SHALE OIL AND GAS PRODUCTION PROCESSES

James G. Speight, PhD, DSc, PhD

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JAMES SPEIGHT
CD & W Inc. Laramie, WY, United States

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About the author

Dr. James G. Speight has doctorate degrees in Chemistry, Geological Sciences, and Petroleum Engineering. He is the author of more than 80 books in petroleum science, fossil fuel science, petroleum engineering, environmental sciences, and ethics.

He has more than fifty years of experience in areas associated with (i) the properties, recovery, and refining of reservoir fluids, conventional petroleum, heavy oil, extra heavy oil, tar sand bitumen, and oil shale, (ii) the properties and refining of natural gas, gaseous fuels, (iii) the production and properties of chemicals from crude oil, coal, and other sources, (iv) the properties and refining of biomass, biofuels, biogas, and the generation of bioenergy, and (v) the environmental and toxicological effects of energy production and fuels use. His work has also focused on safety issues, environmental effects, environmental remediation, and safety issues as well as reactors associated with the production and use of fuels and biofuels.

Although he has always worked in private industry with emphasis on contract-based work leading to commercialization of concepts, Dr. Speight was (among other appointments) a Visiting Professor in the College of Science, University of Mosul (Iraq) and has also been a Visiting Professor in Chemical Engineering at the Technical University of Denmark, (Lyngby, Denmark) and the University of Trinidad and Tobago (Point Lisas, Trinidad).

In 1996, Dr. Speight was elected to the Russian Academy of Sciences and awarded the Academy's Gold Medal of Honor that same year for outstanding contributions to the field of petroleum sciences. In 2001, he received the Scientists without Borders Medal of Honor of the Russian Academy of Sciences and was also awarded the Einstein Medal for outstanding contributions and service in the field of Geological Sciences. In 2005, the Academy awarded Dr. Speight the Gold Medal — Scientists without Frontiers, Russian Academy of Sciences, in recognition of Continuous Encouragement of Scientists to Work Together Across International Borders. In 2007 Dr. Speight received the Methanex Distinguished Professor award at the University of Trinidad and Tobago in recognition of excellence in research. In 2018, he received the American Excellence Award for Excellence in Client Solutions from the United States Institute of Trade and Commerce, Washington, DC.

Preface

Natural gas and crude oil production from hydrocarbon rich deep tight shale formations, known as tight gas and tight oil (also referred to as shale gas and, incorrectly, as shale oil) is one of the most quickly expanding trends in onshore domestic exploration for crude oil and natural gas. In some cases, this has included bringing drilling and production to regions of the country that have seen little or no activity in the past.

Vast new natural gas and oil resources are being discovered every year across North America — drilling activity is at a 25-year high and supplies are rapidly growing. One major source of these resources comes from the development of deep shale formations, typically located many thousands of feet below the surface of the Earth in tight, low permeability formations. Recent technological advancements in horizontal drilling and hydraulic fracturing are unlocking an abundance of deep shale natural gas and oil in the United States. However, the issues of tight gas and tight oil recovery relate to the differences in shale plays.

Natural gas and crude oil from tight formations has not only changed the energy distribution in the United States as a result of this new-found popularity, but development of these resources also brings change to the environmental and socio-economic landscape, particularly in those areas where development is new. With these changes have come questions about the nature of the development of these resources including the potential environmental impacts and the ability of the current regulatory structure to deal with these issues.

Natural gas and crude oil from tight formation such as shale, tight sandstone, and carbonate formations are is considered as unconventional fossil fuels since the gas or oil may be attached to or adsorbed on to organic matter. The gas and oil are contained in difficult-to-produce reservoirs — shale is a rock that can hold huge amount of gas or oil, not only in the zones between the particles, but some of the particles are organic that like sponges also contain hold gas and oil. Thus, evaluation of the potential of sedimentary basins for gas and oil production has now become an important area of development internationally and is of great national interest as these resources will have direct positive impact on energy security of many countries which have sizeable resources in sedimentary basins. However, it will be appreciated that the reserves estimations are not static and are changing annually based upon new discoveries and improvement in drilling and recovery techniques.

The global increasing significance of gas and oil from tight formations has led to the need for deeper understanding of shale behavior. Increased understanding of the tight formations will provide a better decision regarding the development of these resources. To find these reserves may be relatively easy but the technology to produce the natural gas and the crude oil is very expensive. The technique to drill straight through the gas-bearing or oil-bearing rock gives very little exposure to rock for the gas and oil to escape. Hydraulic fracturing is the only way to increase exposure for successful production rate of the gas and the oil.

On the other hand, oil shale is a fine-grained sedimentary rock containing organic matter (commonly called kerogen) that yields substantial amounts of oil and combustible gas upon destructive distillation and in many parts of the world. Most of the organic matter is insoluble in ordinary organic solvents; therefore, it must be decomposed by heating to release such materials. Underlying most definitions of oil shale is its potential for the economic recovery of energy, including shale oil and combustible gas, as well as a number of byproducts. A deposit of oil shale having economic potential is generally one that is at or near enough to the surface to be developed by open-pit or conventional underground mining or by in-situ methods. The properties of shale oil (kerogen-derived oil) vary with the sources and the process by which the shale oil is produced. Thus, shale oil can be a difficult feedstock to processes in refinery operations. Varying quantities of heteroatoms (nitrogen, oxygen, and sulfur as well as metal constituents) offer several difficulties that refiners must face if they are to include shale oil as part of the refinery feedstocks. In addition, the incompatibility of shale oil with typical petroleum feedstocks may also be an issue.

Oil shale deposits are in many parts of the world. They range in age from Cambrian to Tertiary and were formed in a variety of marine, continental, and lacustrine depositional environments. The largest known deposit is in the Green River Formation in the western United States with the potential to produce approximately 1.5 trillion US barrels (1.5 × 1012 US bbls) of shale oil.

The properties of shale oil vary with the sources and the process by which the shale oil is produced. Thus, shale oil can be a difficult feedstock to processes. Varying quantities of heteroatoms (nitrogen, oxygen, and sulfur as well as metal constituents) offer several difficulties that refiners must face if they are to include shale oil as part of the refinery feedstocks. In addition, the incompatibility of shale oil with typical petroleum feedstocks may also be an issue. However, depending on the nature of the upgrading techniques applied, shale oil can be a premium-quality refinery feedstock, comparable and compatible with the best grades of conventional crude oil. In fact, shale oil is considered by some scientific and engineering authorities a better source of jet fuel, diesel fuel, and distillate heating oil than it is of gasoline. Although some technical questions remain, the upgrading and refining processes are well-advanced for the production of premium products.

Thus, the objective of this book is to present an introduction to natural gas and crude oil resources in tight formations as well as offer an understanding of the geomechanical properties of such formations and the need for hydraulic fracturing. The book also introduces the reader to issues regarding the nature of natural gas and crude oil development in tight formations, the potential environmental impacts, and the ability of the current regulatory structure to deal with these issues. The book also serves to introduce scientists, engineers, managers, regulators, policy makers to objective sources of information upon which to make decisions about meeting and managing the challenges that may accompany.

This book presents (i) gas and oil potential from tight formations, (ii) the evolution of shale plays, (iii) exploitation through discovery, drilling and reservoir evaluation, (iv) production, and (v) the efficiency of these completion operations. This book also deals with the production of shale oil (kerogen-derived oil) from oil shale and transports the reader through the various aspects of production with chapters that deal with (i) origin and properties of oil shale, (ii) oil shale resources by country, (iii) the chemical and physical nature of kerogen, the precursor to oil shale, (iv) mining and retorting oil shale, (v) in situ retorting, and (vi) shale oil refining. The environmental aspects of the development of natural gas and crude oil from tight formations are also presented.

The book also serves to introduce scientists, engineers, managers, regulators, policy makers to objective sources of information upon which to make decisions about meeting and managing the challenges that may accompany development of these resources. A descriptive Glossary is also included.

Dr. James G. Speight
CD&W Inc.,
Laramie,
Wyoming, United States

CHAPTER

1

Gas and oil in tight formations

1. Introduction

The generic terms *crude oil* (also referred to as *petroleum*) and *natural gas* and apply to the mixture of liquids and gases, respectively, commonly associated with petroliferous (crude oil-producing, crude oil-containing) geologic formations (Speight, 2014a) and which has been extended to gases and liquids from the recently developed deep shale formations (Speight, 2013b). However, in addition to the natural gas found in crude oil reservoirs, there are also those reservoirs in which natural gas may be the sole occupant. The principal constituent of natural gas is methane, but other hydrocarbon derivatives, such as ethane, propane, and butane, may also be present. Carbon dioxide is also a common constituent of natural gas. Trace amounts of rare gases, such as helium, may also occur, and certain natural gas reservoirs are a source of these rare gases. Just as crude oil can vary in composition, so can natural gas. Differences in natural gas composition occur between different reservoirs, and two wells in the same field may also yield gaseous products that are different in composition (Mokhatab et al., 2006; Speight, 2014a, 2019).

Crude oil and natural gas are the most important raw materials consumed in modern society – they provide raw materials for the ubiquitous plastics and other products as well as fuels for energy, industry, heating, and transportation. From a chemical standpoint, natural gas and crude oil are a mixture of hydrocarbon compounds and non-hydrocarbon compounds with crude oil being much more complex than natural gas (Speight, 2012a, 2014a, 2019). The fuels that are derived from these two natural products supply more than half of the total supply of world energy. Gas (for gas burners and for the manufacture of petrochemicals), gasoline, kerosene, and diesel oil provide fuel for automobiles, tractors, trucks, aircraft, and ships (Speight, 2014a). In addition, fuel oil and natural gas are used to heat homes and commercial buildings, as well as to generate electricity.

Natural gas and crude oil are carbon-based resources and, therefore, the geochemical carbon cycle is also of interest to fossil fuel usage in terms of crude oil formation, use, and the buildup of atmospheric carbon dioxide. Thus, the more efficient use of natural gas and crude oil is of paramount importance and the technology involved in processing both feedstocks will supply the industrialized nations of the world for (at least) the next fifty years until suitable alternative forms of energy are readily available (Boyle, 1996; Ramage, 1997; Speight, 2011a, 2011b, 2011c).

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In this context, it is relevant to introduce the term *peak oil* which refers to the maximum rate of oil production, after which the rate of production of this natural resources (in fact the rate of production of any natural resource) enters a terminal decline (Hubbert, 1956, 1962). Peak oil production usually occurs after approximately half of the recoverable oil in an oil reserve has been produced (i.e., extracted). Peaking means that the rate of world oil production cannot increase, and that oil production will thereafter decrease with time; even if the demand for oil remains the same or increases. Following from this, the term *peak energy* is the point in time after which energy production declines and the production of energy from various energy sources is in decline. In fact, most oil-producing countries – including Indonesia, the United Kingdom, Norway, and the United States – have passed the peak crude oil production apex several years or decades ago. Their production declines have been offset by discoveries and production growth elsewhere in the world and the so-called *peak energy precipice* will be delayed by such discoveries as well as by further development or crude oil and natural gas resources that are held in tight formations and tight shale formations (Islam and Speight, 2016).

However, before progressing any further, a series of definitions are used to explain the terminology used in this book.

2. Definitions

The *definitions* of crude oil and natural gas have been varied and diverse and are the product of many years of the growth of the crude oil and natural gas processing industries. Of the many forms of the definitions that have been used not all have survived but the more common, as illustrated here, are used in this book. Also included for comparison are sources of gas – such as gas hydrates and other sources of gas - that will present an indication of future sources of gaseous energy.

2.1 Crude oil

The term *crude oil* covers a wide assortment of naturally-occurring hydrocarbon-type liquids consisting of mixtures of hydrocarbon derivatives and non-hydrocarbon compounds containing variable amounts of sulfur, nitrogen, and oxygen as well as heavy metals such as nickel and vanadium, which may vary widely in volatility, specific gravity, and viscosity along with varying physical properties such as API gravity and sulfur content (Tables 1.1 and 1.2) as well as being accompanied by variations in color that ranges from colorless to black – the lower API gravity crude oils are darker than the higher API gravity crude oils (Speight, 2012a, 2014a; US EIA, 2014). The metal-containing constituents, notably those compounds consisting of derivatives of vanadium and nickel with, on occasion iron and copper, usually occur in the more viscous crude oils in amounts up to several thousand parts per million and can have serious consequences for the equipment and catalysts used in processing of these feedstocks (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017; Hsu and Robinson, 2017). The presence of iron and copper has been subject to much speculation insofar as it is not clear if these two metals are naturally occurring in the crude oil or whether they are absorbed by the crude oil during recovery and transportation in metals pipelines.

TABLE 1.1 Selected crude oils showing the differences in API gravity and sulfur content.

Country	Crude oil	API	Sulfur % w/w
Abu Dhabi (UAE)	Abu Al Bu Khoosh	31.6	2.00
Abu Dhabi (UAE)	Murban	40.5	0.78
Angola	Cabinda	31.7	0.17
Angola	Palanca	40.1	0.11
Australia	Barrow Island	37.3	0.05
Australia	Griffin	55.0	0.03
Brazil	Garoupa	30.0	0.68
Brazil	Sergipano Platforma	38.4	0.19
Brunei	Champion Export	23.9	0.12
Brunei	Seria	40.5	0.06
Cameroon	Lokele	20.7	0.46
Cameroon	Kole Marine	32.6	0.33
Canada (Alberta)	Wainwright-Kinsella	23.1	2.58
Canada (Alberta)	Rainbow	40.7	0.50
China	Shengli	24.2	1.00
China	Nanhai Light	40.6	0.06
Dubai (UAE)	Fateh	31.1	2.00
Dubai (UAE)	Margham Light	50.3	0.04
Egypt	Ras Gharib	21.5	3.64
Egypt	Gulf of Suez	31.9	1.52
Gabon	Gamba	31.4	0.09
Gabon	Rabi-Kounga	33.5	0.07
Indonesia	Bima	21.1	0.25
Indonesia	Kakap	51.5	0.05
Iran	Aboozar (Ardeshir)	26.9	2.48
Iran	Rostam	35.9	1.55
Iraq	Basrah Heavy	24.7	3.50
Iraq	Basrah Light	33.7	1.95
Libya	Buri	26.2	1.76
Libya	Bu Attifel	43.3	0.04
Malaysia	Bintulu	28.1	0.08
Malaysia	Dulang	39.0	0.12

(*Continued*)

TABLE 1.1 Selected crude oils showing the differences in API gravity and sulfur content.—cont'd

Country	Crude oil	API	Sulfur % w/w
Mexico	Maya	22.2	3.30
Mexico	Olmeca	39.8	0.80
Nigeria	Bonny Medium	25.2	0.23
Nigeria	Brass River	42.8	0.06
North Sea (Norway)	Emerald	22.0	0.75
North Sea (UK)	Innes	45.7	0.13
Qatar	Qatar Marine	36.0	1.42
Qatar	Dukhan (Qatar Land)	40.9	1.27
Saudi Arabia	Arab Heavy (Safaniya)	27.4	2.80
Saudi Arabia	Arab Extra Light (Berri)	37.2	1.15
USA (California)	Huntington Beach	20.7	1.38
USA (Michigan)	Lakehead Sweet	47.0	0.31
Venezeula	Leona	24.4	1.51
Venezuela	Oficina	33.3	0.78

TABLE 1.2 API gravity and sulfur content of selected heavy oils.

Country	Crude oil	API	Sulfur % w/w
Canada (Alberta)	Athabasca	8.0	4.8
Canada (Alberta)	Cold Lake	13.2	4.11
Canada (Alberta)	Lloydminster	16.0	2.60
Canada (Alberta)	Wabasca	19.6	3.90
Chad	Bolobo	16.8	0.14
Chad	Kome	18.5	0.20
China	Qinhuangdao	16.0	0.26
China	Zhao Dong	18.4	0.25
Colombia	Castilla	13.3	0.22
Colombia	Chichimene	19.8	1.12
Ecuador	Ecuador Heavy	18.2	2.23
Ecuador	Napo	19.2	1.98
USA (California)	Midway Sunset	11.0	1.55
USA (California)	Wilmington	18.6	1.59
Venezuela	Boscan	10.1	5.50
Venezuela	Tremblador	19.0	0.80

Crude oil exists in reservoirs that consist of more porous and permeable sediments, such as *sandstone* and *siltstone*. A series of reservoirs within a common rock structure or a series of reservoirs in separate but neighboring formations is commonly referred to as an *oil field*. A group of fields is often found in a single geologic environment is known as a *sedimentary basin* or *province*. In the underground locale, crude oil is much more fluid (mobile) than it is on the surface and is generally much more mobile under reservoir conditions because the elevated temperatures (the *geothermal gradient*) in subterranean formations decreases the viscosity of the oil. Although the geothermal gradient varies from place to place, the increase in temperature with depth below the surface is generally recognized to be on the order of 25–30 °C/km (15 °F/1000 feet or 120 °C/1000 feet, i.e. 0.015 °C per foot of depth or 0.012 °C per foot of depth).

The major components of conventional crude oil are *hydrocarbon derivatives* with *non-hydrocarbon compounds (compounds contain nitrogen oxygen, sulfur, and metals) in the minority and* all of which display a substantial variation in molecular structure. The simplest hydrocarbon derivatives are *paraffin derivatives* which extend from methane (the simplest hydrocarbon, CH_4) to the liquids that are refined into gasoline, diesel fuel, and fuel oil to the highly crystalline wax [$(CH_3CH_2)_nCH_3$, where $n > 15$] and the more complex multi-ring constituents (C_{60+}); the latter constituents (i.e., the more complex multi-ring constituents) are typically non-volatile and are found in the residuum from atmospheric distillation or vacuum distillation.

The *non-hydrocarbon constituents* of crude oil include organic derivatives of nitrogen, oxygen, sulfur, and metals (predominantly nickel and vanadium) and are often referred to as polar aromatics, which include the resin and asphaltene constituents (Fig. 1.1) (Speight, 2014a, 2015a). In the case of heavy (high density low API gravity) crude oils and tar sand bitumen, there is a lesser amount of hydrocarbon constituents (with very little of the material boiling below 200 °C (390 °F) volatile constituents) in favor of increasing amounts of non-hydrocarbon constituents (low-volatile and non-volatile constituents) (Speight, 2014a, 2016c). While most of the higher-boiling constituents are removed during refining by conversion of hydrocarbon products, the low-volatile and non-volatile constituents greatly influence the choice and effectiveness of recovery processes and whether or not fracturing is to be considered as a recovery process enhancement (Speight, 2014a, 2016a,c).

In terms of crude oil recovery, geologic techniques can give valuable information related to the existence of rock formations as well as crude oil properties, drilling is the only sure way to ascertain the presence of crude oil in the formation and the suitability of the crude oil for recovery. With modern rotary equipment, wells can be drilled to depths of more than 30,000 feet. Once oil is found, it may be recovered (brought to the surface) by the reservoir pressure created by presence of natural gas or water within the reservoir. Crude oil can also be brought to the surface by injecting water or steam into the reservoir to raise the pressure artificially, or by injecting such substances as carbon dioxide, polymers, and solvents to reduce crude oil viscosity. Thermal recovery methods are frequently used to enhance the production of heavy crude oils, especially when extraction of the heavy oil is impeded by viscous resistance to flow at reservoir temperatures (Speight, 2014a, 2016a,b).

Crude oil and natural gas reserves are conveniently divided into (i) conventional resources and (ii) unconventional resources (Mokhatab et al., 2006; Speight, 2014a, 2019). However, in a more general sense, unconventional resources also include heavy oil which is not a subject of

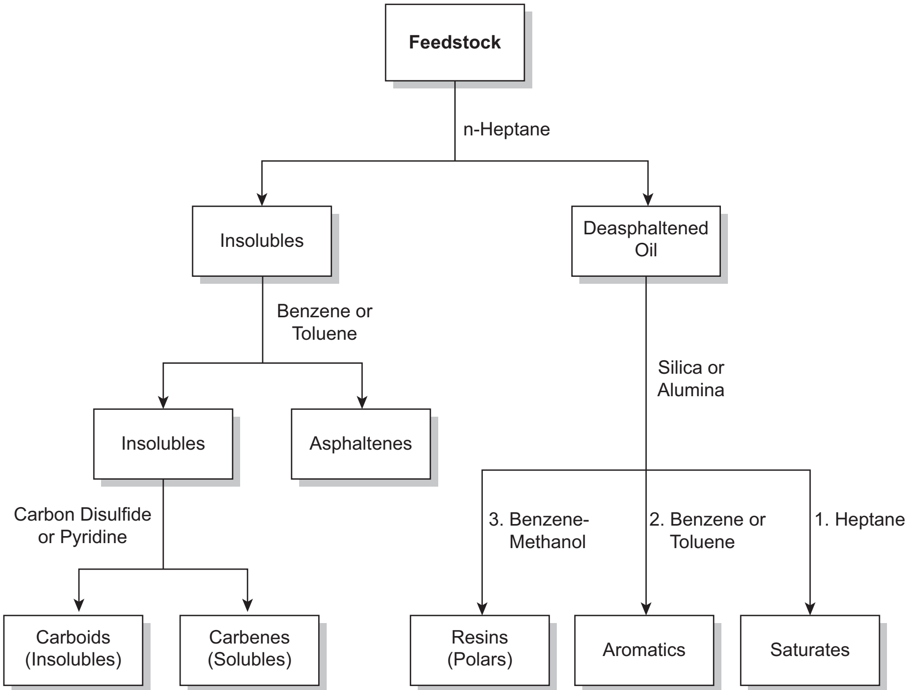

FIG. 1.1 Typical fractionating sequence for conventional crude oil, heavy oil and tar sand bitumen.

this text and crude oil from shale formations and from tight formations. Conventional gas typically is found in reservoirs with a permeability greater than 1 millidarcy (>1 mD) and can be extracted via traditional techniques. A large proportion of the gas produced globally to date is conventional, and is relatively easy and inexpensive to extract. In contrast, unconventional gas is found in reservoirs with relatively low permeability (<1 mD) and hence cannot be extracted by conventional methods. It is the latter type of resources (and crude oil from shale formations and from tight formations) are the subject of this book.

Finally, to complete the definition of unconventional resources, it is the geology of the resource that confers upon the resource it the name *unconventional resource*. Unconventional formations are fine-grained, organic-rich, sedimentary rocks – usually shale formations and similar rocks which are both the source of and the reservoir for oil and natural gas, unlike conventional crude oil reservoirs where the source rock and the reservoir rock are distinctly separate formations. The Society of Petroleum Engineers describes *unconventional resources* as crude oil (or crude oil-type) accumulations that are pervasive throughout a large area and are not significantly affected by pressure exerted by water (hydrodynamic influences). They are also called *continuous-type deposits* or *tight formations*. In contrast, conventional oil and natural gas deposits occur in porous and permeable sandstone and carbonate reservoirs. Under pressure exerted by water, the hydrocarbon derivatives migrated upward from organic sources until an impermeable cap-rock (such as shale) trapped it in the reservoir rock. Although the unconventional formations may be as porous as other sedimentary reservoir rocks, the extremely small pore sizes and lack of permeability make the unconventional formations relatively resistant to fluid flow. The lack of permeability means that the oil and gas typically remain in the source rock unless natural or artificial fractures occur.

2.2 Opportunity crudes

Tight oils are considered opportunity crudes because they are typically less expensive than crude oils produced by traditional drilling methods. Thus, there is the need to include the definition of opportunity crude oil. Processing these cheaper crudes offers the refiner economic incentives but tights oils do come with their own set of unique challenges.

Opportunity crude oils are either new crude oils with unknown or poorly understood properties relating to processing issues or are existing crude oils with well-known properties and processing concerns (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017; Hsu and Robinson, 2017). Opportunity crude oils are often, but not always, high density low API gravity crude oils but in either case are more difficult to process due to high levels of solids (and other contaminants) produced with the oil, high levels of acidity, and high viscosity. These crude oils may also be incompatible with other oils in the refinery feedstock blend and cause excessive equipment fouling when processed either in a blend or separately (Speight, 2015a). There is also the need for a refinery to be configured to accommodate *opportunity crude oils* and/or *high acid crude oils* which, for many purposes are often included with high density low API gravity feedstocks.

In addition to taking preventative measure for the refinery to process these feedstocks without serious deleterious effects on the equipment, refiners need to develop programs for detailed and immediate feedstock evaluation so that they can understand the qualities of a crude oil very quickly and it can be valued appropriately and management of the crude processing can be planned meticulously (Speight, 2014a). For example, the compatibility of opportunity crudes with other opportunity crudes and with conventional crude oil and heavy oil is a very important property to consider when making decisions regarding which crude to purchase. Blending crudes that are incompatible can lead to extensive fouling and processing difficulties due to unstable asphaltene constituents (Speight, 2014a, 2015b). These problems can quickly reduce the benefits of purchasing the opportunity crude in the first place. For example, extensive fouling in the crude preheat train may occur resulting in decreased energy efficiency, increased emissions of carbon dioxide, and increased frequency at which heat exchangers need to be cleaned. In a worst-case scenario, crude throughput may be reduced leading to significant financial losses.

Opportunity crude oils, while offering initial pricing advantages, may have composition problems which can cause severe problems at the refinery, harming infrastructure, yield, and profitability. Before refining, there is the need for comprehensive evaluations of opportunity crudes, giving the potential buyer and seller the needed data to make informed decisions regarding fair pricing and the suitability of a particular opportunity crude oil for a refinery. This will assist the refiner to manage the ever-changing crude oil quality input to a refinery — including quality and quantity requirements and situations, crude oil variations, contractual specifications, and risks associated with such opportunity crude oils (Table 1.3).

TABLE 1.3 Examples of different crude oil quality as expressed by API gravity and sulfur content.

Location[a]	**Low quality range (°API, S% w/w)**	**High quality range (°API, S% w/w)**
Africa	Angola (Kuito) 19°, 0.68%	Nigeria (Agbami Light) 47°, 0.04%
Asia	China (Peng Lai) 22°, 0.29%	Indonesia (Senipah Condensate) 54°, 0.03%
Australia	Enfield 22°, 0.13%	Bayu Undan 56°, 0.07%
Europe	UK (Alba) 19°,1.24%	Norway (Snohvit Condensate) 61°,0.02%
Middle East	Saudi Arabia (SA heavy) 27°, 2.87%	Abu Dhabi (Murban) 39°, 0.8%
North America	Canada (Albian) 19°, 2.1%	US (Williams Sugarland Blend) 41°,0.20%
Latin America	Venezuela (Boscan) 10°, 5.7%	Columbia (Cupiaga) 43°,0.14%
Central Asia	Russia (Espo) 35°, 0.62%	Kumkol (Kazakhstan) 45°,0.81%

[a] *Country or region.*

2.3 Natural gas

The generic term *natural gas* applies to gases commonly associated with petroliferous (crude oil-producing, crude oil-containing) geologic formations. Natural gas is found in deep underground rock formations and is also found in coal seams (coalbed methane) and generally contains high proportions of methane (CH_4) and some of the higher molecular weight higher paraffin derivatives (C_nH_{2n+2}) generally containing up to six or eight carbon atoms may also be present in small quantities (Table 1.4) The hydrocarbon constituents of natural gas are combustible, but non-flammable non-hydrocarbon components such as carbon dioxide, nitrogen, and helium are often present in the minority and are regarded as contaminants that are removed during gas processing (gas cleaning, gas refining) (Mokhatab et al., 2006; Speight, 2014a, 2019).

TABLE 1.4 Constituents of natural gas.

Component	**Formula**	**% v/v**
Methane	CH_4	>85
Ethane	C_2H_6	3–8
Propane	C_3H_8	1–5
Butane	C_4H_{10}	1–2
Pentane$^+$	C_5H_{12}	1–5
Carbon dioxide	CO_2	1–2
Hydrogen sulfide	H_2S	1–2
Nitrogen	N_2	1–5
Helium	He	<0.5

Pentane$^+$: pentane and higher molecular weight, up to and including octane (C_8H_{18}) hydrocarbon derivatives, including benzene and toluene (Speight, 2014).

The hydrocarbon constituents of natural gas are combustible, but non-flammable non-hydrocarbon components such as carbon dioxide, nitrogen, and helium are often present in the minority and are regarded as contaminants. In addition to the natural gas found in crude oil reservoirs, there are also those reservoirs in which natural gas may be the sole occupant. In such cases the liquids that occur with the gas are gas condensate and such reservoirs may also be referred to as *gas condensate reservoirs*. Differences in natural gas composition occur between different reservoirs, and two wells in the same field may also yield gaseous products that are different in composition (Mokhatab et al., 2006; Speight, 2014a, 2019).

In addition to the natural gas that is found in crude oil reservoirs, there are also those reservoirs in which natural gas may be the sole occupant. The principal constituent of this type of natural gas is methane, but other hydrocarbon derivatives, such as ethane, propane, and butane, may (but not always) also be present in somewhat lesser amount than natural gas from a crude oil reservoir. Carbon dioxide is also a common constituent of natural gas. Trace amounts of rare gases, such as helium, may also occur, and certain natural gas reservoirs are a source of these rare gases. Just as crude oil can vary in composition, so can natural gas. Differences in natural gas composition occur between different reservoirs, and two wells in the same field may also yield gaseous products that are different in composition (Speight, 1990, 2014a, 2016a).

Like crude oil resources, natural gas resources are typically divided into two categories: (i) conventional gas and (ii) unconventional gas (Mokhatab et al., 2006; Speight, 2014a, 2019). However, in a more general sense, unconventional resources also include coalbed methane (which is not a subject of this text but which is included for comparison) and natural gas from shale formations and from tight formations. The latter type of resources (natural gas from shale formations and from tight formations such as tight sandstone formations and carbonate formations) are the subject of this book. Conventional gas is typically found in reservoirs with a permeability greater than 1 milliDarcy (>1 mD) and can be extracted by means of traditional recovery methods. In contrast, unconventional gas is found in reservoirs with relatively low permeability (<1 mD) and hence cannot be extracted by conventional methods.

In addition, there are several general definitions that have been applied to natural gas. Thus, *lean* gas is gas in which methane is the major constituent. W*et* gas contains considerable amounts of the higher molecular weight hydrocarbon derivatives and these paraffin derivatives present in the gas, in fact more than 0.1 gal/1000 ft^3. On the other hand, *dry* natural gas indicates that there is less than 0.1 gallon (1 gallon, US, = 264.2 m^3) of gasoline vapor (higher molecular weight paraffin derivatives) per 1000 ft^3 (1 ft^3 = 0.028 m^3). Other terms of interest are sour gas, residual gas, and casinghead gas (casing head gas).

S*our* gas contains hydrogen sulfide whereas *sweet* gas contains very little, if any, hydrogen sulfide. To further define the terms *dry* and *wet* in quantitative measures, the term *dry* natural gas indicates that there is less than 0.1 gallon (1 gallon, US, = 264.2 m^3) of gasoline vapor (higher molecular weight paraffin derivatives) per 1000 ft^3 (1 ft^3 = 0.028 m^3). The term *wet natural gas* indicates that there are such paraffin derivatives present in the gas, in fact more than 0.1 gal/1000 ft^3.

Residue gas is natural gas from which the higher molecular weight hydrocarbon derivatives have been extracted and *casinghead gas* is derived from crude oil but is separated at the separation facility at the well-head.

There are several general definitions that have been applied to natural gas. Thus, *associated natural gas* or *dissolved natural gas* occurs either as free gas or as gas in solution in the crude oil. Gas that occurs as a solution in the crude oil is *dissolved* gas whereas the gas that exists in contact with the crude oil (*gas cap*) is *associated* gas. Such gas typically has higher proportions of the higher boiling hydrocarbon derivatives that commonly occur as low-boiling crude oil constituents (Table 1.5). *Lean* gas is gas in which methane is the major constituent while *t wet* gas contains considerable amounts of the higher molecular weight hydrocarbon derivatives.

Residue gas is natural gas from which the higher molecular weight hydrocarbon derivatives have been extracted and *casing head gas* is derived from crude oil but is separated at the separation facility at the well-head. The use of term *residue* as it is applied to natural gas is in direct contract to the residue left in the distillation tower during crude oil refining – this residue is the high boiling fraction of the crude oil from which the lower boiling constituents have been removed as part of the distillation process.

Other components such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), mercaptans (thiols, RSH), as well as trace amounts of other constituents may also be present. Thus, there is no single composition of components which might be termed *typical* natural gas. Methane and ethane often constitute the bulk of the combustible components; carbon dioxide (CO_2) and nitrogen (N_2) are the major non-combustible (inert) components. Thus, sour gas is

TABLE 1.5 Composition of associated natural gas from a petroleum well.

Category	Component	Amount (%)
Paraffinic	Methane (CH_4)	70–98
	Ethane (C_2H_6)	1–10
	Propane (C_3H_8)	Trace-5
	Butane (C_4H_{10})	Trace-2
	Pentane (C_5H_{12})	Trace-1
	Hexane (C_6H_{14})	Trace-0.5
	Heptane and higher (C_7^+)	None-trace
Cyclic	Cyclopropane (C_3H_6)	Traces
	Cyclohexane (C_6H_{12})	Traces
Aromatic	Benzene (B_6H_6), others	Traces
Non-hydrocarbon	Nitrogen (N_2)	Trace-15
	Carbon dioxide (CO_2)	Trace-1
	Hydrogen sulfide (H_2S)	Trace occasionally
	Helium (He)	Trace-5
	Other sulfur and nitrogen compounds	Trace occasionally
	Water (H_2O)	Trace-5

natural gas that occurs mixed with higher levels of sulfur compounds (such as hydrogen sulfide, H_2S, and mercaptans or thiols, RSH) and which constitutes a corrosive gas (Speight, 2014c). The sour gas requires additional processing for purification (Mokhatab et al., 2006; Speight, 2014a, 2019).

Natural-gas condensate (*gas condensate*, *natural gasoline*) is a low-density low-viscosity mixture of hydrocarbon liquids that may be present as gaseous components under reservoir conditions and which occur in the raw natural gas produced from natural wells. The constituents of *condensate* separate from the untreated (raw) gas if the temperature is reduced to below the hydrocarbon dew point temperature of the raw gas. Briefly, the dew point is the temperature to which a given volume of gas must be cooled, at constant barometric pressure, for vapor to condense into liquid. Thus, the dew point is the saturation point.

On a worldwide scale, there are many gas condensate reservoirs and each has its own unique gas condensate composition. However, in general, gas condensate has a specific gravity on the order of ranging from 0.5 to 0.8, and is composed of hydrocarbon derivatives such as propane, butane, pentane, hexane, heptane and even octane, none and decane in some cases. In addition, the gas condensate may contain additional impurities such as hydrogen sulfide, thiols (mercaptans, RSH), carbon dioxide, cyclohexane (C_6H_{12}), and low molecular weight aromatics such as benzene (C_6H_6), toluene (C_6H5CH_3), ethylbenzene ($C_6H_5CH_2CH_3$), and xylenes ($H_3CC_6H_4CH_3$) (Mokhatab et al., 2006; Speight, 2014a, 2019).

When condensation occurs in the reservoir, the phenomenon known as condensate blockage can halt flow of the liquids to the wellbore. Hydraulic fracturing is the most common mitigating technology in siliciclastic reservoirs (reservoirs composed of clastic rocks), and acidizing is used in carbonate reservoirs (Speight, 2016a). Briefly, clastic rocks are composed of fragments, or clasts, of pre-existing minerals and rock. A clast is a fragment of geological detritus, chunks and smaller grains of rock broken off other rocks by physical weathering. Geologists use the term *clastic* with reference to sedimentary rocks as well as to particles in sediment transport whether in suspension or as bed load, and in sedimentary deposits (Davis, 1992).

In addition, production can be improved with less drawdown in the formation. For some gas-condensate fields, a lower drawdown means single-phase production above the dew point pressure can be extended for a longer time. However, hydraulic fracturing does not generate a permanent conduit past a condensate saturation buildup area. Once the pressure drops below the dew point, saturation will increase around the fracture, just as it did around the well bore. Horizontal or inclined wells are also being used to increase contact area within formations.

2.4 Gas hydrates

Methane hydrates (also called *methane clathrates*) is a resource in which a large amount of methane is trapped within a crystal structure of water, forming a solid similar to ice (Kvenvolden, 1995; Buffett and Archer, 2004; Gao et al., 2005; Gao, 2008; USGS, 2011). Natural gas hydrates are solids that form from a combination of water and one or more hydrocarbon or non-hydrocarbon gases. In physical appearance, gas hydrates resemble packed snow or ice. In a gas hydrate, the gas molecules (such as methane, hence the name *methane hydrates*) are trapped within a cage-like crystal structure composed of water molecules. Gas hydrates are stable only under specific conditions of pressure and temperature. Under the appropriate pressure, they can exist at temperatures significantly above the freezing point of water. The maximum temperature at which gas hydrate can exist depends on pressure and gas composition. For example, methane plus water at 600 psia forms hydrate at 5 °C (41 °F), while at the same pressure, methane with 1% v/v propane forms a gas hydrate at 9.4 °C (49 °F). Hydrate stability can also be influence by other factors, such as salinity (Edmonds et al., 1996).

Per unit volume, gas hydrates contain a high amount of gas. For example, 1 cubic yard of hydrate disassociates at atmospheric temperature and pressure to form approximately 160 cubic yards of natural gas plus 0.8 cubic yards of water (Kvenvolden, 1993). The natural gas component of gas hydrates is typically dominated by methane, but other natural gas components (e.g., ethane, propane, carbon dioxide) can also be incorporated into a hydrate. The origin of the methane in a hydrate can be either thermogenic gas or biogenic gas. Bacterial gas formed during early digenesis of organic matter can become part of a gas hydrate in continental shelf sediment. Similarly, thermogenic gas leaking to the surface from a deep thermogenic gas accumulation can form a gas hydrate in the same continental shelf sediment (Boswell and Collett, 2011; Collett, 2002; Gupta, 2004; Demirbas, 2010a, 2010b, 2010c; Chong et al., 2016).

Generally, methane clathrates are common constituents of the shallow marine geosphere, and they occur both in deep sedimentary structures, and form outcrops on the ocean floor. Methane hydrates are believed to form by migration of gas from depth along geological faults, followed by precipitation, or crystallization, on contact of the rising gas stream with cold sea water. When drilling in crude oil-bearing and gas-bearing formations submerged in deep water, the reservoir gas may flow into the well bore and form gas hydrates owing to the low temperatures and high pressures found during deep water drilling. The gas hydrates may then flow upward with drilling mud or other discharged fluids. When the hydrates rise, the pressure in the annulus decreases and the hydrates dissociate into gas and water. The rapid gas expansion ejects fluid from the well, reducing the pressure further, which leads to more hydrate dissociation (sometimes explosive dissociation) and further fluid ejection.

Estimates of the global inventory of methane clathrate have exceed 10^{19} g of carbon (MacDonald, 1990a,b; Gornitz and Fung, 1994), which is comparable to estimates of potentially recoverable coal, oil, and natural gas. The proximity of this methane reservoir to the seafloor has motivated speculations related to a release of methane in response to climate change (MacDonald, 1990b). Increases in temperature or decreases in pressure (through changes in sea level) tend to dissociate clathrate, releasing methane into the near-surface environment. Release of methane from clathrate has been invoked to explain abrupt increases in the atmospheric concentration of methane during the last glacial cycle.

2.5 Coalbed methane

Natural gas is often located in the same reservoir as with crude oil, but it can also be found trapped in gas reservoirs and within coal seams. The occurrence of methane in coal seams is not a new discovery and methane (called *firedamp* by the miners because of its explosive nature) was known to coal miners for at least one hundred and fifty years (or more) before it was *rediscovered* and developed as coalbed methane (Speight, 2013b). The gas occurs in the pores and cracks in the coal seam and is held there by underground water pressure. To extract the gas, a well is drilled into the coal seam and the water is pumped out (*dewatering*) which allows the gas to be released from the coal and brought to the surface.

Coalbed methane (sometime referred to as *coalmine methane*) is a generic term for the methane found in most coal seams. To the purist, coalmine methane is the fraction of coalbed methane that is released during the mining operation this, in practice, the terms coalbed methane and coalmine methane usually refer to different sources of gas – both forms of gas, whatever the name, are equally dangerous to the miners.

Coalbed methane is a gas formed as part of the geological process of coal generation, and is contained in varying quantities within all coal. Coalbed methane is exceptionally pure compared to conventional natural gas, containing only very small proportions of higher molecular weight hydrocarbon derivatives such as ethane and butane and other gases (such as hydrogen sulfide and carbon dioxide). Coalbed gas is over 90% methane and, subject to gas composition, may be suitable for introduction into a commercial pipeline with little or no treatment (Rice, 1993; Levine, 1993; Mokhatab et al., 2006; Speight, 2013a, 2019). Methane within coalbeds is not structurally trapped by overlying geologic strata, as in the geologic environments typical of conventional gas deposits (Speight, 2013a, 2014a, 2019). Only a small amount (on the order of 5–10% v/v) of the coalbed methane is present as free gas within the joints and cleats of coalbeds. Most of the coalbed methane is contained within the coal itself (adsorbed to the sides of the small pores in the coal).

As the coal forms, large quantities of methane-rich gas are produced and subsequently adsorbed onto (and within) the coal matrix. Because of its many natural cracks and fissures, as well as the porous nature, coal in the seam has a large internal surface area and can store much more gas than a conventional natural gas reservoir of similar rock volume. If a seam is disturbed, either during mining or by drilling into it before mining, methane is released from the surface of the coal. This methane then leaks into any open spaces such as fractures in the coal seam (known as *cleats*). In these cleats, the coalmine methane mixes with nitrogen and carbon dioxide (CO_2). Boreholes or wells can be drilled into the seams to recover the methane. Large amounts of coal are found at shallow depths, where wells to recover the gas are relatively easy to drill at a relatively low cost. At greater depths, increased pressure may have closed the cleats, or minerals may have filled the cleats over time, lowering permeability and making it more difficult for the gas to move through the coal seam. Coalbed methane has been a hazard since mining began. To reduce any danger to coal miners, most effort is addressed at minimizing the presence of coalbed in the mine, predominantly by venting it to the atmosphere. Only during the past two decades has significant effort been devoted to recovering the methane as an energy resource. Another source of methane from a working mine is the methane mixed with ventilation air, the so-called ventilation air methane (VAM). In the mine, ventilation air is circulated in sufficient quantity to dilute the methane to low concentrations for safety reasons. VAM is often too low in concentration to be of commercial value.

In coalbeds (coal seams), methane (the primary component of natural gas) is generally adsorbed to the coal rather than contained in the pore space or structurally trapped in the formation. Although the interstitial spaces in a shale formation are very small they can take up a significant volume of the rock. This allows the shale to hold significant amounts of water, gas or oil but not be able to effectively transmit them because of the low permeability. The oil and gas industry overcomes these limitations of shale by using horizontal drilling and hydraulic fracturing to create artificial porosity and permeability within the rock. Some of the clay minerals that occur in shale have the ability to absorb or adsorb large amounts of water, natural gas, ions or other substances. This property of shale can enable it to selectively and tenaciously hold or freely release fluids or ions.

Thus, this shale gas resource, which is distributed worldwide (Boyer et al., 2011), can be considered a technology-driven resource as achieving gas production out of otherwise unproductive rock requires technology-intensive processes. Maximizing gas recovery requires far more wells than would be the case in conventional natural gas operations. Furthermore, horizontal wells with horizontal legs up to one mile or more in length are widely used to access the reservoir to the greatest extent possible. Pumping the injected and native water out of the coalbeds after fracturing serves to depressurize the coal, thereby allowing the methane to desorb and flow into the well and to the surface. Methane has traditionally posed a hazard to underground coal miners, as the highly flammable gas is released during mining activities. Otherwise inaccessible coal seams can also be tapped to collect this gas, known as coalbed methane, by employing similar well-drilling and hydraulic fracturing techniques as are used in shale gas extraction. Multi-stage hydraulic fracturing (Chapter 5), where the shale is cracked under high pressures at several places along the horizontal section of the well, is used to create conduits through which gas can flow. Micro-seismic imaging allows operators to visualize where this fracture growth is occurring in the reservoir. However, as a technology-driven resource, the rate of development of shale gas may become limited by the availability of required resources, such as fresh water, fracture proppant, or drilling rigs capable of drilling wells several two miles or more in length.

The primary (or natural) permeability of coal is very low, typically ranging from 0.1 to 30 milliDarcys (mD) and, because coal is a very weak (low modulus) material and cannot take much stress without fracturing, coal is almost always highly fractured and cleated. The resulting network of fractures commonly gives coalbeds a high secondary permeability (despite the typical low primary permeability of coal). Groundwater, hydraulic fracturing fluids, and methane gas can more easily flow through the network of fractures. Because hydraulic fracturing generally enlarges pre-existing fractures in addition to creating new fractures, this network of natural fractures is very important to the extraction of methane from the coal.

The gas from coal seams can be extracted by using technologies that are similar to those used to produce conventional gas, such as using well-bores. However, complexity arises from the fact that the coal seams are generally of low permeability and tend to have a lower flow rate (or permeability) than conventional gas systems, gas is only sourced from close to the well and as such a higher density of wells is required to develop a coalbed methane resource as an unconventional resource (such as tight gas) than a conventional gas resource.

Technologies such as horizontal and multilateral drilling with hydraulic fracturing are sometimes used to create longer, more open channels that enhance well productivity but not all coal seam gas wells require application of this technique. Water present in the coal seam, either naturally occurring or introduced during the fracturing operation, is usually removed to reduce the pressure sufficiently to allow the gas to be released, which leads to additional operational requirements, increased investment and environmental concerns. There are some horizontally drilled coalbed methane wells, and some that receive hydraulic fracturing treatments. However, some coalbed methane reservoirs are also underground sources of drinking water, and as such, there are restrictions on hydraulic fracturing operations. The coalbed methane wells are mostly shallow, as the coal matrix does not have the strength to maintain porosity under the pressure of significant overburden thickness.

2.6 Other sources of gas

Biogenic gas (predominantly methane) is produced by certain types of bacteria (methanogens) during the process of breaking down organic matter in an oxygen-free environment. Livestock manure, food waste, and sewage are all potential sources of biogenic gas, or biogas, which is usually considered a form of renewable energy. Small-scale biogas production is a well-established technology in parts of the developing world, particularly Asia, where farmers collect animal manure in vats and capture the methane given off while it decays.

Landfills offer another under-utilized source of biogas. When municipal waste is buried in a landfill, bacteria break down the organic material contained in garbage such as newspapers, cardboard, and food waste, producing gases such as carbon dioxide and methane. Rather than allowing these gases to go into the atmosphere, where they contribute to global warming, landfill gas facilities can capture them, separate the methane, and combust it to generate electricity, heat, or both.

2.7 Wax

Naturally occurring wax, often referred to as *mineral wax*, occurs as a yellow to dark brown, solid substance that is composed largely of paraffin derivatives (Wollrab and Streibl, 1969). Fusion points vary from as low as 37 °C (99 °F) with a boiling range in excess of >370 °C (>700 °F). They are usually found associated with considerable mineral matter, as a filling in veins and fissures or as an interstitial material in porous rocks. The similarity in character of these native products is substantiated by the fact that, with minor exceptions where local names have prevailed, the original term *ozokerite* (*ozocerite*) has served without notable ambiguity for mineral wax deposits.

Ozokerite (*ozocerite*), from the Greek meaning *odoriferous wax*, is a naturally occurring hydrocarbon material composed chiefly of solid paraffin derivatives and cycloparaffin derivatives (i.e. hydrocarbon derivatives) (Wollrab and Streibl, 1969). Ozocerite usually occurs as stringers and veins that fill rock fractures in tectonically disturbed areas. It is predominantly paraffinic material (containing up to 90% non-aromatic hydrocarbon derivatives) with a high content (40%–50%) of normal or slightly branched paraffin derivatives as well as cyclic paraffin derivatives. Ozocerite contains approximately 85% carbon, 14% hydrogen, and 0.3% each of sulfur and nitrogen and is, therefore, predominantly a mixture of pure hydrocarbon derivatives; any non-hydrocarbon constituents are in the minority. Ozocerite is soluble in solvents (such as toluene, benzene, carbon disulfide, chloroform, and ethyl ether) that are commonly employed for dissolution of crude oil derivatives.

While naturally-occurring paraffin wax is of particular interest in some conventional crude oil reservoirs, it occurs in shale as part of the crude oil and becomes of interest when the crude oil from shale formations is blended with other paraffinic liquids that can lead to deposition of the wax during transportation and refining from which fouling can occur (Speight, 2014a, 2015b).

3. Tight gas and tight oil

Shale is a sedimentary rock that is predominantly comprised of very fine-grained clay particles deposited in a thinly laminated texture. These rocks were originally deposited as mud in low energy depositional environments, such as tidal flats and swamps, where the clay particles fall out of suspension. During the deposition of these sediments, organic matter is also deposited, which is measured when quoting the total organic content (TOC) Deep burial of this mud results (through time) in a layered rock (shale), which actually describes the very fine grains and laminar nature of the sediment, not rock composition, which can differ significantly between shale formations.

Shale formations are the most abundant form of sedimentary rock on Earth and they serve as the source rocks for hydrocarbon derivatives migrating into permeable reservoirs and act as seals for trapping oil and gas in underlying sediments. The matrix permeability of a typical shale formation (i.e. the ability of fluids to pass through the formation) is very low (often termed ultra-low) compared to conventional oil and gas reservoirs (Fig. 1.2) which means that hydrocarbon derivatives are effectively trapped and unable to flow under normal circumstances in shale, and usually only able to migrate out over geologic time (i.e. over millennia). The slow migration of hydrocarbon derivatives from shale formations into shallower sandstone and carbonate reservoirs has been the source of most conventional oil and gas fields, hence shales have historically been thought of as source and seal rocks, rather than potential reservoirs, but much of the hydrocarbon still remains bound in the shale.

Until recently, shale formations (and other tight low-permeability formations) were not targeted as source of natural gas and crude oil and, in fact, shale was considered an obstacle when companies were drilling in search for conventional sandstone reservoirs and limestone reservoirs. In fact, organic-rich shale deposits with the potential for the production of natural gas and crude oil referred to as both unconventional reservoirs and resource plays. In addtion, unconventional natural gas and crude oil reservoirs are those reservoirs are those that can be produced neither at economic flow rates nor in economic volumes unless the well is stimulated by hydraulic fracture treatment or accessed by (i) a horizontal wellbore, (ii) a

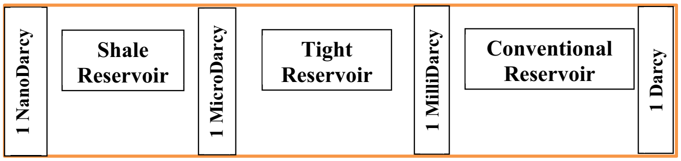

FIG. 1.2 Representation of the differences in permeability of shale reservoirs, tight reservoirs, and conventional reservoirs.

series of multilateral wellbores, or (iii) other techniques that are used to allow access more of the reservoir to the wellbore. This definition is also expanded to include formations composed of tight gas sands and carbonates, as well as resource plays such as coal and shale. The term resource play refers to sediments that act as both the reservoir and the source for natural gas and crude oil and, unlike conventional plays, resource plays cover a wide areal extent and are not typically confined to a specific geologic structure (Zhang et al., 2016).

Following from this, the terms *tight oil* and *tight gas* refer to crude oil (primarily light (low-density) sweet crude oil, i.e. low density, low sulfur crude oil) and natural gas, respectively, that are contained in formations such as shale or tight sandstone, where the low permeability of the formation makes it difficult for producers to extract the crude oil or natural gas except by unconventional techniques such as horizontal drilling and hydraulic fracturing. The term *unconventional oil* or *unconventional gas* are umbrella terms for crude oil and natural gas that are produced by methods that do not meet the criteria for conventional production. Thus, the terms tight oil and tight gas refer to natural gas trapped in organic-rich rocks dominated by shale while tight gas refers to natural gas trapped in sandstone or limestone formations that exhibit very low permeability and such formations may also contain condensate. Given the low permeability of these reservoirs, the gas must be developed via special drilling and production techniques including fracture stimulation (hydraulic fracturing) in order to be produced commercially (Gordon, 2012). Also, because of the haphazard introduction of new names into the crude oil lexicon, There is some confusion over tight oil terminology due to the term *shale gas* being used to describe natural gas in tight in tight formations, there is no correct equivalent for crude oil (Reinsalu and Aarna, 2015). The term *shale oil* is not a type of tight oil. While in a similar geologic formation, it is a formation containing kerogen and requires different production techniques. Before applying such terminology, it would be well to consider the available terminology that has been used by the industry for centuries and the new terminology so as not to confuse the reader.

Unlike conventional mineral formations containing natural gas and crude oil reserves, shale and other tight formations have low permeability, which naturally limits the flow of natural gas and crude oil. In such formations, the natural gas and crude oil are held in largely unconnected pores and natural fractures. Because of this, natural gas and crude oil properties of shale are quite different from conventional reservoirs. In addition to having gas present in the matrix system of pores similar to that found in conventional reservoir rocks, shale also has gas bound or adsorbed to the surface of organic materials in the shale. The relative contributions and combinations of free gas from matrix porosity and from desorption of adsorbed gas is a key determinant of the production profile of the well.

Hydraulic fracturing is the method commonly used to connect these pores and allow the gas to flow. Stimulation by hydraulic fracturing was the first technology used to unlock the natural gas and crude oil that was trapped in shale formations. This practice (Chapter 5) creates permeability in formations where the natural permeability was low-to-non-existent. Fracturing a shale formation (or, for that matter any tight or low-to-no permeability formation) produced high initial production flow rates, followed by rapid falloff. When it was realized that more contact with the reservoir was needed to avoid the rapid decline in production, a second enabling technology was employed − this was the ability to drill extended-reach horizontal wells that allowed contact with significantly more of the reservoir rock than is possible from vertical wellbores.

Thus, the process of producing natural gas and crude oil from tight deposits involves many steps in addition to hydraulic fracturing, all of which involve potential environmental impacts (Chapters 5 and 18) (Speight, 2016b). Hydraulic fracturing is often misused as an umbrella term to include all of the steps involved in gas and oil production from shale formations and tight formations. These steps include road and well pad construction, drilling the well, casing, perforating, hydraulic fracturing, completion, production, abandonment, and reclamation (Chapter 5). Thus, shale formations and other tight formations are impermeable formations that restrict migration of gases and fluids. Economic production of natural gas and crude oil from such formations was, until recently, unfeasible mainly related to the very low to ultralow permeability of the formation, a parameter that determines the connectivity and flow between pores where natural gas and crude oil reside (Chapters 2 and 3).

Tight sandstone formations and shale formations are heterogeneous and vary widely over relatively short distances. Thus, even in a single horizontal drill hole, the amount of gas or oil recovered may vary, as may recovery within a field or even between adjacent wells. This makes evaluation of tight plays (a *play* is a group of fields sharing geological similarities where the reservoir and the trap control the distribution of oil and gas). Because of the variability of the reservoirs − even reservoirs within a play − are different, decisions regarding the profitability of wells on a particular lease difficult. Furthermore, the production of crude oil from tight formations requires that at least 15%−20% v/v of the reservoir pore space is occupied by natural gas to provide the necessary reservoir energy to drive the oil toward the borehole; tight reservoirs which contain only oil cannot be economically produced (US EIA, 2013).

In tight shale reservoirs and other tight reservoirs, there are areas known as *sweet spots* which are preferential targets for drilling and releasing the gas and oil. In these areas, the permeability of the formation is significantly higher than the typical permeability of the majority of the formations. The occurrence of a sweet spot and the higher permeability may often result from open natural fractures, formed in the reservoir by natural stresses, which results in the creation of a dense pattern of fractures. Such fractures may have reclosed, filled in with other materials or may still be open. However, a well that can be connected through hydraulic fracturing to open natural fracture systems can have a significant flow potential.

The development of deep tight natural gas and tight crude oil resources, which are typically found thousands of feet below the surface of the Earth in tight, low-permeability shale formations. Until recently the vast quantities of natural gas in these formations were thought to be unrecoverable. Through the use of hydraulic fracturing, combined with recently improved horizontal drilling techniques, extraordinary amounts of natural gas and crude oil are produced from deep shale formations across the United States.

3.1 Tight gas

In the context of this book, the focus in on *shale gas* and, when necessary, reference will also be made to *tight gas*. In respects of the low permeability of these reservoirs, the gas must be developed via special techniques including stimulation by hydraulic fracturing (or *fraccing*, *fracking*) in order to be produced commercially.

Conventional gas typically is found in reservoirs with permeability greater than 1 milli-Darcy (mD) and can be extracted via traditional techniques (Fig. 1.2). A large proportion of the gas produced globally to date is conventional, and is relatively easy and inexpensive to extract. In contrast, unconventional gas is found in reservoirs with relatively low permeability (less than 1 mD) (Fig. 1.2) and hence cannot be extracted via conventional methods. However, there are several types of unconventional gas resources that are currently under production but the three most common types are (i) shale gas, (ii) tight gas, and (iii) coal bed methane although methane hydrates are often included with these gases under the general umbrella of *unconventional gas* but while included here for comparison and not the subject of this text. Generally, natural gas and crude oil are contained in the predominantly fine, low permeable sedimentary rocks, in consolidated clay-sized particles, at the scale of nanometers.

Shale formations are ubiquitous in sedimentary basins: they typically form approximately 80% of what a well will drill through. As a result, the main organic-rich shale formations have already been identified in most regions of the world. Their depths vary from near surface to several thousand feet underground, while their thickness varies from a tens of feet to several hundred feet. Often, enough is known related to the geological history (Table 1.6) to infer

TABLE 1.6 The geologic timescale.

Era	Period	Epoch	Duration (years × 10^6)[a]	Years ago (× 10^6)[a]
Cenozoic	Quaternary	Holocene	10,000 years ago[b]	
		Pleistocene	2	0.01
	Tertiary	Pliocene	11	2
		Miocene	12	13
		Oligocene	11	25
		Eocene	22	36
		Paleocene	71	58
Mesozoic	Cretaceous		71	65
	Jurassic		54	136
	Triassic		35	190
Paleozoic	Permian		55	225
	Carboniferous		65	280
	Devonian		60	345
	Silurian		20	405
	Ordovician		75	425
	Cambrian		100	500
Precambrian			3,380	600

[a] *Approximate.*
[b] *To the present.*

which shale formations are likely to contain gas (or oil, or a mixture of both). In that sense there may appear to be no real need for a major exploration effort and expense required for shale gas. However, the amount of gas present and particularly the amount of gas that can be recovered technically and economically cannot be known until a number of wells have been drilled and tested. In fact, it has been estimated that the amount of gas in shale formations is equivalent to the sum of coalbed methane and tight sandstone gas (Kuuskraa, 2006).

The existing form of shale gas is different from other natural gas. In the case of shale gas, the gas is stored by multiple mechanisms including slightly dissolved gas, free gas in macropores and natural fractures, and adsorbed gas on the internal surfaces of organic matter and micropores. Many factors have significant effects on the amount of gas that can be adsorbed (Kuuskraa, 2006; Jing et al., 2011). The content of organic matter and clay minerals is much higher in shale gas and the specific surface area of pores is large, which induces the content of adsorbed gas to be 20%–85% (Curtis, 2002). In the early development period, production arises mainly from free gas in macropores and fractures. The adsorbed gas desorbs gradually from the surface of micropores as formation pressure declines and then flows to the bottom of the well. The desorbed gas is the main yield source in the future for a long period. As a result, desorption of adsorbed gas is dominant in the exploitation of shale gas reservoirs.

For the most part, shale is composed of sedimentary rocks containing 30%–50% clay minerals (30–50% w/w), quartz (15–25% w/w), and organic matter (4–30% w/w) and the gas is in the form of dissolved gas, free gas, and adsorbed gas, and the adsorption mechanisms are similar (Kuuskraa, 2006). Thus, it must be recognized that each shale formation has different geological characteristics that affect the way gas can be produced, the technologies needed and the economics of production. Different parts of the (generally large) shale deposits will also have different characteristics: *small sweet spots* or *core areas* may provide much better production than the remainder of the formation, often because of the presence of natural fractures that enhance permeability (Hunter and Young, 1953).

Thus, natural gas and crude oil are found in organic-rich formations that are both source rock and reservoir. The expected value of permeability to gas flow is in the range of micro-to nanodarcy. The gas retained in such deposits is in form of adsorbed material on rock, trapped in pore spaces and as an inter-bedding material with shales (Kuuskraa, 2006). Although the shale gas is usually very clean, it is hard to recover from deposits because of the structural complexity and low hydrodynamic conductivity of shales.

Shale gas is part of a continuum of unconventional gas that progresses from tight gas sand formations, tight gas shale formations to coalbed methane in which horizontal drilling and fracture stimulation technology can enhance the natural fractures and recover gas from rocks with low permeability. Gas can be found in the pores and fractures of shales and also bound to the matrix, by a process known as adsorption, where the gas molecules adhere to the surfaces within the shale. During enhanced fracture stimulation drilling technology, fluid is pumped into the ground to make the reservoir more permeable, then the fractures are propped open by small particles, and can enable the released gas to flow at commercial rates. By drilling multi-lateral horizontal wells followed by hydraulic fracturing (Chapter 5), a greater rock volume can be accessed.

More specifically, shale gas is natural gas that is produced from a type of sedimentary rock derived from clastic sources often including mudstones or siltstones, which is known as shale. Clastic sedimentary rocks are composed of fragments (clasts) of pre-existing rocks that have been eroded, transported, deposited and lithified (hardened) into new rocks. Shales contain organic material which was laid down along with the rock fragments. In areas where conventional resource plays are located, shales can be found in the underlying rock strata and can be the source of the hydrocarbon derivatives that have migrated upwards into the reservoir rock. Furthermore, a tight-gas reservoir is commonly defined as is a rock with matrix porosity of 10% or less and permeability of 0.1 milliDarcy or less, exclusive of fracture permeability.

Shale gas resource plays differ from conventional gas plays in that the shale acts as both the source for the gas, and also the zone (also known as the reservoir) in which the gas is trapped. The very low permeability of the rock causes the rock to trap the gas and prevent it from migrating toward the surface. Also, the gas can be held in natural fractures or pore spaces, or can be adsorbed on to organic material. With the advancement of drilling and completion technology, this gas can be successfully exploited and extracted commercially as has been proven in various basins in North America. Aside from permeability, the key properties of shale, when considering gas potential – and the adsorption/desorption process – such as (i) pressure, (ii) temperature, (iii) the composition of shale, (iv) moisture, (v) the composition of the shale gas, and the thermal maturity of the shale rock system (Jing et al., 2011).

Pressure is an important factor that influences adsorption/desorption. When the pressure is low, the adsorption capacities increase sharply as the pressure increases; when the pressure reaches a critical desorption value, the adsorption is nearly saturated and adsorption tends to be stable, because the probability of gas molecules striking the shale surface and the absorption rate go up. At the same time, the density of gas molecules on the shale surface is increased. But a sufficiently specific interaction achieved when pressure reached the critical value. Because physisorption is reversible, the adsorbed gas begins to desorb when the pressure decreases. However, the desorption rate is slow as the pressure decreases when it is above the critical desorption pressure; when the pressure drops below the critical desorption pressure, shale gas starts to desorb rapidly.

Temperature has a considerable effect on adsorption capacity. The higher the temperature, the more intensely the gas molecules move because the kinetic energy is higher.

The *composition of the shale* through the total organic carbon content (TOC) of the shale – the total amount of organic material present in the rock, expressed as a percentage by weight – is also a key factor that influences the content of adsorbed gas. At the same temperature, the higher the total organic carbon content the better the adsorption capacity. Also, the higher the total organic carbon content, the more structured the microstructure is and the stronger the adsorption capacity is. Also, when the total organic carbon content is higher, a sufficient number of micropores exist in the organic matter (Sondergeld et al., 2010), which increases the specific surface area and adsorption volume.

The total organic carbon (TOC) is a fundamental attribute of shale and is a measure of organic richness. The total organic carbon content, together with the thickness of organic shale and organic maturity, are key attributes that aid in determining the economic viability of a shale play (Table 1.7). There is no unique combination or minimum amount of these factors that determines economic viability. The factors are highly variable between shale of different ages and can vary, in fact, within a single deposit or stratum of shale over short distances. At the low end of these factors, there is very little gas generated. At higher values,

TABLE 1.7 Example of the properties of selected shale plays.

	Antrim shale	Bakken shale	Barnett shale	Fayetteville shale	Haynesville shale
Basin	Michigan	Williston	Fort Worth	Arkoma	Texas-Louisiana Salt Basin
Basin area (square miles, approximate)	12,000	200,000	5,000	9,000	9000
Depth (ft)	500–2,500	2,000–10,000	7,000–8,500	3,000–5,000	10,500–13,500
Horizontal length (feet)		4,000–10,000	3,000–5,000	4,000–7,000	
Thickness (feet)	160	55–150	200–400	200–300	200–300
Age	Devonian	Late Devonian	Mississippian	Mississippian	Jurassic
Mineralogy (non-clay)	55–70		45–70		65–75
Thickness (ft)	160	140	200–400	200–300	200–300
Porosity % (min)	5	1	3	4	8
Porosity % (max)	12	15	7	9	9
Total organic carbon, % w/w (min)	5	4	2	2	0.5
Total organic carbon, % w/w (max)	15	11	5	5	4

more gas is generated and stored in the shale (if it has not been expelled from the source rock), and the shale can be a target for exploration and production. However, the presence of sufficient quantities of gas does not guarantee economic success, since shale has very low permeability and the withdrawal of gas is a difficult proposition that depends largely upon efficient drilling and completion techniques.

In more general terms, the higher the total organic content, the better the potential for hydrocarbon generation. The *thermal maturity* of the rock is a measure of the degree to which organic matter contained in the rock has been heated over time, and potentially converted into liquid and/or gaseous hydrocarbon derivatives. Because of the special techniques required for extraction, shale gas can be more expensive than conventional gas to extract. On the other hand, the in-place gas resource can be very large given the significant lateral extent and thickness of many shale formations. However, only a small portion of a shale gas resource may be theoretically producible and even less likely to be producible in a commercially viable manner. Therefore a key determinant of the success of a shale play is whether, and how much, gas can be recovered to surface and at what cost.

Moisture also affects the adsorption capacity of shale gas for hydrocarbon derivatives (Ross and Bustin, 2007). The adsorption capacity declines as the moisture increases and increased moisture will resulted in decreased adsorption of methane due to the competitive adsorption. Although there is no certain relation between moisture and adsorbed capacities of gas molecules, shale with a higher moisture content has a lower adsorption capacity than shale with a lower moisture content (Ross and Bustin, 2009; Jing et al., 2011).

The *composition of the shale gas* also affects the also influence the adsorption/desorption process. The gas adsorbed on shale is not always pure methane and also contains appreciable amounts of carbon dioxide, nitrogen as well as hydrocarbon derivatives of higher molecular weight the methane. The adsorption type of these gases is physisorption, and the interaction force is van der Waals forces. The greater the polarizability and ionization potential, the greater the van der Waals forces and the depth of potential well are. Because the polarizability and ionization potential of carbon dioxide, methane, and nitrogen decrease successively and the order of the relative adsorption capacities of these gases is carbon dioxide > methane > nitrogen (Jing et al., 2011).

The thermal maturity of the organic carbon-rock system is also a key property that affect the adsorption/desorption of gas from the shale. The thermal maturity of the rock is a measure of the degree to which organic matter contained in the rock has been heated over time, and potentially converted into liquid and/or gaseous hydrocarbon derivatives. Thermal maturity is measured using vitrinite reflectance (R_o).

3.2 Tight oil

In addition, oil from tight sandstone and from shale formations (*tight oil*) is another type of crude oil which various from a gas condensate-type liquid to a highly-volatile liquid (Table 1.8) (McCain, 1990; Dandekar, 2013; Speight, 2014a, 2016b; Terry and Rogers, 2014). Tight oil refers to the oil preserved in tight sandstone or tight carbonate rocks with low matrix permeability – in these reservoirs, the individual wells generally have no natural productivity or their natural productivity is lower than the lower limit of industrial oil flow, but

TABLE 1.8 Typical properties of fluids occurring in shale formations and in tight formations.

Constituents (% v/v)	Dry gas	Wet gas	Condensate	Volatile oil[a]
Carbon dioxide (CO_2)	0.1	1.4	2.4	1.8
Nitrogen (N_2)	2.1	0.3	0.3	0.2
Methane (C_1)	86.1	92.5	73.2	57.6
Ethane (C_2)	5.9	3.2	7.8	7.4
Propane (C_3)	3.6	1.0	3.6	4.2
Butane derivatives (C_4)	1.7	0.5	2.2	2.8
Pentane derivatives (C_5)	0.5	0.2	1.3	1.5
Hexane derivatives (C_{6+})		0.1	1.1	1.9
Heptane derivatives (C_{7+})		0.8	8.2	22.6

[a] *Representative of crude oil from tight formations.*

industrial oil production can be obtained under certain economic conditions and technical measures. Such measures include acid fracturing, multi-stage fracturing, horizontal wells, and multi-lateral wells.

The term *light tight oil* is also used to describe oil from shale reservoirs and tight reservoirs because the crude oil produced from these formations is light (low density, high API gravity) crude oil. The term *light crude oil* refers to low-density crude oil that flows freely at room temperature and these light crude oils have a higher proportion of low boiling hydrocarbon fractions resulting in higher API gravities (between 37° and 42°) (Speight, 2014a). However, the crude oil contained in shale reservoirs and in tight reservoirs will not flow to the wellbore without assistance from advanced drilling (such as horizontal drilling) and fracturing (hydraulic fracturing) techniques. There has been a tendency to refer to this oil as *shale oil*. This terminology is incorrect insofar as it is confusing and the use of such terminology should be discouraged as illogical since shale oil has (for decades, even centuries) been the name given to the distillate produced from oil shale by thermal decomposition (Lee, 1996; Scouten, 1990; Speight, 2012b, 2014a, 2016b). There has been the recent (and logical) suggestion that shale oil can be referred to as *kerogen oil* (IEA, 2013).

The challenges associated with the production of crude oil from shale formations are a function of the compositional complexity and the varied geological formations where they are found. These crude oils are light (low density), but they often contain high proportions of waxy constitunets and, for the most part, reside in oil-wet formations. These phenomena create some of the predominant difficulties associated with crude oil extraction from the shale formations, and include: (i) scale formation, (ii) salt deposition, (iii) paraffin wax deposits, (iv) destabilized asphaltene constituents, (v) equipment corrosion, and (vi) bacteria growth. Thus, multi-component chemical additives are added to the stimulation fluid to control these problems.

While crude oil from tight shale formations is characterized by a low content of asphaltene constituents and low-sulfur content, there can be a significant proportion of wax constitunets in the oil. These constituents may exhibit a broad distribution of the molecular weight. For example, paraffin carbon chains of C_{10} to C_{60} have been found and some tight crude oil may even have hydrocarbon carbon chains (wax) up to C_{72}. While this may be a relief from recovery of high-asphaltene high density low API gravity oils, the joy is short-lived and the deposition of waxy constituents can cause as many problems as asphaltene incompatibility. To control deposition and plugging in formations due to paraffin, a variety of wax dispersants are available for use. In upstream applications, the paraffin wax dispersants are applied as part of multifunctional additive packages where, for convenience, asphaltene stability and corrosion control can also be addressed simultaneously.

Scale deposits of calcite ($CaCO_3$), carbonate minerals, and silicate minerals must also be controlled during production or plugging problems arise. A wide range of scale additives is available. These additives can be highly effective when selected appropriately. Depending on the nature of the well and the operational conditions, a specific chemistry is recommended or blends of products are used to address scale deposition.

The most notable tight oil plays in North America include the Bakken shale, the Niobrara formation, the Barnett shale, the Eagle Ford shale, and the and the Miocene Monterey play of the San Joaquin Basin (California) in the United States, and the Cardium play (Alberta) in Canada. In many of these tight formations, the existence of large quantities of oil has been known for decades and efforts to commercially produce those resources have occurred sporadically with typically disappointing results. However, starting in the mid-decade of the current century, advancements in well drilling and stimulation technologies combined with high oil prices have turned tight oil resources into one of the most actively explored and produced targets in North America.

Furthermore, of the tight oil plays, perhaps the best understood is the Bakken which straddles the border between Canada and the US in North Dakota, Montana, and Saskatchewan. Much of what is known related to the exploitation of tight oil resources comes from industry experiences in the Bakken and the predictions of future tight oil resource development described in this study are largely based on that knowledge. The Bakken tight oil play historically includes three zones, or members, within the Bakken Formation. The upper and lower members of the Bakken are organic rich shales which serve as oil source rocks, while the rocks of the middle member may be siltstone formations, sandstone formations, or carbonate formations that are also typically characterized by low permeability and high oil content. Since 2008 the Three Forks Formation, another tight oil-rich formation which directly underlies the lower Bakken shale, has also yielded highly productive oil wells. Drilling, completion, and stimulation strategies for wells in the Three Forks Formation are similar to those in the Bakken and the light (low density, high API gravity) sweet crude oil that is produced from both plays has been geochemically determined to be essentially identical. Generally, the Three Forks Formation is considered to be part of the Bakken play, though the authors of published works will sometimes refer to it as the Bakken-Three Forks play.

Using the Bakken formation as a further example, the lower and upper Bakken shales are in the Williston Basin, sourcing reservoirs in the Bakken, upper Three Forks, and lower Lodgepole formations, which comprise the economically significant Bakken crude oil system (BPS). Estimates of the crude oil available are on the order of 10–400 billion barrels ($10-400 \times 10^9$ bbls). Important geochemical characteristic parameters of the Bakken shales – such as organic richness, kerogen type, source rock maturity, and kinetics – are derived from the total organic carbon (TOC) and pyrolysis analysis in Rock-Eval. Based on the total organic carbon content and pyrolysis results of Bakken samples, the lower and upper Bakken shales exhibit a wide range of total organic carbon, laterally from 1% w/w at shallower basin margins up to 35% w/w in the deeper basin, and vertically with recurrent patterns in each shale section. This high variation of the content of the total organic carbon content may result from mixed effects of the original depositional environment and progressive maturation.

Other known tight formations (on a worldwide basis) include the R'Mah Formation in Syria, the Sargelu Formation in the northern Persian Gulf region, the Athel Formation in Oman, the Bazhenov formation and Achimov Formation in West Siberia, Russia, the Coober Pedy in Australia, the Chicontepex formation in Mexico, and the Vaca Muerta field in Argentina (US EIA, 2011, 2013). However, tight oil formations are heterogeneous and vary widely over relatively short distances. Thus, even in a single horizontal drill hole, the amount of oil recovered may vary as may recovery within a field or even between adjacent wells. This makes evaluation of *shale plays* and decisions regarding the profitability of wells on a particular lease difficult and a tight reservoir which contains only crude oil (without natural gas as the pressurizing agent) cannot be economically produced (US EIA, 2011, 2013).

Success in extracting crude oil and natural gas from shale reservoirs depends largely on the hydraulic-fracturing process (Speight, 2016b) that requires an understanding of the mechanical properties of the subject and confining formations. In hydraulic-fracturing design, Young's modulus is a criterion used to determine the most-appropriate fracturing fluid and other design considerations. Young's modulus provides an indication of the fracture conductivity that can be expected under the width and embedment considerations. Without adequate fracture conductivity, production from the hydraulic fracture will be minimal, or nonexistent (Akrad et al., 2011; Speight, 2016b).

Typical of the crude oil from tight formations (*tight oil* — *tight light oil, and tight shale oil* have been suggested as alternate terms) is the Bakken crude oil, which is a low density, high API gravity highly volatile crude oil. Briefly, Bakken crude oil is a low density, high API gravity sweet (low-sulfur) crude oil that has a relatively high proportion of volatile constituents. The production of the oil also yields a significant amount of volatile gases (including propane and butane) and low-boiling liquids (such as pentane and natural gasoline), which are often referred to collectively as (light low boiling) naphtha. By definition, natural gasoline (sometime also referred to as *gas condensate*) is a mixture of low-boiling liquid hydrocarbon derivatives isolate from crude oil and natural gas wells suitable for blending with low boiling naphtha and/or refinery gasoline (Mokhatab et al., 2006; Speight, 2014a, 2019). Because of the presence of low-boiling hydrocarbon derivatives, low-boiling naphtha can become extremely explosive, even at relatively low ambient temperatures. Some of these gases may be burned off (flared) at the field well-head, but others remain in the liquid products extracted from the well (Speight, 2014a).

Bakken crude oil is considered to be a low-sulfur (*swee*t) crude oil and there have been increasing observations of elevated levels of hydrogen sulfide (H_2S) in the oil. Hydrogen sulfide is a toxic, highly flammable, corrosive, explosive gas (hydrogen sulfide) and there have been increasing observations of elevated levels of hydrogen sulfide in Bakken oil. Thus, the liquids stream produced from the Bakken formation will include the crude oil, the low-boiling liquids, and gases that were not flared, along with the materials and by-products of the hydraulic fracturing process. These products are then mechanically separated into three streams: (i) produced salt water, often referred to as brine, (ii) gases, and (iii) crude oil liquids, which include condensates, natural gas liquids, and low density high API gravity crude oil. Depending on the effectiveness and appropriate calibration of the separation equipment, which is controlled by the oil producers, varying quantities of gases remain dissolved and/or mixed in the liquids, and the whole is then transported from the separation equipment to the well-pad storage tanks, where emissions of volatile hydrocarbon derivatives have been detected as emanating from the oil.

Oil from tight shale formation is characterized by low-asphaltene content, low-sulfur content and a significant molecular weight distribution of the paraffinic wax content (Speight, 2014a, 2015a). Paraffin carbon chains of C_{10} to C_{60} have been found, with some shale oils containing carbon chains up to C_{72}. To control deposition and plugging in formations due to paraffin derivatives, the dispersants are commonly used. In upstream applications, these paraffin dispersants are applied as part of multifunctional additive packages where asphaltene stability and corrosion control are also addressed simultaneously (Speight, 2014a,b,c, 2015a,b). In addition, scale deposits of calcite ($CaCO_3$), other carbonate minerals (minerals containing the carbonate ion, CO_3^{2-}), and silicate minerals (minerals classified on the basis of the structure of the silicate group, which contains different ratios of silicon and oxygen) must be controlled during production or plugging problems arise. A wide range of scale additives is available which can be highly effective when selected appropriately. Depending on the nature of the well and the operational conditions, a specific chemistry is recommended or blends of products are used to address scale deposition.

Another challenge encountered with oil from tight shale formations – many of which have been identified but undeveloped – is the general lack (until recently) of transportation infrastructure. Rapid distribution of the crude oil to the refineries is necessary to maintain consistent refinery throughput – a necessary aspect of refinery design. Some pipelines are in use, and additional pipelines are being (and need to be) constructed to provide consistent supply of the oil to the refinery. During the interim, barges and railcars are being used, along with a significant expansion in trucking to bring the various the crude oil to the refinery. For example, with development of suitable transportation infrastructure, production of Eagle Ford tight oil is estimated to increase by a substantial amount to approximately 2,000,000 bpd by 2017. Similar expansion in crude oil production is estimated for Bakken and other identified (and perhaps as yet unidentified and, if identified, undeveloped) tight formations.

While the basic approach toward developing a tight oil play are expected to be similar from area to area, the application of specific strategies, especially with respect to well completion and stimulation techniques, will almost certainly differ from play to play, and often even within a given play. The differences depend on the geology (which can be very heterogeneous, even within a play) and reflect the evolution of technologies over time with increased experience and availability.

Finally, the properties of tight oil are highly variable. Density and other properties can show wide variation, even within the same field. The Bakken crude is a light sweet crude oil with an API of 42° and a sulfur content of 0.19% w/w. Similarly, Eagle Ford is a light sweet crude oil, with a sulfur content of approximately 0.1% w/w and with published API gravity between 40° API and 62° API.

In terms of refining, although tight oil is considered sweet (low sulfur content) and amenable to refinery options, this is not always the case. Hydrogen sulfide gas, which is flammable and poisonous, comes out of the ground with the crude oil and must be monitored at the drilling site as well as during transportation. Amine-based hydrogen sulfide scavengers are added to the crude oil prior to transport to refineries. However, mixing during transportation due to movement, along with a change in temperature that raises the vapor pressure of the oil, can cause the release of entrained hydrogen sulfide during offloading, thereby creating a safety hazard. For example, such crude oil that is loaded on railcars in winter and then transported to a warmer climate becomes hazardous clue to the higher vapor pressure. The shippers and receivers of the oil should be aware of such risks.

The constituents of *paraffin wax* [e.g. $CH_3(CH_2)_nCH_3$, where $n > 15$] are present in tight oil and remain on the walls of railcars, tank walls, and piping. The wax constituents are also known to foul the preheat sections of crude heat exchangers (before they are removed in the crude desalter) (Speight, 2015b). Paraffin wax constituents that stick to piping and vessel walls can trap amines against the walls which can create localized corrosion (Speight, 2014c). *Filterable solids* also contribute to fouling in the crude preheat exchangers and a tight crude can contain over seven times more filterable solids than a traditional crude oil. To mitigate filter plugging, the filters at the entrance of the refinery require automated monitoring because they need to capture large volumes of solids. In addition, wetting agents are added to the desalter to help capture excess solids in the water, rather than allowing the undesired solids to travel further downstream into the process.

In many refineries, *blending two or more crude oils* as the refinery feedstock is now standard operating procedure which allows the refiner to achieve the right balance of feedstock qualities. However, the blending of the different crude oils may cause problems if the crude oils being mixed are incompatible (Chapter 17) (Speight, 2014a). When crude oils are incompatible, there is increased deposition of any asphaltene constituents or the formation of two phases which accelerates fouling in the heat exchanger train downstream of the crude desalter (Speight, 2014a,c, 2015b). Accelerated fouling increases the amount of energy that must be supplied by the crude fired heater, which limits throughput when the fired heater reaches its maximum capacity and may also necessitate an earlier shutdown of the system for cleaning.

Mixing stable crude oil blends with asphaltic and paraffinic oils creates the potential for precipitating the unstable asphaltene constituents − a high content of paraffinic naphtha in tight oils also creates favorable conditions for precipitation of the asphaltene constituents (Speight, 2014a,c). It should be noted that the ratio of crude oils in a blend may have an impact on crude incompatibility. For example, a low amount of tight oil in a blend may not cause accelerated fouling whereas a blend containing a higher amount of tight oil may cause accelerated fouling. The key is the separation of any constituents that can cause fouling (Speight, 2014c).

Shale gas (also called *tight gas*) is a description for a field in which natural gas accumulation is locked in tiny bubble-like pockets within layered low-permeability sedimentary rock such as shale. The terms *shale gas* and *tight gas* are often used interchangeably but there are differences − while shale gas is trapped in rock, tight gas describes natural gas that is dispersed within low-porosity silt or sand areas that create a tight-fitting environment for the gas. Typically, tight gas refers to natural gas that has migrated into a reservoir rock with high porosity but low permeability. These types of reservoirs are not usually associated with oil and commonly require horizontal drilling and hydraulic fracturing to increase well output to cost-effective levels. In general, the same drilling and completion technology that is effective with shale gas can also be used to access and extract tight gas. Shell uses proven technology in responsible ways to access this needed resource.

Tight gas is the fastest growing natural gas resource in the United States and worldwide as a result of several recent developments (Nehring, 2008). Advances in horizontal drilling technology allow a single well to pass through larger volumes of a shale gas reservoir and, thus, produce more gas. The development of hydraulic fracturing technology has also improved access to shale gas deposits. This process requires injecting large volumes of water mixed with sand and fluid chemicals into the well at high pressure to fracture the rock, increasing permeability and production rates.

To extract tight gas, a production well is drilled vertically until it reaches the shale formation, at which point the wellbore turns to follow the shale horizontally. As drilling proceeds, the portion of the well within the shale is lined with steel tubing (casing.). After drilling is completed, small explosive charges are detonated to create holes in the casing at intervals where hydraulic fracturing is to occur. In a hydraulic fracturing operation, the fracturing fluid is pumped in at a carefully controlled pressure to fracture the rock out to several hundred feet from the well. Sand mixed with the fracturing fluid acts to prop these cracks open when the fluids are subsequently pumped out. After fracturing, gas will flow into the well bore and up to the surface, where it is collected for processing and sales.

Shale gas is natural gas produced from shale formations that typically function as both the reservoir and source rocks for the natural gas. In terms of chemical makeup, shale gas is typically a dry gas composed primarily of methane (60–95% v/v), but some formations do produce wet gas. The Antrim and New Albany plays have typically produced water and gas. Gas shale formations are organic-rich shale formations that were previously regarded only as source rocks and seals for gas accumulating in the strata near sandstone and carbonate reservoirs of traditional onshore gas development.

Thus, by definition, *shale gas* in the hydrocarbon gas present in organic rich, fine grained, sedimentary rocks (shale and associated lithofacies). The gas is generated and stored *in situ* in gas shale as both adsorbed gas (on organic matter) and free gas (in fractures or pores). As such, shale containing gas is a self-sourced reservoir. Low-permeable shale requires extensive fractures (natural or induced) to produce commercial quantities of gas.

Shale is a very fine-grained sedimentary rock, which is easily breakable into thin, parallel layers. It is a very soft rock, but it does not disintegrate when it becomes wet. The shale formations can contain natural gas, usually when two thick, black shale deposits *sandwich* a thinner area of shale. Because of some of the properties of the shale deposits, the extraction of natural gas from shale formations is more difficult and perhaps more expensive than that of conventional natural gas. Shale basins are scattered across the United States (Fig. 1.3).

There are several types of unconventional gas resources that are currently produced (i) deep natural gas – natural gas that exists in deposits very far underground, beyond conventional drilling depths, typically 15,000 feet or more, (ii) shale gas – natural gas that occurs in low-permeability shale formations, (iii) tight natural gas – natural gas that occurs in low-permeability formations, (iv) geo-pressurized zones – natural underground formations that are under unusually high pressure for their depth, (v) coalbed methane – natural gas that occurs in conjunction with coal seams, and (vi) methane hydrates – natural gas that occurs at low temperature and high pressure regions such as the sea bed and is made up of a lattice of frozen water, which forms a *cage* around the methane.

Coalbed methane is produced from wells drilled into coal seams which act as source and reservoir to the produced gas (Speight, 2013b). These wells often produce water in the initial production phase, as well as natural gas. Economic coalbed methane reservoirs are normally shallow, as the coal matrix tends to have insufficient strength to maintain porosity at depth. On the other hand, shale gas is obtained from ultra-low permeability shale formations that may also be the source rock for other gas reservoirs. The natural gas volumes can be stored in fracture porosity, within the micropores of the shale itself, or adsorbed onto the shale (Kuuskraa, 2006).

To prevent the fractures from closing when the pressure is reduced several tons of sand or other *proppant* is pumped down the well and into the pressurized portion of the hole. When the fracturing occurs millions of sand grains are forced into the fractures. If enough sand grains are trapped in the fracture, it will be propped partially open when the pressure is reduced. This provides an improved permeability for the flow of gas to the well.

It has been estimated that there is on the order of 750 trillion cubic feet (Tcf, 1×10^{12} ft^3) of technically recoverable shale gas resources in the United States and represents a large and very important share of the United States recoverable resource base and in addition, by

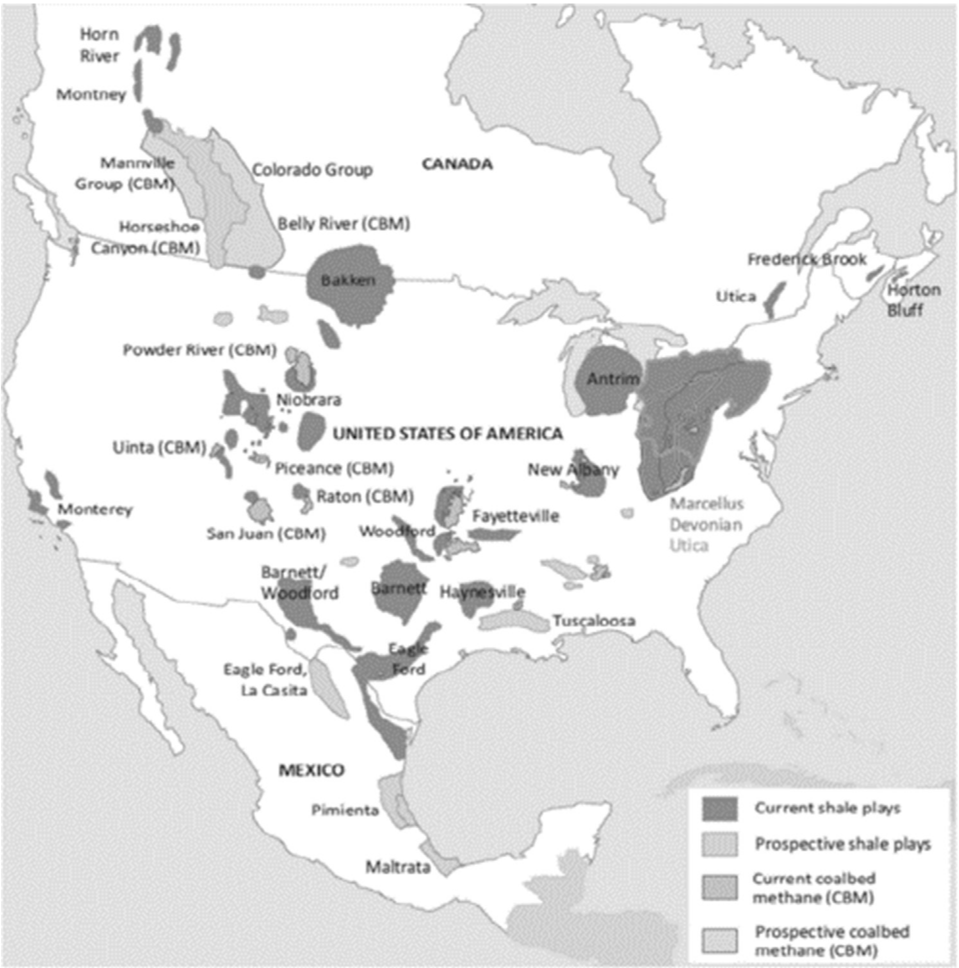

FIG. 1.3 Shale gas resources (shale gas plays) in the contiguous United States, Canada, and Mexico. *Adapted from Energy Information Administration, United States Department of Energy, Washington, DC.*

2035 approximately 46% of the natural gas supply of the United States will come from shale gas (US EIA, 2011).

Tight gas is a form of unconventional natural gas that is contained in a very low-permeability formation underground – usually hard rock or a sandstone or limestone formation that is unusually impermeable and non-porous (tight sand). In a conventional natural gas deposit, once drilled, the gas can usually be extracted quite readily and easily (Speight, 2019). Like shale gas reservoirs, tight gas reservoirs are generally defined as having low permeability (in many cases less than 0.1 milliDarcy (mD)) (Law and Spencer, 1993). Tight gas makes up a significant portion of the natural gas resource base – more than 21% v/v of the total recoverable natural gas in the United States is in tight formations and represents an extremely important portion of natural gas resources (GAO, 2012).

In tight gas sands (low-porosity sandstones and carbonate reservoirs), gas is produced through wells and the gas arose from a source outside the reservoir and migrates into the reservoir over geological time. Some *tight gas reservoirs* have also been found to be sourced by underlying coal and shale formation source rocks, as appears to be the case in the *basin-centered gas accumulations*.

However, extracting gas from a tight formation requires more severe extraction methods — several such methods do exist that allow natural gas to be extracted, including hydraulic fracturing and acidizing. It has been projected that shale formations and tight formations containing natural gas and crude oil with a permeability as low as one nanoDarcy may be economically productive with optimized spacing and completion of staged fractures to maximize yield with respect to cost. In any case, with all unconventional natural gas and crude oil reserves, the economic incentive must be there to encourage companies to extract this gas and oil instead of more easily obtainable, conventional natural gas and crude oil.

4. Origin

Unlike oil shale projects (Scouten, 1990; Lee, 1991; Speight, 2008, 2012b; Lee et al., 2014), the producible portions of deep shale oil and natural gas formations exist many thousands of feet below the surface — typically at depths ranging from 5000 to 12,000 feet underground. Tight formations scattered thought North America have the potential to produce not only gas (*tight gas*) but also crude oil (*tight oil*) (Law and Spencer, 1993; US EIA, 2011, 2013; Speight, 2013a; Islam, 2014). Such formations might be composted of shale sediments or sandstone sediments. In a conventional sandstone reservoir, the pores are interconnected so gas and oil can flow easily from the rock to a wellbore. In tight sandstones, the pores are smaller and are poorly connected by very narrow capillaries which results in low permeability. Tight gas and tight oil occur in sandstone sediments that have an effective permeability of less than 1 milliDarcy (<1 mD) (Fig. 1.2) and in addition, the tight oil is light oil with a high volatility (Tables 1.8 and 1.9). In addition, application of typical fractionating techniques (Fig. 1.1) to oil from tight formations would show very little, if any, resin and asphaltene constituents. The majority of the crude oil is typically low-boiling paraffin constituents and aromatic constituents.

One of the newest terms in the crude oil lexicon is the arbitrarily-named (even erroneously-named) *shale oil* which is used to describe crude oil that is produced from tight shale formations. This use of this term should be discontinued and when used it should not be confused with the older term *shale oil*, which is crude oil that is produced by the thermal treatment of oil shale and the ensuing decomposition of the kerogen contained within the shale (Scouten, 1990; Speight, 2012b) and does not fall under the umbrella definition of tight oil. Oil shale represents one of the largest unconventional hydrocarbon deposits in the world with an estimated eight trillion barrels (8×10^{12} bbls) of oil-in-place. Approximately six trillion barrels of oil-in-place is located in the United States including the richest and most concentrated deposits found in the Green River Formation in Colorado, Utah and Wyoming. Documented efforts to develop oil shale to produce shale oil in the US go back to approximate 1900, even earlier in Scotland (Scouten, 1990; Lee, 1991; Speight, 2008, 2012b; Lee et al., 2014). These

TABLE 1.9 Simplified differentiation between conventional crude oil and crude oil from shale formations.

Conventional crude oil
Medium-to-high API gravity Low-to-medium sulfur content Mobile in the reservoir High-permeability reservoir Primary recovery Secondary recovery May use tertiary recovery when reservoir energy is depleted
Tight oil
High API gravity Low sulfur content Immobile in the reservoir Low-to-zero permeability reservoir Primary, secondary, and tertiary methods of recovery ineffective Horizontal drilling into reservoir Fracturing (typically multi-fracturing) to release reservoir fluids

prior efforts have produced a wealth of knowledge regarding the geological description as well as technical options and challenges for development. Thus far, however, none of these efforts have produced a commercially viable business in the United States. There needs to be economically viable, socially acceptable and environmentally responsible development solutions.

Recently, the introduction of the term *shale oil* to define crude oil from tight shale formations is the latest term to add confusion to the system of nomenclature of crude oil-heavy oil-bitumen materials. The term has been used without any consideration of the original term shale oil produced by the thermal decompositon of kerogen in oil shale It is not quite analogous, but is certainly similarly confusing, to the term *black oil* that has been used to define crude oil by color rather than by any meaningful properties or recovery behavior (Speight, 2014a, 2015a).

Briefly, the characteristic feature of oil shale is the presence of kerogen (organic matter) from which oil is obtained by thermal treatment in the absence of oxygen (Scouten, 1990; Lee, 1991; Speight, 2008, 2012b; Lee et al., 2014). Shale oil is the main product of oil shale thermal treatment or processing (sometimes also called retorting). Utilization of oil shale is technically and economically feasible only if can at least 20% of its kerogen be converted into oil by thermal processing. If oil yield is less, there is a notation that the low-yield rock is a type of low-kerogen rock and is not true oil shale (Scouten, 1990; Lee, 1991; Speight, 2008, 2012b; Lee et al., 2014).

Generally, unconventional tight oil and natural gas are found at considerable depths in sedimentary rock formations that are characterized by very low permeability. While some of the tight oil plays produce oil directly from shales, tight oil resources are also produced from low-permeability siltstone formations, sandstone formations, and carbonate formations that occur in close association with a shale source rock. It is important to note that in the context of this text, the term tight oil does not include resources that are commonly known as "oil shales" which refers to oil or kerogen-rich shale formations that are either heated *in situ* and produced or if surface accessible mined and heated (Scouten, 1990; Lee, 1991; Speight, 2008, 2012b; Lee et al., 2014).

4.1 Origin

In the same manner as conventional natural gas and crude oil, natural gas in shale formations and in tight formations has, essentially, formed from the remains of plants, animals, and micro-organisms that lived millions of years ago. Though there are different theories on the origins of fossil fuels, the most widely accepted is that they are formed when organic matter (such as the remains of a plant or animal) is buried and compressed (even heated but the actual temperature of the maturation process remains unknown and, at best, is only speculative) for geological long time (millions of years).

More specifically, natural gas and crude oil in shale formations and in tight formations is generated in two different ways: (i) as a thermogenic product that is generated thermally from the organic matter in the matrix and (ii) as a biogenic product – an example is the Antrim shale gas field in Michigan in which the gas has been generated from microbes in areas of fresh water recharge (Shurr and Ridgley, 2002; Martini et al., 1998, 2003, 2004). Generally, more mature organic matter should generate higher gas-in-place resources than less mature organic matter, all other factors being equal. Organic maturity is often expressed in terms of vitrinite reflectance (% R_o), where a value above approximately 1.0%–1.1%, which indicates that the organic matter is sufficiently mature to generate gas and could be an effective source rock.

By way of explanation, the origin of natural gas and crude oil is an important aspect of evaluating shale reservoirs. For example, thermogenic systems often produce natural gas liquids with the methane, which can add value to production, whereas biogenic systems typically generate methane only. Thermogenic systems can also lead to the generation of carbon dioxide as an impurity in the natural gas, which must be removed during the gas processing operations (Chapter 8). Also, reservoirs classed as having thermogenic origins tend to flow at high rates, but are normally exploited through the extensive use of horizontal drilling and are therefore more expensive to develop than biogenic plays, which flow at lower rates and are exploited through shallow, closely spaced vertical wells instead.

Thus, the thermogenic product is associated with mature organic matter that has been subjected to relatively high temperature and pressure in order to generate hydrocarbon derivatives. Moreover, all other factors being equal the more mature organic matter should generate higher gas-in-place resources than less mature organic matter (Schettler and Parmely, 1990; Martini et al., 1998). However, generation of the gas and oil within individual shale formations and tight formations may differ significantly. Better knowledge is needed e.g. on basin modeling, petrophysical characterization, or gas flow in shales for an improved understanding of unconventional reservoirs.

Thermogenic maturation is a primary control on the proportion and composition of gas and liquids generated in shale during burial. As temperature increases, gas forms by decomposition of the organic matter and though decomposition of any retained oil. Highly mature systems tend to have much higher initial gas flow rates than low maturity systems because of gas charge and storage mechanisms. Thermal maturation increases the porosity associated with the structural transformation and conversion of organic matter. At low to medium thermal maturity, adsorption of hydrocarbon derivatives on organic matter may significantly contribute to oil retention and subsequent secondary thermal decomposition to gas. Fluid pressure buildup as a result of gas generation may also result in the formation of natural hydraulic fractures as well as microfractures, providing flow path for production as described in the Marcellus shale play.

The biogenic product can be associated with either mature or immature organic matter, and can add substantially to shale gas reserves. For example, the San Juan Basin coalbed methane (CBM) gas field is a mixture of both gases and has generated much of its gas from biogenic processes (Scott et al., 1994). Likewise, gas from the Antrim Shale Formation in the Michigan Basin is largely biogenic gas that has been generated in the last 10,000−20,000 years (Martini et al., 1998, 2003, 2004) and has produced more than 2.4 Tcf as of 2006. A mixture of gases is suggested for the New Albany Shale formation in the Illinois Basin (Wipf and Party, 2006) and is certainly possible in Alberta shale.

Tight gas resources and tight oil resources differ from conventional natural gas resources insofar as the shale acts as both the source for the gas and oil, and also the zone (the reservoir) in which the gas and oil are trapped. The very low permeability of the rock causes the rock to trap the gas or oil and prevent it from migrating toward the surface. The gas and oil can be held in natural fractures or pore spaces, or can be adsorbed onto organic material. With the advancement of drilling and completion technology, this gas can be successfully exploited and extracted commercially as has been proven in various basins in North America.

In the case of gas in shale formations, the path is similar to the formation of natural gas and crude oil in conventional reservoirs but the low permeability of the shale formation adds an extra dimension to the origin of the gas. Thus, as the ancient mud turns into shale during shallow burial, generally several hundred feet deep, in the so-called *nursery* (the place where the evolution of the organic matter commences), bacteria feed on the available organic matter (up to 10% w/w of the rock volume but generally less than five% w/w) and release biogenic methane as a byproduct. Natural gas is also generated during deep burial while the shale is in the *kitchen*, generally one mile or more deep, where heat and pressure crack the organic matter, including any oil already produced by the same heat and pressure, into smaller hydrocarbon derivatives, creating thermogenic methane. The actual temperature of the so-called kitchen is debatable and depends upon several factors, including the geothermal gradient (Speight, 2014a).

Some of the oil and gas manages to escape and migrate into the more porous rock of conventional reservoirs. In fact, the vast bulk of the conventional reserves of oil and gas in the world were generated in and escaped from organic-rich shales. But some oil and gas does not escape, as it is either trapped in the micropore spaces or attached to the organic matter within the shale. For example, the natural gas produced from the Second White Specks Shale of Alberta and Saskatchewan comes from shallow burial (it is shallow enough that gas is still being generated by bacteria), while the natural gas from the Devonian Horn River Basin and Triassic Montney shales was generated during deep burial. The Utica Shale of Quebec has both shallow and deep sections and there is potential for both biogenic and thermogenic natural gas, respectively (Shurr and Ridgley, 2002).

Thus, the origins of natural gas become important when evaluating shale-gas prospects. For example, thermogenic systems often produce natural gas liquids with the methane, which can add value to production, whereas biogenic systems generate methane only. Thermogenic systems can also lead to the generation of carbon dioxide as an impurity in the natural gas, which can increase greenhouse-gas emissions. Thermogenic plays tend to flow at high rates, but are normally exploited through the extensive use of horizontal drilling and are therefore more expensive to develop than biogenic plays, which flow at lower rates and are exploited through shallow, closely spaced vertical wells instead.

Kerogen is often cited as the precursor to oil and gas but, however, the role played by kerogen in the natural gas and crude oil maturation process is not fully understood (Tissot and Welte, 1978; Durand, 1980; Hunt, 1996; Scouten, 1990; Speight, 2014a). What obviously needs to be addressed more fully in terms of kerogen participation in crude oil generation is the potential to produce crude oil constituents from kerogen by low-temperature processes rather than by processes that involve the use of temperatures in excess of 250 °C (>480 °F) (Burnham and McConaghy, 2006; Speight, 2014a). If such geochemical studies are to be pursued, a thorough investigation is needed to determine the potential for such high temperatures being present during the main phase, or even various phases, of crude oil generation on order to give stronger indications that kerogen is a precursor to crude oil (Speight, 2014a).

4.2 Shale formations

In conventional gas reservoirs (GAO, 2012; Speight, 2014a, 2019), oil and gas are fairly mobile and easily move through the permeable formation because of buoyancy (they have a lower density than the water in the same formation and therefore rise) until they are trapped against an impermeable rock (i.e. a seal) that prevents further movement. This leads to localized pools of oil and gas while the rest of the formation is filled with water. However, both biogenic and thermogenic shale gas, remains where it was first generated and can be found in three forms: (i) free gas in the pore spaces and fractures, (ii) adsorbed gas, where the gas is electrically stuck to the organic matter and clay, and (iii) a small amount of dissolved gas that is dissolved in the organic matter. In such reservoirs, typically an impermeable shale formation is either the basement rock or the cap rock of a sandstone formation thereby preventing any fluids within the sandstone from escaping from the formation or migrating to another formation.

By way of definition and in the context of this book, a shale play is a defined geographic area containing an organic-rich fine-grained sedimentary rock that underwent physical and chemical compaction during diagenesis to produce the following characteristics: (i) clay to silt sized particles, (ii) high % of silica, and sometimes carbonate minerals, (iii) thermally mature, (iv) hydrocarbon-filled porosity − on the order of 6%−14%, (v) low permeability − on the order of <0.1 mD, (vi) large areal distribution, and (vii) fracture stimulation required for economic production.

In the current context, natural gas and crude oil from shale formations are natural gas and crude oil that is produced from a type of sedimentary rock derived from clastic sources often including mudstone or siltstone, which is known as shale. Clastic sedimentary rocks are composed of fragments (clasts) of pre-existing rocks that have been eroded, transported, deposited and lithified (hardened) into new rocks. Shale deposits typically contain organic material which was laid down along with the rock fragments.

Shale is a sedimentary rock that was once deposited as mud (clay and silt) and is generally a combination of clay minerals, silica minerals (e.g. quartz), carbonate minerals (calcite or dolomite), and organic material. While shale formations are generally considered to be rich in clay minerals, the proportions of the constituents are more than likely to be highly variable.

Shale formations and silt formations are the most abundant sedimentary rocks in the crust of the Earth. In crude oil geology, organic shale formations are source rocks as well as seal rocks that trap oil and gas (Speight, 2014a,b,c). In reservoir engineering, shale formations are flow barriers. In drilling, the bit often encounters greater shale volumes than reservoir sands. In seismic exploration, shale formations interfacing with other rocks often form good seismic reflectors. As a result, seismic and petrophysical properties of shale formations and the relationships among these properties are important for both exploration and reservoir management. Shale formations are a worldwide occurrence and the organic-rich shale deposits with potential for natural gas and crude oil production hydrocarbon production are referred to as both unconventional reservoirs and resource plays – unconventional reservoirs refer to low-permeability to ultralow-permeability sediments. Also, unconventional reservoirs are those reservoirs from which the resource (natural gas or crude oil) cannot be produced neither at economic flow rates nor in economic volumes unless the well is stimulated by hydraulic fracture treatment or accessed by a horizontal wellbore, multilateral well bores or some other technique to expose more of the reservoir to the wellbore. This definition includes formations composed of tight sands and carbonates, as well as coal seams and oil shale formations (Scouten, 1990; Speight, 2013b). The term resource play refers to sediments that act as both the reservoir and the source for hydrocarbon derivatives. Unlike conventional plays, resource plays cover a wide areal extent and are not typically confined to any particular geologic structure.

More specifically, shale is a geological rock formation rich in clay, typically derived from fine sediments, deposited in fairly quiet environments at the bottom of seas or lakes, having then been buried over the course of millions of years. Shale formations can serve as pressure barriers in basins, as top seals, and as reservoirs in shale gas plays. More technically, shale is a fissile, terrigenous sedimentary rock in which particles are mostly of silt and clay size (Blatt and Tracy, 2000). In this definition, *fissile* refers to the ability of the shale to split into thin sheets along bedding and *terrigenous* refers to the origin of the sediment. In many basins, the fluid pressure of the aqueous system becomes significantly elevated, leading to the formation of a hydro-fracture, and fluid bleed-off. However, the occurrence of a natural hydro-fracture is an unlikely process in the circumstances that exist in most basins.

Shale is composed mainly of clay-size mineral grains, which are usually clay minerals such as illite, kaolinite and smectite. Shale usually contains other clay-size mineral particles such as quartz, chert, and feldspar. Other constituents might include organic particles, carbonate minerals, iron oxide minerals, sulfide minerals and heavy mineral grains and the presence of such minerals in shale is determined by the environment under which the shale constituents were. Shale formations may also exist in thin beds or laminae of sandstone (SiO_2), limestone ($CaCO_3$), or dolostone, a sedimentary carbonate rock that contains a high proportion of the mineral dolomite ($CaCO_3 \cdot MgCO_3$). The mud – in the form of microscopic mineral particles – was deposited in deep, quiet (calm) water such as in large lakes or deep seas and oceans. The organic matter in the mud was algae, plant matter, or plankton that died and sank to the sea floor or lake bed before being buried.

Shale comes in two general varieties based on organic content: (i) dark colored or (ii) light colored. Dark colored shale formations (sometime referred to as black shale formations) are organic-rich, whereas the lighter colored shale formations have a relatively content of organic material and are often referred to as organic-lean formations. Organic-rich shale formations were deposited under conditions of little or no oxygen in the water, which preserved the organic material from decay. The organic matter was mostly plant debris that had accumulated with the sediment. Black organic shale formations are the source rock for many of the oil and natural gas deposits of the world. These black shale formations obtain their black color from tiny particles of organic matter that were deposited with the mud from which the shale formed. As the mud was buried and warmed within the Earth some of the organic material was transformed into oil and natural gas.

Thus, a *shale reservoir* (*shale play*) is similar on a worldwide basis insofar as organic-rich, gas-prone shale is generally difficult to *discover*. In all cases, a thorough understanding of the fundamental geochemical and geological attributes of shale is essential for resource assessment, development and environmental stewardship. Four properties that are important characteristics in each shale gas play are: (i) the maturity of the organic matter, (ii) the type of gas generated and stored in the reservoir – biogenic gas or thermogenic gas, (iii) the total organic carbon content of the strata, and (iv) the permeability of the reservoir. A *tight reservoir* (*tight sands*) is a low-permeability sandstone reservoir that produce primarily dry natural gas. A tight gas reservoir is one that cannot be produced at economic flow rates or recover economic volumes of gas unless the well is stimulated by a large hydraulic fracture treatment and/or produced using horizontal wellbores. This definition also applies to coalbed methane and tight carbonate reservoirs – shale gas reservoirs are also included by some observers (bit not in this text).

A black color in sedimentary rocks almost always indicates the presence of organic materials. Just one or two percent organic materials can impart a dark gray or black color to the rock. In addition, this black color almost always implies that the shale formed from sediment deposited in an oxygen-deficient environment. Any oxygen that entered the environment quickly reacted with the decaying organic debris. If a large amount of oxygen was present the organic debris would all have decayed. An oxygen-poor environment also provides the proper conditions for the formation of sulfide minerals such as pyrite, another important mineral found in most black shale sediments or formations. The presence of organic debris in black shale formations makes them the candidates for oil and gas generation. If the organic material is preserved and properly heated after burial oil and natural gas might be produced. The Barnett Shale, Marcellus Shale, Haynesville Shale Fayetteville Shale and other gas producing rocks are all dark gray or black shale formations that yield natural gas.

Specifically, the Barnett Shale of Texas was the first major natural gas field developed in a shale reservoir rock. Producing gas from the Barnett Shale was a challenge because the pore spaces in shale are so tiny that the gas has difficulty moving through the shale and into the well. Drillers discovered that the permeability of the shale could be increased by pumping water down the well under pressure that was high enough to fracture the shale. These fractures liberated some of the gas from the pore spaces and allowed that gas to flow to the well (hydraulic fracturing, hydrofracing).

The oil and natural gas migrated out of the shale and upwards through the sediment mass because of their low density. The oil and gas were often trapped within the pore spaces of an overlying rock unit such as a sandstone formation. These types of oil and gas deposits are known as *conventional reservoirs* because the fluids can easily flow through the pores of the rock and into the extraction well.

A more technical definition of a *shale formation* is: a fissile, terrigenous sedimentary rock in which particles are mostly of silt and clay size in which the term *fissile* refers to the ability of the rock to split into thin sheets along bedding while the term *terrigenous* refers to the origin of the sediment and that it (the sediment) is the product of weathering of rocks (Blatt and Tracy, 2000). In addition, a *bed* is layer of sediment thicker than 1 cm, whereas a lamina (plural: laminae) is a layer of sediment, typically thinner than one centimeter (Blatt and Tracy, 2000). Also, the pore spaces in shale, through which the natural gas must move if the gas is to flow into any well, are on the order of one thousand times smaller than the pores in a conventional sandstone reservoir (Bowker, 2007). The gaps that connect pores (the pore throats) are smaller still, only 20 times larger than a single methane molecule. Therefore, a shale formation has very low permeability. However, fractures (natural fractures) which act as conduits for the movements for natural gas, may naturally exist in the shale and increase the permeability of the formation.

On a more physical note, typical shale formations can be anywhere from twenty feet to a mile or so thick and extend over very wide geographic areas, a gas shale reservoirs is often referred to as a *resource play*, where natural gas resources are widely distributed over extensive areas (perhaps several fields) rather than concentrated in a specific location. The volume of natural gas contained within a resource play increases as the thickness and areal extent of the deposit grows. Individual gas shale formations may have a billion cubic feet (1×10^9 ft^3) or even e a trillion cubic feet (1×10^{12} ft^3) of gas in place spread over hundreds to thousands of square miles. The difficulty lies in extracting even a small fraction of that gas.

Shale formations exhibit a wide range of mechanical properties and significant anisotropy reflecting their wide range of material composition and fabric anisotropy (Sone, 2012). The elastic properties of these shale rocks are successfully described by tracking the relative amount soft components (clay and solid organic materials) in the rock and also acknowledging the anisotropic distribution of the soft components. Gas shale formations also possess relatively stronger degree of anisotropy compared to other organic-rich shale formations, possibly due to the fact that these rocks come from peak-maturity source rocks. The deformational properties are influenced by the amount of soft components in the rock and exhibited mechanical anisotropy. The pore spaces in shale, through which the natural gas must move if the gas is to flow into any well, are as much as one thousand times smaller than pores in conventional sandstone reservoirs. The gaps that connect pores (the pore throats) are smaller still, only twenty times larger than a single methane molecule. Therefore, shale has very low permeability but natural or induced fractures, which act as conduits for the movement for natural gas, will increase the permeability of the shale. There is also the possibility (only assiduous geological studies will tell) of hybrid gas shale formation, where the originally deposited mud was rich in sand or silt. These foreign minerals (sand, silt) result in a natural higher permeability for the shale formation and result in greater susceptibility of the shale to hydraulic fracturing.

A shale reservoir originated as a formation that is an organic-rich, and fine-grained sediment that contains natural gas or crude oil (Bustin, 2006; Bustin et al., 2008). When a significant amount of organic matter has been deposited with the sediments, the shale rock can contain organic solid material (kerogen). The properties and composition of shale place it in the category of sedimentary rocks known as *mudstones*. Shale is distinguished from other mudstones because it is laminated and fissile — the shale is composed of many thin layers and readily splits into thin pieces along the laminations.

However, the term *shale* is used very loosely and does not describe the lithology of the reservoir. Lithological variations in American shale gas reservoirs indicate that natural gas is retained in the reservoir not only in shale but also a wide spectrum of lithology and texture from mudstone (i.e., non-fissile shale) to siltstone and fine-grained sandstone, any of which may be of siliceous or carbonate composition. For example, in many basins, much of what is described as shale is often siltstone, or encompasses multiple rock types, such as siltstone or sandstone laminations interbedded with shale laminations or beds. The presence of multiple rock types in organic-rich shale formations implies that there are multiple gas and oil storage mechanisms, as gas or oil constitunets may be adsorbed on organic matter and stored as free gas in micropores and macropores. Laminations serve a dual purpose because they both store free gas and oil and transmit gas and oil desorbed from organic matter in shale to the well bore. The determination of the permeability and porosity of the laminations, and the linking of these laminations via a hydraulic fracture to the well bore, are key requirements for efficient development.

Briefly, horizontal drilling and hydraulic fracturing revolutionized drilling technology and paved the way for developing several giant natural gas fields. These include the Marcellus Shale in the Appalachians, the Haynesville Shale in Louisiana and the Fayetteville Shale in Arkansas. These enormous shale reservoirs hold enough natural gas to serve all of the requirements of the United States for twenty years or more. Hydraulic properties are characteristics of a rock such as permeability and porosity that reflect its ability to hold and transmit fluids such as water, oil or natural gas. In this respect, shale has a very small particle size so the interstitial spaces are very small. In fact they are so small that oil, natural gas and water have difficulty moving through the rock. Shale can therefore serve as a cap rock for oil and natural gas traps and it also is an aquiclude that blocks or limits the flow of underground water.

Additionally, solute or solution gas may be held in micropores and nano-pores of bitumen (Bustin, 2006) and may be an additional source of gas, although traditionally this is thought to be a minor component. Free gas may be a more dominant source of production than desorbed gas or solute gas in a shale gas reservoir. Determining the percentage of free gas versus solute gas versus desorbed gas is important for resource and reserve evaluation and is a significant issue in gas production and reserve calculations, as desorbed gas diffuses at a lower pressure than free gas.

In areas where conventional resources are located, shale can be found in the underlying rock strata and can be the source of the hydrocarbon derivatives that have migrated upwards into the reservoir rock. Over time, as the rock matures, hydrocarbon derivatives are produced from the kerogen. These may then migrate, as either a liquid (crude oil) or a gas (natural gas), through existing fissures and fractures in the rock until they reach the surface of the Earth or until the hydrocarbon derivatives become trapped by strata of impermeable rock. Porous areas beneath these traps collect the hydrocarbon derivatives in a conventional reservoir, frequently of sandstone.

Shale gas reservoirs generally allow recovery of less gas (from <5 to 20% v/v) relative to conventional gas reservoirs (approximately 50–90% v/v) (Faraj et al., 2004), although the naturally well-fractured Antrim Shale may have a recovery factor as high as 50–60% v/v. More recently, there have been suggestions that the Haynesville shale in Louisiana may have a recovery factor as high as 30% (Durham, 2008). To increase the recovery factor, innovation in drilling and completion technology is paramount in low-permeability shale reservoirs. In the initial state of pool development, permeability *sweet spots* are often sought because they result in higher rates of daily production and increased recovery of gas compared to less permeable shale.

Shale gas reservoirs generally recover less gas (from <5 to 20% v/v) relative to conventional gas reservoirs (approximately 50–90% v/v) (Faraj et al., 2004), although the naturally well-fractured Antrim Shale may have a recovery factor as high as 50–60% v/v. More recently, there have been suggestions that the Haynesville shale in Louisiana may have a recovery factor as high as 30% (Durham, 2008). To increase the recovery factor, innovation in drilling and completion technology is paramount in low-permeability shale reservoirs. In the initial state of pool development, permeability *sweet spots* are often sought because they result in higher rates of daily production and increased recovery of gas compared to less permeable shale. But these sweet spots are small, relative to the size of unconventional pools, so horizontal drilling and new completion techniques (such as *staged fracs* and *simultaneous fracs*) (Cramer, 2008) were developed to improve economics both inside and outside of *sweet spots*. The result is a significant increase in economically producible reserves and a substantial extension of the area of economically producible gas.

Shale gas resources differ from conventional natural gas resources insofar as the shale acts as both the source for the gas, and also the zone (the reservoir) in which the gas is trapped. The very low permeability of the rock causes the rock to trap the gas and prevent it from migrating toward the surface. The gas can be held in natural fractures or pore spaces, or can be adsorbed onto organic material. With the advancement of drilling and completion technology, this gas can be successfully exploited and extracted commercially as has been proven in various basins in North America. However, well-fractured shale that typically contains an abundance of mature organic matter and is deep or under high pressure will yield a high initial flow rate. For example, horizontal wells in the Barnett with a high initial reservoir pressure can yield an initial flow rate of a few million cubic feet per day after induced fracturing. However, after the first year gas flow may be dominated by the rate of diffusion from the matrix to the induced fractures (Bustin et al., 2008).

Aside from permeability, the key properties of shale, when considering gas and oil potential, are (i) total organic content and (ii) thermal maturity. The *total organic content* is the total amount of organic material present in the rock, expressed as a percentage by weight. Generally, the higher the total organic content, the better the potential for hydrocarbon generation. The *thermal maturity* of the rock is a measure of the degree to which organic matter contained in the rock has been heated over time, and potentially converted into liquid and/or gaseous hydrocarbon derivatives.

The gas and oil storage properties of shale are quite different from conventional reservoirs. In addition to having gas or oil present in the matrix system of pores similar to that found in conventional reservoir rocks, shale also has gas bound or adsorbed to the surface of organic materials in the shale. The relative contributions and combinations of free gas from matrix porosity and from desorption of adsorbed gas is a key determinant of the production profile of the well.

The amount and distribution of gas or oil within the shale is determined by, among other things, the initial reservoir pressure, the petrophysical properties of the rock, and its adsorption characteristics. During production there are three main processes at play. Initial gas production is dominated by depletion of gas from the fracture network. This form of production declines rapidly due to limited storage capacity. After the initial decline rate stabilizes, the depletion of gas stored in the matrix becomes the primary process involved in production. The amount of gas or oil held in the matrix is dependent on the particular properties of the shale reservoir which can be hard to estimate. Secondary to this depletion process is desorption whereby adsorbed gas is released from the rock as pressure in the reservoir declines. The rate of gas production via the desorption process depends on there being a significant drop in reservoir pressure. Pressure changes typically advance through the rock very slowly due to low permeability. Tight well spacing can therefore be required to lower the reservoir pressure enough to cause significant amounts of adsorbed gas to be desorbed.

The ultimate recovery (Chapter 4) of the gas or oil in place surrounding a particular shale well can be in the order of 28%−40% of the original volume in place whereas the recovery per conventional well may be as high as 60%−80% v/v. The development of shale gas plays, therefore, differs significantly from the development of conventional resources. With a conventional reservoir, each well is capable of draining oil or gas over a relatively large area (dependent on reservoir properties). As such, only a few wells (normally vertical) are required to produce commercial volumes from the field. With shale gas projects, a large number of relatively closely spaced wells are required to produce large enough volumes to make the plays economic. As a result, many wells must be drilled in a shale play to drain the reservoir sufficiently − in the Barnett shale resource in the US, the drilling density can exceed one well per 60 acres.

Total organic carbon (TOC) is a fundamental attribute of tight gas and tight oil formations and is a measure of organic richness. The content of total organic carbon together with the thickness of organic shale and organic maturity are key indicators that can be used to determine the economic viability of a shale gas play. There is no unique combination or minimum amount of these factors that determines economic viability. The factors are highly variable between shale of different ages and can vary, in fact, within a single deposit or stratum of shale over short distances.

Induced fracturing may occur many times during the productive life of a shale gas reservoir (Walser and Pursell, 2007). Shale, in particular, exhibits permeability lower than coalbed methane or tight gas and, because of this, forms the source and seal of many conventional oil and gas pools. Hence, not all shale is capable of sustaining an economic rate of production. In this respect, permeability of the shale matrix is the most important parameter influencing sustainable shale gas production (Bennett et al., 1991a,b; Davies et al., 1991; Davies and Vessell, 2002; Gingras et al., 2004; Pemberton and Gingras, 2005; Bustin et al., 2008).

To sustain yearly production, gas must diffuse from the low-permeability matrix to induced or natural fractures. Generally, higher matrix permeability results in a higher rate of diffusion to fractures and a higher rate of flow to the wellbore (Bustin et al., 2008).

Furthermore, more fractured shale (i.e., shorter fracture spacing), given sufficient matrix permeability, should result in higher production rates (Bustin et al., 2008), a greater recovery of hydrocarbon derivatives and a larger drainage area (Cramer, 2008; Walser and Pursell, 2007). Additionally, microfractures within shale matrix may be important for economic production; however, these microfractures are not easily determined *in situ* in a reservoir (Tinker and Potter, 2007), and only further research and analysis will determine their role in shale gas production.

An additional factor to consider is shale thickness. The substantial thickness of shale is one of the primary reasons, along with a large surface area of fine-grained sediment and organic matter for adsorption of gas, that shale resource evaluations yield such high values. Therefore, a general rule is that thicker shale is a better target. Shale targets such as the Bakken oil play in the Williston Basin (itself a hybrid conventional-unconventional play), however, are less than 50 m thick in many areas and are yielding apparently economic rates of flow. The required thickness to economically develop a shale gas target may decrease as drilling and completion techniques improve, as porosity and permeability detection techniques progress in unconventional targets and, perhaps, as the price of gas increases. Such a situation would add a substantial amount of resources and reserves to the province.

4.3 Tight formations

The term *tight formation* refers to a formation consisting of extraordinarily impermeable, hard rock. Tight formations are relatively low permeability, non-shale, sedimentary formations that can contain oil and gas.

A *tight reservoir* (*tight sands*) is a low-permeability sandstone reservoir that produce primarily dry natural gas. A tight gas reservoir is one that cannot be produced at economic flow rates or recover economic volumes of gas unless the well is stimulated by a large hydraulic fracture treatment and/or produced using horizontal wellbores. This definition also applies to coalbed methane and tight carbonate reservoirs − shale gas reservoirs are also included by some observers (but not in this text). Typically, tight formations which formed under marine conditions contain less clay and are more brittle, and thus more suitable for hydraulic fracturing than formations formed in fresh water which may contain more clay. The formations become more brittle with an increase in quartz content (SiO_2) and carbonate content (such as calcium carbonate, $CaCO_3$, or dolomite, $CaCO_3 \cdot MgCO_3$).

By way of explanation, in a conventional sandstone reservoir the pores are interconnected so that natural gas and crude oil can flow easily through the reservoir and to the production well. However, in tight sandstone formations, the pores are smaller and are poorly connected (if at all) by very narrow capillaries which results in low permeability and immobility of the natural gas and crude oil. Such sediments typically have an effective permeability of less than 1 milliDarcy (<1 mD) (Fig. 1.2) and, in the case of a crude oil reservoir, the oil is a highly volatile low density high API gravity low sulfur crude oil (Tables 1.8 and 1.9). In addition, application of typical fractionating techniques (Fig. 1.1) to the crude oil from tight formations shows the relative absence (compared to conventional crude oil) of resin constituents and asphaltene constituents. The majority of the crude oil is typically low-boiling paraffin constituents (including high molecular weight waxy constitunets) and aromatic constituents.

4.4 Geopressurized zones

Geopressurized zones are natural underground formations that are under high pressure that is not always expected from the depth of the zone. These areas are formed by layers of clay minerals that are deposited and compacted on top of (or above) more porous, absorbent material such as sandstone or silt. Water and natural gas that are present in this clay formation are forced out by the rapid compression and enter into the more porous sandstone or silt deposits. The natural gas or crude oil is deposited in this sandstone or silt under very high pressure (*geopressure*). Geopressurized zones are typically located at great depths − on the order of, usually 10,000−25,000 feet below the surface of the Earth. The combination of the above factors makes the extraction of natural gas or crude oil located in geopressurized zones quite complicated.

Most of the geopressurized natural gas in the US is located in the Gulf Coast region. Although the amount of natural gas in these geopressurized zones is uncertain, it is estimated to be on the order of 5000−49,000 trillion cubic feet (5000 to 49,000 $\times 10^{12}$ ft^3) or 5−49 quadrillion cubic feet (5 to 40 $\times 10^{15}$ ft^3). Thus, geopressurized zones offer an incredible opportunity for increasing the natural gas supply of the United States.

5. Oil shale and shale oil

Reference was made earlier to the erratic and incorrect terminology by which tight oil has been referred to as *shale oil*. This terminology is also confusing and the use of such terminology should be discouraged as illogical since shale oil has been (for decades) the name given to the distillate produced from oil shale by thermal decomposition (Lee, 1996; Scouten, 1990; Speight, 2012b, 2014a, 2016b). Therefore, it is appropriate at this point to clarify the names oil shale and shale oil.

Oil shale is found at shallow depths, from surface outcrops to 3000 feet deep. It is a very low-permeability sedimentary rock that contains a large proportion of kerogen, a mixture of solid organic compounds. In kerogen-containing shale reservoirs (IEA, 2013), conversion of the kerogen into liquid oil (shale oil, kerogen oil) has not taken place because the high temperatures required have not been experienced. Oil shale consists of minerals of variable composition mixed with organic matter commonly occurring finely dispersed in the matrix or in thin laminae (Eseme et al., 2007). To allow an appreciation of their complex behavior especially at high temperature, it is useful to consider an oil shale as a three-phase material: (i) minerals, (ii) kerogen, and (iii) pore fill − the bulk mechanical properties strongly depend on the volume fractions of these phases. Most studies on mechanical properties of oil shales are accompanied by an indication of organic matter content. Commonly, the parameter reported is the oil yield given in gallons per ton (GPT, 1 gallon = 4.2 L) determined by the standardized Fischer assay technique (heating 100 g of crushed rock to 500 °C, 930 °F).

Oil shale is a prolific synthetic fuel resources on Earth and copious deposits of oil shale are found in a number of countries, including Australia, Brazil, China, Estonia, Israel, Jordan, Mongolia, and the United States. Preliminary geologic surveys and evidence from oil shale outcrops indicate that Mongolia may also have oil shale resources of a size and quality that are commercially viable. The United States is recognized as having the largest oil shale deposits in the world, the richest of which are located in the Green River Basin, an overlapping area of Colorado, Utah, and Wyoming. Estimates of the total resource that could be conceivably recovered, exceeds 2 trillion barrels (2 × 1012 bbls) of thermally-produced shale oil.

In the context of this book – natural gas and crude oil from tight formations, including shale formations – this is the point at which a comparison between shale oil and oil from tight shales should end. With the evolution of tight oil production, there has been confusion regarding the difference between tight oil and shale oil. Often, the terms are used incorrectly and often interchangeably, thereby adding further confusing to their distinction. The two resources are vastly different and markedly different in composition and methods of production.

By definition, oil shale is shale that contains a carbonaceous immobile material (kerogen) which, by the application of heat, can be converted into gas and synthetic crude oil – only applied heat will produce shale oil (a synthetic crude oil) from oil shale. Furthermore, the term synthetic crude oil is typically applied to oil that is produced by thermal means and which contains constituents that are not indigenous to the oil or to the shale formation. There is no requirement for elaborate horizontal drilling or hydraulic fracturing of the shale deposit to allow flow paths through which the oil and gas will be produced. On the other hand, tight oil is a conventional crude oil that is created naturally through the maturation process but is trapped in shale deposits. Shale gas is similarly produced from precursors that were trapped within the shale formations.

5.1 Oil shale

The term *oil shale* describes an organic-rich rock from which little carbonaceous material can be removed by extraction (with common crude oil-based solvents) but which produces variable quantities of distillate (*shale oil*) when raised to temperatures in excess of 350 °C (660 °F). Thus, oil shale is assessed by the ability of the mineral to produce shale oil in terms of gallons per ton (g/t) by means of a test method (Fischer Assay) in which the oil shale is heated to 500 °C (930 °F).

Oil shale represents a large and mostly untapped hydrocarbon resource. Like tar sand (*oil sand* in Canada) and coal, oil shale is considered unconventional because oil cannot be produced directly from the resource by sinking a well and pumping. Oil has to be produced thermally from the shale. The organic material contained in the shale is called *kerogen*, a solid material intimately bound within the mineral matrix (Baughman, 1978; Allred, 1982; Scouten, 1990; Lee, 1991; Speight, 2008, 2013b, 2014a).

Oil shale is distributed widely throughout the world with known deposits in every continent. Oil shale ranging from Cambrian to Tertiary in age (Table 1.6) occurs in many parts of the world. Deposits range from small occurrences of little or no economic value to those of enormous size that occupy thousands of square miles and contain many billions of barrels of potentially extractable shale oil. However, crude oil-based crude oil is cheaper to produce today than shale oil because of the additional costs of mining and extracting the energy from oil shale. Because of these higher costs, only a few deposits of oil shale are currently being exploited in China, Brazil, and Estonia. However, with the continuing decline of crude oil supplies, accompanied by increasing costs of crude oil-based products, oil shale presents opportunities for supplying some of the fossil energy needs of the world in the future (Culbertson and Pitman, 1973; Bartis et al., 2005; Andrews, 2006).

Oil shale is not generally regarded as true shale by geologists nor does it contain appreciable quantities of free oil (Scouten, 1990; Speight, 2008). The fracture resistance of all oil shales varies with the organic content of the individual lamina and fractures preferentially initiate and propagate along the leaner horizontal laminas of the depositional bed.

Oil shale was deposited in a wide variety of environments including freshwater to saline ponds and lakes, epicontinental marine basins, and related subtidal shelves as well as shallow ponds or lakes associated with coal-forming peat in limnic and coastal swamp depositional environments. This give rise to a variety of different oil shale types (Hutton, 1987, 1991) and it is not surprising, therefore, that oil shale exhibits a wide range in organic and mineral composition (Scouten, 1990; Mason, 2006; Ots, 2014; Wang et al., 2009). Most oil shale contains organic matter derived from varied types of marine and lacustrine algae, with some debris of land plants, depending upon the depositional environment and sediment sources.

Organic matter in oil shale is a complex moisture and is derived from includes the carbon-containing remains of algae, spores, pollen, plant cuticle and corky fragments of herbaceous and woody plants, plant resins, and other cellular remains of lacustrine plants, marine plants, and land plants (Scouten, 1990; Dyni, 2003, 2006). These materials are composed chiefly of carbon, hydrogen, oxygen, nitrogen, and sulfur. Generally, the organic matter is unstructured and is best described as amorphous (*bituminite*) – the origin of which has not been conclusively identified but is theorized to be a mixture of degraded algal or bacterial remains. Other carbon-containing materials such as phosphate and carbonate minerals may also be present which, although of organic origin, are excluded from the definition of organic matter in oil shale and are considered to be part of the mineral matrix of the oil shale.

Finally, much of the work performed on oil shale has referenced the oil shale from the Green River formation in the western United States. Thus, unless otherwise stated, the shale referenced in the following text is the Green river shale.

5.1.1 General properties

Oil shale is typically a fine-grained sedimentary rock containing relatively large amounts of organic matter (*kerogen*) from which significant amounts of shale oil and combustible gas can be extracted by thermal deposition with ensuing distillation from the reaction zone. However, oil shale does not contain any oil – this must be produced by a process in which the kerogen is thermally decomposed (cracked) to produce the liquid product (shale oil). The mineral matter (shale) consists of fine-grained silicate and carbonate minerals. The ratio of kerogen-to-shale for commercial grades of oil shale is typically in the range 0.75:5 to 1.5:5 – as a comparison, for coal the organic matter-to-mineral matter ratio in coal is usually greater than 4.75:5 (Speight, 2013b).

In the United States there are two principal oil shale types, the shale from the Green River Formation in Colorado, Utah, and Wyoming, and the Devonian-Mississippian black shale of the East and Midwest (Baughman, 1978). The Green River shale is considerably richer, occurs in thicker seams, and has received the most attention for synthetic fuel.

The common property of these two types of oil shale is the presence of the ill-defined kerogen. The chemical composition of the kerogen has been the subject of many studies (Scouten, 1990) but whether or not the data are indicative of the true nature of the kerogen is extremely speculative. Based on solubility/insolubility in various solvents (Koel et al., 2001) it is, however, a reasonable premise (remembering that regional and local variations in the flora that were the precursors to kerogen) led to differences in kerogen composition and properties kerogen from different shale samples – similar to the varying in quality, composition, and properties of crude oil from different reservoirs (Speight, 2014a).

The organic matter is derived from the varied types of marine and lacustrine algae, with some debris of land plants, is largely dependent on the depositional environment and sediment sources. Bacterial processes were probably important during the deposition and early diagenesis of most oil shale deposits – these processes could produce significant quantities of biogenic methane, carbon dioxide, hydrogen sulfide, and ammonia. These gases in turn could react with dissolved ions in the sediment waters to form authigenic minerals (minerals generated where they were found or observed) such as calcite ($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$), pyrite (FeS_2), and even such rare authigenic minerals as buddingtonite (ammonium feldspar – $NH_4 \cdot Al \cdot Si_3O_8 \cdot 0.5H_2O$).

5.1.2 Mineral constituents

Oil shale has often been termed as (incorrectly and for various illogical reasons) high-mineral coal. Nothing could be further from the truth than this misleading terminology. Coal and oil shale are fraught with considerable differences (Speight, 2008, 2013b) and such terminology should be frowned upon.

In terms of mineral and elemental content, oil shale differs from coal in several distinct ways. Oil shale typically contains much larger amounts of inert mineral matter (60%–90%) than coal, which has been defined as containing less than 40% mineral matter (Speight, 2013b). The organic matter of oil shale, which is the source of liquid and gaseous hydrocarbon derivatives, typically has a higher hydrogen and lower oxygen content than that of lignite and bituminous coal.

The mineral component of some oil shale deposits is composed of carbonates including calcite ($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$), siderite ($FeCO_3$), nahcolite ($NaHCO_3$), dawsonite [$NaAl(OH)_2CO_3$], with lesser amounts of aluminosilicates – such as alum [$KAl(SO_4)_2 \cdot 12H_2O$] – and sulfur, ammonium sulfate, vanadium, zinc, copper, and uranium, which add by-product value (Beard et al., 1974). For other deposits, the reverse is true – silicates including quartz (SiO_2), feldspar [$xAl(Al \cdot Si)_3O_8$, where x can be sodium (Na), and/or calcium (Ca), and/or potassium (K)], and clay minerals are dominant and carbonates are a minor component.

Briefly, clay minerals are the characteristic minerals of the near surface environments of the Earth. They form in soils and sediments, and by diagenetic and hydrothermal alteration of rocks. Water is essential for clay mineral formation and most clay minerals are described as hydrous alumino silicates. Structurally, the clay minerals are composed of planes of cations, arranged in sheets, which may be tetrahedral-coordinated or octahedrally-coordinated with oxygen, which in turn are arranged into layers often described as 2:1 if they involve units composed of two tetrahedral and one octahedral sheet or 1:1 if they involve units of alternating tetrahedral and octahedral sheets. Additionally some 2:1 clay minerals have interlayers sites between successive 2:1 units which may be occupied by interlayer cations, which are often hydrated. The planar structure of clay minerals give rise to characteristic platy habit of many and to perfect cleavage, as seen for example in larger hand specimens of mica minerals.

Many oil-shale deposits contain small, but ubiquitous, amounts of sulfides including pyrite (FeS_2) and marcasite (FeS_2, but which physically and crystallographically distinct from pyrite), indicating that the sediments probably accumulated in dysaerobic (a depositional environment with 0.1–1.0 mL of dissolved oxygen per liter of water) to anoxic waters that prevented the destruction of the organic matter by burrowing organisms and oxidation.

Green River oil shale contains abundant carbonate minerals including dolomite, nahcolite, and dawsonite. The latter two minerals have potential by-product value for their soda ash and alumina content, respectively. The oil shale deposits of the eastern United States are low in carbonate content but contain notable quantities of metals, including uranium, vanadium, molybdenum, and others which could add significant by-product value to these deposits. There is the potential for low emissions due to the inherent presence of carbonate minerals. Calcium carbonate present in oil shale ash binds sulfur dioxide and it is not necessary to add limestone for desulfurization:

$$CaCO_3 \rightarrow CaO + CO_2$$

$$2CaO + SO_2 + O_2 \rightarrow CaSO_4$$

Illite (a layered alumino-silicate, $[(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2,(H_2O)]$) is ever-present in Green River oil shale – it is generally associated with other clay minerals but frequently occurs as the only clay mineral found in the oil shale (Tank, 1972). Smectite (a group of clay minerals that includes montmorillonite, which tends to swell when exposed to water) is present in all three members of the Green River Formation, but its presence frequently shows an inverse relationship to both analcime (a white, gray, or colorless tectosilicate mineral which consists of hydrated sodium aluminum silicate, $NaAlSi_2O_6 \cdot H_2O$) and loughlinite (a silicate of magnesium, $Na_2Mg_3Si_6O_{16} \cdot 8(H_2O)$. Chlorite (a group of mostly monoclinic but also triclinic or orthorhombic micaceous phyllosilicate minerals) occurs only in the silty and sandy beds of the Tipton Shale Member. The distribution of random mixed-layer structures and amorphous material is irregular. Several independent lines of evidence favor an *in situ* origin for many of the clay minerals. Apparently the geochemical conditions favoring the accumulation of the oil shale also favored *in situ* generation of illite.

Finally, precious metals and uranium are contained in good amounts in oil shale of the Eastern United States. It may not be in the near future to recover these mineral resources, since a commercially favorable recovery process has not yet been developed. However, there are many patents on recovery of alumina from Dawsonite-bearing beds $[NaAl(CO_3)(OH)_2]$ by leaching, precipitation, and calcination.

5.1.3 Grade

The grade of oil shale has been determined by many different methods with the results expressed in a variety of units (Scouten, 1990; Dyni, 2003, 2006). For example, the heating value is useful for determining the quality of an oil shale that is burned directly in a power plant to produce electricity. Although the heating value of a given oil shale is a useful and fundamental property of the rock, it does not provide information on the amounts of shale oil (which does not fall under the definition of *tight oil*) or combustible gas that would be yielded by retorting (destructive distillation). Alternatively, the grade of oil shale can be determined by measuring the yield of distillable oil produced from a shale sample in a laboratory retort (Scouten, 1990). This is perhaps the most common type of analysis that has been, and still is, used to evaluate an oil-shale resource – however the end result of the evaluation depends upon the source of the sample and whether or not the sample is representative of the deposit.

The method commonly used in the United States is the *modified Fischer assay* test method (ASTM D3904). However, the test method has been withdrawn (but still used in many laboratories) consists of heating a 100-g sample crushed to -8 mesh (2.38-mm) screen in a small aluminum retort to 500 °C (930 °F) at a rate of 12 °C (21.6 °F) per minute and held at that temperature for 40 min. The distilled vapors of oil, gas, and water are passed through a condenser cooled with ice water into a graduated centrifuge tube. The oil and water are then separated by centrifuging. The quantities reported are the weight percentages of shale oil (and its specific gravity), water, shale residue, and (by difference) gas plus losses. Some laboratories have further modified the Fischer assay method to better evaluate different types of oil shale and different methods of oil-shale processing.

Another method for characterizing organic richness of oil shale is a pyrolysis test developed by the Institut Français du Pétrole for analyzing source rocks (Allix et al., 2011). The Rock-Eval test heats a 50-mg to 100-mg sample through several temperature stages to determine the amounts of hydrocarbon and carbon dioxide generated. The results can be interpreted for kerogen type and potential for oil and gas generation. The method is faster than the Fischer assay and requires less sample material (Kalkreuth and Macauley, 1987).

5.1.4 Porosity

The porosity (void fraction) is a measure of the void spaces in a material such as a reservoir rock, and is a fraction of the volume of void space over the total volume, between and is expressed as a fractional number between 0 and 1, or as a percentage between 0 and 100.

The porosity of porous material can be measured in a number of different ways, depending on what specific pores are looked at and how the void volumes are measured. They include: (i) inter-particle porosity, (ii) intra-particle porosity, (iii) internal porosity, (iv) porosity by liquid penetration, (v) porosity by saturation, (vi) porosity by liquid absorption, (vii) superficial porosity, (viii) total open porosity, (ix) bed porosity, which is the bed void fraction, and (x) packing porosity.

Except for the two low-yield oil shale samples, naturally occurring porosities in the raw oil shales are almost negligible and they do not afford access to gases. Porosity may exist to some degree in the oil shale formation where fractures, faults, or other structural defects occurred. It is also believed that a good portion of pores is either blind or very inaccessible. Cracking and fractures, or other structural defects often create new pores and also break up some of the blind pores – closed or blind pores are normally not accessible by mercury porosimetry even at high pressures. Due to the severity of mercury poisoning, the instrument based on pressurized mercury penetration through pores is no longer used.

5.1.5 Permeability

The permeability of raw oil shale is essentially zero, because the pores are filled with a non-displaceable organic material. In general, oil shale constitutes a highly impervious system. Thus, one of the major challenges of any *in-situ* retorting project is in the creation of a suitable degree of permeability in the formation. This is why an appropriate rubbelization technique is essential in the success of an *in situ* pyrolysis project.

Of practical interest is the dependency of porosity or permeability on temperature and organic contents. Upon heating to 510 °C (950 °F), an obvious increase in oil shale porosity is noticed. These porosities, which vary from 3 to 6% v/v of the initial bulk oil shale volume, represented essentially the volumes occupied by the organic matter before the retorting treatment. Therefore, the oil shale porosity increases as the extent of pyrolysis reaction proceeds.

5.1.6 Compressive strength

Raw oil shale has high compressive strengths both perpendicular and parallel to the bedding plane (Eseme et al., 2007). After heating, the inorganic matrices of low-yield Fischer assay oil shale retain high compressive strength in both perpendicular and parallel planes. This indicates that a high degree of inorganic cementation exists between the mineral particles comprising each lamina and between adjacent laminae. With an increase in organic matter of oil shale the compressive strength of the respective organic-free mineral matrices decreases, and it becomes very low in those rich oil shales.

5.1.7 Thermal conductivity

Measurements of thermal conductivity of oil shale show that blocks of oil shale are anisotropic related to the bedding plane and thermal conductivity as a function of temperature, oil shale assay and direction of heat flow, parallel to the bedding plane (parallel to the surface of the Earth for a flat oil shale bed), was slightly higher than the thermal conductivity perpendicular to the bedding plane. As layers of material were laid to form the oil shale bed over a long period of geological years, the resulting continuous strata have slightly higher resistance to heat flow perpendicular to the strata than parallel to the strata.

The thermal conductivity of oil shale is, in general, only weakly dependent on the temperature. However, extreme caution needs to be exercised in the interpretation of results at temperatures close to the decomposition temperature of the shale organic matter. This is due to the fact that the kerogen decomposition reaction (or, pyrolysis reaction) is endothermic in nature and as such the temperature transients can be confounded between the true rate of heat conduction and the rate of heat of reaction.

5.1.8 Thermal decomposition

High-yield oil shale sustains combustion hence the name older Native American name *the rock that burns* but in the absence of air (oxygen) three carbonaceous end products result when oil shale is thermally decomposed. Distillable oil is produced as are non-combustible gases and a carbonaceous (high-carbon) deposit remains on the rock on (the surface or in the pores) as char − a coke-like residue similar. The relative proportions of oil, gas, and char vary with the pyrolysis temperature and to some extent with the organic content of the raw shale. All three products are contaminated with nonhydrocarbon compounds and the amounts of the contaminants also vary with the pyrolysis temperature (Bozak and Garcia, 1976; Scouten, 1990).

At temperatures on the order of 500−520 °C (930−970 °F), oil shale produces shale oil while the mineral matter of the oil shale is not decomposed. The yield and quality of the products depend on a number of factors, whose impact has been identified and quantified for some of the deposits, notably the US Green River deposits and the Estonian Deposits (Brendow, 2003, 2009). A major factor is that oil shale ranges widely in organic content and oil yield. Commercial grades of oil shale, as determined by the yield of shale oil range from approximately 25–50 gallons per ton of rock (typically using the Fischer Assay method).

One simple aspect of the thermal decomposition of oil shale kerogen is the relationships of the organic hydrogen and nitrogen contents, and Fischer assay oil yields. Stoichiometry suggests that kerogen with a higher organic hydrogen-to-carbon atomic ratio can yield more oil per weight of carbon than kerogen that is relatively hydrogen-poor (Scouten, 1990). However, the hydrogen-to-carbon atomic ration is not the only important factor. South African kerogen with an atomic hydrogen-to-carbon ratio of 1.35 has a lower oil yield than Brazilian kerogen with an atomic hydrogen-to-carbon ratio of 1.57. In general, the oil shale containing kerogen that is converted efficiently to oil contains relatively low levels of nitrogen (Scouten, 1990). Furthermore, variation of [product distribution with time in the reaction zone can cause a change in product distribution (Hubbard and Robinson, 1950).

During retorting, kerogen decomposes into three organic fractions: (i) shale oil, (ii) gas, and (iii) carbonaceous residue. Oil shale decomposition begins at relatively low retort temperatures (300 °C, 572 °F) but proceeds more rapidly and more completely at higher temperatures (Scouten, 1990). The highest rate of kerogen decomposition occurs at retort temperatures of 480–520 °C (895–970 °F). In general, the yield of shale oil yield decreases, the yield of gas yield increases, and the aromaticity of the oil increases with increasing decomposition temperature (Dinneen, 1976; Scouten, 1990).

However, there is an upper limit on optimal retorting temperature as the mineral content of the shale may decompose if the temperature is too high. For example, the predominant mineral component of Estonian kukersite shales is calcium carbonate ($CaCO_3$), a compound that dissociates at high temperatures (600–750 °C, 1110–1380 °F for dolomite ($CaCO_3 \cdot MgCO_3$), and 600–900 °C, 1110–1650 °F for calcite ($CaCO_3$)). Thus carbon must be anticipated as a product of and oil shale decomposition process, which will dilute the off-gases (adding to emissions issues) produced from the retorting process. The gases and vapors leaving the retort are cooled to condense the reaction products, including oils and water.

The active devolatilization of oil shale begins at approximately 350–400 °C (660–750 °F), with the peak rate of oil evolution at approximately 425 °C (800 °F), and with devolatilization essentially complete in the range of 470–500 °C (890–930 °F) (Hubbard and Robinson, 1950; Shih and Sohn, 1980). At temperatures near 500 °C (930 °F), the mineral matter, consisting mainly of calcium/magnesium and calcium carbonates, begins to decompose yielding carbon dioxide as the principal product. The properties of crude shale oil are dependent on the retorting temperature, but more importantly on the temperature-time history because of the secondary reactions accompanying the evolution of the liquid and gaseous products. The produced shale oil is dark brown, odoriferous, and tending to waxy oil.

Kinetic studies (Scouten, 1990) indicate that below 500 °C (930 °F) the kerogen (organic matter) decomposes into an extractable product (*bitumen*) with subsequent decomposition into oil, gas, and carbon residue. The actual kinetic picture is influenced by the longer time required to heat the organic material, which is dispersed throughout the mineral matrix, and to the increased resistance to the outward diffusion of the products by the matrix which does not decompose. From the practical standpoint of oil shale retorting, the rate of oil production is the important aspect of kerogen decomposition.

Contrary to other oil shales, obtaining high oil yields of distillable oil from kukersite needs specific conditions of processing. It can be explained by the fact that on thermal processing of kukersite, its elevated moisture percentage and the predominance of calcium carbonate in its mineral part result in high values of specific heat consumption in the process (Yefimov and Purre, 1993). Also shale is rich in organic matter and must pass the temperatures of thermobitumen formation and coking at a relatively high speed to avoid caking and secondary pyrolysis of oil.

5.2 Kerogen and shale oil

The name *kerogen* is also generally used for organic matter in sedimentary rocks that is insoluble in common organic and inorganic solvents. Thus, the term *kerogen* is used throughout this text to mean the carbonaceous material that occurs in sedimentary rocks, carbonaceous shale, and oil shale. This carbonaceous material is, for the most part, insoluble in common organic solvents. A soluble fraction, *bitumen*, co-exists with the kerogen. The bitumen is not to be confused with the material found in tar sand deposits (Speight, 2008, 2009, 2014a). However, like many naturally-occurring organic materials, kerogen does yields a hydrocarbonaceous oil when heated to temperatures sufficiently high (Typically >300 °C, 570 °F) to cause thermal decomposition with simultaneous removal of distillate.

Kerogen is the naturally occurring, solid, insoluble organic matter that occurs in source rocks and can yield oil upon heating. Typical organic constituents of kerogen are algae and woody plant material. Kerogen has a high molecular weight and is generally insoluble in typical organic solvents (Speight, 2009, 2014a) and has been conveniently divided into four types: (i) Type I kerogen, which consists mainly algal and amorphous constituents, (ii) Type II kerogen, which consists of mixed terrestrial and marine source material, (iii) Type III kerogen, which consists of woody terrestrial source material, and (iv) Type IV kerogen, which consists mostly of decomposed organic matter in the form of polycyclic aromatic hydrocarbon derivatives and has a low (<0.5) hydrogen-to-carbon (H/C) atomic ratio.

Kerogen is a solid, waxy, organic substance that forms when pressure and heat from the Earth act on the remains of plants and animals. Given geological time, it has been proposed that kerogen converts to various liquid and gaseous *hydrocarbon derivatives* at a depth of approximately 4.5 miles or more (approximately 7 km) and a temperature between 50 and 100 °C (122 and 212 °F) (USGS, 1995), which has been assigned to the presence of the *thermal gradient*.

Briefly, the *geothermal gradient* is the variation of temperature with depth in subterranean formations of the Earth. Although the geothermal gradient varies from place to place, it is generally on the order of (22 °F per 1000 feet of depth or 12 °C per 1000 feet of depth, i.e. 0.022 °F per foot of depth or 0.012 °C per foot of depth). This would require a depth on the order of 25,000 to attain temperatures of 300 °C (570 °F). However, the thermal evolution of kerogen is unknown and the role of kerogen in crude oil formation is at best, highly speculative.

The precise structure of kerogen is unknown and the precise role of kerogen-rock interactions in determining the properties of oil shale is also unknown. In addition, the precise role played by kerogen in the natural gas and crude oil maturation process is not fully understood (Tissot and Welte, 1978; Durand, 1980; Hunt, 1996; Scouten, 1990; Speight, 2014a). What obviously needs to be addressed more fully in terms of kerogen participation in crude oil generation is the potential to produce crude oil constituents from kerogen by low-temperature processes rather than by processes that involve the use of temperatures in excess of 250 °C (>480 °F) (Burnham and McConaghy, 2006; Speight, 2014a).

6. Resources and reserves

Throughout this book there is frequent reference to resources and reserves (such as in Chapters 2 and 12) and it is appropriate to present explanation of these terms and any related terms (Fig. 1.4). Thus, terms such as (i) original oil in place, OOIP, or original gas in place, OGIP, (ii) ultimately recoverable resources, URR, (iii) technically recoverable resources, TRR (iv) estimate ultimate recovery, EUR, (v) economically recoverable resources, ERR, (vi) proved reserves, (vii) probable reserves, and (viii) possible reserves.

First and foremost, the resources of natural gas and crude oil are the natural concentrations of natural gas and crude oil that are, or may become, of potential economic interest and which will also be present in sufficient quantity to make natural gas and crude oil of intrinsic economic interest. The status of the resources in economic terms may change with time as product specifications change, as markets decline or expand, as transport links improve, and as extraction and processing technology improve. Resources that might previously have remained unworked, because of (i) the poor quality of the resource, (ii) the resource was beneath excessive overburden thickness, or (iii) the natural gas and crude oil was

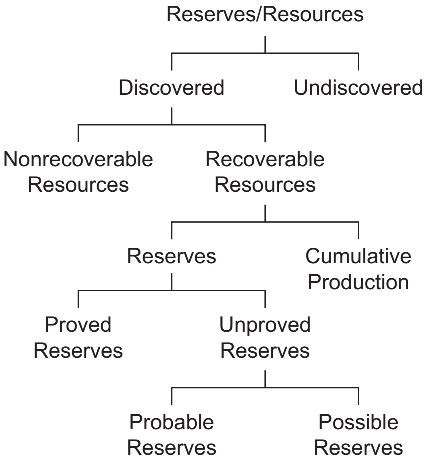

FIG. 1.4 Simplified sub-division of resources and reserves.

contained in a low permeability (tight) formation are increasingly being considered as potential sources of supply.

The presence of an otherwise economically viable aggregate resource is not in itself sufficient to ensure that extraction of the natural gas and crude oil will take place. This is because, in common with most other forms of development, natural gas and crude oil extraction (i.e. recovery) and related activities such as processing facilities, require planning permission before any development can take place. Without the consent to proceed, no natural gas and crude oil can legally take place and consequently the inherent economic value of a mineral resource cannot be released and resulting wealth created.

The *original oil or gas in place* (OOIP or OGIP) is the total volume of the resource that is estimated to be present in a given field, play, or region. However, it is not possible to recover all (100%) of the volume in place and the amount that is recoverable is referred to by a *recovery factor*. This factor is a key factor in the estimation of natural gas or crude oil availability and can vary significantly depending on geological conditions, recovery technology employed, and the economic environment (such as cost of recovery, gas or oil price).

The *ultimately recoverable resources* (URRs) is the sum of all natural gas or crude oil that expected to be produced from a field or region over the lifetime of the production site. This estimate includes not only (i) the gas or oil already produced, (ii) the gas or oil resources already discovered, but also (iii) the natural gas and crude oil which is not currently producible either technically or economically but is expected to be so in the future as recovery technology evolves, and (iv) undiscovered gas or oil which is expected to be discovered in the future. This definition is very dependent upon the assumption employed in the estimation, such as future gas and oil prices, future developments in recovery technology, and future discoveries of gas or oil. The estimate for *ultimately recoverable resources* is closely related to *estimated ultimate recovery* (EUR) which is commonly used to refer to the production from a single well but for all other purposes is synonymous with the definition of *ultimately recoverable resources*.

The *technically recoverable resources* (TRRs) is the natural gas or crude oil that can be recovered (produced) using currently available recover technology, but this definition tends to exclude any economic aspect of the recovery operations. However, there is some ambiguity as to whether this classification includes undiscovered gas or oil but the majority of evidence suggests that undiscovered gas oil should be included. Another definition, *remaining technically recoverable resources* (RTRRs), can be used to exclude the cumulative production.

The *economically recoverable resources* (ERRs) defines the technically *and* economically producible gas given current technical and economic conditions. As such this definition is highly sensitive to changes in economic conditions and it is difficult to defend the basis for any assumptions on the economic producibility of undiscovered gas and gas resources.

The economic potential of a natural gas or crude oil resource can only be proved by a detailed evaluation program which involves drilling and associated test work to prove that a resource of sufficient quantity and quality is present. Such an investigation is an essential precursor to submitting a planning for natural gas or crude oil recovery. Since there is no guarantee that planning permission will be granted, the capital involved in acquiring a site and evaluating its economic potential is at risk. In addtion, the part of a natural gas or crude oil resource which has been fully evaluated and is deemed commercially viable to work is called referred to as the reserves of natural gas or the reserves of crude oil. However, in the context of land-use planning, the term *reserves* should be further restricted to the natural gas or crude oil to which the company has been granted legal access and for which a valid planning permission for extraction also exists (i.e. permitted reserves). Without a valid planning consent, the development of natural gas or crude oil resources cannot legally occur. Because of increasing concerns about the environmental and social impact of the development of natural gas or crude oil resources, access to the formations containing natural gas or crude oil has now become the major determinant of where mineral extraction may or may not take place.

Reserves will need to meet not only the requirements of geological certainty and economic viability but also accessibility based on legal permission to extract the natural gas or crude oil. The important point is to recognize is that permitted reserves may only be a small part of total resource. The ultimate fate of a natural gas or crude oil reserve is to be either physically worked out or to be made non-viable by changing economic, technological, environmental and/or social circumstances. Reserves are of crucial importance to the natural gas or crude oil industry since they represent future assets of the industry. They are also of crucial importance to the planning process in ensuring that an adequate and steady supply of natural gas or crude oil aggregate is available to meet the future demand.

In terms of definitions of reserves, there are the probabilistic definitions: (i) proved reserves, (ii) probable reserves, and (iii) possible reserves.

The term *proved reserves* (*proven reserves*) is typically limited to those quantities that are commercial under current economic conditions, while probable and possible reserves may be based on future economic conditions. In general, quantities should not be classified as reserves unless there is an expectation that the accumulation will be developed and placed on production within a reasonable timeframe. On the other hand, the *probable reserves* are those reserves of natural gas or crude oil that are nearly certain but about which a slight doubt exists while *possible reserves* are those reserves of crude oil with an even greater degree of uncertainty related to recovery but about which there is some information. An additional term *potential reserves* is also used on occasion; these reserves are based upon geological information related to the types of sediments where such resources are likely to occur and they are considered to represent an educated guess. The term *inferred reserves* is also commonly used in addition to, or in place of, *potential reserves*. Inferred reserves are regarded as of a higher degree of accuracy than potential reserves, and the term is applied to those reserves that are estimated using an improved understanding of reservoir frameworks. The term also usually includes those reserves that can be recovered by further development of recovery technologies.

Proved reserves is sometimes referred to as P90 (or P_{90}) and represents an estimate with a 90% probability of being exceeded. *Proved and probable reserves* (*2P*) is sometimes referred to as P50 (or P_{50}) and represents an estimate with a 50% chance of being exceeded (the median estimate). *Proved*, *probable* and *possible reserves* (*3P*) is sometimes referred to as P10 (or P_{10}) and represents an estimate with a 10% chance of being exceeded.

Caution is advised when using these definitions and care must be taken to define each term carefully with the explanation of any assumptions so that anyone following the definitions can know precisely what is expected from the definition. In summary, the use of resource and reserve definitions is inconsistent with variations between company definitions and government definitions. Thus, when reporting reserve and resource data, it is essential to be explicit related to resource definitions.

Finally, a *stranded resource* (*stranded reserve*) is a resource (reserve) that is not economical to recover and transport to an existing market. The resource (reserve) may be too remote from a market, making construction of a pipeline prohibitively expensive or the resource (reserve) may be in a region where demand for gas or oil is saturated and the cost of exporting gas beyond this region is excessive. Such a resource (reserve) is likely to be developed in the future when existing sources begin to deplete.

7. Tight oil, tight gas, and energy security

Energy security is the continuous and uninterrupted availability of energy, to a specific country or region. The security of energy supply conducts a crucial role in decisions that are related to the formulation of energy policy strategies. The economies of many countries are depended by the energy imports in the notion that their balance of payments is affected by the magnitude of the vulnerability that the countries have in crude oil and natural gas (Speight, 2011b).

Energy security has been an on-again-off-again political issue in the United States since the first Arab oil embargo in 1973. Since that time, the speeches of various Presidents and the Congress of the United States have continued to call for an end to the dependence on foreign oil and gas by the United States. However, the congressional rhetoric of energy security and energy independence continues but meaningful suggestions of how to successfully address this issue remain few and far between.

The energy literature and numerous statements by officials of oil-and-gas-producing and oil-and-gas-consuming countries indicate that the concept of energy security is elusive. Definitions of energy security range from uninterrupted oil supplies to the physical security of energy facilities to support for bio-fuels and renewable energy resources. Historically, experts and politicians referred to *security of oil supplies* as *energy security*. Only recently policy makers started to include natural gas supplies in the portfolio of energy definitions.

The security aspects of natural gas are similar, but not identical, to those of crude oil. Compared with crude oil imports, natural gas imports play a smaller role in most importing countries – mainly because it is less costly to transport liquid crude oil and crude oil products than natural gas. Natural gas is transported by pipeline over long distances because of the pressurization costs of transmission; the need to finance the cost of these pipelines encourages long-term contracts that dampen price volatility.

The past decade has yielded substantial change in the natural gas industry. Specifically, there has been rapid development of technology allowing the recovery of natural gas from shale formations. During the last two decades, rapid growth in the production of natural gas and crude oil from shale formations in North America has dramatically altered the global natural gas market landscape. Indeed, the emergence of tight gas and tight oil is perhaps the most intriguing development in the natural gas and crude oil markets in recent memory.

Historically, producing hydrocarbon derivatives from shale deposits is not a new venture – the practice predates the modern natural gas and crude oil industries. In 1821, a commercial shale gas well was drilled in Fredonia, New York, USA. By the 1920s, prolific natural gas production came from shale deposits in the nearby Appalachian basin. The methods used then for exploiting gas-containing shale formations bears little resemblance to the current practices. The gas recovery operations consisted of vertical wells drilled into the formation but which produced low flow rates.

Development of the Barnett Shale (in northeast Texas) commenced in 1981 but there was little commercial viability in terms of the production of gas from the shale and the project offered little in terms of future energy security. Hydraulic fracture stimulation was the first technology to unlock the gas trapped in shales. The process showed high initial production flow rates but was followed by rapid decrease in production. Realizing that more contact with the reservoir was needed to avoid these rapid declines, the operators introduced the concept of horizontal wells, along with the hydraulic fracturing technique, which allowed contact with significantly more reservoir rock than is possible from vertical wellbores. Thus, by applying these two technologies together, economic volumes of the resource could be liberated from the shale source rocks. Following this success, similar basins were investigated to find shale formations that had been largely ignored by the industry where resources could be recovered economically.

Thus, beginning with the Barnett shale, the application of innovative new techniques involving the use of horizontal drilling with hydraulic fracturing has resulted in the rapid growth in production of natural gas from shale. Knowledge of the shale gas resource is not new as geologists have long known related to the existence of shale formations, and accessing those resources was long held in the geology community to be an issue of technology and cost. In the past decade, innovations have yielded substantial cost reductions, making shale gas production a commercial reality. In fact, shale gas production in the United States has increased from virtually nothing in the year 2000 to over 10 billion cubic feet per day (bcfd, 10×10^9 ft^3 per day) in 2010, and it is expected to more than quadruple by the year 2040, reaching 50% or more of total US natural gas production by the decade starting in the year 2030.

Natural gas – if not placed at a disadvantage by government policies that protect competing fuels, such as coal, although at the time of writing the protection of coal does seem unlikely – stands to play a very important role in the energy mix of the United States for decades to come. But coal must not be forgotten – a turn in the energy policies could bring coal back to the limelight. The increasing production of tight gas and tight oil has already delivered large beneficial impacts to the United States. These resources are generally located in close proximity to end-use markets where natural gas is utilized to fuel industry, generate electricity and heat homes. This offers both security of supply and economic benefits (Medlock et al., 2011).

The *Energy Independence and Security Act of 2007* (originally named the *Clean Energy Act of 2007*) is an Act of Congress concerning the energy policy of the United States. The stated purpose of the act is (quote) to move the United States toward greater energy independence and energy security, to increase the production of clean renewable fuels, to protect consumers, to increase the efficiency of products, buildings, and vehicles, to promote research on and deploy greenhouse gas capture and storage options, and to improve the energy performance of the Federal Government, and for other purposes (end quote).

The Act originally sought to cut subsidies to the crude oil industry in order to promote crude oil independence and different forms of alternative energy. These tax changes were ultimately dropped after opposition in the Senate, and the final bill focused on automobile fuel economy, development of biofuels, and energy efficiency in public buildings and lighting. It was, and still is, felt by many observers that there should have been greater recognition of the role that natural gas can play in energy security. In fact, viewed from the perspective of the energy-importing countries as a whole, diversification in oil supplies has remained constant over the last decade while diversification in natural gas supplies has steadily increased. Given the increasing importance of tight gas and tight oil in energy use in the United States, this is an indicator of an increase in overall energy security (Cohen et al., 2011).

However, tight gas and tight oil are attractive resources and, accordingly, analysts predict significant future growth in consumption worldwide. Current trends suggest that tight gas and tight oil will gradually become global commodities with a single world market. The outcome of a global tight gas market and a tight oil market is inevitable; once this occurs, the tendency will be toward a world price of natural gas and crude oil and the prices of natural gas and crude oil each will reach a global equivalence based on energy content (Deutch, 2010).

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CHAPTER

2

Resources

1. Introduction

By way of introduction, a natural gas or crude oil resources is a concentration or occurrence of natural gas or crude oil in the crust of the Earth in such form and quantity and of such a grade or quality that the natural gas or crude oil has reasonable-to-good prospects for economic extraction (Chapter 1). The location, quantity, grade, geological characteristics, and continuity of a natural gas or crude oil resource are known, estimated, or interpreted from specific geological evidence and knowledge.

Natural gas or crude oil resources are sub-divided, in order of increasing geological confidence, into *inferred*, *indicated*, and *measured* categories (Fig. 2.1) (CIM, 2014) – these terms tend to be company-dependent in their meaning – and the confidence level in *inferred resources* should be sufficiently high to allow the application of technical and economic parameters or to enable an evaluation of economic viability worthy of public disclosure. As already discussed (Chapter 1), a natural gas or crude oil reserve is the economically recoverable part of a resource that has been demonstrated by at least a preliminary feasibility study. Furthermore, natural gas or crude oil reserves are sub-divided in order of increasing confidence into *probable reserves* and *proven reserves*, which those parts of the resource that, after the application of all recovery factors, are the basis of an economically viable project after taking account of all relevant processing, metallurgical, economic, marketing, legal, environment, socio-economic and government factors.

Unconventional resources such as natural gas and crude oil from tight formations have evolved into an important resource play in North America and can take on an important energy-source role in Europe and other countries (Law and Curtis, 2002). The shale formations and other tight formations (sandstone formations and carbonate formation) are composed of fine-grained particles with pores that are typically on the nanometer scale. Shale acts as source rock only or both source rock and reservoir rock. Organic materials deposited in shale were buried with time. With the increase of temperature and pressure, organic materials, such as lipid derivatives from animal tissue and plant matter, or lignin derivatives from plant cells, were transformed into kerogen. Depending on organic materials, pressure, and temperature, kerogen was converted to oil, wet gas, and dry gas. In some shale formations, natural gas or crude oil migrated from shale through fractures and faults due to expansion. However, the natural gas or the crude oil did not migrate in

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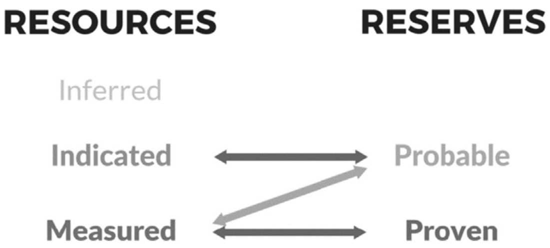

FIG. 2.1 Relationship between natural gas and crude oil resources and reserves.

some shale rocks. In that case, shale is defined both as source rock and reservoir rock, which is the case of shale gas and oil reservoirs (Curtis, 2002; Boyer et al., 2011; Kok and Merey, 2014).

These tight formations, such as the organic-rich shale formations of the United States and Canada (Table 2.1) have become an attractive target for development and recovery of the resource because these formations a substantial resource of natural gas, natural gas liquids, gas condensate, and. These (typically) black organic shale formations that were formed millions of years ago (Table 2.2) obtain their black color from the organic matter that was deposited with the primordial from of the shale that developed into shale geologic time. The non-shale sedimentary *tight formation* consists of extraordinarily impermeable, hard rock (usually sandstone or carbonate rock) which exhibit relatively low permeability that can contain oil and gas (Chapter 3). In both cases, some of the organic material was transformed into natural gas and/or crude oil during geologic time (millions of years) and remained in (or was unable to migrate out of) the formation. In other instances, the formed crude oil and natural gas migrated into reservoir formations while the organic material that did not migrate remained in the original rock as kerogen. In the former case (the shale formation or the tight formation that presented migration of the fluids) the source rock and reservoir rock become one and the same.

Generally, a black color in shale formations and in sedimentary rock formations almost always indicates the presence of organic material, typically as little as one-to-two percent w/w can impart a dark gray or black color to the shale or sedimentary rock. However, a note of caution. Gray shale formations sometimes contain a small amount of organic matter but may also contain calcareous materials or simply clay minerals that result in a gray coloration of the formation. Generally, it can be assumed that the black color of the shale implies that the shale was formed from a mud-like sediment which was deposited in an oxygen-deficient environment. Any oxygen that entered the environment quickly reacted with the decaying organic debris and, if the amount of oxygen was plentiful, the organic debris decayed to produce carbon dioxide and water.

$$[4CH] + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

An oxygen-poor environment also provides the proper conditions for the formation of sulfide minerals such as pyrite (FeS_2), which is also found in many black shale formations. The Barnett shale formation, the Marcellus shale formation, the Haynesville shale formation, the Fayetteville shale formation and other gas-producing rocks are all dark gray or black shale

TABLE 2.1 Shale gas formations in the United States and Canada.

Formation	Geological period	Location
Antrim shale	Late Devonian	Michigan basin, Michigan
Baxter shale	Late Cretaceous	Vermillion basin, Colorado, Wyoming
Barnett shale	Mississippian	Fort Worth and Permian basins, Texas
Bend shale	Pennsylvanian	Palo Duro basin, Texas
Cane Creek shale	Pennsylvanian	Paradox basin, Utah
Caney shale	Mississippian	Arkoma basin, Oklahoma
Chattanooga shale	Late Devonian	Alabama, Arkansas, Kentucky, Tennessee
Chimney Rock shale	Pennsylvanian	Paradox basin, Colorado, Utah
Cleveland shale	Devonian	Eastern Kentucky
Clinton shale	Early Silurian	Eastern Kentucky
Cody shale	Cretaceous	Oklahoma, Texas
Colorado shale	Cretaceous	Central Alberta, Saskatchewan
Conasauga shale	Middle Cambrian	Black Warrior basin, Alabama
Dunkirk shale	Upper Devonian	Western New York
Duvernay shale	Late Devonian	West central Alberta
Eagle Ford shale	Late Cretaceous	Maverick basin, Texas
Ellsworth shale	Late Devonian	Michigan basin, Michigan
Excello shale	Pennsylvanian	Kansas, Oklahoma
Exshaw shale	Devonian-Mississippian	Alberta, northeast British Columbia
Fayetteville shale	Mississippian	Arkoma basin, Arkansas
Fernie shale	Jurassic	West central Alberta, northeast British Columbia
Floyd/Neal shale	Late Mississippian	Black Warrior basin, Alabama, Mississippi
Frederick Brook shale	Mississippian	New Brunswick, Nova Scotia
Gammon shale	Late Cretaceous	Williston basin, Montana
Gordondale shale	Early Jurassic	Northeast British Columbia
Gothic shale	Pennsylvanian	Paradox basin, Colorado, Utah
Green River shale	Eocene	Colorado, Utah
Haynesville/Bossier shale	Late Jurassic	Louisiana, east Texas
Horn River shale	Middle Devonian	Northeast British Columbia
Horton Bluff shale	Early Mississippian	Nova Scotia

(*Continued*)

TABLE 2.1 Shale gas formations in the United States and Canada.—cont'd

Formation	Geological period	Location
Hovenweep shale	Pennsylvanian	Paradox basin, Colorado, Utah
Huron shale	Devonian	East Kentucky, Ohio, Virginia, West Virginia
Klua/Evie shale	Middle Devonian	Northeast British Columbia
Lewis shale	Late Cretaceous	Colorado, New Mexico
Mancos shale	Cretaceous	San Juan basin, New Mexico, Uinta basin, Utah
Manning Canyon shale	Mississippian	Central Utah
Marcellus shale	Devonian	New York, Ohio, Pennsylvania, West Virginia
McClure shale	Miocene	San Joaquin basin, California
Monterey shale	Miocene	Santa Maria basin, California
Montney-Doig shale	Triassic	Alberta, northeast British Columbia
Moorefield shale	Mississippian	Arkoma basin, Arkansas
Mowry shale	Cretaceous	Bighorn and Powder River basins, Wyoming
Muskwa shale	Late Devonian	Northeast British Columbia
New Albany shale	Devonian-Mississippian	Illinois basin, Illinois, Indiana
Niobrara shale	Late Cretaceous	Denver basin, Colorado
Nordegg/Gordondale shale	Late Jurassic	Alberta, northeast British Columbia
Ohio shale	Devonian	East Kentucky, Ohio, West Virginia
Pearsall shale	Cretaceous	Maverick basin, Texas
Percha shale	Devonian-Mississippian	West Texas
Pierre shale	Cretaceous	Raton basin, Colorado
Poker Chip shale	Jurassic	West central Alberta, northeast British Columbia
Queenston shale	Ordovician	New York
Rhinestreet shale	Devonian	Appalachian basin
Second White Speckled shale	Late Cretaceous	Southern Alberta
Sunbury shale	Mississippian	Appalachian basin
Utica shale	Ordovician	New York, Ohio, Pennsylvania, West Virginia, Quebec
Wilrich/Buckinghorse/Garbutt/Moosebar shale	Early Cretaceous	West central Alberta, northeast British Columbia
Woodford shale	Devonian-Mississippian	Oklahoma, Texas

TABLE 2.2 The geologic timescale.[a]

Era	Period	Epoch	Millions of years ago
Cenozoic	Quaternary	Holocene	
		Pleistocene	0.01
	Tertiary	Pliocene	2
		Miocene	13
		Oligocene	25
		Eocene	36
		Paleocene	58
Mesozoic	Cretaceous		65
	Jurassic		136
	Triassic		190
Paleozoic	Permian		225
	Carboniferous		280
	Devonian		345
	Silurian		405
	Ordovician		425
	Cambrian		500
Precambrian			600

[a] *The numbers are approximate (±5%) due to variability of the data in literature sources; nevertheless, the numbers do give an indication of the extent of geologic time.*

formations that yield natural gas. The Bakken shale formation of North Dakota and the Eagle Ford shale formation of Texas are examples of shale formations that yield crude oil.

Because of the presence of these shale formations, natural gas production and crude oil production in the United States has grown significantly in recent years as improvements in horizontal drilling and hydraulic fracturing technologies have made it commercially viable to recover gas trapped in tight formations, such as shale and coal. The United States is now the number one natural gas producer in the world and, together with Canada, accounts for more than 25% of global natural gas production (BP, 2015), which will play an ever-increasing role in this resource base and economic outlook of the United States Furthermore, production of shale gas is projected to increase to 49% v/v of total gas production in the United States by 2035, up from 23% v/v in 2010, highlighting the significance of shale gas in the future energy mix in the United States and Canada (Bonakdarpour et al., 2011; Dong et al., 2013).

Determining the amount of gas in place in unconventional reservoirs is complex because of the heterogeneous structure of the reservoirs as well as the potential conflicts in the definitions of resources and reserves (Chapter 1). Moreover, assessing productivity is dependent on a detailed investigation of the characteristics of the reservoir, which can vary not only between reservoirs but also horizontally and vertically in any given reservoir. As an approximate estimate, ultimately recoverable unconventional gas resources, excluding methane hydrates, are estimated close to 12.0 quadrillion cubic feet (12.0×10^{15} ft^3; 340 trillion cubic meters, 340×10^{12} m^3). Of this amount, 24% v/v can be found in countries of the Organization for Economic Co-operation and Development (OECD) Americas, 28% v/v in Asia Pacific countries, 14% v/v in Latin American countries, and 13% v/v in Eastern Europe countries and Eurasian countries with smaller shares in African countries, the OECD European countries, and the Middle Eastern countries (IEA, 2012, 2013). With remaining recoverable resources of conventional natural gas at 16.3 quadrillion cubic feet (16.3×10^{15} ft^3) and unconventional gas at 12.0 quadrillion cubic feet (12.0×10^{15} ft^3), together they can sustain more than 200 years of production at current rates. The future potential for unconventional gas production remains contentious, with questions over the size and recoverability of the physical resource being central to the debate. While interest has focused upon shale gas in recent years, there is also considerable potential for coal bed methane (CBM) and tight gas to contribute to global gas supply. However, despite recent advances there remains considerable uncertainty over the size of recoverable resources for each type of gas, at both the regional and global level. This even applies to the United States, where the development of shale natural gas resources and shale crude oil resources are relatively advanced.

However, estimating the technically recoverable oil and natural gas resource base in the United States is an evolving process and the evolution of resource estimates is likely to continue for some time. The *true size* (*estimated true size*, that is) of the technically recoverable natural gas and crude oil resource base in the United States becomes evident only as the gas and oil producers drill into geologic deposits in which natural gas and crude reside and the potential for production of these resources on a commercial basis becomes real. As producers find plays that contain more crude oil or natural gas than expected, resource estimates have to be adjusted to reflect the latest information. Thus, estimates of the technically recoverable resource base will be continuously adjusted as knowledge of the resource base and future technologies and management practices improve. Consequently, it is advisable to recognize that the resource estimates in any current (recently-published) report may not be the actual estimates by the time the report is published since, in the interim time period between data acquisitions and publication, the estimates change as more wells are drilled and completed, technologies evolve, and the long-term performance of the wells to produce natural gas and crude oil becomes better established.

Furthermore, not all tight shale formations and tight non-shale formations are newly discovered. In many parts of the natural gas and crude oil producing world, a reexamination of old drilling records is opening up opportunities for the *rediscovery* of natural gas and crude oil resources that were rejected as worthy of development at an earlier time because of lower resources prices and/or more limited recovery technology (i.e., the technology is inadequate to the task of efficient recovery). This is especially true with natural gas and crude oil, which in many instances was a *stranded* resource having little or no market value. Also until quite recently with improvements in recovery technology, natural gas in tight sand or shale reservoirs could not be produced at commercial rates. There are more than fifty shale gas resource for formations in the United States and Canada, some of which are older (known) shale formation and other which are more recent and new (Table 2.1).

Shale gas reserves in the United States are considerable and not concentrated in any particular area (USGS, 2014). The estimates place 482 trillion cubic feet (482×10^{12} ft^3) of technically recoverable shale gas resources in the rower forty-eight states with the largest portions in the Northeastern states (63% v/v), Gulf Coast states (13% v/v), and Southwestern states (10% v/v), respectively. The largest shale gas resources (*plays*) are the Marcellus shale (141 trillion cubic feet, 141×10^{12} ft^3), Haynesville shale (74.7 trillion cubic feet, 74.7×10^{12} ft^3), and Barnett shale (43.4 trillion cubic feet, 43.4×10^{12} ft^3). Activity in new shale resources has increased shale gas production in the United States from 388 billion cubic feet (388×10^9 ft^3) in the year 2000 to 4944 billion cubic feet (4944×10^9 ft^3) in the year 2010 (US EIA, 2011a). This production potential has the ability to change the nature of the energy mix in the United states and the natural gas resource base could support supply for five or more decades at current or greatly expanded levels of use (NPC, 2011). However, in addition to these data and possibly because of the uncertainty of calculating reserve estimates, there are indications from numbers recently released that the estimated shale gas resource for the continental United States doubled from 2010 to 2011 to approximately eight hundred and sixty-two trillion cubic feet (862×10^{12} ft^3) and from 2006 to 2010 annual shale gas production in the United States almost quintupled to four point eight trillion cubic feet (from 1.0×10^{12} ft^3 to 4.8×10^{12} ft^3) (EIUT, 2012).

Finally, it must always be remembered that each of the shale basins is different and each has a unique set of exploration criteria and operational challenges that need consideration in any development program. Because of these differences, the development of shale formation resources and tight formation resources in each of these areas poses potential challenges not only to the resource developers but also to the surrounding communities and ecosystems. For example, the Antrim and New Albany Shale formations are shallower shale formations which produce significant volumes of formation water unlike most of the other gas shale formations. This is water that cannot be ignored for recycle use as well as purification so that contamination of aquifers does not occur (Chapter 18).

At this stage, a comment on each of the tight formations in the various countries is warranted, especially the United States and Canada where the majority of the pioneering work has been done. Finally a word about estimates of the available tight gas and tight oil resources.

The estimates of technically recoverable tight gas resources and tight oil resources remain uncertain and often speculative, even in regions with a relatively long history of tight gas and tight oil production. The estimates can be based upon the extrapolation of previous production experience in developed areas, or from the geological appraisal of undeveloped areas. Much of the variation in published estimates may be a function of the rapid advances in the extraction of natural gas and crude oil from tight formations over the past few years, and the limited production history that is available for analysis. Another challenge is the proprietary nature of much of the data required for third party assessment of resource estimates.

It is not surprising that there are substantial difficulties in assessing the recoverable volumes of shale gas and that current resource estimates should be treated with considerable caution. Most existing studies lack a rigorous approach to assessing uncertainty and provide estimates that are highly sensitive to key variables that are poorly defined − such as the assumed ratio of gas-in-place to recovered gas (the recovery factor) and the assumed ultimate recovery from individual wells (McGlade et al., 2013).

The data presented in this chapter and for kerogen-containing shale (Chapter 12) are selected because of their potential; reliability to present an estimate of the various resources that *might* be available for future development. However, because of the magnitude of uncertainties described above, current resource estimates should be treated with caution.

2. Natural gas in tight formations

Conventional resources of natural gas (or for that matter, any fossil fuel) exist in discrete, well-defined subsurface accumulations (reservoirs), with permeability values greater than a specified lower limit. Such conventional gas resources can usually be developed using vertical wells, and generally yield the high recovery factors. Briefly, permeability is a measure of the ability of a porous medium, such as that found in a hydrocarbon reservoir, to transmit fluids, such as gas, oil or water, in response to a pressure differential across the medium. In petroleum engineering, permeability is usually measured in units of millidarcies (mD).

By contrast, unconventional resources are found in accumulations where permeability is low (<0.1 mD) (Law and Curtis, 2002). Such accumulations include *tight* sandstone formations, coal beds (coal bed methane, CBM) and shale formations (Fig. 2.2). Unconventional resource accumulations tend to be distributed over a larger area than conventional accumulations and usually require advanced technology such as horizontal wells or artificial stimulation in order to be economically productive; recovery factors are much lower — typically of the order of 15%—30% of the gas initially in place (GIIP). The mature, organic-rich shale formations that serve as sources for gas and which have received considerable interest, have

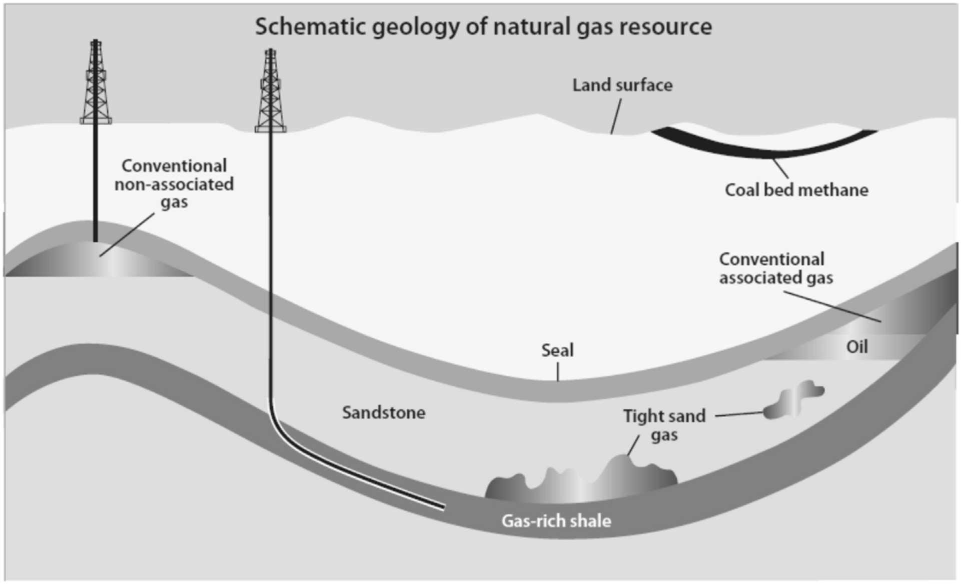

FIG. 2.2 Illustration of the conventional and unconventional gas reservoirs. *From:* EIA (2011a). *Energy Information Administration, United States Department of Energy, Washington, DC.*

become an attractive target because they represent a huge resource (500–780 × 10^{12} ft^3) and are distributed throughout the forty eight contiguous United States (Fig. 2.3) (Hill and Nelson, 2000; US EIA, 2011a).

Due to the unique nature of shale, every basin, play, well and pay zone may require a unique treatment. Briefly comparing the characteristics of some of the current hottest plays can help illustrate the impact of these differences throughout development. It is necessary

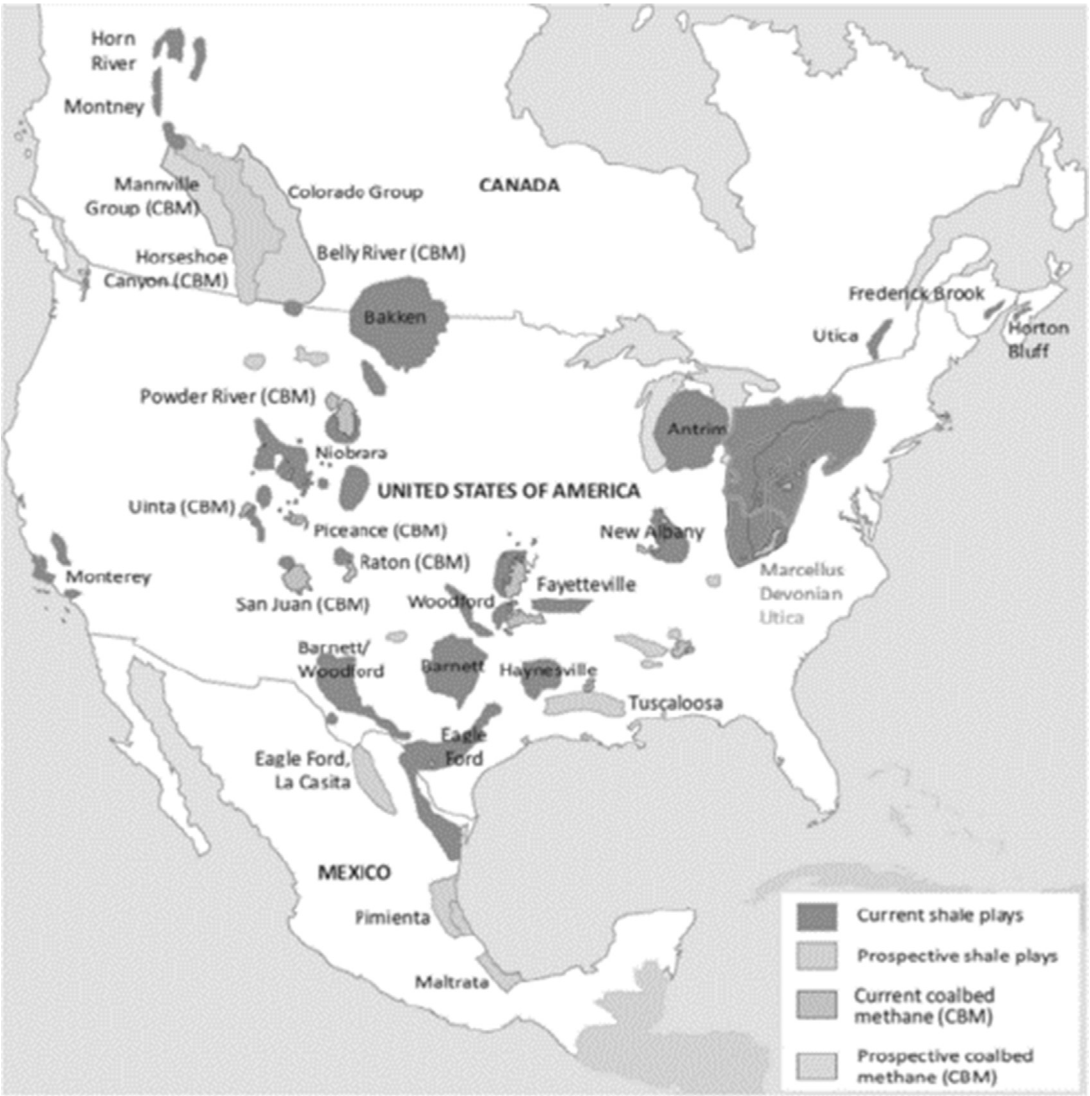

FIG. 2.3 Shale gas resources (shale gas plays) in the contiguous United States, Canada, and Mexico. *Adapted from US EIA (2012). Energy Information Administration, United States Department of Energy, Washington, DC.*

to study and understand key reservoir parameters for gas shale deposits and these parameters include: (i) thermal maturity, (ii) reservoir thickness, (iii) total organic carbon (TOC) content, (iv) adsorbed gas fraction, (v) free gas within the pores and fractures, and (vi) permeability (Chapter 4). The first two parameters are routinely measured. Thermal maturity is commonly measured in core analysis and reservoir thickness is routinely measured with logs. The calculation of the final four parameters requires a novel approach.

2.1 US resources

Almost all (96% v/v) of the shale natural gas in proved reserves in 2010 came from the six largest shale plays in the United States (US EIA, 2012). The Barnett again ranked as the largest shale gas play in the United States, significantly higher increases over 2009 proved reserves were registered by the Haynesville/Bossier (which more than doubled 2009 volumes) and the Marcellus (which nearly tripled). Among these six shale plays, the only decline from 2009 volumes was in the Antrim of northern Michigan — a mature, shallow biogenic shale gas play discovered in 1986 that is no longer being developed at the same pace as the other leading shale resources.

However, there are other gas shale resources that are of increasing importance to the United States energy balance and economics. These must not be ignored and the predominant shale gas resources in the United states are listed below in *alphabetical order* and not in order of preference or importance.

2.1.1 *Antrim shale*

The Antrim shale is a shallow shale gas play in the Michigan Basin (Table 2.3) whose development was accelerated due to the non-conventional gas tax incentives of the 1980s (Hill and Nelson, 2000; Curtis, 2002). The play is part of an extensive, organic-rich shale

TABLE 2.3 Geological, geochemical, and reservoir parameters for five shale-gas systems.

Property	Antrim	Ohio	New Albany	Barnett	Lewis
Depth (ft)	600–2400	2000–5000	600–4900	6500–8500	3000–6000
Bottom-hole temperature (°F)	75	100	80–105	200	130–170
Total organic carbon (%)	0.3–24	0–4.7	1–25	4.50	0.45–2.5
Vitrinite reflectance (% Ro)	0.4–0.6	0.4–1.3	0.4–1.0	1.0–1.3	1.6–1.88
Total porosity (%)	9	4.7	10–14	4–5	3–5.5
Gas-filled porosity (%)	4	2.0	5	2.5	1–3.5
Water-filled porosity (%)	4	2.5–3.0	4–8	1.9	1–2
Gas content (scf/ton)	40–100	60–100	40–80	300–350	15–45
Adsorbed gas (%)	70	50	40–60	20	60–85
Reservoir pressure (psi)	400	500–2000	300–600	3000–4000	1000–1500

depositional system that covered large areas of the ancestral North American continent in the Middle-to-Late Devonian. The intracratonic Michigan basin was one of several depocenters situated along the Eastern Interior Seaway. The basin has been filled with more than 17,000 feet of sediment, 900 feet of which comprises the Antrim Shale and associated Devonian-Mississippian rocks. The base of the Antrim, near the center of the modern structural basin, is approximately 2400 feet below sea level (Braithwaite, 2009; US EIA, 2011a).

The Antrim shale is a black, organic rich bituminous shale which is divided into four members, from base to top: the Norwood, Paxton, Lachine, and upper members. The upper members are overlaid by the Greenish-gray Ellsworth Shale. The stratigraphy of the Antrim shale stratigraphy is relatively straightforward and wells are typically completed in the Lachine and Norwood members of the lower Antrim, whose aggregate thickness approaches 160 feet. The total organic carbon (TOC) content of the Lachine and Norwood ranges from 0.5% to 24% w/w. These black shale formations are silica rich (20%—41% microcrystalline quartz and wind-blown silt) and contain abundant dolomite and limestone concretions and carbonate, sulfide, and sulfate cements. The remaining lower Antrim unit, the Paxton, is a mixture of lime mudstone and gray shale lithology (Martini et al., 1998) containing 0.3—8% w/w total organic carbon and 7—30% w/w silica. Correlation of the fossil alga *Foerstia* has established time equivalence among the upper part of the Antrim Shale, the Huron Member of the Ohio Shale of the Appalachian basin, and the Clegg Creek Member of the New Albany Shale of the Illinois basin (Roen, 1993).

Typical depths for the entire Antrim shale unit range from 500 to 2300 feet and the areal extent is roughly approximately 30,000 square miles (Gutschick and Sandberg, 1991; Braithwaite, 2009; US EIA, 2011a). The entire area is overlain by Devonian and Mississippian sediments and hundreds of feet of glacial till. The Antrim mineralogy shows the shale to be laminated with very fine grains. The composition consists mainly of illite and quartz with small quantities of organic material and pyrite.

The Antrim Shale has an organic matter up to 20% w/w, and is mainly made up of algal material. The vitrinite reflectance is in the range of 0.4—0.6, indicating that the shale is thermally immature. The shale is also shallow and there is a high concentration of methane in the composition, which would lead one to assume the gas is of a microbial origin, but, $\delta^{13}C$ values indicate a more thermogenic origin (Martini et al., 1996). For shallow wells in the Antrim shale, the gas is of microbial origin. Deeper wells have a mix of thermogenic gas and microbial gas. For gas compositions with C1/(C2+C3) <100 the gas origin is thermogenic, and this occurs for the gas present in the Niagaran formation which under lays the Antrim Shale. Since the Antrim has so many natural fractures, it is reasonable to assume there is migration of gas from the Niagaran formation in to the Antrim Shale.

The Antrim shale has two main ways of storing gas: absorption and free gas in the pore volume. The lower Norwood member has a higher adsorption capacity (approximately 115 ft^3 per ton) than the Lachine member (approximately 85 ft^3 per ton) (Kuuskraa et al., 1992). This is an important factor to consider when designing a fracture treatment because it would be more beneficial to have more of the proppant in the zone with the highest gas content. The free gas in the pore space can account for up to 10% of the total gas in place, but it is still not clear on how dependant the free gas is on the water in place. The very low permeability of the matrix could make it very difficult if not impossible to remove a significant portion of the free gas.

Two dominant sets of natural fractures have been identified in the northern producing trend, one oriented toward the northwest and the other to the northeast and both exhibiting sub-vertical to vertical inclinations. These fractures, generally uncemented or lined by thin coatings of calcite (Holst and Foote, 1981; Martini et al., 1998), have been mapped for several meters in the vertical direction and tens of meters horizontally in surface exposures. Attempts to establish production in the Antrim outside this trend have commonly encountered organic, gas-rich shale but minimal natural fracturing and, hence, permeability (Hill and Nelson, 2000).

Thus, the Antrim Shale is highly fractured for a shale reservoir. Fracture spacing can be as close as 1–2 feet, compared to 10–20 feet for the Barnett shale. These fractures can create permeability-thicknesses in the range of 50–5000 md-ft, which increases gas production. But, it also helps water flow, and thus most wells produce large amounts of water which must be disposed (Kuuskraa et al., 1992).

2.1.2 *Bakken shale*

The Bakken Shale of the Williston Basin of Montana and North Dakota has seen a similar growth rate to the Barnett. The Bakken is another technical play in which the development of this unconventional resource has benefitted from the technological advances in horizontal wells and hydraulic fracturing (Cohen, 2008; Cox et al., 2008; Braithwaite, 2009). In April 2008, the United States Geological Survey (USGS) released an updated assessment of the undiscovered technically recoverable reserves for this shale play estimating there are 3.65 billion barrels (3.65×10^9 bbls) of oil, 1.85 trillion cubic feet (1.85×10^{12} ft^3) of associated natural gas, and 148 million barrels (148×10^6 bbls) of natural gas liquids in the play (USGS, 2008; US EIA, 2011a).

The Bakken shale formation differs from other shale plays in that it is an oil reservoir, a dolomite layered between two shale formations, with depths ranging from around 8000 to 10,000 feet from which oil, gas and natural gas liquids are produced. Each succeeding member of the Bakken formation – lower shale, middle sandstone and upper shale member – is geographically larger than the one below. Both the upper and lower shale formations, which are the crude oil source rocks, present fairly consistent lithology, while the middle sandstone member varies in thickness, lithology and petrophysical properties.

The Bakken shale formation is not as naturally fractured as the Barnett shale formation and, therefore, requires more traditional fracture geometry with both longitudinal and transverse fractures. Diversion methods are used throughout hydraulic fracture treatments, which primarily use gelled water fracture fluids, although there is a growing trend toward the use of an intermediate strength proppant. Recently, the Bakken gas shale has seen an increase in activity, and the trend is toward longer laterals – up to 10,000 feet for single laterals in some cases. In addition, there is also a trend to drill below the lower Bakken shale and fracture upwards.

2.1.3 *Barnett shale*

The Barnett shale formation is the oldest of the shale gas plays (Montgomery et al., 2005). Much of the technology used in drilling and production of shale gas has been developed on this play. The Barnett shale formation lies around the Dallas-Ft. Worth area of Texas and produces at depths of 6500–9500 feet. The wedge-shaped Fort Worth basin covers approximately 15,000 square miles in North-Central Texas and is centered along the north-south direction, deepening to the north and outcropping at the Liano uplift in Liano County (Bowker, 2007a, 2007b; Jarvie et al., 2007; Zhao et al., 2007). The Cambrian Riley and Hickory formations are overlaid by the Viola-Simpson and Ellenburger groups. The Viola-Simpson limestone group is found in Tarrant and Parker counties and acts as a barrier between the Barnett and the Ellenburger formation. The Ellenburger formation is a very porous aquifer (Zuber et al., 2002) that if fractured will produce copious amounts of highly saline water, effectively shutting down a well with water disposal cost.

Geochemical and reservoir parameters for the Barnett Shalein the Fort Worth basin differ markedly from those of other gas-productive shales, particularly with respect to gas in place. For example, Barnett shale gas is thermogenic in origin and hydrocarbon generation began in the Late Paleozoic, continued through the Mesozoic, and ceased with uplift and cooling during the Cretaceous (Jarvie et al., 2001, 2007). In addition, organic matter in the Barnett shale formation has generated liquid hydrocarbon derivatives and Barnett-sourced oils in other formations, ranging from Ordovician to Pennsylvanian in age, in the western Fort Worth basin (Jarvie et al., 2001, 2007) – cracking of this oil may have contributed to the gas-in-place resource.

The Mississippian-age Barnett Shale overlies the Viola-Simpson group. The Barnett shale is varies in thickness from 150 to 800 feet, and is the most productive gas shale in Texas. The permeability ranges from 7 to 50 nanodarcies and the porosity from 4% to 6% (Montgomery et al., 2005; Cipolla et al., 2010). In addition, well performance of the Barnett Shale changes significantly with changing produced fluid type, depth and formation thickness (Hale and William, 2010) and on the type of completion method implemented and the large hydraulic fracture treatments (Ezisi et al., 2012).

The three most important production related structures in the basin include both major and minor faulting, fracturing, and karst-related collapse features (Frantz et al., 2005). Fracturing is important to gas production because it provides a conduit for gas to flow from the pores to the wellbore, and it also increases exposure of the well to the formation. The Barnett shale formation exhibits complex fracture geometry which often creates difficulty in estimating fracture length and exposure to the formation due to the complex geometry. The fracturing is believed to be caused by the cracking of oil into gas. This cracking can cause a tenfold increase in the hydrocarbon volume, increasing the pressure until the formation breaks. The precipitation of calcium carbonate in the fractures can cut down on the conductivity of the fractures. This precipitation is hard to detect on logs, and can cause a well location that appears to be good on seismic into an unproductive well. This precipitation is also hard to treat with acidization due to the long distances the acid is required to travel before making a noticeable impact on production.

Change in gas content with pressure occurs in the Barnett shale with a typical reservoir pressure in the range of 3000–4000 psi (Frantz et al., 2005). In low permeability formations, pseudo radial flow can take over 100 years to be established. Thus, most gas flow in the reservoir is a linear flow from the near fracture area toward the nearest fracture face. Faulting and karst-related collapse features are important mainly in the Ellenburger formation.

Horizontal drilling and hydraulic fracturing are the key enabling technologies that first made recovery of Barnett shale gas economically viable in the mid-1990s. The completion and drilling techniques are well established there and drilling efficiency continues to improve even as laterals extend to increasing lengths. A typical lateral is 2500 feet to 3000 feet. Use of water-based muds is standard, as is cementing with acid soluble cement. In addition to drilling longer laterals, current trends in the Barnett are toward bigger frac jobs and more stages. Infills are being drilled and testing of spacing is down to 10 acres, while re-fracturing of the first horizontal wells from 2003 to 2004 has commenced; both infills and refracturing efforts are expected to improve the estimated Ultimate Recovery from 11% to 18%. In addition, pad drilling, especially in urban areas, and recycling of water are growing trends in the Barnett, as elsewhere.

In addition to drilling longer laterals, current trends in the Barnett are toward bigger hydraulic fracturing projects and more stages. Infills are being drilled and testing of spacing is down to 10 acres, while re-fracturing of the first horizontal wells from 2003 to 2004 has commenced; both infills and refracturing are expected to improve the *estimated ultimate recovery* from 11 to 18% v/v. In addition, pad drilling (Chapter 4), especially in urban areas, and recycling of water (Chapter 6) are growing trends in the Barnett shale and in other shale formations.

2.1.4 Baxter shale

The Baxter Shale is stratigraphically equivalent to the Mancos, Cody, Steele, Hilliard, and Niobrara/Pierre formations (Braithwaite, 2009; Mauro et al., 2010; US EIA, 2011a) and was deposited in hundreds of feet of water in the Western Interior Seaway from approximately ninety to eighty million years ago (Coniacean to lower Campanian) and consists of approximately two thousand five hundred feet of dominantly siliceous, illitic, and calcareous shale that contains regionally correlative coarsening-upward sequences of quartz-and carbonate-rich siltstones several tens of feet thick. The total organic carbon content ranges from 0.5 to 2.5% w/w in the shale and from 0.25 to 0.75% w/w in the siltstones. Measured porosities in both the shale and siltstones typically range from 3% to 6% with matrix permeability of 100−1500 nanodarcies.

Gas production has been established from the Baxter Shale in twenty two vertical wells and three horizontal wells in the Vermillion Basin of northwestern Colorado and adjacent Wyoming. Production comes mainly from the silt-rich intervals as determined by production logs. The productive area in the Baxter Shale has vitrinite reflectance values approaching 2% and is in the dry gas generation window.

The resource area is defined by numerous wells with gas shows and over-pressuring in the Baxter shale with gradients ranging from 0.6 to 0.8 psi/ft at depths greater than ten thousand feet.

A challenge within this reservoir is the ability to economically access this large unconventional gas accumulation. This is not a classic 100- to 300-foot-thick organic-rich shale gas reservoir. Instead it is a very large hydrocarbon resource stored in two thousand five hundred feet of shale with interbedded siltstone intervals. 3-D seismic data have proved useful in helping define potential fracture networks in the Baxter shale that can be targeted with horizontal wells.

2.1.5 *Big Sandy*

The Devonian Big Sandy shale gas play includes the Huron, Cleveland and Rhinestreet formations located within the Appalachian Basin in Kentucky, Virginia and West Virginia. For modeling purposes, the Big Sandy was divided into two main units: the Developed Area and Undeveloped Area.

The total area for the Big Sandy shale play as 10,669 square miles (6,828,000 acres). The shale play has an average estimated ultimate recovery on the order of 0.325 billion cubic feet (0.325×10^9 ft^3) per well and approximately 7.4 trillion cubic feet (7.4×10^{12} ft^3) of technically recoverable gas. Big Sandy has a total active area of approximately 8675 square miles and an undeveloped area of 1994 square miles with a well spacing of 80 acres per well.

2.1.6 *Caney shale*

The Caney Shale (Arkoma Basin, Oklahoma) is the stratigraphic equivalent of the Barnett Shale in the Ft. Worth Basin (Fig. 2.4) (Boardman and Puckette, 2006; Andrews, 2007, 2012; Jacobi et al., 2009). The formation has become a gas producer since the large success of the Barnett shale formation. The Caney Shale, Chesterian age, was deposited in the Oklahoma part of the Arkoma Basin one of a series of foreland basins that formed progressively westward along the Ouachita Fold Belt from the Black Warrior Basin in Mississippi to basins in southwest Texas. The Arkoma Basin in Oklahoma is in the Southeast corner of the state north and northwest of the Ouachita Mountains. The Caney shale formation dips southward from a depth of three thousand feet in northern McIntosh County, Oklahoma to twelve thousand feet north of the Choctaw thrust. The Caney formation thickens toward the southeast along

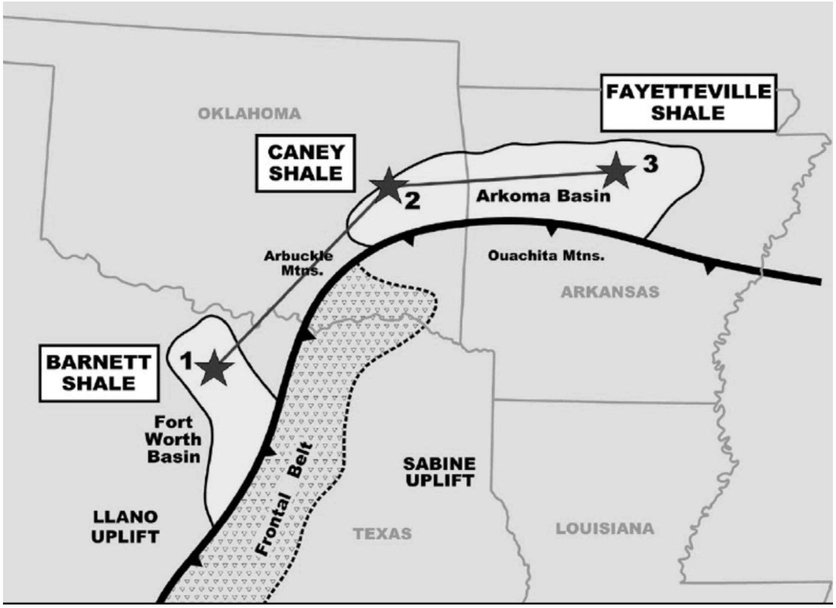

FIG. 2.4 Deposition of shale during the Mississippian sub-period. The Mississippian is a sub-period of the Carboniferous Period in the Geological Time Scale (Chapter 1).

the Choctaw fault in the south. It can be subdivided into six intervals based on characteristics of the density and resistivity logs.

Reported average total organic carbon values the Caney formation range from 5 to 8% w/w, which show a linear correlation with density. Mud log gas shows have a strong correlation with desorbed gas values that range from one hundred and twenty to one hundred and fifty cubic feet per ton of shale. Estimates of gas in place for the Caney range from thirty to forty billion cubic feet ($30-40 \times 10^9$ ft^3).

2.1.7 *Chattanooga shale*

The Chattanooga Shale (Black Warrior Basin) and has been considered as a rich oil shale formation (Rheams and Neathery, 1988). The Chattanooga sits within the thermogenic gas window in much of the Black Warrior Basin (Carroll et al., 1995) and may thus contain significant prospects for natural gas. The Chattanooga formation overlies Ordovician through Devonian strata, and the time value of the disconformity increases northward (Thomas, 1988). The Chattanooga is overlain sharply by the Lower Mississippian Maury Shale, which is commonly thinner than 2 feet, and the Maury is in turn overlain by the micritic Fort Payne Chert. The Chattanooga Shale in Alabama was apparently deposited in dysoxic to anoxic subtidal environments and can be considered as a cratonic extension of the Acadian foreland basin (Ettensohn, 1985).

The thickness of the Chattanooga varies significantly within the Black Warrior Basin. The shale is thinner than 10 feet and is locally absent in much of Lamar, Fayette, and Pickens Counties, which is the principal area of conventional oil and gas production in the Black Warrior Basin. For this reason, the Chattanooga has not been considered to be the principal source rock for the conventional oil and gas reservoirs in this area. The shale is thicker than 30 feet in a belt that extends northwestward from Blount County into Franklin and Colbert Counties. A prominent depocenter is developed along the southwestern basin margin in Tuscaloosa and Greene Counties. Here, the shale is consistently thicker than 30 feet and is locally thicker than 90 feet.

The Chattanooga Shale is in some respects analogous to the Barnett Shale of the Fort Worth Basin in that it is an organic-rich black shale bounded by thick, mechanically stiff limestone units that may help confine induced hydrofractures within the shale (Hill and Jarvie, 2007; Gale et al., 2007). Because the Chattanooga is relatively thin, horizontal drilling combined with controlled hydrofracturing may maximize production rates.

2.1.8 *Conasauga shale*

The Conasauga Formation of the Appalachian thrust belt is geologically the oldest and most structurally complex shale formation from which gas production has been established. The Conasauga differs from other gas shale formations in several respects. The productive lithology is thinly interbedded shale and micritic limestone that can contain more than 3% total organic carbon.

The Conasauga is of Middle Cambrian age and can be characterized as a shoaling-upward succession in which shale passes vertically into a broad array of inner ramp carbonate facies. The shale was deposited on the outer ramp, and the shale is thickest in basement grabens that formed during late Precambrian to Cambrian Iapetan rifiting (Thomas et al., 2000). The shale facies of the Conasauga is part of the weak litho-tectonic unit that hosts the basal detachment of the Appalachian Thrust Belt in Alabama (Thomas, 2001; Thomas and Bayona, 2005). The shale has been thickened tectonically into antiformal stacks that have been interpreted as giant shale duplexes, or mushwads (Thomas, 2001). In places, the shale is thicker than 8000 feet, and the shale is complexly folded and faulted at outcrop scale.

The Conasauga shale gas formation (Conesauga shale gas formation, Alabama) continues to be developed primarily in northeast Alabama (US EIA, 2011a). With the exception of one well in Etowah County and one well in Cullman County, all of the development has been in St. Clair County. Etowah and St. Clair Counties are located northeast of Birmingham in the Valley and Ridge Province of Alabama. Cullman County is north of Birmingham in the Cumberland Plateau Province.

This shale formation it represents the first commercial gas production from shale in Alabama, but because it is geologically the oldest and most structurally complex shale formation from which gas production has been established. The Conasauga differs from other gas shale formations in several respects. The productive lithology is thinly inter-bedded shale and micritic limestone that can contain more than 3% total organic carbon.

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Surface mapping and seismic exploration reveal that at least three Conasauga anti-forms are preserved in the Alabama Appalachians. Exploration has focused primarily on the southeastern portion of the Gadsden anti-form, which is in St. Clair and Etowah Counties. The Palmerdale and Bessemer anti-forms constitute the core of the Birmingham anticlinorium. The Palmerdale and Bessemer structures are overlain by a thin roof of brittle Cambrian-Ordovician carbonate rocks, and Conasauga shale facies are exposed locally. The Palmerdale structure is in the heart of the Birmingham metropolitan area and thus may be difficult to develop, whereas the southwestern part of the Bessemer structure is in rural areas and may be a more attractive exploration target. Additional thick shale bodies may be concealed below the shallow Rome thrust sheet in Cherokee and northeastern Etowah Counties and perhaps in adjacent parts of Georgia (Mittenthal and Harry, 2004).

2.1.9 Devonian Low Thermal Maturity play and Greater Siltstone shale gas play

The Devonian Low Thermal Maturity shale gas play, also known as the Northwestern Ohio shale, is located within the Appalachian Basin in Kentucky, New York, Ohio, Pennsylvania, Tennessee and West Virginia. The location of the Greater Siltstone is also within the Appalachian Basin in New York, Ohio, Pennsylvania, Virginia and West Virginia.

The estimated a total area for the Low Thermal Maturity as 45,844 square miles (29,340,000 acres) and a total area of 22,914 square miles (14,665,000 acres) for the Greater Siltstone shale play. The Devonian Low Thermal Maturity has an average estimated ultimate resource of 0.3 billion cubic feet (0.3×10^9 ft^3) per well and approximately 13.5

trillion cubic feet (13.5×10^{12} ft^3) of technically recoverable gas. The Devonian Greater Siltstone has an average estimated ultimate recovery of 0.19 billion cubic feet (0.19×10^9 ft^3) per well and approximately 8.5 trillion cubic feet (8.5×10^{12} ft^3) of technically recoverable gas.

2.1.10 Eagle Ford shale

The Eagle Ford shale (discovered in 2008) is a sedimentary rock formation from the Late Cretaceous age underlying much of South Texas which covers three thousand square miles and consists of an organic-rich marine shale that also has been found to appear in outcrops (Braithwaite, 2009; US EIA, 2011a). The shale formation has a high carbonate content, up to 70%, which makes it brittle and facilitates hydraulic fracturing. During the Cretaceous time the tectonic movements caused the land masses in the south-east, in the direction of the Mexican gulf, to be pressed down. These movements caused a steep slope in the geological layers and brought once submerged areas, rich in organic matter, onshore. For this reason the depth of the oil and gas findings in the Eagle Ford varies from approximately one to two miles with an average thickness of 240 feet. West of Dallas, Texas, the Eagle Ford formation can be seen on the surface.

The fact that the Eagle Ford shale occurs at different depths is the reason for the occurrence of oil, wet gas/condensate and dry gas in different regions (Satter et al., 2008). Thus, dry gas reservoirs are categorized as reservoirs with hydrocarbon derivatives in the gas phase alone, remaining in the gas phase during production. In wet gas reservoirs the hydrocarbon derivatives are initially all in the gas phase but during production some of the extracted gas condenses to the liquid phase because they are heavier (having lower API gravity). Further, the hydrocarbon derivatives in the oil reservoirs are in the liquid phase within the reservoir.

This hydrocarbon-producing formation rich in oil and natural gas extends from the Texas-Mexico border in Webb and Maverick counties and extends 400 miles toward East Texas. The formation is fifty miles wide and an average of two hundred and fifty feet thick at a depth between four thousand and twelve thousand feet. The shale contains a high amount of carbonate which makes it brittle and easier to apply hydraulic fracturing to produce the oil or gas.

The Eagle Ford shale formation is estimated to have 20.81 trillion cubic feet (20.81×1012 ft^3) of natural gas and 3.351 billion barrels (3351×109 bbls) of oil.

2.1.11 Fayetteville shale

The Fayetteville shale is an unconventional gas reservoir located on the Arkansas side of the Arkoma Basin. The shale ranges in thickness from 50 to 550 feet at a depth of 1500–6500 feet. With productive wells penetrating the Fayetteville shale (Arkoma Basin), this formation is somewhat shallower than the Barnett shale formation (Braithwaite, 2009; US EIA, 2011a). Mediocre production from early vertical wells stalled development in the vertically fractured Fayetteville, and only with recent introduction of horizontal drilling and hydraulic fracturing has drilling activity increased.

In the most active Central Fayetteville Shale, horizontal wells are drilled using oil-based mud in most cases, and water-based mud in others. In addition, 3-D seismic is gaining importance as longer laterals of 3000-plus feet are drilled and more stages are required for hydraulic fracturing. With growing numbers of wells and a need for more infrastructure – pad drilling is another trend emerging in the Fayetteville.

2.1.12 *Floyd shale*

The Upper Mississippian Floyd Shale is an equivalent of the prolific Barnett Shale of the Fort Worth Basin. The shale is an organic-rich interval in the lower part of the Floyd Shale that is informally called the Neal shale, which is an organic-rich, starved-basin deposit that is considered to be the principal source rock for conventional hydrocarbon derivatives in the Black Warrior basin.

The Floyd shale is a black marine shale located stratigraphically below the Mississippian Carter sandstone and above the Mississippian Lewis sandstone (US EIA, 2011a). Although the Carter and Lewis sandstones have historically been the most prolific gas-producing zones in the Black Warrior Basin Region of Alabama, there has been no prior production history reported for the Floyd Shale. The Chattanooga Shale is located below the Floyd and is separated from it in most areas by the Tuscumbia Limestone and the Fort Payne Chert.

The Mississippian Floyd Shale is an equivalent of the prolific Barnett Shale of the Fort Worth Basin and the Fayetteville Shale of the Arkoma Basin and has thus been the subject of intense interest. The Floyd is a broadly defined formation that is dominated by shale and limestone and extends from the Appalachian Thrust Belt of Georgia to the Black Warrior Basin of Mississippi.

Usage of the term, Floyd, can be confusing. In Georgia, the type Floyd Shale includes strata equivalent to the Tuscumbia Limestone, and in Alabama and Mississippi, complex facies relationships place the Floyd above the Tuscumbia Limestone, Pride Mountain Formation, or Hartselle Sandstone and below the first sandstone in the Parkwood Formation. Importantly, not all Floyd facies are prospective as gas reservoirs. Drillers have long recognized a resistive, organic-rich shale interval in the lower part of the Floyd Shale that is called informally the Neal shale (Cleaves and Broussard, 1980; Pashin, 1994). In addition to being the probable source rock for conventional oil and gas in the Black Warrior Basin, the Neal has the greatest potential as a shale-gas reservoir in the Mississippian section of Alabama and Mississippi. Accordingly, usage of the term, Neal, helps specify the facies of the Floyd that contains prospective hydrocarbon source rocks and shale-gas reservoirs.

2.1.13 *Haynesville shale*

The Haynesville Shale (also known as the Haynesville-Bossier shale) is situated in the North Louisiana Salt Basin in northern Louisiana and eastern Texas with depths ranging from 10,500 to 13,500 feet (Braithwaite, 2009; Parker et al., 2009; US EIA, 2011a). The Haynesville is an Upper Jurassic-age shale bounded by sandstone (Cotton Valley Group) above and limestone (Smackover Formation) below.

The Haynesville Shale covers an area of approximately 9000 square miles with an average thickness of 200–300 feet. The thickness and areal extent of the Haynesville has allowed operators to evaluate a wider variety of spacing intervals ranging from 40 to 560 acres per well. Gas content estimates for the play are 100 to 330 scf/ton. The Haynesville formation has the potential to become a significant shale gas resource for the United States with original gas-in-place estimates of 717 trillion cubic feet (717×10^{12} ft^3) and technically recoverable resources estimated at 251 trillion cubic feet (251×10^{12} ft^3).

Compared to the Barnett shale, the Haynesville shale is extremely laminated, and the reservoir changes over intervals as small as four inches to one foot. In addition, at depths of 10,500—13,500 feet, this play is deeper than typical shale gas formations creating hostile conditions. Average well depths are 11,800 feet with bottomhole temperatures averaging 155 °C (300 °F) and wellhead treating pressures that exceed 10,000 psi. As a result, wells in the Haynesville require almost twice the amount of hydraulic horsepower, higher treating pressures and more advanced fluid chemistry than the Barnett and Woodford shale formations.

The high-temperature range, from 125 °C (260 °F) to 195 °C (380 °F), creates additional problems in horizontal wells, requiring rugged, high-temperature/high-pressure logging evaluation equipment. The formation depth and high-fracture gradient demand long pump times at pressures above 12,000 psi. In deep wells, there is also concern related to the ability to sustain production with adequate fracture conductivity. In large volumes of water for fracturing, making water conservation and disposal a primary issue.

The Bossier Shale, often linked with the Haynesville shale is a geological formation that produces hydrocarbon and delivers large amounts of natural gas when properly treated. While there is some confusion when distinguishing Haynesville shale from the Bossier Shale, it is a relatively simple comparison — the Bossier Shale lies directly above the Haynesville shale but lies under the Cotton Valley sandstones. However, some geologists still consider the Haynesville shale and the Bossier Shale one in the same.

The thickness of the Bossier Shale is approximately 1800 feet in the area of interest. The productive zone is located in the upper 500—600 feet of the shale. The Bossier shale is located in eastern Texas and northern Louisiana.

The Upper Jurassic (Kimmeridgian to Lower Tithonian) Haynesville and Bossier hale formations of East Texas and northwest Louisiana are currently one of the most important shale-gas plays in North America, exhibiting overpressure and high temperature, steep decline rates, and resources estimated together in the hundreds of trillions of cubic feet. These shale-gas resources have been studied extensively by companies and academic institutions within the last year, but to date the depositional setting, facies, diagenesis, pore evolution, petrophysics, best completion techniques, and geochemical characteristics of the Haynesville and Bossier shales are still poorly understood. Our work represents new insights into Haynesville and Bossier Shale facies, deposition, geochemistry, petrophysics, reservoir quality, and stratigraphy in light of paleographic setting and regional tectonics.

Haynesville and Bossier Shale deposition was influenced by basement structures, local carbonate platforms, and salt movement associated with the opening of the Gulf of Mexico basin. The deep basin was surrounded by carbonate shelves of the Smackover/Haynesville Lime Louark sequence in the north and east and local platforms within the basin. The basin periodically exhibited restricted environment and reducing anoxic conditions, as indicated by variably increased molybdenum content, presence of framboidal pyrite, and TOC-S-Fe relationships. These organic-rich intervals are concentrated along and between platforms and islands that provided restrictive and anoxic conditions during Haynesville and part of Bossier times.

The mudrock facies range from calcareous-dominated facies near the carbonate platforms and islands to siliceous-dominated lithologies in areas where deltas prograded into the basin and diluted organic matter (e.g., northern Louisiana and northeast Texas). These facies are a direct response to a second-order transgression that lasted from the early Kimmeridgian to the Berriasian. Haynesville and Bossier shales each compose three upward-coarsening cycles that probably represent third-order sequences within the larger second-order transgressive systems and early highstand systems tracts, respectively. Each Haynesville third-order cycle is characterized by unlaminated mudstone grading into laminated and bioturbated mudstone. Most of the three Bossier third-order cycles are dominated by varying amounts of siliciclastic mudstones and siltstones. However, the third Bossier cycle exhibits higher carbonate and an increase in organic productivity in a southern restricted area (beyond the basinward limits of Cotton Valley progradation), creating another productive gas-shale opportunity. This organic-rich Bossier cycle extends across the Sabine Island complex and the Mt. Enterprise Fault Zone in a narrow trough from Nacogdoches County, Texas, to Red River Parish, Louisiana. Similar to the organic-rich Haynesville cycles, each third-order cycle grades from unlaminated into laminated mudstone and is capped by bioturbated, carbonate-rich mudstone facies. Best reservoir properties are commonly found in facies with the highest TOC, lowest siliciclastics, highest level of maturity, and highest porosity. Most porosity in the Haynesville and Bossier is related to interparticle nano- and micropores and, to a minor degree, by porosity in organic matter.

Haynesville and Bossier gas shales are distinctive on wireline logs—high gamma ray, low density, low neutron porosity, high sonic travel time, moderately high resistivity. Persistence of distinctive log signatures is similar for the organic-rich Bossier Shale and the Haynesville Shale across the study area, suggesting that favorable conditions for shale-gas production extend beyond established producing areas.

2.1.14 Hermosa shale

The black shale of the Hermosa Group (Utah) consists of nearly equal portions of clay-sized quartz, dolomite and other carbonate minerals, and various clay minerals. The clay is mainly illite with minor amounts of chlorite and mixed layer chlorite-smectite (Hite et al., 1984).

The area of interest for the Hermosa Group black shale is the northeast half of the Paradox basin, the portion referred to as the fold and fault belt. This is the area of thick halite deposits in the Paradox Formation, and consequently narrow salt walls and broad interdome depressions. To the southwest of this stratigraphically controlled structural zone the black shale intervals are fewer and thinner, and they lack the excellent seals provided by the halite. The area encompasses eastern Wayne and Emery Counties, southern Grand County and the northeast third of San Juan County (Schamel, 2005, 2006). The kerogen in the shale is predominantly gas-prone humic type III and mixed type II–III (Nuccio and Condon, 1996).

Numerous factors favor the possible development of shale gas in the black shale intervals of the Hermosa Group. First, the shale are very organic-rich, on the whole the most carbonaceous shale in Utah, and they are inherently gas-prone. Second, they have reached relatively high degrees of thermal maturity across much of the basin. Third and perhaps most significant, the shale is encased in halite and anhydride which retard gas leakage, even by diffusion. Yet it is curious that the Paradox basin is largely an oil province (Morgan, 1992; Montgomery, 1992) in which gas production is historically secondary and associated gas, which relates to the concentration of crude oil development in the shallower targets on the southwest basin margin and in the anticlines.

2.1.15 *Huron shale*

The Huron shale formation lies at a depth between 1000 and 7000 feet and stretches across portions of West Virginia, Ohio, and Northeast Kentucky. Most development and production in the Huron are occurring in West Virginia. The vertical thickness of this rock formation varies between 200 and 2000 feet.

2.1.16 *Lewis shale*

The Lewis Shale (San Juan Basin) is a quartz-rich mudstone that was deposited in a shallow, off-shore marine setting during an early Campanian transgression southwestward across shoreline deposits of the underlying pro-gradational Cliffhouse Sandstone Member of the Mancos Formation (Nummendal and Molenaar, 1995; US EIA, 2011a). The gas resources of the Lewis Shale are currently being developed, principally through recompletions of existing wells targeting deeper, conventional sandstone gas reservoirs (Dube et al., 2000; Braithwaite, 2009).

The 1000−1500 feet thick Lewis Shale is lowermost shore-face and pro-delta deposits composed of thinly laminated (locally bioturbated) siltstones, mudstones and shale. The average clay fraction is just 25%, but quartz is 56%. The rocks are very tight. Average matrix gas porosity is 1.7% and the average gas permeability is 0.0001 mD. The rocks also are organically lean, with an average total organic carbon content is only 1.0%; the range is 0.5%−1.6%. The reservoir temperature is 46 °C (140 °F). Yet the adsorptive capacity of the rock is 13−38 scf/ton, or approximately 22 billion cubic feet per quarter section (i.e., per 160 acres) (Jennings et al., 1997).

Four intervals and a conspicuous, basin-wide bentonite marker are recognizable in the shale. The greatest permeability is found in the lowermost two-thirds of the section, which may be the result of an increase in grain size and micro-fracturing associated with the regional north-south/east-west fracture system (Hill and Nelson, 2000).

2.1.17 *Mancos shale*

The Mancos shale formation (Uintah Basin) is an emerging shale-gas resource (US EIA, 2011a). The thickness of the Mancos (averaging four thousand feet in the Uinta Basin) and the variable lithology present drillers with a wide range of potential stimulation targets. The area of interest for the Mancos Shale is the southern two-thirds of the greater Uinta Basin, including the northern parts of the Wasatch Plateau. In the northern one-third of the basin there have been two few well penetrations of the Mancos Shale, and it is too deep to warrant commercial exploitation of a “low density” resource such as shale gas. The area is within Duchesne, Uintah, Grand, Carbon and the northern part of Emery Counties (Schamel, 2005, 2006; Braithwaite, 2009).

The Mancos Shale is dominated by mudrock that accumulated in offshore and open-marine environments of the Cretaceous Interior seaway. It is 3450−4150 feet thick where exposed in the southern part of the Piceance and Uinta Basins, and geophysical logs indicate the Mancos to be approximately 5400 feet thick in the central part of the Uinta Basin. The upper part of the formation is inter-tongues with the Mesaverde Group − these tongues typically have sharp basal contacts and gradational upper contacts. Named tongues include the Buck and the Anchor Mine Tongues. An important hydrocarbon-producing unit in the middle part of the

Mancos was referred to as the Mancos B Formation, which consists of thinly interbedded and interlaminated, very fine grained to fine-grained sandstone, siltstone, and clay that was interpreted to have accumulated as north-prograding fore slope sets within an open-marine environment. The Mancos B has been incorporated into a thicker stratigraphic unit identified as the Prairie Canyon Member of the Mancos, which is approximately 1200 feet thick (Hettinger and Kirschbaum, 2003).

At least four members of the Mancos have shale-gas potential: (i) the Prairie Canyon (Mancos B), (ii) the Lower Blue Gate Shale, (iii) the Juana Lopez, and (iv) the Tropic-Tununk Shale. Organic matter in the shale has a large fraction of Terrigenous material derived from the shorelines of the Sevier belt. The thickness of the organic-rich zones within individual system tracts exceeds twelve feet. Vitrinite reflectance values from a limited number of samples at the top of the Mancos range from 0.65% at the Uinta Basin margins to >1.5% in the central basin.

Across most of Utah the Mancos Shale has not been sufficiently buried to have attained the levels of organic maturity required for substantial generation of natural gas, even in the humic kerogen-dominant (type II–III) shale that characterize this group (Schamel 2005, 2006). However, vitrinite reflectance values beneath the central and southern Uinta Basin are well within the gas generation window at the level of the Tununk Shale, and even the higher members of the Mancos Shale. In addition to the in situ gas within the shale, it is likely that some of the gas reservoired in the silty shale intervals has migrated from deeper source units, such as the Tununk Shale or coals in the Dakota.

The Mancos Shale warrants consideration as the significant gas reservoir and improved methods for fracture stimulation tailored to the specific rock characteristics of the Mancos lithology are required. The well completion technologies used in the sandstones cannot be applied to the shale rocks without some reservoir damage.

2.1.18 Marcellus shale

The Marcellus Shale (Appalachian Basin), also referred to as the Marcellus Formation, is a Middle Devonian black, low density, carbonaceous (organic rich) shale that occurs in the subsurface beneath much of Ohio, West Virginia, Pennsylvania, and New York. It is shallow at depths of 2000–8000 feet and 300–1000 feet thick. Small areas of Maryland, Kentucky, Tennessee, and Virginia are also underlain by the Marcellus Shale (Braithwaite, 2009; Bruner and Smosna, 2011; US EIA, 2011a).

The Marcellus Shale formations are 400 million years in the making, stretching from western Maryland to New York, Pennsylvania and West Virginia and encompassing the Appalachian region of Ohio along the Ohio River. It has been estimate that the Marcellus shale formation could contain as much as 489 trillion cubic feet of natural gas, a level that would establish the Marcellus as the largest natural gas resource in North America and the second largest in the world. The Marcellus shale ranges in depth from 4000 to 8500 feet, with gas currently produced from hydraulically fractured horizontal wellbores. Horizontal lateral lengths exceed 2000 feet, and, typically, completions involve multistage fracturing with more than three stages per well.

Throughout most of its extent, the Marcellus is nearly a mile or more below the surface. These great depths make the Marcellus Formation a very expensive target. Successful wells must yield large volumes of gas to pay for the drilling costs that can easily exceed a million dollars for a traditional vertical well and much more for a horizontal well with hydraulic fracturing. There are areas where the thick Marcellus Shale can be drilled at minimum depths and tends to correlate with the heavy leasing activity that has occurred in parts of northern Pennsylvania and western New York.

Natural gas occurs within the Marcellus Shale in three ways: (i) within the pore spaces of the shale, (ii) within vertical fractures (joints) that break through the shale, and (iii) adsorbed on mineral grains and organic material. Most of the recoverable gas is contained in the pore spaces. However, the gas has difficulty escaping through the pore spaces because they are very tiny and poorly connected. The active area of the play is 10,622 square miles and has a total technically recoverable resource 177.9 trillion cubic feet (177.9×10^{12} ft^3), which is equivalent to 3.5 Bcf per well. At the well level, the overwhelming majority of reported estimated ultimate recovery ranges between 3 and 4 billion cubic feet ($3-4 \times 109$ ft^3) of gas. Due to a development moratorium in New York, access to resource, lack of current production, and other issues in the undeveloped section of the Marcellus, the number of drilling locations and the total technically recoverable resources is still open to question. However, at the well level the estimated ultimate recovery of the gas is on the order of 1.15 billion cubic feet (1.5×10^9 ft^3).

The gas in the Marcellus Shale is a result of its contained organic content. Logic therefore suggests that the more organic material there is contained in the rock the greater its ability to yield gas. The areas with the greatest production potential might be where the net thickness of organic-rich shale within the Marcellus Formation is greatest. Northeastern Pennsylvania is where the thick organic-rich shale intervals are located.

Before the year 2000, many successful natural gas wells had been completed in the Marcellus shale. The yields of these wells were often unimpressive upon completion. However, many of these older wells in the Marcellus have a sustained production that decreases slowly over time and many of them continued to produce gas for decades. To exhibit the interest in this shale formation, The Pennsylvania Department of Environmental Protection reports that the number of drilled wells in the Marcellus Shale has been increasing rapidly. In 2007, 27 Marcellus Shale wells were drilled in the state, however, in 2011 the number of wells drilled had risen to more than 2000.

For new wells drilled with the new horizontal drilling and hydraulic fracturing technologies the initial production can be much higher than what was seen in the old wells. Early production rates from some of the new wells have been over one million cubic feet of natural gas per day. The technology is so new that long term production data is not available. As with most gas wells, production rates will decline over time, however, a second hydraulic fracturing treatment could stimulate further production.

2.1.19 Neal shale

The Neal shale is an organic-rich facies of the Upper Mississippian age Floyd shale formation. The Neal shale formation has long been recognized as the principal source rock that charged conventional sandstone reservoirs in the Black Warrior Basin (Telle et al., 1987; Carroll et al., 1995; US EIA, 2011a) and has been the subject of intensive shale-gas exploration in recent years.

The Neal shale is developed mainly in the southwestern part of the Black Warrior Basin and is in facies relationship with strata of the Pride Mountain Formation, Hartselle

Sandstone, the Bangor Limestone, and the lower Parkwood Formation. The Pride Mountain-Bangor interval in the northeastern part of the basin constitutes a progradational parasequence set in which numerous stratigraphic markers can be traced southwestward into the Neal shale. Individual parasequences tend to thin southwestward and define a clinoform stratal geometry in which near-shore facies of the Pride Mountain-Bangor interval pass into condensed, starved-basin facies of the Neal shale.

The Neal formation maintains the resistivity pattern of the Pride Mountain-Bangor interval, which facilitates regional correlation and assessment of reservoir quality at the parasequence level. The Neal shale and equivalent strata were subdivided into three major intervals, and isopach maps were made to define the depositional framework and to illustrate the stratigraphic evolution of the Black Warrior Basin in Alabama (Pashin, 1993). The first interval includes strata equivalent to the Pride Mountain Formation and the Hartselle Sandstone and thus shows the early configuration of the Neal basin. The Pride Mountain-Hartselle interval contains barrier-strand plain deposits (Cleaves and Broussard, 1980; Thomas and Mack, 1982). Isopach contours define the area of the barrier-strand plain system in the northeastern part of the basin, and closely spaced contours where the interval is between 25 and 225 feet thick define a southwestward slope that turns sharply and faces southeastward in western Marion County. The Neal starved basin is in the southwestern part of the map area, where this interval is thinner than 25 feet.

The second interval includes strata equivalent to the bulk of the Bangor Limestone. A generalized area of inner ramp carbonate sedimentation is defined in the northeastern part of the formation where the interval is thicker than 300 feet. Muddy, outer-ramp facies are concentrated where this interval thins from 300 to 100 feet, and the northeastern margin of the Neal starved basin is marked by the 100-foot contour. Importantly, this interval contains the vast majority of the prospective Neal reservoir facies, and the isopach pattern indicates that the slope had prograded more than 25 miles southwestward during Bangor deposition.

The final interval includes strata equivalent to the lower Parkwood Formation. The lower Parkwood separates the Neal shale and the main part of the Bangor Limestone from carbonate-dominated strata of the middle Parkwood Formation, which includes a tongue of the Bangor that is called the *Millerella* limestone. The Lower Parkwood is a succession of siliciclastic deltaic sediment that prograded onto the Bangor ramp in the northeastern part of the study area and into the Neal basin in the southern part and contains the most prolific conventional reservoirs in the Black Warrior Basin (Cleaves, 1983; Pashin and Kugler, 1992; Mars and Thomas, 1999). The lower Parkwood is thinner than 25 feet above the inner Bangor ramp and includes a variegated shale interval containing abundant slickensides and calcareous nodules, which are suggestive of exposure and soil formation. The area of deltaic sedimentation is where the lower Parkwood is thicker than 50 feet and includes constructive deltaic facies in the Neal basin and destructive, shoal-water deltaic facies along the margin of the Bangor ramp. In the southern part of the study area, the 25-foot contour defines a remnant of the Neal basin that persisted through lower Parkwood deposition. In this area, condensation of lower Parkwood sediment brings middle Parkwood carbonate rocks within 25 feet of the resistive Neal shale.

2.1.20 New Albany shale

The New Albany shale (Illinois Basin) is a black organic-rich Devonian shale located over a large area in southern Indiana and Illinois and in Northern Kentucky (Zuber et al., 2002; Braithwaite, 2009; US EIA, 2011a). The depth of the producing interval varies from 500 feet to 2000 feet depth, with thicknesses of approximately 100 feet. The shale is generally subdivided into four stratigraphic intervals: from top to bottom, these are (i) Clegg Creek, (ii) Camp Run/Morgan Trail, (iii) Selmier, and (iv) Blocher intervals.

The New Albany shale can be considered to be a *mixed source rock* in which some parts of the basin produced thermogenic gas, and other parts produced biogenic gas. This is indicated by the vitrinite reflectance in the basin, varying from 0.6 to 1.3 (Faraj et al., 2004). It is not known whether circulating ground waters recently generated this biogenic gas or whether it is original biogenic gas generated shortly after the time of deposition.

Most gas production from the New Albany comes from approximately sixty fields in northwestern Kentucky and adjacent southern Indiana. However, past and current production is substantially less than that from either the Antrim Shale or Ohio Shale. Exploration and development of the New Albany Shale was spurred by the spectacular development of the Antrim Shale resource in Michigan, but results have not been as favorable (Hill and Nelson, 2000).

Production of New Albany Shale gas, which is considered to be biogenic, is accompanied by large volumes of formation water (Walter et al., 2000). The presence of water would seem to indicate some level of formation permeability. The mechanisms that control gas occurrence and productivity are not as well understood as those for the Antrim and Ohio shale formations (Hill and Nelson, 2000).

2.1.21 Niobrara shale

The Niobrara shale formation (Denver-Julesburg Basin, Colorado) is a shale rock formation located in Northeast Colorado. Northwest Kansas, Southwest Nebraska, and Southeast Wyoming. Oil and natural gas can be found deep below the surface of the Earth at depths of three thousand to fourteen thousand. Companies drill these wells vertically and even horizontally to get at the oil and natural gas in the Niobrara Formation.

The Niobrara Shale is located in the Denver-Julesburg basin which is often referred to as the DJ Basin. This resource exciting oil shale play is being compared to the Bakken shale resource, is located in North Dakota.

2.1.22 Ohio shale

The Devonian shale in the Appalachian Basin was the first produced in the 1820s. The resource extends from Central Tennessee to Southwestern New-York and also contains the Marcellus shale formation. The Middle and Upper Devonian shale formations underlie approximately 128,000 square miles and crop out around the rim of the basin. Subsurface formation thicknesses exceed 5000 feet and organic-rich black shale exceeds 500 feet (152 m) in net thickness (DeWitt et al., 1993).

In general, the Ohio Shale (Appalachian Basin) differs in many respects from the Antrim Shale system. Locally, the stratigraphy is considerably more complex as a result of variations in depositional setting across the basin (Kepferle, 1993; Roen, 1993). The shale formations can be further subdivided into five cycles of alternating carbonaceous shale formations and coarser grained clastic materials (Ettensohn, 1985). These five shale cycles developed in response to the dynamics of the Acadian orogeny and westward progradation of the Catskill delta.

The Ohio Shale, within the Devonian Shale, consists of two major stratigraphic intervals: (i) the Chagrin Shale and (ii) the underlying Lower Huron Shale.

The Chagrin Shale consists of 700–900 feet of gray shale (Curtis, 2002; Jochen and Lancaster, 1993), which thins gradually from East to West. Within the lower 100–150 feet, a transition zone consisting of inter-bedded black and gray shale lithology announces the underlying Lower Huron formation. The Lower Huron shale is 200–275 feet of dominantly black shale, with moderate amounts of gray shale and minor siltstone. Essentially all the organic matter contained in the lower Huron is thermally mature for hydrocarbon generation, based on vitrinite reflectance studies.

The vitrinite reflectance of the Ohio Shale varies from 1% to 1.3%, which indicates that the rock is thermally mature for gas generation (Faraj et al., 2004). The gas in the Ohio Shale is consequently of thermogenic origin. The productive capacity of the shale is a combination of gas storage and deliverability (Kubik et al., 1993). Gas storage is associated with both classic matrix porosity as well as gas adsorption onto clay and non-volatile organic material. Deliverability is related to matrix permeability although highly limited (10^{-9} to 10^{-7} millidarcies) and a well-developed fracture system.

2.1.23 *Pearsall shale*

The Pearsall Shale is a gas bearing formation that garnered attention near the Texas-Mexico border in the Maverick Basin before development of the Eagle Ford shale truly commenced. The Pearsall Shale formation is found below the Eagle Ford formation at depths of seven thousand to twelve thousand feet with a thickness of six hundred to nine hundred feet (Braithwaite, 2009).

The formation does have the potential to produce liquids east of the Maverick Basin. As of 2012, only a few wells had been drilled in the play outside of the Maverick Basin but early results indicate there is potential that has largely been overlooked.

2.1.24 *Pierre shale*

The Pierre Shale, located in Colorado, produced two million cubic feet of gas in 2008. Drilling operators are still developing this rock formation, which lies at depths that vary between 2500 and 5000 feet, and will not know its full potential until more wells provide greater information related to its limits (Braithwaite, 2009).

The Pierre shale formation is a division of Upper Cretaceous rocks laid down from approximately one hundred and forty six million to sixty five million years ago and is named for exposures studied near old Fort Pierre, South Dakota. In addition to Colorado, the formation also occurs in South Dakota, Montana, Colorado, Minnesota, New Mexico, Wyoming, and Nebraska.

The formation consists of approximately 2000 feet of dark gray shale, some sandstone, and many layers of bentonite (altered volcanic-ash falls that look and feel much like soapy clays). In some regions the Pierre Shale may be as little as seven hundred feet feet thick.

The lower Pierre Shale represents a time of significant changes in the Cretaceous Western Interior Seaway, resulting from complex interactions of tectonism and eustatic sea level changes. The recognition and redefinition of the units of the lower Pierre Shale has facilitated understanding of the dynamics of the basin. The Burning Brule Member of the Sharon Springs Formation is restricted to the northern part of the basin and represents tectonically influenced sequences. These sequences are a response to rapid subsidence of the axial basin and the Williston Basin corresponding to tectonic activity along the Absoroka Thrust in Wyoming. Unconformities associated with the Burning Brule Member record a migrating peripheral bulge in the Black Hills region corresponding to a single tectonic pulse on the Absoroka Thrust. Migration of deposition and unconformities supports an elastic model for the formation and migration of the peripheral bulge and its interaction with the Williston Basin (Bertog, 2010).

2.1.25 Utah shale

There are five kerogen-rich shale units as having reasonable potential for commercial development as shale gas reservoirs. These are (i) four members of the Mancos Shale in northeast Utah - the Prairie Canyon, the Juana Lopez, the Lower Blue Gate, and the Tununk, and (ii) the black shale facies within the Hermosa Group in southeast Utah (Schamel, 2005).

The Prairie Canyon and Juana Lopez Members are both detached mudstone-siltstone-sandstone successions embedded within the Mancos Shale in northeast Utah. The Prairie Canyon Member is up to 1200 feet thick, but the stratigraphically deeper Juana Lopez Member is less than 100 feet. Both are similar in lithology and basin setting to the gas-productive Lewis Shale in the San Juan basin. As in the Lewis Shale, the lean, dominantly humic, kerogen is contained in the shale interlaminated with the siltstone-sandstone. The high quartz content is likely to result in a higher degree of natural fracturing than the enclosing clay-mudstone rocks. Thus, they may respond well to hydraulic fracturing. Also the porosity of the sandstone interbeds averaging 5.4% can enhance gas storage. Both units extend beneath the southeast Uinta basin reaching depths sufficient for gas generation and retention from the gas-prone kerogen. Although not known to be producing natural gas at present, both units are worthy of testing for add-on gas, especially in wells that are programmed to target Lower Cretaceous or Jurassic objectives.

The Lower Blue Gate and Tropic-Tununk shales generally lack the abundant siltstone-sandstone interbeds that would promote natural and induced fracturing, but they do have zones of observed organic richness in excess of 2.0% that might prove to be suitable places for shale gas where the rocks are sufficiently buried beneath the southern Uinta basin and perhaps parts of the Wasatch Plateau.

The black shale facies in the Hermosa Group of the Paradox basin is enigmatic. These shale formations contain mixed type II–III kerogen that should favor gas generation, yet oil with associated gas dominate current production. They are relatively thin, just a few tens of feet thick on average, yet they are encased in excellent sealing rocks, salt and anhydride. In the salt walls (anticlines) the shale formations are complexly deformed making them difficult to develop even with directional drilling methods, but where they are likely less deformed in the interdome areas (synclines) they are very deep. Yet in these deep areas one can expect peak gas generation. The shale formations are over-pressured, which suggests generation currently or in the recent past. Prospects are good that shale gas reservoirs can be developed in the Paradox basin, but it may prove to be technically and economically challenging (Schamel, 2005).

2.1.26 Utica shale

The Utica shale is a rock unit located approximately four thousand to fourteen thousand feet below the Marcellus shale and has the potential to become an enormous natural gas resource. The boundaries of the deeper Utica Shale formation extend under the Marcellus Shale region and beyond. The Utica shale encompasses New York, Pennsylvania, West Virginia, Maryland and even Virginia. The Utica Shale is thicker than the Marcellus and has already proven its ability to support commercial gas production.

The geologic boundaries of the Utica Shale formation extend beyond those of the Marcellus Shale. The Utica formation, which was deposited 40–60 million years ($40–60 \times 10^6$ years) before the Marcellus formation during the Paleozoic Era, is thousands of feet beneath the Marcellus formation. The depth of Utica Shale in the core production area of the Marcellus shale formation production area creates a more expensive environment in which to develop the Utica shale formations. However, in Ohio the Utica shale formation is as little as 3000 feet below the Marcellus Shale, whereas in sections of Pennsylvania the Utica formation is as deep as 7000 feet below the Marcellus formation creating a better economic environment to achieve production from the Utica shale formation in Ohio. Furthermore, the investments in the infrastructure to extract natural gas from the Marcellus shale formation also increase the economic efficiency of extracting natural gas from the Utica shale.

Although the Marcellus Shale is the current unconventional shale drilling target in Pennsylvania. Another rock unit with enormous potential is a few thousand feet below the Marcellus.

The potential source rock portion of the Utica Shale is extensive and underlies portions of Kentucky, Maryland, New York, Ohio, Pennsylvania, Tennessee, West Virginia and Virginia. It is also present beneath parts of Lake Ontario, Lake Erie and part of Ontario, Canada. This geographic extent of potential Utica Shale source rock along with the equivalent Antes Shale of central Pennsylvania and Point Pleasant Shale of. In keeping with this areal extent, the Utica Shale has been estimated to contain (at least) thirty eight trillion cubic feet (38×10^{12} $\mathrm{ft}^{3)}$ of technically recoverable natural gas (at the mean estimate) according to the first assessment of this continuous (unconventional) natural gas accumulation by the US Geological Survey.

In addition to natural gas, the Utica Shale is also yielding significant amounts of natural gas liquids and oil in the western portion of its extent and has been estimated to contain on the order of nine hundred and forty million barrels (940×10^6 bbls) of unconventional oil resources and approximately two hundred and eight million barrels (208×10^6 bbls) of unconventional natural gas liquids. A wider estimate place gas resources of the Utica shale, from 2 trillion cubic feet to 69 trillion cubic feet ($2–69 \times 10^{12}$ ft^3), which put this shale on the same resource level as the Barnett shale, the Marcellus shale, and the Haynesville shale formations.

2.1.27 *Woodford shale*

The Woodford Shale, located in south-central Oklahoma, ranges in depth from 6000 to 11,000 feet (Abousleiman et al., 2007; Braithwaite, 2009; Jacobi et al., 2009; US EIA, 2011a). This formation is a Devonian-age shale bounded by limestone (Osage Lime) above and undifferentiated strata below. Recent natural gas production in the Woodford Shale began in 2003 and 2004 with vertical well completions only. However, horizontal drilling has been adopted in the Woodford, as in other shale gas plays, due to its success in the Barnett Shale.

The Woodford Shale play encompasses an area of nearly 11,000 square miles. The Woodford play is in an early stage of development and is occurring at a spacing interval of 640 acres per well. The average thickness of the Woodford Shale varies from 120 to 220 feet across the play. The gas content in the Woodford Shale is higher on average than some of the other shale gas plays at 200—300 scf/ton. The original gas-in-place estimate for the Woodford Shale is similar to the Fayetteville Shale at 23 trillion cubic feet (23×10^{12} ft^3) while the technically recoverable resources are estimate at 11.4 trillion cubic feet (11.4×10^{12} ft^3).

The Woodford shale stratigraphy and organic content are well understood, but due to their complexity compared to the Barnett shale, the formations are more difficult to drill and fracture. As in the Barnett, horizontal wells are drilled, although oil-based mud is used in the Woodford shale and the formation is harder to drill. In addition to containing chert and pyrite, the Woodford formation is more faulted, making it easy to drill out of the interval; sometimes crossing several faults in a single wellbore is required.

Like the Barnett shale, higher silica rocks are predominant in the best zones for fracturing in the Woodford formation, although the Woodford has deeper and higher fracture gradients. Due to heavy faulting, 3-D seismic is extremely important, as the Woodford formation trends toward longer laterals exceeding 3000 feet with bigger fracture projects and more stages. Pad drilling also will increase as the Woodford shale formation continues expanding to the Ardmore Basin and to West Central Oklahoma in Canadian County.

2.2 World resources

Significant amounts of shale gas occur outside of the United States in other countries. The initial estimate of technically recoverable shale gas resources in the 32 countries 5760 trillion cubic feet (5760×10^{12} ft^3) (US EIA, 2011b). Adding the US estimate of the shale gas technically recoverable resources of 862 trillion cubic feet (862×10^{12} ft^3) results in a total shale gas resource base estimate of 6622 trillion cubic feet (6622×10^{12} ft^3) for the United States and the other 32 countries assessed. To put this shale gas resource estimate in context, the technically recoverable gas resources worldwide are approximately 16,000 trillion cubic feet ($16{,}000 \times 10^{12}$ ft^3), largely excluding shale gas (US EIA, 2011b). Thus, adding the identified shale gas resources to other gas resources increases total world technically recoverable gas resources by more than 40% to 22,600 trillion cubic feet ($22{,}600 \times 10^{12}$ ft^3).

At a country level, there are two country groupings that emerge where shale gas development appears most attractive. The first group consists of countries that are currently highly dependent upon natural gas imports, have at least some gas production infrastructure, and their estimated shale gas resources are substantial relative to their current gas consumption.

For these countries, shale gas development could significantly alter their future gas balance, which may motivate development. The second group consists of those countries where the shale gas resource estimate is large (>200 trillion cubic feet, $>200 \times 10^{12}$ ft^3) and there already exists a significant natural gas production infrastructure for internal use or for export. Existing infrastructure would aid in the timely conversion of the resource into production, but could also lead to competition with other natural gas supply sources. For an individual country the situation could be more complex.

The predominant shale gas resources are found in countries (listed alphabetically below).

2.2.1 Argentina

Argentina (the Neuquén Basin) has 774 trillion cubic feet (774×10^{12} ft^3) of technically recoverable shale gas, making it the third-largest resource on the world behind the United States and China. Located on the border of Argentina with Chile, the Neuquén Basin is the largest source of hydrocarbon derivatives, holding 35% of the oil reserves and 47% of the gas reserves of Argentina. Within the basin, the Vaca Muerta Shale formation may hold as much as 240 trillion cubic feet (240×10^{12} ft^3) of exploitable gas.

Unconventional shale oil and natural gas have been found in the Mendoza province, confirming the extension of the massive Vaca Muerta area. Exploration at the Payun Oeste and Valle del Rio Grande blocks pointed to an estimated one billion barrels (1×10^9 bbls) of oil equivalent (boe) in unconventional oil and gas in Mendoza. Energy resources and reserves in the province, which border the Andes mountain range in western Argentina, currently stand at 685 million barrels of oil equivalent (685×10^6 boe).

2.2.2 Canada

Recent estimates (NEB, 2009) in indicate that there is the potential for one quadrillion cubic feet (1×10^{15} ft^3) of gas in place in shale formation in Canada located in different areas but predominantly in the Western Canada Sedimentary basin (WCSB) (Fig. 2.5). However, high uncertainty, because gas shale formations are still in the initial stages of evaluation across Canada, precludes calculating more rigorous resource estimates for Canada at the current time (NEB, 2009; Rokosh et al., 2009; Boyer et al., 2011).

2.2.2.1 Colorado Group

The Colorado Group consists of various shale-containing horizons deposited throughout southern Alberta and Saskatchewan during globally high sea levels of the middle Cretaceous, including the Medicine Hat and Milk River shale-containing sandstones, which have been producing natural gas for over 100 years, and the Second White Speckled Shale, which has been producing natural gas for decades (Beaton et al., 2009).

In the Wildmere area of Alberta, the Colorado Shale is approximately six hundred and fifty feet thick, from which natural gas has potential to produce from five intervals. Unlike shale formations from the Horn River Basin and the Utica Group of Quebec, shale from the Colorado Group produces through thin sand beds and lamina, making it a hybrid gas shale like the Montney shale. Furthermore, the gas produced in the Colorado has biogenic rather than thermogenic origins. This would suggest very low potential for natural gas liquids and an under-pressured reservoir, which is more difficult to hydraulically fracture. Colorado Group

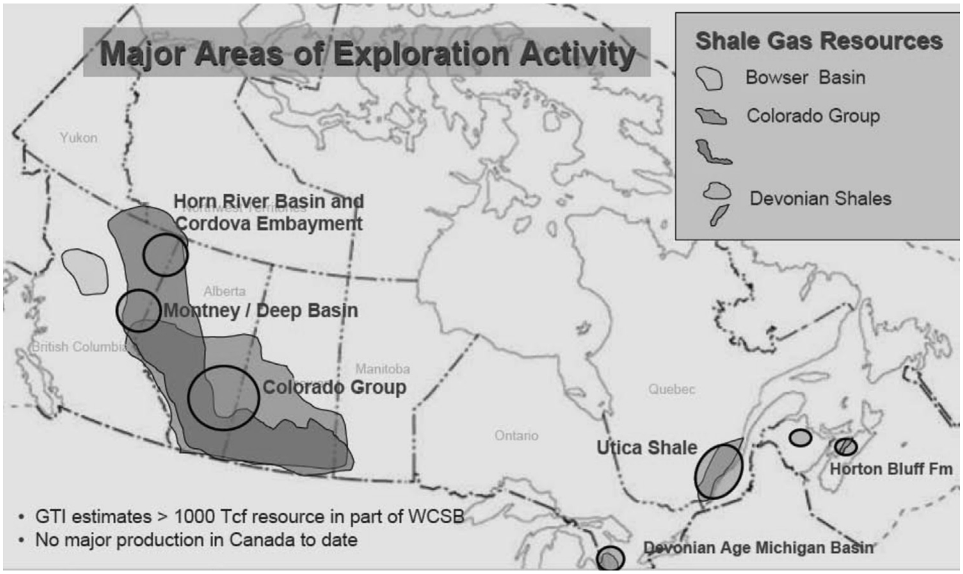

FIG. 2.5 Occurrence of shale gas in Canada, especially the Western Canada Sedimentary Basin (WCSB). *Adapted from NEB (2009). A Primer for understanding Canadian shale gas. National Energy Board, Calgary, Alberta, Canada. November.*

shale formations are sensitive to water, which makes them sensitive to fluids used during hydraulic fracturing.

The total volume of gas in the Colorado Group is very difficult to estimate given the wide lateral extent of the shale and variability of the reservoir and the absence of independent and publicly available analyses. However, there could be at least one hundred trillion cubic feet (100×10^{12} ft^3) of gas in place.

2.2.2.2 Duvernay shale

The Devonian Duvernay shale is an oil and natural gas field located in Alberta, Canada (in the Kaybob area) which extends into British Columbia. The Duvernay Formation (Devonian-Frasnian) of Alberta, Canada is a Type II marine, proven source rock which has yielded much of the oil and gas to the adjacent classical Devonian, conventional fields in carbonate reefs and platform carbonates. Production in these conventional fields is in decline and exploration and development has now shifted to their source, the Duvernay shale. The Devonian is considered the source rock for the Leduc reefs light oil resources, the discovery of which in 1947 was one of the defining moments in the past-present-and-future Western Canadian oil and gas industry.

The Duvernay shale, which can be found just north of the Montney shale is distributed over most of central Alberta and absent in areas of Leduc reef growth, except beneath the Duhamel reef, where it may be represented by a thin development of calcilutite (a dolomite or limestone formed of calcareous rock flour that is typically non-siliceous). At its type section in the East Shale Basin it is the shale formation is 174 feet) thick – it thickens to (246 feet east and southeastward toward the Southern Alberta Shelf. Northeastward the formation reaches 394 feet at its truncation in the subsurface at the pre-Cretaceous unconformity. In the West Shale Basin it averages 197 feet thick and thickens northward, attaining over 820 feet to the east of Lesser Slave Lake.

The formation consists of interbedded dark brown bituminous shale sediments, dark brown, black and occasionally gray-green calcareous shale sediments and dense argillaceous limestone sediments. The shale formations are characteristically petroliferous and exhibit plane parallel millimeter lamination.

Based on petrophysics calibrated to core and cuttings samples, the Duvernay is characterized by porosity of 6.0%—7.5%, permeability of 236—805 nD, and total organic carbon content 2.0—7.5% w/w. X-ray diffraction results from core and cuttings samples indicate it is likely very brittle with a low clay content (26% w/w), amorphous biogenic silica (47% w/w), and a calcite and dolomite matrix (20% w/w) (Switzer et al., 1994; Fowler et al., 2003).

2.2.2.3 Horn River basin

Devonian Horn River Basin shale formations were deposited in deep waters at the foot of the Slave Point carbonate platform in northeast British Columbia, which has been producing conventional natural gas for many decades. Horn River Basin shale formations are silica-rich (approximately 55% v/v silica) and approximately four hundred and fifty feet thick. The total organic content is one to six per cent. The rocks are mature, having been heated far into the thermogenic gas window. The Horn River Shale Formation located in British Columbia, is the largest shale gas field in Canada and part of Canadian deposits that amount to as much as 250 trillion cubic feet (250×10^{12} ft^3) of natural gas (Ross and Bustin, 2008).

It should be noted that the Horn River Basin shale gas play also includes the Cordova Embayment and the whole formation extends into both the Yukon Territory and the Northwest Territories, although its northward extent beyond provincial/territorial borders is poorly defined.

2.2.2.4 Horton Bluff Group

Lacustrine muds of the Horton Bluff Group of the Canadian Maritime Provinces were deposited in the Early Mississippian (approximately three hundred and sixty million years ago) during regional subsidence (NEB, 2009). The silica content in the Frederick Brook Shale of the Horton Bluff Group in New Brunswick averages 38% v/v but the clay content is also high, averaging 42% v/v. There are indications that organic contents of the Frederick Brook member in Nova Scotia are significantly higher than other Canadian gas shale formations, at 10% v/v, and the pay zone appears to be over five hundred feet thick, sometimes exceeding two thousand five hundred feet in New Brunswick.

There are also indications that most of the gas is adsorbed onto clay and organic matter, and it will take very effective reservoir stimulation to achieve significant production from Nova Scotia shale formations. It is unclear at this time at what proportion of gas is adsorbed onto clay and organic matter in the New Brunswick shale formations.

Analysis indicates that sixty seven trillion cubic feet (67×10^{12} ft^3) of free gas in place is present in the Frederick Brook shale of the Sussex/Elgin sub-basins of southern New Brunswick and sixty nine trillion cubic feet (69×10^{12} ft^3) of gas is present on the Windsor land block in Nova Scotia.

2.2.2.5 Montney shale

The Montney Shale formation is a shale rock deposit located deep below British Columbia, Canada and is located in the Dawson Creek area just south of the Horn Rover shale formation as well as the Duvernay shale formation. Natural gas can be found in large quantities trapped in this tight shale formation (Williams and Kramer, 2011).

The Triassic Montney Formation of northeastern British Columbia spans a wide variety of depositional environments, from shallow-water sands in the east to offshore muds to the west. Natural gas is currently produced from conventional shallow-water shoreface sandstones at the eastern edge of the Montney and from deep-water tight sands at the foot of the ramp. However, hybrid shale gas potential is being realized in two other zones: (i) the Lower Montney, in sandy, silty shales of the offshore transition and offshore-marine parts of the Basin, and (ii) the Upper Montney, below the shoreface, where silts have buried the tight sands at the foot of the ramp. The Montney formation is so thick (well over 1000 feet in some places) that some operators are planning to pursue stacked horizontal wells, where horizontal legs are drilled at two elevations in the same well, penetrating and fraccing both the Upper and Lower Montney. The total organic carbon in Montney shale is up to seven per cent and the rocks were heated until they were well into the thermogenic gas window.

The formation is a hybrid between a tight gas and shale gas resource and the sandy mudstone formation dates back to the Triassic period and is located beneath the Doig formation at depths ranging from 5500 to 13,500 feet and is up to 1000 feet thick in places. As such, the Montney shale is poised to become one of the most significant shale gas resources in Canada.

However, complicating reservoir characterization is the upper and lower Montney zones in the same area have different mineralogy which affects the formation evaluation data. The lower Montney is especially difficult as conventional open hole logs have historically caused people to believe that the lower Montney to be very tight. While the lower Montney has less porosity than the upper Montney formation, core data over the lower zone has porosity higher than expected (Williams and Kramer, 2011).

The gas shale formation play is estimated to contain up to fifty trillion cubic feet (50×10^{12} ft^3) of natural gas trapped within poor permeability shale and siltstone. Horizontal wells are drilled at depths from 5500 to 13,500 feet and hydraulic fracturing enables the gas to flow more easily. Microseismic monitoring techniques can be used to assess fracture stimulations by locating events along each stage of the fracture and calculating the dimensions, geometry and effective fracture volume. The Montney shale is a unique resource play in that it is a hybrid between tight gas and traditional shale.

The Montney formation is rich in silt and sand (characteristics similar to tight gas) but the source of the natural gas originated from its own organic matter like shale plays. Due to the presence of siltstone and sand, the Montney formation has extremely low permeability and requires higher levels of fracture stimulation.

2.2.2.6 Utica Group

The Upper Ordovician Utica Shale is located between Montreal and Quebec City and was deposited in deep waters at the foot of the Trenton carbonate platform. Later, the shale was caught up in early Appalachian Mountain growth and became faulted and folded on its southeastern side. The Utica is approximately five hundred feet thick and has a total organic content of one to three per cent and has been known for decades as a crude oil source rock for associated conventional reservoirs. However, unlike other Canadian gas shale formations, the Utica has higher concentrations of calcite, which occur at the expense of some silica (Theriault, 2008). While calcite is still brittle, hydraulic fractures do not transmit as well through it.

Biogenic gas can be found in the Utica in shallow areas, while thermogenic methane can be found in medium-deep and structured shale formations. The reservoir has an advantage over others in that it is folded and faulted, which increases the potential for the presence of natural fractures.

2.2.3 *China*

In 2011, China was estimated that to have 1275 trillion cubic feet (1275×10^{12} ft^3) of technically recoverable shale gas. Since then a government geological survey confirmed a total of 882 trillion cubic feet (882×10^{12} ft^3) of technically recoverable shale gas, excluding Tibet. The Sichuan Basin, located in south central China, accounts for 40% of the shale resources in China.

2.2.4 *India*

In India, gas wells have been in Damodar Valley Mainly Cambay (in Gujarat), Assam-Arakan (in the North-East), Krishna Godavari, Cauvery and Gondwana (in central India) are the shale gas prospective sedimentary basins in India. Besides these, there are many other sedimentary basins which are not studied for their shale gas potential (Mohan, 1995; Raju, 1969; Banerjee, 2002; Borah, 2014). Although US geological survey estimated the recoverable shale gas reserves is 63 trillion cubic feet (63×10^{12} ft^3), proper studies and development can enhanced the estimated results and the actual value may be much greater (Boruah, 2014).

The Cambay shale Formation in Cambay Basin is organically rich with average 2500 thickness. The kerogen type of the shale is both type II and III both oil and gas prone. The original generation potential is approximately 8 mg of hydrocarbon derivatives per gram of rock and calculated maturity value ranges from oil window to gas window (0.4–1.7). The maturity level of the Cambay shale is higher (>0.7) at the Tankari lows, which are depressions of Broach and Ahmedabad- Mehsana blocks. In the northern part of the basin, most of the places Olpad formation is within gas window with marginal source rock potential (Benerjee et al., 2002). Although the shales have good values of the total organic carbon and gas prone kerogen, the prospect of shale gas is expected at higher depth and higher maturity level i.e., within gas window zone.

Gas is expected to be generated within the rock from cracking of kerogen and crude oil retained in the shales and accumulated due to lack of migration pathways. Although the petrophysical analysis is not included in this study, it is one of the important factors as the earlier studies are showing most of the commercial production of shale gas from brittle shale (Bowker, 2007a).

Raniganj, south Karanpura, North Karanpura coal fields that are promising shale gas fields in Damodar Valley Basin. Gondwana sediments in India comprise of clastic sediments of fluviatile and lacustrine origin. Age is Upper Carboniferous to Lower Cretaceous.

The Sedimentary deposits can be divided into three types: (i) glaciogenic sedimentation, (ii) continental fluviatile deposits, and (iii) marine deposits.

The Damodar Valley Basin is part of the Gondwana basins of India characterized by their mostly non-marine sedimentary fill and narrow graben structures. Although filled with mostly Late Permian to Triassic terrestrial sediment, there is a significant thickness the Barren measures, so called as it is barren of coal. Barren Measure Formation of Permian age is identified as the shale gas prospective horizon based on thickness (2000 feet), higher content of organic matter (4–20% w/w) and a higher degree of thermal maturity (>7). Based on available data, the south-western part of the Raniganj coalfield is expected to be the most promising area for exploration as well as exploitation of shale gas.

The sediment deposition of Barren measure formation is thick at the end of Barakar Formation. Sediments comprise of dark gray to black shale with ironstone bands/nodules. The Barren Measure is best developed (3500 feet) in the western part of the Raniganj coalfield at the Suraj Nager area. The Barakar Formation also shows good organic content and higher maturity value than Barren Measure formation.

In the Krishna Godavari basin, the prospective formation is the Kommugudem shale formation of (up to 3000 feet thickness) Permian age. The basin is a Late Permian to Tertiary age basin in eastern India consisting of a series of horst and graben. The cyclothermic sequences of carbonaceous shale, coal and sandstone are deposited under fluvio-lacustrine environment. The shale formations are dark gray to black hard compact, silty and occasionally carbonaceous.

The inter-bedded sandstone formations in coal-shale are dirty white, medium to coarse grained, feldspathic. Glauconite and pyrites are often found. Kaolinite dominating along with chlorite, smectite and illite. The increasing accommodation to sediment influx further enhanced for preservation of organic contents and the coal-shale developed within the sequence acts as a good gaseous source facies. The shale is has more than 2% w/w total organic carbon and is kerogen Type II and Type III. The Cretaceous-Cenozoic Cauvery basin in south eastern India is another basin with prospective shales. The formations of interest are the early Cretaceous Andimadam Formation and the Sattapadi shale its stratigraphic equivalents. The shales are interpreted to have been deposited in marine environments. The Sattapadi Shale contains 2–2.5% w/w total organic carbon and is thermally mature for hydrocarbon generation in deeper parts of the basin. The kerogen types are predominantly Type III with minor amounts of Type II.

2.2.5 Poland

There are several shale plays in Europe of which Poland is among the most advanced in terms of exploration for and appraisal of unconventional gas resources. The shale formation occur in three basins: (i) the Baltic basin in the north, (ii) the Lublin basin in the south, and (iii) the Podlasie basin in the east. The organically rich shales in these three basins appear to have favorable characteristics for shale gas exploration. In fact, estimates indicate that Poland has 792 trillion cubic feet (792×10^{12} ft^3) of shale gas-in place, comprising 514 trillion cubic feet (514×10^{12} ft^3) in the Baltic Basin, 222 trillion cubic feet (222×10^{12} ft^3) in the Lublin Basin, and 56 trillion cubic feet (56×10^{12} ft^3) in the Podlasie Basin of which the technically recoverable shale gas resource is on the order of 187 trillion cubic feet (187×10^{12} ft^3) from these three basins (US EIA, 2013; Anthonsen et al., 2016; Zijp et al., 2017).

2.2.6 South Africa

In addition to being an area fertile in fossil remains, the Karoo Supergroup (South Africa) might also be one of the most plentiful sources of shale gas in the world. The area is constituted mainly of shale and sandstone and underlies more than two-thirds of the entire area of South Africa and contains an estimated 485 trillion cubic feet ($485 \times 10^{12}\ \mathrm{ft}^3$) of technically recoverable gas. Shale gas could reduce the dependence of South Africa on coal to supply 85% of the energy needs.

2.2.7 Turkey

Turkey has shale gas potentials in Southeast Anatolia Basin and Thrace Basin. Moreover, Turkey may have shale potential in the Taurus Basins and Black Sea Basin (US EIA, 2011b; Kok and Merey, 2014). The Southeast Anatolia Basin has the Dadas shale – the depth of this shale ranges from 6560 to 9840 feet. The Dadas shale has three members with the gross thickness of 1300 feet. Of these three members, the Dadas I formation (the thickness is approximately 150 feet) is very rich with organic materials compared to the other two members. The total organic carbon (TOC) changes from 2% to 16% and it is estimated that Dadas shale contains 43 trillion cubic feet ($43 \times 10^{12}\ \mathrm{ft}^3$) gas-in-place of which 9 trillion cubic feet ($9 \times 10^{12}\ \mathrm{ft}^3$) of this gas is technically recoverable (US EIA, 2011b).

The Thrace Basin has two formations with shale gas potential: (i) the Hamitabat formation (the Lower Mid-Eocene) and (ii) the Mezardere formation (the Lower Oligocene). The Hamitabat formation consists of sandstone, shale, and marl deposited in a shallow marine environment. The Hamitabat shale ranges from 12,100 to 16,400 feet and the total organic carbon ranges from 1.5 to 6.4% w/w. The net shale thickness is 344 feet. Hamitabat shale contains an estimated 14 trillion cubic feet ($14 \times 10^{12}\ \mathrm{ft}^3$) of gas in place of which and 4 trillion cubic feet ($4 \times 10^{12}\ \mathrm{ft}^3$) of this gas is technically recoverable (US EIA, 2011b).

The Mezardere formation consists of sandstone, shale, and marl deposited in a deltaic environment and the shale depth changes from 8200 to 10,168 feet. The total organic carbon ranges from 1 to 4% w/w and the shale thickness is 295 feet. The formation contains an estimated 7 trillion cubic feet ($7 \times 10^{12}\ \mathrm{ft}^3$) gas in place of which and 2 trillion cubic feet ($2 \times 10^{12}\ \mathrm{ft}^3$) of this gas is technically recoverable (US EIA, 2011b).

3. Oil in tight formations

Conventional resources of crude oil (or for that matter, any fossil fuel) exist in discrete, well-defined subsurface accumulations (reservoirs), with permeability values greater than a specified lower limit. Such conventional gas resources can usually be developed using vertical wells, and generally yield the high recovery factors.

Briefly, permeability is a measure of the ability of a porous medium, such as that found in a hydrocarbon reservoir, to transmit fluids, such as gas, oil or water, in response to a pressure differential across the medium. In petroleum engineering, permeability is usually measured in units of milliDarcys (mD).

By contrast, unconventional resources are found in accumulations where permeability is low (<0.1 mD). Such accumulations include *tight* sandstone formations, coal beds (coal bed methane, CBM) and shale formations. Tight sandstone formations can be sandstones originally formed as beaches or estuaries with relatively little organic matter but later sealed with cap rock, and thus becoming low permeability traps, which captured hydrocarbon derivatives seeping upwards from lower source rocks. Also, unconventional resource accumulations tend to be distributed over a larger area than conventional accumulations and usually require advanced technology such as horizontal wells or artificial stimulation in order to be economically productive; recovery factors are much lower — typically of the order of 15%−30% of the gas initially in place (GIIP). While the horizontal wells and multi-stage fracture completions are more expensive than non-fractured vertical wells, they generate a higher initial rate of oil production than even the best vertical wells. In addition, eight or more horizontal wells can be drilled from the same surface location which simplifies tie-ins and minimizes the cost and environmental impact of having to build more roads, pipelines and well pads.

3.1 United States

The mature, organic-rich shale formations that serve as sources for natural gas and crude oil predominantly in the United States and Canada (Figs. 2.3 and 2.6) and which have received considerable interest, have become an attractive target because they represent a substantial resource of natural gas and crude oil and are distributed throughout the forty-eight contiguous United States as well as Western Canada (Hill and Nelson, 2000; Curtis, 2002; Law and Curtis, 2002; NEB, 2009; IEA, 2012).

Due to the unique nature of shale, every basin, play, well and pay zone may require a unique treatment. Briefly comparing the characteristics of some of the current hottest plays can help illustrate the impact of these differences throughout development. It is necessary to study and understand key reservoir parameters for gas shale deposits and these parameters include: (i) thermal maturity, (ii) reservoir thickness, (iii) total organic carbon (TOC) content, (iv) adsorbed gas fraction, (v) free gas within the pores and fractures, and (vi) permeability (Chapter 3, Chapter 4). The first two parameters are routinely measured. Thermal maturity is commonly measured in core analysis and reservoir thickness is routinely measured with logs. The calculation of the final four parameters requires a novel approach.

Almost all (96% v/v) of the shale natural gas in proved reserves in 2010 came from the six largest shale plays in the United States (US EIA, 2012). The Barnett again ranked as the largest shale gas play in the United States, significantly higher increases over 2009 proved reserves were registered by the Haynesville/Bossier (which more than doubled 2009 volumes) and the Marcellus (which nearly tripled). Among these six shale plays, the only decline from 2009 volumes was in the Antrim of northern Michigan − a mature, shallow biogenic shale gas play discovered in 1986 that is no longer being developed at the same pace as the other leading shale resources.

The first Barnett Shale gas production, by Mitchell Energy & Development Corp, took place in the Fort Worth Basin in 1981. Until Barnett Shale successes, it was believed that natural fractures had to be present in gas shale. A low-permeability gas-shale play is presently viewed as a technological play. Advances in micro-seismic fracture mapping, 3D seismic, horizontal drilling, fracture stimulation and multiple fracturing stages, have all contributed

FIG. 2.6 Major basins with the potential for tight oil development. *Adapted from* US EIA (2012). *Energy Information Administration, United States Department of Energy, Washington, DC.*

to successful gas shale wells. By the early part of the 21st Century the main gas resources to that point had been: Antrim Shale in the northern Michigan Basin; Barnett Shale in the Fort Worth Basin, Texas; Lewis Shale in the San Juan Basin; New Albany Shale in the Illinois Basin; and the Ohio Shale in the Appalachian Basin (GAO, 2012). More recent development of gas shale resources includes (alphabetically): (i) the Fayetteville Shale in Arkansas. (ii) The Eagle Ford Shale in Texas, (iii) the Haynesville Shale in Louisiana, (iv) the Marcellus Shale in the Appalachian Basin, (v) Utica Shale in New York and Quebec, Canada, and (vi) the Woodford Shale in Oklahoma.

However, there are other gas shale resources that are of increasing importance to the United States energy balance and economics. These must not be ignored and the predominant natural shale gas and crude oil resources in the United States and the formations are formations presented below are not listed in any particular order of preference or importance, other than *alphabetical order* for ease of location.

3.1.1 Antrim shale

The Antrim Shale, one of the largest unconventional natural gas reserves in North America, is a finely laminated, pyritic, organic-matter rich, thermally immature Devonian black shale located in the Michigan Basin in the northern part of Michigan State and is part of an extensive, organic-rich shale depositional system that covered large areas of the ancestral North American continent in the Middle-to-Late Devonian. The intracratonic Michigan basin was one of several deposition centers situated along the Eastern Interior Seaway. The basin has been filled with more than 17,000 feet of sediment, 900 feet of which comprises the Antrim Shale and associated Devonian-Mississippian rocks. The base of the Antrim, near the center of the modern structural basin, is approximately 2400 feet below sea level (Braithwaite, 2009; US EIA, 2011a). The Antrim shale is a black, organic rich bituminous shale which is divided into four members, from base to top: Norwood, Paxton, Lachine, and upper members. The play and ranges from 600 to 2200 feet deep and is 70–120 feet think The total area of the Antrim shale play is approximately 12,000 square miles, which includes the developed and undeveloped area of the play. The shale gas play has an average expected ultimate recovery of approximately 19.9 trillion cubic feet (19.9×10^{12} ft^3) of technically recoverable gas. The upper members are overlaid by the Greenish-gray Ellsworth Shale.

The stratigraphy of the Antrim shale stratigraphy is relatively straightforward and wells are typically completed in the Lachine and Norwood members of the lower Antrim, whose aggregate thickness approaches 160 feet. The total organic carbon (TOC) content of the Lachine and Norwood ranges from 0.5 to 24% w/w. These black shale formations are silica rich (20%–41% microcrystalline quartz and wind-blown silt) and contain abundant dolomite and limestone concretions and carbonate, sulfide, and sulfate cements. The remaining lower Antrim unit, the Paxton, is a mixture of lime mudstone and gray shale lithology (Martini et al., 1998) containing 0.3–8% w/w total organic carbon and 7–30% w/w silica. Correlation of the fossil alga *Foerstia* has established time equivalence among the upper part of the Antrim Shale, the Huron Member of the Ohio Shale of the Appalachian basin, and the Clegg Creek Member of the New Albany Shale of the Illinois basin (Roen, 1993).

Typical depths for the entire Antrim shale unit range from 500 to 2300 feet and the areal extent is roughly approximately 30,000 square miles (Gutschick and Sandberg, 1991; Braithwaite, 2009; US EIA, 2011a). The entire area is overlain by Devonian and Mississippian sediments and hundreds of feet of glacial till. The Antrim mineralogy shows the shale to be laminated with very fine grains. The composition consists mainly of illite and quartz with small quantities of organic material and pyrite.

The Antrim Shale has an organic matter up to 20% w/w, and is mainly made up of algal material. The vitrinite reflectance is in the range of 0.4–0.6, indicating that the shale is thermally immature. The shale is also shallow and there is a high concentration of methane in the composition, which would lead one to assume the gas is of a microbial origin, but, $\delta^{13}C$ values indicate a more thermogenic origin (Martini et al., 1996).

For shallow wells in the Antrim shale, the gas is of microbial origin. Deeper wells have a mix of thermogenic gas and microbial gas. For gas compositions with $C1/(C2+C3) < 100$ the gas origin is thermogenic, and this occurs for the gas present in the Niagaran formation which under lays the Antrim Shale. Since the Antrim has so many natural fractures, it is reasonable to assume there is migration of gas from the Niagaran formation in to the Antrim Shale.

The Antrim shale has two main ways of storing gas: absorption and free gas in the pore volume. The lower Norwood member has a higher adsorption capacity (approximately 115 ft^3 per ton) than the Lachine member (approximately 85 ft^3 per ton) (Kuuskraa et al., 1992). This is an important factor to consider when designing a fracture treatment because it would be more beneficial to have more of the proppant in the zone with the highest gas content. The free gas in the pore space can account for up to 10% of the total gas in place, but it is still not clear on how dependant the free gas is on the water in place. The very low permeability of the matrix could make it very difficult if not impossible to remove a significant portion of the free gas.

Two dominant sets of natural fractures have been identified in the northern producing trend, one oriented toward the northwest and the other to the northeast and both exhibiting sub-vertical to vertical inclinations. These fractures, generally uncemented or lined by thin coatings of calcite (Holst and Foote, 1981; Martini et al., 1998), have been mapped for several meters in the vertical direction and tens of meters horizontally in surface exposures. Attempts to establish production in the Antrim outside this trend have commonly encountered organic, gas-rich shale but minimal natural fracturing and, hence, permeability (Hill and Nelson, 2000).

Thus, the Antrim Shale is highly fractured for a shale reservoir. Fracture spacing can be as close as 1–2 feet, compared to 10–20 feet for the Barnett shale. These fractures can create permeability-thicknesses in the range of 50–5000 md/foot, which increases gas production. But, it also helps water flow, and thus most wells produce large amounts of water which must be disposed (Kuuskraa et al., 1992).

3.1.2 *Avalon and Bone Springs shale*

The Avalon and Bone Springs shale oil play is located in the Permian Basin in Southeast New Mexico and West Texas and has a reported depth from 6000 to 13,000 feet and a thickness ranging from 900 to 1700 feet. The area of the play has been estimated to be approximately 1313 square miles with approximately 1.58 billion barrels (1.58×10^9 bbls) of technically recoverable oil.

3.1.3 *Bakken shale*

The Bakken shale oil play is located within the Williston Basin in Montana and North Dakota and has an area on the order of approximately 6522 square miles in the United States. This discovery, first made in 1951, was not considered significant until 2004, when the employment of horizontal drilling and hydraulic fracturing ("fracking") in combination demonstrated that this "shale oil" could be efficiently and economically produced.

The play has seen a similar growth rate to the Barnett and is another technical play in which the development of this unconventional resource has benefitted from the technological advances in horizontal wells and hydraulic fracturing (Cohen, 2008; Cox et al., 2008; Braithwaite, 2009). In April 2008, the United States Geological Survey (USGS) released an updated assessment of the undiscovered technically recoverable reserves for this shale play estimating there are 3.65 billion barrels (3.65×10^9 bbls) of oil, 1.85 trillion cubic feet (1.85×10^{12} ft^3) of associated natural gas, and 148 million barrels (148×10^6 bbls) of natural gas liquids in the play (USGS, 2008; US EIA, 2011a).

The Bakken shale formation differs from other shale plays in that it is an oil reservoir, a dolomite layered between two shale formations, with depths ranging from around 8000 to 10,000 feet from which oil, gas and natural gas liquids are produced. The formation contains approximately 3.59 billion barrels (3.59×10^9 bbls) of technically recoverable oil. The shale formation ranges from 4500 to 7500 feet deep with a mean of 6000 feet and an average thickness of 22 feet.

Each succeeding member of the Bakken formation – lower shale, middle sandstone and upper shale member – is geographically larger than the one below. Both the upper and lower shale formations, which are the crude oil source rocks, present fairly consistent lithology, while the middle sandstone member varies in thickness, lithology and petrophysical properties.

The Bakken shale formation is not as naturally fractured as the Barnett shale formation and, therefore, requires more traditional fracture geometry with both longitudinal and transverse fractures. Diversion methods are used throughout hydraulic fracture treatments, which primarily use gelled water fracture fluids, although there is a growing trend toward the use of an intermediate strength proppant. Recently, the Bakken gas shale has seen an increase in activity, and the trend is toward longer laterals – up to 10,000 feet for single laterals in some cases. In addition, there is also a trend to drill below the lower Bakken shale and fracture upwards.

Interestingly, this shale formation was estimated by industry experts to contain up to 24 billion barrels (24×10^9 bbls) of total oil. Currently, more than 200 drilling rigs are using these techniques developing new wells at the rate of one each eight weeks or less. Production in the Bakken is on the order of 450,000 barrels of crude oil per day and estimate are for a steady increase in production for the next several years. In terms of transportation, rail is supplementing the pipeline capacity to transport the crude to refining centers. A key driver for the refinery development in the area is the rapidly growing availability of the crude oil, which has less than 0.005% w/w sulfur and more on the order of 0.0015% w/w sulfur. This crude oil is also light (low in density) at API specific gravity of approximately 42, compared to an API gravity of 39.6 for West Texas Intermediate. The laboratory distillation of Bakken crude shows high yields of naphtha and mid-distillates (kerosene and diesel) and low residual fuel oil and asphaltene constituents.

3.1.4 Barnett shale

The Barnett shale gas play is located within the Fort Worth and Permian Basins in Texas. The Barnett shale is divided into two sections: the "Core/Tier I" and the Undeveloped. The Core/Tier I section corresponds to the areas of the Barnett Shale that are currently under development. It is primarily located in the Parker, Wise, Johnson, and other neighboring counties (Bowker, 2007a).

The wedge-shaped Fort Worth basin covers approximately 15,000 square miles in North-Central Texas and is centered along the north-south direction, deepening to the north and outcropping at the Liano uplift in Liano County (Bowker, 2007a, 2007b; Jarvine et al., 2007). The Cambrian Riley and Hickory formations are overlaid by the Viola-Simpson and

Ellenburger groups. The Viola-Simpson limestone group is found in Tarrant and Parker counties and acts as a barrier between the Barnett and the Ellenburger formation. The Ellenburger formation is a very porous aquifer (Zuber et al., 2002) that if fractured will produce copious amounts of highly saline water, effectively shutting down a well with water disposal cost.

Geochemical and reservoir parameters for the Barnett Shalein the Fort Worth basin differ markedly from those of other gas-productive shale formations, particularly with respect to gas in place. For example, Barnett shale gas is thermogenic in origin and hydrocarbon generation began in the Late Paleozoic, continued through the Mesozoic, and ceased with uplift and cooling during the Cretaceous (Jarvie et al., 2001, 2007). In addition, organic matter in the Barnett shale formation has generated liquid hydrocarbon derivatives and Barnett-sourced oils in other formations, ranging from Ordovician to Pennsylvanian in age, in the western Fort Worth basin (Jarvie et al., 2001, 2007) – cracking of this oil may have contributed to the gas-in-place resource.

The Mississippian-age Barnett Shale overlies the Viola-Simpson group. The Barnett shale varies in thickness from 150 to 800 feet, and is the most productive gas shale in Texas. The permeability ranges from 7 to 50 nanoDarcys and the porosity from 4% to 6% (Montgomery et al., 2005; Cipolla et al., 2010). In addition, well performance of the Barnett Shale changes significantly with changing produced fluid type, depth and formation thickness (Hale and William, 2010) and on the type of completion method implemented and the large hydraulic fracture treatments (Ezisi et al., 2012).

The three most important production related structures in the basin include both major and minor faulting, fracturing, and karst-related collapse features (Frantz et al., 2005). Fracturing is important to gas production because it provides a conduit for gas to flow from the pores to the wellbore, and it also increases exposure of the well to the formation. The Barnett shale formation exhibits complex fracture geometry which often creates difficulty in estimating fracture length and exposure to the formation due to the complex geometry. The fracturing is believed to be caused by the cracking of oil into gas. This cracking can cause a ten-fold increase in the hydrocarbon volume, increasing the pressure until the formation breaks. The precipitation of calcium carbonate in the fractures can cut down on the conductivity of the fractures. This precipitation is hard to detect on logs, and can cause a well location that appears to be good on seismic into an unproductive well. This precipitation is also hard to treat with acidization due to the long distances the acid is required to travel before making a noticeable impact on production.

Change in gas content with pressure occurs in the Barnett shale with a typical reservoir pressure in the range of 3000–4000 psi (Frantz et al., 2005). In low permeability formations, pseudo radial flow can take over 100 years to be established. Thus, most gas flow in the reservoir is a linear flow from the near fracture area toward the nearest fracture face. Faulting and karst-related collapse features are important mainly in the Ellenburger formation.

In addition to drilling longer laterals, current trends in the Barnett are toward bigger hydraulic fracturing projects and more stages. Infills are being drilled and testing of spacing is down to 10 acres, while re-fracturing of the first horizontal wells from 2003 to 2004 has commenced; both infills and refracturing methods are expected to improve the *estimated ultimate recovery* from 11 to 18% v/v.

The total area for the Barnett formation, as estimated by USGS is 6458 square miles. This area is subdivided into two sections – (i) the Greater Newark East Frac-Barrier Continuous Barnett Shale Gas (1555 square miles) and (ii) the Extended Continuous Barnett Shale Gas (4903 square miles). As the development of the Barnett extended beyond the Newark East field, the active section of the Barnett was also extended. The remaining area is considered to be undeveloped section of the Barnett. The Barnett shale gas play, including the active and undeveloped areas, is approximately 43.37 trillion cubic feet (43.37×10^{12} ft^3) of technically recoverable gas.

The Barnett-Woodford shale gas play is located in the Permian Basin in West Texas and has an area of approximately 2691 square miles and ranges from 5100 to 15,300 feet deep and 400–800 feet thick with an estimated recovery of approximately 32.2 trillion cubic feet (32.2×10^{12} ft^3) of technically recoverable gas.

3.1.5 Baxter shale

The Baxter Shale is stratigraphically equivalent to the Mancos, Cody, Steele, Hilliard, and Niobrara/Pierre formations (Braithwaite, 2009; Mauro et al., 2010; US EIA, 2011a) and was deposited in hundreds of feet of water in the Western Interior Seaway from approximately ninety to eighty million years ago (Coniacean to lower Campanian) and consists of approximately two thousand five hundred feet of dominantly siliceous, illitic, and calcareous shale that contains regionally correlative coarsening-upward sequences of quartz-and carbonate-rich siltstones several tens of feet thick. The total organic carbon content ranges from 0.5% to 2.5% in the shale and from 0.25% to 0.75% in the siltstones. Measured porosities in both the shale and siltstones typically range from 3% to 6% with matrix permeability of 100–1500 nanoDarcys.

Gas production has been established from the Baxter Shale in twenty-two vertical wells and three horizontal wells in the Vermillion Basin of northwestern Colorado and adjacent Wyoming. Production comes mainly from the silt-rich intervals as determined by production logs. The productive area in the Baxter Shale has vitrinite reflectance values approaching 2% and is in the dry gas generation window.

The resource area is defined by numerous wells with gas shows and over-pressuring in the Baxter shale with gradients ranging from 0.6 to 0.8 psi/foot at depths greater than ten thousand feet.

A challenge within this reservoir is the ability to economically access this large unconventional gas accumulation. This is not a classic 100- to 300-foot-thick organic-rich shale gas reservoir. Instead it is a very large hydrocarbon resource stored in two thousand five hundred feet of shale with interbedded siltstone intervals. 3-D seismic data have proved useful in helping define potential fracture networks in the Baxter shale that can be targeted with horizontal wells.

The Hilliard-Baxter-Mancos shale gas play is located in the Greater Green River Basin in Wyoming and Colorado and the depth for the shale ranges from 10,000 to 19,500 square miles and is 2850 to 3300 feet thick. The total active area for the play is 16,416 square miles with approximately 3.77 trillion cubic feet (3.77×10^{12} ft^3) of technically recoverable gas.

3.1.6 Big Sandy

The Devonian Big Sandy shale gas play includes the Huron, Cleveland and Rhinestreet formations located within the Appalachian Basin in Kentucky, Virginia and West Virginia.

The United States Geological Survey (USGS) has estimated a total area for the Big Sandy shale play as 10,669 square miles (6,828,000 acres). The shale play has an average expected ultimate recovery of approximately 7.4 trillion cubic feet (7.4×10^{12} ft^3) of technically recoverable gas. Big Sandy has a total active area of approximately 8675 square miles and an undeveloped area of 1994 square miles with a well spacing of 80 acres per well. The formation ranges from 1600 to 6000 feet deep and has a thickness of 50–300 feet.

3.1.7 Caney shale

The Caney Shale (Arkoma Basin, Oklahoma) is the stratigraphic equivalent of the Barnett Shale in the Ft. Worth Basin (Boardman and Puckette, 2006; Andrews, 2007, 2012; Jacobi et al., 2009). The formation has become a gas producer since the large success of the Barnett shale formation.

The Caney Shale, Chesterian age, was deposited in the Oklahoma part of the Arkoma Basin one of a series of foreland basins that formed progressively westward along the Ouachita Fold Belt from the Black Warrior Basin in Mississippi to basins in southwest Texas. The Arkoma Basin in Oklahoma is in the Southeast corner of the state north and northwest of the Ouachita Mountains. The formation dips southward from a depth of three thousand feet in northern McIntosh County, Oklahoma to twelve thousand feet north of the Choctaw thrust. The Caney formation thickens toward the southeast from the northwest edge to the Choctaw fault in the south. It can be subdivided into six intervals based on characteristics of the density and resistivity logs.

Reported average total organic carbon values the Caney formation range from 5 to 8% w/w, which show a linear correlation with density. Mud log gas shows have a strong correlation with desorbed gas values that range from one hundred and twenty to one hundred and fifty cubic feet per ton of shale. Estimates of gas in place for the Caney range from thirty to forty billion cubic feet ($30-40 \times 10^9$ ft^3).

3.1.8 Chattanooga shale

The Chattanooga Shale (Black Warrior Basin) and has been considered as a rich shale formation (Rheams and Neathery, 1988). The shale formation sits within the thermogenic gas window in much of the Black Warrior Basin (Carroll et al., 1995) and may thus contain significant prospects for natural gas. The Chattanooga disconformity overlies Ordovician through Devonian strata, and the time value of the disconformity increases northward (Thomas, 1988). The Chattanooga is overlain sharply by the Lower Mississippian Maury Shale, which is commonly thinner than 2 feet, and the Maury is in turn overlain by the micritic Fort Payne Chert. The Chattanooga Shale in Alabama was apparently deposited in dysoxic to anoxic subtidal environments and can be considered as a cratonic extension of the Acadian foreland basin (Ettensohn, 1985).

The thickness of the Chattanooga varies significantly within the Black Warrior Basin. The shale is thinner than 10 feet and is locally absent in much of Lamar, Fayette, and Pickens Counties, which is the principal area of conventional oil and gas production in the Black Warrior Basin. For this reason, the Chattanooga has not been considered to be the principal source rock for the conventional oil and gas reservoirs in this area. The shale is thicker than 30 feet in a belt that extends northwestward from Blount County into Franklin and Colbert Counties. A prominent deposition center is developed along the southwestern basin margin in Tuscaloosa and Greene Counties. Here, the shale is consistently thicker than 30 feet and is locally thicker than 90 feet.

The Chattanooga Shale is in some respects analogous to the Barnett Shale of the Fort Worth Basin in that it is an organic-rich black shale bounded by thick, mechanically stiff limestone units that may help confine induced hydrofractures within the shale (Hill and Jarvie, 2007; Gale et al., 2007).

3.1.9 Conasauga shale

The Conasauga shale gas formation (Conesauga shale gas formation, Alabama) continues to be developed primarily in northeast Alabama (US EIA, 2011a). With the exception of one well in Etowah County and one well in Cullman County, all of the development has been in St. Clair County. Etowah and St. Clair Counties are located northeast of Birmingham in the Valley and Ridge Province of Alabama. Cullman County is north of Birmingham in the Cumberland Plateau Province. This shale formation represents the first commercial gas production from shale in Alabama, but because it is geologically the oldest and most structurally complex shale formation from which gas production has been established. The Conasauga differs from other gas shale formations in several respects. The productive lithology is thinly inter-bedded shale and micritic limestone that can contain more than 3% total organic carbon.

The Conasauga shale is of Middle Cambrian age and can be characterized as a shoaling-upward succession in which shale passes vertically into a broad array of inner ramp carbonate facies. The shale was deposited on the outer ramp, and the shale is thickest in basement grabens that formed during late Precambrian to Cambrian Iapetan rifting (Thomas et al., 2000). The shale facies of the Conasauga is part of the weak litho-tectonic unit that hosts the basal detachment of the Appalachian Thrust Belt in Alabama (Thomas, 2001; Thomas and Bayona, 2005). The shale has been thickened tectonically into anti-formal stacks that have been interpreted as giant shale duplexes, or mushwads (Thomas, 2001). In places, the shale is thicker than 8000 feet, and the shale is complexly folded and faulted at outcrop scale.

Surface mapping and seismic exploration reveal that at least three Conasauga anti-forms are preserved in the Alabama Appalachians. Exploration has focused primarily on the southeastern portion of the Gadsden anti-form, which is in St. Clair and Etowah Counties. The Palmerdale and Bessemer anti-forms constitute the core of the Birmingham anticlinorium. The Palmerdale and Bessemer structures are overlain by a thin roof of brittle Cambrian-Ordovician carbonate rocks, and Conasauga shale facies are exposed locally. The Palmerdale structure is in the heart of the Birmingham metropolitan area and thus may be difficult to develop, whereas the southwestern part of the Bessemer structure is in rural areas and may be a more attractive exploration target. Additional thick shale bodies may be concealed below the shallow Rome thrust sheet in Cherokee and northeastern Etowah Counties and perhaps in adjacent parts of Georgia (Mittenthal and Harry, 2004).

3.1.10 Eagle Ford shale

The Eagle Ford shale (Eagleford shale) (discovered in 2008) is a sedimentary rock formation from the Late Cretaceous age underlying much of South Texas which covers three thousand square miles and consists of an organic-rich marine shale that also has been found to appear in outcrops (Braithwaite, 2009; US EIA, 2011a). The Eagle Ford is a geological formation directly beneath the Austin Chalk and is considered to be the source rock of hydrocarbon derivatives that are contained in the Austin Chalk above the play.

The play is located within the Texas Maverick Basin and contains a high liquid component and takes its name from the town of Eagle Ford Texas where the shale outcrops at the surface in clay form. The Eagle Ford is an extremely active shale play with over one hundred active rigs in operation. This hydrocarbon-producing formation rich in oil and natural gas extends from the Texas-Mexico border in Webb and Maverick counties and extends 400 miles toward East Texas. The formation is fifty miles wide and an average of two hundred and fifty feet thick at a depth between four thousand and twelve thousand feet. The shale contains a high amount of carbonate which makes it brittle and easier to apply hydraulic fracturing to produce the oil or gas.

The formation is best known for producing variable amounts of dry gas, wet gas, natural gas liquids (NGLs), gas condensate, and crude oil. The most active area lies above the Edwards Reef Trend where the formation yields a gas-condensate production stream. The Eagle Ford shale formation is estimated to have 20.81 trillion cubic feet (20.81 × 1012 ft^3) of natural gas and 3.351 billion barrels (3351 × 109 bbls) of oil.

3.1.11 Fayetteville shale

The Fayetteville shale gas play is a geologic formation of Mississippian age (354−323 million years ago) composed of tight shale within the Arkoma basin of Arkansas. The play is divided into two main units, Central and Western based on the location of the shale. The shale ranges from 1000 to 7000 feet deep and 20−200 feet thick. With productive wells penetrating the Fayetteville shale (Arkoma Basin) at depths between a few hundred and 7000 feet, this formation is somewhat shallower than the Barnett shale formation (Braithwaite, 2009; US EIA, 2011a). Mediocre production from early vertical wells stalled development in the vertically fractured Fayetteville, and only with recent introduction of horizontal drilling and hydraulic fracturing has drilling activity increased.

In the most active Central Fayetteville Shale, horizontal wells are drilled using oil-based mud in most cases, and water-based mud in others. In addition, 3-D seismic is gaining importance as longer laterals of 3000-plus feet are drilled and more stages are required for hydraulic fracturing. With growing numbers of wells and a need for more infrastructure − pad drilling is another trend emerging in the Fayetteville.

The total area for the Fayetteville shale play, including Central and Western Fayetteville, is 9000 square miles. Fayetteville Central is 4000 square miles and the remaining shale, Fayetteville Western, is approximately 5000 square miles. The shale gas play is estimated to have approximately 31.96 trillion cubic feet (31.96×10^{12} ft^3) of technically recoverable gas.

3.1.12 Floyd shale

The Upper Mississippian Floyd Shale is an equivalent of the prolific Barnett Shale of the Fort Worth Basin. The shale is an organic-rich interval in the lower part of the Floyd Shale that is informally called the Neal shale, which is an organic-rich, starved-basin deposit that is considered to be the principal source rock for conventional hydrocarbon derivatives in the Black Warrior basin.

The Floyd shale is a black marine shale located stratigraphically below the Mississippian Carter sandstone and above the Mississippian Lewis sandstone (US EIA, 2011a). Although the Carter and Lewis sandstones have historically been the most prolific gas-producing zones in the Black Warrior Basin Region of Alabama, there has been no prior production history reported for the Floyd Shale. The Chattanooga Shale is located below the Floyd and is separated from it in most areas by the Tuscumbia Limestone and the Fort Payne Chert.

The Mississippian Floyd Shale is an equivalent of the prolific Barnett Shale of the Fort Worth Basin and the Fayetteville Shale of the Arkoma Basin and has thus been the subject of intense interest. The Floyd is a broadly defined formation that is dominated by shale and limestone and extends from the Appalachian Thrust Belt of Georgia to the Black Warrior Basin of Mississippi.

Usage of the term, Floyd, can be confusing. In Georgia, the type Floyd Shale includes strata equivalent to the Tuscumbia Limestone, and in Alabama and Mississippi, complex facies relationships place the Floyd above the Tuscumbia Limestone, Pride Mountain Formation, or Hartselle Sandstone and below the first sandstone in the Parkwood Formation. Importantly, not all Floyd facies are prospective as gas reservoirs. Drillers have long recognized a resistive, organic-rich shale interval in the lower part of the Floyd Shale that is called informally the Neal shale (Cleaves and Broussard, 1980; Pashin, 1994). In addition to being the probable source rock for conventional oil and gas in the Black Warrior Basin, the Neal has the greatest potential as a shale-gas reservoir in the Mississippian section of Alabama and Mississippi. Accordingly, usage of the term, Neal, helps specify the facies of the Floyd that contains prospective hydrocarbon source rocks and shale-gas reservoirs.

The expected ultimate recovery is on the order of 4.37 trillion cubic feet (4.37×10^{12} ft^3) of technically recoverable gas. The shale ranges from 6000 to 10,000 feet deep and 80–180 feet thick with a well spacing of 2 well per square mile (320 acres per well).

3.1.13 Gammon shale

The Gammon shale is a Cretaceous marine mudstone that is typical of gas-bearing rocks and contains large quantities of biogenic methane (Gautier, 1981). Organic matter in the low-permeability reservoirs served as the source of biogenic methane, and capillary forces acted as the trapping mechanism for gas accumulation. The Gammon member of the Pierre shale of the northern Great Plains, USA, contains abundant siderite concretions (Gautier, 1982).

At Little Missouri field, southwestern North Dakota, Gammon reservoirs consist of discontinuous lenses and laminae of siltstone, less than 10 mm thick, enclosed by silty clay shale. Large amounts of allogenic clay, including highly expansible mixed-layer illite-smectite cause great water sensitivity and high measured and calculated water-saturation values. The shale layers are practically impermeable whereas siltstone microlenses are porous (30%–40%) and have a permeability on the order of 3–30 milliDarcys. Reservoir continuity between siltstone layers is poor and, overall, reservoir permeability is probably less than 0.4 milliDarcys. Connecting passageways between siltstone lenses are 0.1 μm or less in diameter. The reservoirs and non-reservoirs cannot be distinguished on the basis of lithology, and much of the Gammon interval is potentially economic.

3.1.14 *Haynesville shale*

The Haynesville Shale (also known as the Haynesville/Bossier) is situated in the North Louisiana Salt Basin in northern Louisiana and eastern Texas with depths ranging from 10,500 to 13,500 feet (Braithwaite, 2009; Parker et al., 2009; US EIA, 2011a). The Haynesville is an Upper Jurassic-age shale bounded by sandstone (Cotton Valley Group) above and limestone (Smackover Formation) below.

The Haynesville Shale covers an area of approximately 9000 square miles with an average thickness of 200−300 feet. The thickness and areal extent of the Haynesville has allowed operators to evaluate a wider variety of spacing intervals ranging from 40 to 560 acres per well. Gas content estimates for the play are 100−330 scf/ton. The Haynesville formation has the potential to become a significant shale gas resource for the United States with original gas-in-place estimates of 717 trillion cubic feet (717×10^{12} ft^3) and technically recoverable resources estimated at 251 trillion cubic feet (251×10^{12} ft^3).

Compared to the Barnett shale, the Haynesville shale is extremely laminated, and the reservoir changes over intervals as small as four inches to one foot. In addition, at depths of 10,500 to 13,500 feet, this play is deeper than typical shale gas formations creating hostile conditions. Average well depths are 11,800 feet with bottomhole temperatures averaging 155 °C (300 °F) and wellhead treating pressures that exceed 10,000 psi. As a result, wells in the Haynesville require almost twice the amount of hydraulic horsepower, higher treating pressures and more advanced fluid chemistry than the Barnett and Woodford shale formations.

The high-temperature range, from 125 °C (260 °F) to 195 °C (380 °F), creates additional problems in horizontal wells, requiring rugged, high-temperature/high-pressure logging evaluation equipment. The formation depth and high-fracture gradient demand long pump times at pressures above 12,000 psi. In deep wells, there is also concern related to the ability to sustain production with adequate fracture conductivity. In large volumes of water for fracturing, making water conservation and disposal a primary issue.

The Bossier Shale, often linked with the Haynesville shale is a geological formation that produces hydrocarbon and delivers large amounts of natural gas when properly treated. While there is some confusion when distinguishing Haynesville shale from the Bossier Shale, it is a relatively simple comparison − the Bossier Shale lies directly above the Haynesville shale but lies under the Cotton Valley sandstones. However, some geologists still consider the Haynesville shale and the Bossier Shale one in the same. The thickness of the Bossier Shale is approximately 1800 feet in the area of interest. The productive zone is located in the upper 500−600 feet of the shale. The Bossier shale is located in eastern Texas and northern Louisiana.

The Upper Jurassic (Kimmeridgian to Lower Tithonian) Haynesville and Bossier shale formations of East Texas and northwest Louisiana are currently one of the most important shale-gas plays in North America, exhibiting overpressure and high temperature, steep decline rates, and resources estimated together in the hundreds of trillions of cubic feet. These shale-gas resources have been studied extensively by companies and academic institutions within the last year, but to date the depositional setting, facies, diagenesis, pore evolution, petrophysics, best completion techniques, and geochemical characteristics of the Haynesville shale formation and the Bossier shale formations are still not fully characterized and understood. Our work represents new insights into Haynesville and Bossier Shale facies, deposition, geochemistry, petrophysics, reservoir quality, and stratigraphy in light of paleographic setting and regional tectonics.

Haynesville and Bossier Shale deposition was influenced by basement structures, local carbonate platforms, and salt movement associated with the opening of the Gulf of Mexico basin. The deep basin was surrounded by carbonate shelves of the Smackover/Haynesville Lime Louark sequence in the north and east and local platforms within the basin. The basin periodically exhibited restricted environment and reducing anoxic conditions, as indicated by variably increased molybdenum content, presence of framboidal pyrite, and TOC-S-Fe relationships. These organic-rich intervals are concentrated along and between platforms and islands that provided restrictive and anoxic conditions during Haynesville and part of Bossier times.

The mudrock facies range from calcareous-dominated facies near the carbonate platforms and islands to siliceous-dominated lithology in areas where deltas prograded into the basin and diluted organic matter (e.g., northern Louisiana and northeast Texas). These facies are a direct response to a second-order transgression that lasted from the early Kimmeridgian to the Berriasian. The Haynesville shale formation and the Bossier shale formation each compose three upward-coarsening cycles that probably represent third-order sequences within the larger second-order transgressive systems and early highstand systems tracts, respectively. Each Haynesville shale formation is characterized by unlaminated mudstone grading into laminated and bioturbated mudstone. Most of the three Bossier third-order cycles are dominated by varying amounts of siliciclastic mudstones and siltstones. However, the third Bossier formation exhibits higher carbonate and an increase in organic productivity in a southern restricted area (beyond the basinward limits of Cotton Valley progradation), creating another productive gas-shale opportunity. This organic-rich Bossier formation extends across the Sabine Island complex and the Mt. Enterprise Fault Zone in a narrow trough from Nacogdoches County, Texas, to Red River Parish, Louisiana. Similar to the organic-rich Haynesville cycles, each third-order cycle grades from unlaminated into laminated mudstone and is capped by bioturbated, carbonate-rich mudstone facies. Best reservoir properties are commonly found in facies with the highest TOC, lowest siliciclastics, highest level of maturity, and highest porosity. Most porosity in the Haynesville and Bossier is related to interparticle nano- and micropores and, to a minor degree, by porosity in organic matter.

The Haynesville shale formation and the Bossier shale formation are distinctive on wireline logs: high gamma ray, low density, low neutron porosity, high sonic travel time, moderately high resistivity. A multiline log model seems to predict the total organic content of the formations from the logs. Persistence of distinctive log signatures is similar for the organic-rich Bossier shale formation and the Haynesville shale formation across the study area, suggesting that favorable conditions for shale-gas production extend beyond established producing areas.

3.1.15 Hermosa shale

The black shale of the Hermosa Group (Utah) consists of nearly equal portions of clay-sized quartz, dolomite and other carbonate minerals, and various clay minerals. The clay is mainly illite with minor amounts of chlorite and mixed layer chlorite-smectite (Hite et al., 1984).

The area of interest for the Hermosa Group black shale is the northeast half of the Paradox basin, the portion referred to as the fold and fault belt. This is the area of thick halite deposits in the Paradox Formation, and consequently narrow salt walls and broad interdome depressions. To the southwest of this stratigraphically controlled structural zone the black shale intervals are fewer and thinner, and they lack the excellent seals provided by the halite. The area encompasses eastern Wayne and Emery Counties, southern Grand County and the northeast third of San Juan County (Schamel, 2005, 2006). The kerogen in the shale is predominantly gas-prone humic type III and mixed type II–III (Nuccio and Condon, 1996).

Numerous factors favor the possible development of shale gas in the black shale intervals of the Hermosa Group. First, the shale is very organic-rich, on the whole the most carbonaceous shale in Utah, and they are inherently gas-prone. Second, they have reached relatively high degrees of thermal maturity across much of the basin. Third and perhaps most significant, the shale is encased in halite and anhydride which retard gas leakage, even by diffusion. Yet it is curious that the Paradox basin is largely an oil province (Morgan, 1992; Montgomery, 1992) in which gas production is historically secondary and associated gas, which relates to the concentration of crude oil development in the shallower targets on the southwest basin margin and in the salt-core anticlines.

3.1.16 Lewis shale

The Lewis shale gas play is located in the San Juan Basin in Colorado and New Mexico. And has an area of approximately 7506 square miles. The depth of the Lewis shale ranges from 1640 to 8202 feet deep and is 200–300 feet thick with approximately 11.6 trillion cubic feet (11.6×10^{12} ft^3) of technically recoverable gas.

The Lewis Shale (San Juan Basin) is a quartz-rich mudstone that was deposited in a shallow, off-shore marine setting during an early Campanian transgression southwestward across shoreline deposits of the underlying pro-gradational Cliffhouse Sandstone Member of the Mancos Formation (Nummendal and Molenaar, 1995; US EIA, 2011a). The gas resources of the Lewis Shale are currently being developed, principally through recompletions of existing wells targeting deeper, conventional sandstone gas reservoirs (Dube et al., 2000; Braithwaite, 2009). Current estimates place the expected ultimate recovery of gas on the order of 21.02 trillion cubic feet (21.02×10^{12} ft^3) of technically recoverable gas.

The 1000–1500 feet thick Lewis Shale is lowermost shore-face and pro-delta deposits composed of thinly laminated (locally bioturbated) siltstones, mudstones and shale. The average clay fraction is just 25%, but quartz is 56%. The rocks are very tight. Average matrix gas porosity is 1.7% and the average gas permeability is 0.0001 milliDarcy. The rocks also are organically lean, with an average total organic carbon content is only 1.0%; the range is 0.5–1.6%. The reservoir temperature is 46 °C (140 °F). Yet the adsorptive capacity of the rock is 13–38 scf/ton, or approximately 22 billion cubic feet per quarter section (i.e., per 160 acres) (Jennings et al., 1997).

Four intervals and a conspicuous, basin-wide bentonite marker are recognizable in the shale. The greatest permeability is found in the lowermost two-thirds of the section, which may be the result of an increase in grain size and micro-fracturing associated with the regional north-south/east-west fracture system (Hill and Nelson, 2000).

3.1.17 Mancos shale

The Mancos shale formation (Uintah Basin) is an emerging shale-gas resource (US EIA, 2011a). The thickness of the Mancos (averaging four thousand feet in the Uinta Basin) and the variable lithology present drillers with a wide range of potential stimulation targets. The area of interest for the Mancos Shale is the southern two-thirds of the greater Uinta Basin, including the northern parts of the Wasatch Plateau. In the northern one-third of the basin there have been two few well penetrations of the Mancos Shale, and it is too deep to warrant commercial exploitation of a “low density” resource such as shale gas. The area is within Duchesne, Uintah, Grand, Carbon and the northern part of Emery Counties (Schamel, 2005, 2006; Braithwaite, 2009).

The Mancos Shale is dominated by mudrock that accumulated in offshore and open-marine environments of the Cretaceous Interior seaway. It is 3450–4150 feet thick where exposed in the southern part of the Piceance and Uinta Basins, and geophysical logs indicate the Mancos to be approximately 5400 feet thick in the central part of the Uinta Basin. The upper part of the formation is inter-tongues with the Mesaverde Group – these tongues typically have sharp basal contacts and gradational upper contacts. Named tongues include the Buck and the Anchor Mine Tongues. An important hydrocarbon-producing unit in the middle part of the Mancos was referred to as the Mancos B Formation, which consists of thinly interbedded and interlaminated, very fine grained to fine-grained sandstone, siltstone, and clay that was interpreted to have accumulated as north-prograding fore slope sets within an open-marine environment. The Mancos B has been incorporated into a thicker stratigraphic unit identified as the Prairie Canyon Member of the Mancos, which is approximately 1200 feet thick (Hettinger and Kirschbaum, 2003).

At least four members of the Mancos have shale-gas potential: (i) the Prairie Canyon (Mancos B), (ii) the Lower Blue Gate Shale, (iii) the Juana Lopez, and (iv) the Tropic-Tununk Shale. Organic matter in the shale has a large fraction of Terrigenous material derived from the shorelines of the Sevier belt. The thickness of the organic-rich zones within individual system tracts exceeds twelve feet. Vitrinite reflectance values from a limited number of samples at the top of the Mancos range from 0.65% at the Uinta Basin margins to >1.5% in the central basin.

Across most of Utah the Mancos Shale has not been sufficiently buried to have attained the levels of organic maturity required for substantial generation of natural gas, even in the humic kerogen-dominant (type II–III) shale that characterize this group (Schamel 2005, 2006). However, vitrinite reflectance values beneath the central and southern Uinta Basin are well within the gas generation window at the level of the Tununk Shale, and even the higher members of the Mancos Shale. In addition to the in situ gas within the shale, it is likely that some of the gas found a reservoir in the silty shale intervals has migrated from deeper source units, such as the Tununk Shale or coals in the Dakota.

The Mancos Shale warrants consideration as the significant gas reservoir and improved methods for fracture stimulation tailored to the specific rock characteristics of the Mancos lithology are required. The well completion technologies used in the sandstones cannot be applied to the shale rocks without some reservoir damage.

3.1.18 Marcellus shale

The Marcellus Shale (Appalachian Basin), also referred to as the Marcellus Formation, is located in the Appalachian Basin across the Eastern Part of the United States. The Marcellus Shale formations are 400 million years old and extend from western Maryland to New York, Pennsylvania and West Virginia and encompassing the Appalachian region of Ohio along the Ohio River. The formation is a Middle Devonian black, low density, carbonaceous (organic rich) shale that occurs in the subsurface beneath much of Ohio, West Virginia, Pennsylvania, and New York. Small areas of Maryland, Kentucky, Tennessee, and Virginia are also underlain by the Marcellus Shale (Braithwaite, 2009; Bruner and Smosna, 2011; US EIA, 2011a). It has been estimated that the Marcellus shale formation could contain as much as 489 trillion cubic feet of natural gas, a level that would establish the Marcellus as the largest natural gas resource in North America and the second largest in the world.

Throughout most of its extent, the Marcellus is nearly a mile or more below the surface. These great depths make the Marcellus Formation a very expensive target. Successful wells must yield large volumes of gas to pay for the drilling costs that can easily exceed a million dollars for a traditional vertical well and much more for a horizontal well with hydraulic fracturing. There are areas where the thick Marcellus Shale can be drilled at minimum depths and tends to correlate with the heavy leasing activity that has occurred in parts of northern Pennsylvania and western New York.

Natural gas occurs within the Marcellus Shale in three ways: (i) within the pore spaces of the shale, (ii) within vertical fractures (joints) that break through the shale, and (iii) adsorbed on mineral grains and organic material. Most of the recoverable gas is contained in the pore spaces. However, the gas has difficulty escaping through the pore spaces because they are very tiny and poorly connected. The gas in the Marcellus Shale is a result of its contained organic content. Logic therefore suggests that the more organic material there is contained in the rock the greater its ability to yield gas. The areas with the greatest production potential might be where the net thickness of organic-rich shale within the Marcellus Formation is greatest. Northeastern Pennsylvania is where the thick organic-rich shale intervals are located. The Marcellus shale ranges in depth from 4000 to 8500 feet, with gas currently produced from hydraulically fractured horizontal wellbores. Horizontal lateral lengths exceed 2000 feet, and, typically, completions involve multistage fracturing with more than three stages per well.

Before the year 2000, many successful natural gas wells had been completed in the Marcellus shale. The yields of these wells were often unimpressive upon completion. However, many of these older wells in the Marcellus have a sustained production that decreases slowly over time and many of them continued to produce gas for decades. To exhibit the interest in this shale formation, The Pennsylvania Department of Environmental Protection reports that the number of drilled wells in the Marcellus Shale has been increasing rapidly. In 2007, 27 Marcellus Shale wells were drilled in the state, however, in 2011 the number of wells drilled had risen to more than 2000.

For new wells drilled with the new horizontal drilling and hydraulic fracturing technologies the initial production can be much higher than what was seen in the old wells. Early production rates from some of the new wells have been over one million cubic feet of natural gas per day. The technology is so new that long term production data is not available. As with most gas wells, production rates will decline over time, however, a second hydraulic fracturing treatment could stimulate further production.

3.1.19 Monterey/Santos shale

The Monterey/Santos shale oil play includes the Lower Monterey shale formation and the Santos shale formation and is located in the San Joaquin and Los Angeles Basins in California. The active area for the Monterey/Santos shale play is approximately 1752 square miles. The depth of the shale ranges from 8000 to 14,000 feet deep and is between 1000 and 3000 feet thick with approximately 15.42 billion barrels (15.42×10^9 bbls) of technically recoverable oil.

3.1.20 Neal shale

The Neal shale is an organic-rich facies of the Upper Mississippian age Floyd shale formation. The Neal shale formation has long been recognized as the principal source rock that charged conventional sandstone reservoirs in the Black Warrior Basin (Telle et al., 1987; Carroll et al., 1995; US EIA, 2011a) and has been the subject of intensive shale-gas exploration in recent years.

The Neal shale is developed mainly in the southwestern part of the Black Warrior Basin and is in facies relationship with strata of the Pride Mountain Formation, Hartselle Sandstone, the Bangor Limestone, and the lower Parkwood Formation. The Pride Mountain-Bangor interval in the northeastern part of the basin constitutes a progradational parasequence set in which numerous stratigraphic markers can be traced southwestward into the Neal shale (Pashin, 1993). Individual parasequences tend to thin southwestward and define a clinoform stratal geometry in which near-shore facies of the Pride Mountain-Bangor interval pass into condensed, starved-basin facies of the Neal shale.

The Neal formation maintains the resistivity pattern of the Pride Mountain-Bangor interval, which facilitates regional correlation and assessment of reservoir quality at the parasequence level. The Neal shale and equivalent strata were subdivided into three major intervals, and isopach maps were made to define the depositional framework and to illustrate the stratigraphic evolution of the Black Warrior Basin in Alabama (Pashin, 1993). The first interval includes strata equivalent to the Pride Mountain Formation and the Hartselle Sandstone and thus shows the early configuration of the Neal basin. The Pride Mountain-Hartselle interval contains barrier-strand plain deposits (Cleaves and Broussard, 1980; Thomas and Mack, 1982). Isopach contours define the area of the barrier-strand plain system in the northeastern part of the basin, and closely spaced contours where the interval is between 25 and 225 feet thick define a southwestward slope that turns sharply and faces southeastward in western Marion County. The Neal starved basin is in the southwestern part of the map area, where this interval is thinner than 25 feet.

The second interval includes strata equivalent to the bulk of the Bangor Limestone. A generalized area of inner ramp carbonate sedimentation is defined in the northeastern part of the formation where the interval is thicker than 300 feet. Muddy, outer-ramp facies are concentrated where this interval thins from 300 to 100 feet, and the northeastern margin of the Neal starved basin is marked by the 100-foot contour. Importantly, this interval contains the vast majority of the prospective Neal reservoir facies, and the isopach pattern indicates that the slope had prograded more than 25 miles southwestward during Bangor deposition.

The final interval includes strata equivalent to the lower Parkwood Formation. The lower Parkwood separates the Neal shale and the main part of the Bangor Limestone from carbonate-dominated strata of the middle Parkwood Formation, which includes a tongue of the Bangor that is called the *Millerella* limestone. The Lower Parkwood is a succession of siliciclastic deltaic sediment that prograded onto the Bangor ramp in the northeastern part of the study area and into the Neal basin in the southern part and contains the most prolific conventional reservoirs in the Black Warrior Basin (Cleaves, 1983; Pashin and Kugler, 1992; Mars and Thomas, 1999). The lower Parkwood is thinner than 25 feet above the inner Bangor ramp and includes a variegated shale interval containing abundant slickensides and calcareous nodules, which are suggestive of exposure and vertical soil formation. The area of deltaic sedimentation is where the lower Parkwood is thicker than 50 feet and includes constructive deltaic facies in the Neal basin and destructive, shoal-water deltaic facies along the margin of the Bangor ramp. In the southern part of the study area, the 25-foot contour defines a remnant of the Neal basin that persisted through lower Parkwood deposition. In this area, condensation of lower Parkwood sediment brings middle Parkwood carbonate rocks within 25 feet of the resistive Neal shale.

3.1.21 New Albany shale

The New Albany shale gas play (Illinois Basin, Illinois, Indiana and Kentucky) is organic-rich shale located over a large area in southern Indiana and Illinois and in Northern Kentucky (Zuber et al., 2002; Braithwaite, 2009; US EIA, 2011a). The depth of the producing interval varies from 500 feet to 2000 feet depth, with thicknesses of approximately 100 feet. The shale is generally sub-divided into four stratigraphic intervals: from top to bottom, these are (i) Clegg Creek, (ii) Camp Run/Morgan Trail, (iii) Selmier, and (iv) Blocher intervals.

The total area for the New Albany shale play is approximately 43,500 square miles. The total area includes an active and undeveloped area of the play – the total active area is on the order of 1600 square miles and the remaining area (41,900) square miles and is characterized as undeveloped area. The New Albany formation has an expected ultimate recovery of 10.95 trillion cubic feet (10.95×10^{12} ft^3) of technically recoverable gas. The depth of the formation ranges from 1000 to 4500 and is 100–300 feet thick.

The New Albany shale can be considered to be a *mixed source rock* in which some parts of the basin produced thermogenic gas, and other parts produced biogenic gas. This is indicated by the vitrinite reflectance in the basin, varying from 0.6 to 1.3 (Faraj et al., 2004). It is not known whether circulating ground waters recently generated this biogenic gas or whether it is original biogenic gas generated shortly after the time of deposition.

Most gas production from the New Albany comes from approximately sixty fields in northwestern Kentucky and adjacent southern Indiana. However, past and current production is substantially less than that from either the Antrim Shale or Ohio Shale. Exploration and development of the New Albany Shale was spurred by the spectacular development of the Antrim Shale resource in Michigan, but results have not been as favorable (Hill and Nelson, 2000).

Production of New Albany Shale gas, which is considered to be biogenic, is accompanied by large volumes of formation water (Walter et al., 2000). The presence of water would seem to indicate some level of formation permeability. The mechanisms that control gas occurrence and productivity are not as well understood as those for the Antrim and Ohio shale formations (Hill and Nelson, 2000).

3.1.22 Niobrara shale

The Niobrara shale formation (Denver-Julesburg Basin, Colorado) is a shale rock formation located in Northeast Colorado. Northwest Kansas, Southwest Nebraska, and Southeast Wyoming. Oil and natural gas can be found deep below the surface of the Earth at depths of three thousand to fourteen thousand feet. Companies drill these wells vertically and even horizontally to get at the oil and natural gas in the Niobrara Formation.

The Niobrara Shale is located in the Denver-Julesburg basin which is often referred to as the DJ Basin. This resource exciting oil shale play is being compared to the Bakken shale resource, is located in North Dakota.

3.1.23 Ohio shale

The Devonian shale in the Appalachian Basin was the first produced in the 1820s. The resource extends from Central Tennessee to Southwestern New-York and also contains the Marcellus shale formation. The Middle and Upper Devonian shale formations underlie approximately 128,000 square miles and crop out around the rim of the basin. Subsurface formation thicknesses exceed 5000 feet and organic-rich black shale exceeds 500 feet (152 m) in net thickness (DeWitt et al., 1993).

The Ohio Shale (Appalachian Basin) differs in many respects from the Antrim Shale crude oil system. Locally, the stratigraphy is considerably more complex as a result of variations in depositional setting across the basin (Kepferle, 1993; Roen, 1993). The shale formations can be further subdivided into five cycles of alternating carbonaceous shale formations and coarser grained clastic materials (Ettensohn, 1985). These five shale cycles developed in response to the dynamics of the Acadian orogeny and westward progradation of the Catskill delta.

The Ohio Shale, within the Devonian Shale, consists of two major stratigraphic intervals: (i) the Chagrin Shale and (ii) the underlying Lower Huron Shale.

The Chagrin Shale consists of 700−900 feet of gray shale (Curtis, 2002; Jochen and Lancaster, 1993), which thins gradually from East to West. Within the lower 100−150 feet, a transition zone consisting of inter-bedded black and gray shale lithology announces the underlying Lower Huron formation. The Lower Huron shale is 200−275 feet of dominantly black shale, with moderate amounts of gray shale and minor siltstone. Essentially all the organic matter contained in the lower Huron is thermally mature for hydrocarbon generation, based on vitrinite reflectance studies.

The vitrinite reflectance of the Ohio Shale varies from 1% to 1.3%, which indicates that the rock is thermally mature for gas generation (Faraj et al., 2004). The gas in the Ohio Shale is consequently of thermogenic origin. The productive capacity of the shale is a combination of gas storage and deliverability (Kubik and Lowry, 1993). Gas storage is associated with both classic matrix porosity as well as gas adsorption onto clay and non-volatile organic material. Deliverability is related to matrix permeability although highly limited (10^{-9} to 10^{-7} milliDarcys) and a well-developed fracture system.

3.1.24 Pearsall shale

The Pearsall Shale is a gas bearing formation that garnered attention near the Texas-Mexico border in the Maverick Basin before development of the Eagle Ford shale truly commenced. The Pearsall Shale formation is found below the Eagle Ford formation at depths of seven thousand to twelve thousand feet with a thickness of six hundred to nine hundred feet (Braithwaite, 2009).

The formation does have the potential to produce liquids east of the Maverick Basin. As of 2012, only a few wells had been drilled in the play outside of the Maverick Basin but early results indicate there is potential that has largely been overlooked.

3.1.25 Pierre shale

The Pierre Shale, located in Colorado, produced two million cubic feet of gas in 2008. Drilling operators are still developing this rock formation, which lies at depths that vary between 2500 and 5000 feet, and will not know its full potential until more wells provide greater information related to its limits (Braithwaite, 2009).

The Pierre shale formation is a division of Upper Cretaceous rocks laid down from approximately one hundred and forty-six million to sixty-five million years ago and is named for exposures studied near old Fort Pierre, South Dakota. In addition to Colorado, the formation also occurs in South Dakota, Montana, Colorado, Minnesota, New Mexico, Wyoming, and Nebraska.

The formation consists of approximately 2000 feet of dark gray shale, some sandstone, and many layers of bentonite (altered volcanic-ash falls that look and feel much like soapy clays). In some regions the Pierre Shale may be as little as seven hundred feet feet thick.

The lower Pierre Shale represents a time of significant changes in the Cretaceous Western Interior Seaway, resulting from complex interactions of tectonism and eustatic sea level changes. The recognition and redefinition of the units of the lower Pierre Shale has facilitated understanding of the dynamics of the basin. The Burning Brule Member of the Sharon Springs Formation is restricted to the northern part of the basin and represents tectonically influenced sequences. These sequences are a response to rapid subsidence of the axial basin and the Williston Basin corresponding to tectonic activity along the Absoroka Thrust in Wyoming. Unconformities associated with the Burning Brule Member record a migrating peripheral bulge in the Black Hills region corresponding to a single tectonic pulse on the Absoroka Thrust. Migration of deposition and unconformities supports an elastic model for the formation and migration of the peripheral bulge and its interaction with the Williston Basin (Bertog, 2010).

3.1.26 Utah shale

There are five kerogen-rich shale units as having reasonable potential for commercial development as shale gas reservoirs. These are (i) four members of the Mancos Shale in northeast Utah - the Prairie Canyon, the Juana Lopez, the Lower Blue Gate, and the Tununk, and (ii) the black shale facies within the Hermosa Group in southeast Utah (Schamel, 2005).

The Prairie Canyon and Juana Lopez Members are both detached mudstone-siltstone-sandstone successions embedded within the Mancos Shale in northeast Utah. The Prairie Canyon Member is up to 1200 feet thick, but the stratigraphically deeper Juana Lopez

Member is less than 100 feet. Both are similar in lithology and basin setting to the gas-productive Lewis Shale in the San Juan basin. As in the Lewis Shale, the lean, dominantly humic, kerogen is contained in the shale interlaminated with the siltstone-sandstone. The high quartz content is likely to result in a higher degree of natural fracturing than the enclosing clay-mudstone rocks. Thus, they may respond well to hydraulic fracturing. Also the porosity of the sandstone interbeds averaging 5.4% can enhance gas storage. Both units extend beneath the southeast Uinta basin reaching depths sufficient for gas generation and retention from the gas-prone kerogen. Although not known to be producing natural gas at present, both units are worthy of testing for add-on gas, especially in wells that are programmed to target Lower Cretaceous or Jurassic objectives.

The Lower Blue Gate shale formation and the Tropic-Tununk shale formation generally lack the abundant siltstone-sandstone interbeds that would promote natural and induced fracturing, but they do have zones of observed organic richness in excess of 3.1.0% that might prove to be suitable places for shale gas where the rocks are sufficiently buried beneath the southern Uinta basin and perhaps parts of the Wasatch Plateau.

The black shale facies in the Hermosa Group of the Paradox basin is enigmatic. These shale formations contain mixed type II—III kerogen that should favor gas generation, yet oil with associated gas dominate current production. They are relatively thin, just a few tens of feet thick on average, yet they are encased in excellent sealing rocks, salt and anhydride. In the salt walls (anticlines) the shale formations are complexly deformed making them difficult to develop even with directional drilling methods, but where they are likely less deformed in the interdome areas (synclines) they are very deep. Yet in these deep areas one can expect peak gas generation. The shale formations are over-pressured, which suggests generation currently or in the recent past. Prospects are good that shale gas reservoirs can be developed in the Paradox basin, but it may prove to be technically and economically challenging (Schamel, 2005).

3.1.27 Utica shale

The Utica shale is a rock unit located approximately four thousand to fourteen thousand feet below the Marcellus shale and has the potential to become an enormous natural gas resource. The boundaries of the deeper Utica Shale formation extend under the Marcellus Shale region and beyond. The Utica shale encompasses New York, Pennsylvania, West Virginia, Maryland and even Virginia. The Utica Shale is thicker than the Marcellus and has already proven its ability to support commercial gas production.

The geologic boundaries of the Utica Shale formation extend beyond those of the Marcellus Shale. The Utica formation, which was deposited 40—60 million years ($40-60 \times 10^6$ years) before the Marcellus formation during the Paleozoic Era, is thousands of feet beneath the Marcellus formation. The depth of Utica Shale in the core production area of the Marcellus shale formation production area creates a more expensive environment in which to develop the Utica shale formations. However, in Ohio the Utica shale formation is as little as 3000 feet below the Marcellus Shale, whereas in sections of Pennsylvania the Utica formation is as deep as 7000 feet below the Marcellus formation creating a better economic environment to achieve production from the Utica shale formation in Ohio. Furthermore, the investments in the infrastructure to extract natural gas from the Marcellus shale formation also increase the economic efficiency of extracting natural gas from the Utica shale. Although the Marcellus Shale is the current unconventional shale drilling target in Pennsylvania. Another rock unit with enormous potential is a few thousand feet below the Marcellus formation.

The potential source rock portion of the Utica Shale is extensive and underlies portions of Kentucky, Maryland, New York, Ohio, Pennsylvania, Tennessee, West Virginia and Virginia. It is also present beneath parts of Lake Ontario, Lake Erie and part of Ontario, Canada. This geographic extent of potential Utica Shale source rock along with the equivalent Antes Shale of central Pennsylvania and Point Pleasant Shale of. In keeping with this areal extent, the Utica Shale has been estimated to contain (at least) thirty-eight trillion cubic feet (38×10^{12} ft^3) of technically recoverable natural gas (at the mean estimate) according to the first assessment of this continuous (unconventional) natural gas accumulation by the US Geological Survey.

In addition to natural gas, the Utica Shale is also yielding significant amounts of natural gas liquids and oil in the western portion of its extent and has been estimated to contain on the order of nine hundred and forty million barrels (940×10^6 bbls) of unconventional oil resources and approximately two hundred and eight million barrels (208×10^6 bbls) of unconventional natural gas liquids. A wider estimate place gas resources of the Utica shale, from 2 trillion cubic feet to 69 trillion cubic feet ($2-69 \times 10^{12}$ ft^3), which put this shale on the same resource level as the Barnett shale, the Marcellus shale, and the Haynesville shale formations.

3.1.28 Woodford shale

The Woodford Shale, located in south-central Oklahoma, ranges in depth from 6000 to 11,000 feet (Abousleiman et al., 2007; Braithwaite, 2009; Jacobi et al., 2009; US EIA, 2011a). This formation is a Devonian-age shale bounded by limestone (Osage Lime) above and undifferentiated strata below. Recent natural gas production in the Woodford Shale began in 2003 and 2004 with vertical well completions only. However, horizontal drilling has been adopted in the Woodford, as in other shale gas plays, due to its success in the Barnett Shale.

The Woodford Shale play encompasses an area of nearly 11,000 square miles. The Woodford play is in an early stage of development and is occurring at a spacing interval of 640 acres per well. The average thickness of the Woodford Shale varies from 120 to 220 feet across the play. The gas content in the Woodford Shale is higher on average than some of the other shale gas plays at 200–300 scf/ton. The original gas-in-place estimate for the Woodford Shale is similar to the Fayetteville Shale at 23 trillion cubic feet (23×10^{12} ft^3) while the technically recoverable resources are estimate at 11.4 trillion cubic feet (11.4×10^{12} ft^3).

Woodford shale stratigraphy and organic content are well understood, but due to their complexity compared to the Barnett shale, the formations are more difficult to drill and fracture. As in the Barnett, horizontal wells are drilled, although oil-based mud is used in the Woodford shale and the formation is harder to drill. In addition to containing chert and pyrite, the Woodford formation is more faulted, making it easy to drill out of the interval; sometimes crossing several faults in a single wellbore is required.

Like the Barnett shale, higher silica rocks are predominant in the best zones for fracturing in the Woodford formation, although the Woodford has deeper and higher fracture gradients. Due to heavy faulting, 3-D seismic is extremely important, as the Woodford formation trends toward longer laterals exceeding 3000 feet with bigger fracture projects and more stages. Pad drilling also will increase as the Woodford shale formation continues expanding to the Ardmore Basin and to West Central Oklahoma in Canadian County.

The Cana Woodford formation is an emerging gas play located within the Oklahoma Anadarko Basin, approximately 40 miles west of Oklahoma City. It has been estimated that the Cana Woodford play contains a high liquid content of approximately 65% v/v gas, 30% v/v natural gas liquids (NGLs), and 5% v/v crude oil. The active area for Cana Woodford is approximately 688 square miles with depths that range from approximately 11,500 to 14,500 feet.

3.2 Canada

A number of tight oil formations are found in the Western Canada Sedimentary Basin, and most have seen production in the past at relatively low rate and low recovery, while others are just recently attracting attention for potential development with horizontal multi-stage fracturing techniques (Ross and Bustin, 2008). Generally, these crude oil resources were known to exist but large areas of the shale/tight formations were considered to be uneconomic when compared to production through conventional vertical wells.

Recent estimates (NEB, 2009) in indicate that there is the potential for one quadrillion cubic feet (1×10^{15} ft^3) of gas in place in shale formation in Canada located in different areas but predominantly in the Western Canada Sedimentary basin which includes (i) the Cardium Group, (ii) the Colorado Group, (iii) the Duvernay Shale, (iv) the Horn River Basin, and (v) the Montney Shale and which also show significant coalbed methane resources (WCSBs) (Figs. 2.3 and 2.6). As more shale and tight formations are investigated and identified, estimates of the resources are expected to show significant increases (NEB, 2009).

3.2.1 Cardium Group

The Cardium formation consists of tight inter-bedded shale layers and sandstone layers and is found in much of west central area of the Province of Alberta. The formation depth varies from 3900 to 7500 feet and the average thickness of the oil-bearing strata is on the order of 3–10 feet (Peachey, 2014). Some higher quality parts of the formation in the Pembina Oil Field (one of the largest oil fields in Canada) have higher porosity beds of sands and gravel conglomerates, which have already seen production.

The original conventional Cardium oil fields contained 10.6 billion barrels (10.6×10^9 bbls) of light oil, or approximately 16% of all of the conventional oil resources found in Alberta. The areas around the main pools, currently being developed, may contain an additional 1–3 billion barrels ($1–3 \times 10^9$ bbls) of light oil bbls, although estimates vary and so far 130 million barrels (130×10^6 bbls), or 5%–10% of the original oil in place, have been claimed as proved and probable reserves which might be technically and economically produced.

At the onset of oil and gas formation, the Cardium, may not have contained much organic matter but the formations now contain natural gas and crude oil which may have migrated into the formations from deeper shale formations. Within the Cardium formation there are areas of the reservoir which lack the highly permeable conglomerate zones, or where there are tight zones above or below the conglomerates which are not connected to the flow system leading to a producing vertical well. While these zones contain considerable amounts of light crude oil, they did not allow for commercial rates of production with vertical wells. However, the introduction of long horizontal wells within the formation, and a series of fracture stages to connect the horizontal wells to various layers in the formation results in economic oil production rates, even in relatively poor reservoir rock. Some of the oil found in the Cardium Group may be referred to as *halo oil* which is oil that exists on the fringe regions of existing oil fields that surround the areas of historical production. Traditional technology cannot produce this oil because of the low permeability of the reservoir matrix.

3.2.2 Colorado Group

The Colorado Group consists of various shale-containing horizons deposited throughout southern Alberta and Saskatchewan during the middle Cretaceous Period – including the Medicine Hat and Milk River shale-containing sandstones – when globally high sea levels caused the deposition of these formations of the, which have been producing natural gas for over 100 years (NEB, 2009). There is also the Second White Speckled Shale, which has been producing natural gas for decades (Beaton et al., 2009).

In the Wildmere area of Alberta, the Colorado Shale is approximately six hundred and fifty feet thick, from which natural gas has potential to produce from five intervals. Unlike shale formations from the Horn River Basin and the Utica Group of Quebec, shale from the Colorado Group produces through thin sand beds and lamina, making it a hybrid gas shale like the Montney shale. Furthermore, the gas produced in the Colorado has biogenic rather than thermogenic origins. This would suggest very low potential for natural gas liquids and an under-pressured reservoir, which is more difficult to hydraulically fracture. Colorado Group shale formations are sensitive to water, which makes them sensitive to fluids used during hydraulic fracturing.

The total volume of gas in the Colorado Group is very difficult to estimate given the wide lateral extent of the shale and variability of the reservoir and the absence of independent and publicly available analyses. However, there could be at least one hundred trillion cubic feet (100×10^{12} ft^3) of gas in place.

3.2.3 Duvernay shale

The Devonian Duvernay shale is an oil and natural gas field located in Alberta, Canada (in the Kaybob area) which extends into British Columbia. The Devonian formation is considered the source rock for the Leduc reefs light oil resources, the discovery of which in 1947 was one of the defining moments in the past-present-and-future Western Canadian oil and gas industry.

The Duvernay Formation (Devonian-Frasnian) of Alberta, Canada is a proven source rock of marine origin which has yielded much of the crude oil and natural gas to the adjacent classical Devonian, conventional fields in carbonate reefs and platform carbonates. Production in these conventional fields is in decline and exploration and development has now shifted to their source, the Duvernay shale.

The deeper Duvernay shale formation underlies much of the Cardium and the portions of the Duvernay formation that underlie the Cardium formation appear to be more likely to contain natural gas reserves than crude oil reserves (NEB, 2009; Peachey, 2014).

The Duvernay shale, which can be found just north of the Montney shale is distributed over most of central Alberta and absent in areas of Leduc reef growth, except beneath the Duhamel reef, where it may be represented by a thin development of calcilutite (a dolomite or limestone formed of calcareous rock flour that is typically non-siliceous). In the East Shale Basin, the formation is approximately 175 feet thick and thickens to 246 feet east and southeastward toward the Southern Alberta Shelf. In a northeast direction, the formation reaches approximately 395 feet at its truncation in the subsurface at the pre-Cretaceous unconformity. In the West Shale Basin, the formation is approximately 195 feet thick and thickens northward, attaining a thickness in excess of 820 feet to the east of Lesser Slave Lake.

The formation consists of interbedded dark brown bituminous shale sediments, dark brown, black and occasionally gray-green calcareous shale sediments and dense argillaceous limestone sediments. The shale formations are characteristically petroliferous and exhibit plane parallel millimeter lamination. The formation is characterized by (i) a porosity on the order of 6.0%—7.5%, (ii) a permeability on the order of 236—805 nanoDarcys, and (iii) total organic carbon content 3.1.0—7.5% w/w. X-ray diffraction results from core and cuttings samples indicate it is likely very brittle with a low clay content (26% w/w), amorphous biogenic silica (47% w/w), and a calcite ($CaCO_3$) and dolomite ($CaCO_3 \cdot MgCO_3$) matrix (Switzer et al., 1994; Fowler et al., 2003).

3.2.4 *Horn River basin*

The Horn River Basin encompasses approximately 2.5 million acres of land in northeastern British Columbia, north of Fort Nelson and south of the Northwest Territories border. This is an unconventional shale play targeting dry gas from mid-Devonian aged over pressured shale formations of the Muskwa, Otter Park and Evie Formations. The Horn River Basin is confined to the west by the Bovie Lake Fault Zone and to the East and South by the time equivalent Devonian Carbonate Barrier Complex (NEB, 2009; BCOGC, 2014).

Stratigraphically, the organic rich siliciclastic Muskwa, Otter Park and Evie shale formations of the Horn River group are overlain by the Fort Simpson shale and underlain by the Keg River platform carbonates. The Evie Shale consists of dark gray to black, organic rich, pyritic, variably calcareous and siliceous shale. This shale exhibits relatively high gamma ray readings and high resistivity on well logs. The unit is at its thickest immediately west of the barrier reef complex, generally thinning westward toward the Bovie Lake Fault Structure. The Otter Park Shale thickens considerably in the southeast corner of the Basin, characterized by increasingly argillaceous and calcareous facies. Limestone marls were deposited at the expense of shale. The unit thins to the north and west, exhibiting higher gamma ray readings. The Muskwa Shale consists of gray to black, organic rich, pyritic, siliceous shale. A gradational contact exists between the overlying silt-rich shale of the Fort Simpson Formation. Generally, the Muskwa Formation thickens westward toward the Bovie Lake Structure. This shale thins and extends over the top of the barrier reef complex and continues eastward into Alberta, stratigraphically equivalent to the Duvernay Shale. Muskwa and Otter Park formations were mapped in combination and analyzed as one interval. From a geomechanical perspective, the Muskwa and Otter Park Formations are considered as one flow unit after hydraulic fracturing with few barriers to fracture propagation. The Evie formation was evaluated and mapped as a separate unit. Mapping completed thus far has defined areas of reservoir variability within the Basin, particularly within the Otter Park Formation.

The Devonian Horn River Basin shale formations were deposited in deep waters at the foot of the Slave Point carbonate platform in northeast British Columbia. The shale formations are silica-rich (approximately 55% v/v silica) and approximately four hundred and fifty feet thick. The total organic content is 1−6% w/w and the formations have been producing conventional natural gas for many decades. The Horn River Shale Formation located in British Columbia, is the largest shale gas field in Canada and contain an estimated 250 trillion cubic feet (250×10^{12} ft^3) of natural gas (Ross and Bustin, 2008). This shale gas play also includes the Cordova Embayment and the whole formation extends into both the Yukon Territory and the Northwest Territories, although its northward extent beyond provincial/territorial borders is poorly defined.

The advent of horizontal drilling combined with multi-stage hydraulic fracturing increased interest in unlocking the potential of shale gas. Prior to 2005, operators were targeting Devonian pinnacle reefs, with the basin shale formations then considered a seal and source rock for gas. After 2005, operators began applying horizontal drilling and multi-stage hydraulic fracturing technology from the analogous Barnett shale in Texas to investigate economic recovery in the Horn River Basin.

3.2.5 *Horton Bluff Group*

Lacustrine muds of the Horton Bluff Group of the Canadian Maritime Provinces were deposited in the Early Mississippian Period (approximately three hundred and sixty million years ago) (Table 2.2) during regional subsidence (NEB, 2009). The silica content in the Frederick Brook Shale of the Horton Bluff Group in New Brunswick is approximately 38% v/v but the clay content is also high, on the order of 42% v/v. There are indications that organic contents of the Frederick Brook member in Nova Scotia are significantly higher than other Canadian gas shale formations, at 10% v/v, and the pay zone appears to be over five hundred feet thick, sometimes exceeding two thousand five hundred feet in New Brunswick.

There are also indications that most of the gas is adsorbed onto clay and organic matter, and it will take very effective reservoir stimulation to achieve significant production from Nova Scotia shale formations. It is unclear at this time at what proportion of gas is adsorbed onto clay and organic matter in the New Brunswick shale formations.

Analysis indicates that sixty-seven trillion cubic feet (67×10^{12} ft^3) of free gas in place is present in the Frederick Brook shale of the Sussex/Elgin sub-basins of southern New Brunswick and sixty-nine trillion cubic feet (69×10^{12} ft^3) of gas is present on the Windsor land block in Nova Scotia.

3.2.6 *Montney shale*

The Montney shale is a unique resource play in that it is a hybrid between tight gas and traditional shale. The formation is rich in silt and sand (characteristics similar to tight gas) but the source of the natural gas originated from its own organic matter like shale plays. Due to the presence of siltstone and sand, the Montney formation has extremely low permeability and requires higher levels of fracture stimulation. However, the reservoir characterization is complicated because the upper and lower Montney zones in the same area have different mineralogy (hence, different properties) which affects the formation evaluation data. The lower Montney is especially difficult as conventional open hole logs have historically led investigators to believe that the lower Montney was a very tight formation but the porosity was higher than expected but still lower than the porosity of the upper Montney formation (Williams and Kramer, 2011; NEB, 2009).

The Montney Shale formation is a shale rock deposit located deep below British Columbia, Canada and is located in the Dawson Creek area just south of the Horn Rover shale formation as well as the Duvernay shale formation. The Triassic Montney formation spans a wide variety of depositional environments, from shallow-water sands in the east to offshore muds to the west. Natural gas is currently produced from conventional shallow-water shore-face sandstones at the eastern edge of the Montney and from deep-water tight sands at the foot of the ramp. However, hybrid shale gas potential is being realized in two other zones: (i) the Lower Montney, in sandy, silty shales of the offshore transition and offshore-marine parts of the basin, and (ii) the Upper Montney, below the shore-face, where silt has buried the tight sands at the foot of the ramp. The Montney is so thick (well over 1000 feet in some places) that it lends itself to the stacked horizontal well concept, where horizontal legs are drilled at two elevations in the same well, penetrating and fracturing both the Upper Montney formation and the Lower Montney formation. The total organic carbon in Montney shale is on the order of 7% w/w (maximum) the rocks were heated until they were well into the thermogenic gas window.

As a result, natural gas can be found in large quantities trapped in this tight shale formation (Williams and Kramer, 2011). The formation is a hybrid between a tight gas and shale gas resource and the sandy mudstone formation dates back to the Triassic period and is located beneath the Doig formation at depths ranging from 5500 to 13,500 feet and is up to 1000 feet thick in places. With these parameters, the Montney shale has the potential to become one of the most significant sources of shale gas in Canada.

The play has been estimated to contain as much as fifty trillion cubic feet (50×10^{12} ft^3) of natural gas trapped within low-permeability shale and siltstone formation. Horizontal wells are drilled at depths from 5500 to 13,500 feet and hydraulic fracturing enables the gas to flow more easily. Microseismic monitoring techniques can be used to assess fracture stimulations by locating events along each stage of the fracture and calculating the dimensions, geometry and effective fracture volume.

3.2.7 *Utica Group*

The Upper Ordovician Utica Shale is located between Montreal and Quebec City and was deposited in deep waters at the foot of the Trenton carbonate platform (NEB, 2009). Over geologic time, the shale formation evolved and was changed due to early Appalachian Mountain growth which resulted in faulting and folding and formation on its southeastern side. The formation is approximately five hundred feet thick and has a total organic content of one to three per cent (w/w) and was identified in the early-to-mid 20th Century as a source rock for associated conventional crude oil reservoirs.

However, unlike other Canadian gas shale formations, the Utica has higher concentrations of calcite ($CaCO_3$), which occur at the expense of some silica (SiO_2) (Theriault, 2008). While the calcite in the formation is brittle, hydraulic fractures do not transmit as well through it.

3.3 Other countries

Significant amounts of shale gas occur outside of the United States and Canada and the potential natural gas and crude oil resources in tight formations (Table 2.4) rivals the resource estimates from conventional gas and oil accumulations and could help meet the burgeoning demand of the world countries for energy, which is forecast to increase 60% by 2035 (Khlaifat et al., 2011; Aguilera et al., 2012; Islam and Speight, 2016). However, the technical and environmental challenges as well as the economic challenges involved in the commercialization of these largely untapped vast resources requires a multi-disciplinary approach involving geoscience, engineering and economics. Nevertheless, natural gas and crude oil from tight formations have the potential to contribute a significant volume of the gas that is needed to satisfy global primary energy consumption up to and beyond 2035.

In addition, to the United States and Canada, China and Argentina are currently (at the time of writing) the only countries in the world that are producing commercial volumes of either natural gas from tight formation (shale formations) or crude oil from tight formations (tight oil). The United States is by far the dominant producer of both shale gas and tight oil. In China, Sinopec and PetroChina have reported commercial production of shale gas from fields in the Sichuan Basin. In Argentina, tight oil production comes mainly from the Neuquen Basin where the national oil company YPF (Yacimientos Petrolíferos Fiscales) is producing approximately 20,000 barrels of tight oil per day from the Loma Campana area.

The initial estimate of shale gas resources in the 42 countries (other than the United States and Canada) is on the order of 6381 trillion cubic feet (6381×10^{12} ft^3) (US EIA, 2011b, 2015; DECC, 2013; NRF, 2013). Adding the US estimate of the shale resources of results in a total shale gas resource base estimate of 7576 trillion cubic feet (7576×10^{12} ft^3) for the United States and the other 42 countries assessed. To put this shale gas resource estimate in context, the technically recoverable gas resources worldwide are approximately 16,000 trillion cubic feet ($16{,}000 \times 10^{12}$ ft^3), largely excluding shale gas (US EIA, 2011b). Thus, adding the identified shale gas resources to other gas resources increases total world technically recoverable gas resources by more than 40% to 22,600 trillion cubic feet ($22{,}600 \times 10^{12}$ ft^3) (ERA, 2011b). In terms of light oil from tight formations, estimates (excluding Canada and the United States) are on the order of 332 billion barrels (331.8×10^9 bbls) of crude oil in tight formations spread over forty-two countries (Table 2.4).

At a country level, there are two country groupings that emerge where shale gas development appears most attractive. The first group consists of countries that are currently highly dependent upon natural gas imports, have at least some gas production infrastructure, and their estimated shale gas resources are substantial relative to their current gas consumption. For these countries, shale gas development could significantly alter their future gas balance, which may motivate development. The second group consists of those countries where the shale gas resource estimate is large (>200 trillion cubic feet, $>200 \times 10^{12}$ ft^3) and there already exists a significant natural gas production infrastructure for internal use or for export. Existing infrastructure would aid in the timely conversion of the resource into production, but could also lead to competition with other natural gas supply sources. For an individual country the situation could be more complex.

The predominant resources of tight oil are found in many countries (Table 2.4). The resources of crude oil in these countries is still under investigation and estimates are tentative

TABLE 2.4 Estimated of shale gas and tight oil in various countries.

	Shale gas	Tight oil
Country	**10^{12} ft^3**	**10^9 bbls**
Algeria	706.9	5.7
Argentina	801.5	27
Australia	429.3	15.6
Bolivia	36.4	0.6
Brazil	244.9	5.3
Bulgaria	16.6	0.2
Chad	44.4	16.2
Chile	48.5	2.3
China	1115.2	32.2
Colombia	54.7	6.8
Denmark	31.7	0
Egypt	100	4.6
France	136.7	4.7
Germany	17	0.7
India	96.4	3.8
Indonesia	46.4	7.9
Jordan	6.8	0.1
Kazakhstan	27.5	10.6
Libya	121.6	26.1
Lithuania/Kaliningrad	2.4	1.4
Mexico	545.2	13.1
Mongolia	4.4	3.4
Morocco	11.9	0
Netherlands	25.9	2.9
Oman	48.3	6.2
Pakistan	105.2	9.1
Paraguay	75.3	3.7
Poland	145.8	1.8
Romania	50.7	0.3
Russia	284.5	74.6

TABLE 2.4 Estimated of shale gas and tight oil in various countries.—cont'd

	Shale gas	**Tight oil**
Country	**10^{12} ft^3**	**10^9 bbls**
South Africa	389.7	0
Spain	8.4	0.1
Sweden	9.8	0
Thailand	5.4	0
Tunisia	22.7	1.5
Turkey	23.6	4.7
Ukraine	127.9	1.1
United Arab Emirates	205.3	22.6
United Kingdom	25.8	0.7
Uruguay	4.6	0.6
Venezuela	167.3	13.4
West Sahara	8.6	0.2
Total[a]	6381.2	331.8

[a] *Excluding the United States and Canada.*

but show promise for the future and there is also the need to define the methods by which other countries determine the amount of resources of shale gas and tight oil and to assure the reliability comparative data (US EIA, 2013). As an example of different terminology for the definitions of the reservoirs, while many countries use the reservoir properties to define a tight reservoir, some countries may use the flow rate of the natural gas or crude oil to define a tight formation whether or not the flow rate is due to the reservoir properties.

In addition, the nomenclature and methods used in reserve estimation is also subject to question, especially the issue of the volumetric capacity of the reservoir to hold natural gas and crude oil and the means by which the reservoir volumetric capacity was determined. For example, it is important to distinguish between a technically recoverable resource and an economically recoverable resource (US EIA, 2013, 2015). Technically recoverable resources represent the volumes of natural gas and crude oil gas that can be recovered using current technology, regardless of the prices for natural gas and crude oil and natural gas as well as production costs. On the other hand, economically recoverable resources are resources that can be profitably produced under the current market price. Moreover, economic recoverability can be significantly influenced not only by subterranean geology but also by above-the-ground factors which include (i) private ownership of subsurface rights, (ii) the availability of many independent operators and supporting contractors with critical expertize and suitable drilling rigs, (iii) the preexisting gathering and pipeline infrastructure, (iv) the availability of water resources for use in hydraulic fracturing (US EIA, 2013, 2015). Not all of these factors are equal in all countries.

4. The future of resources in tight formations

The storage properties of shale formations and tight formations for natural gas and crude oil are quite different from the storage properties of conventional reservoirs (Chapters 1 and 3). In addition to having gas present in the matrix system of pores similar to that found in conventional reservoir rocks, shale formations and tight formations also have gas or oil bound or adsorbed not only to the inorganic surface of the formation but also bound or adsorbed to surface of organic material in the shale. The relative contributions and combinations of free gas from matrix porosity and from desorption of adsorbed gas and oil is a key determinant of the production profile of the well.

The amount and distribution of gas within the shale is determined by, among other things, (i) the initial reservoir pressure, (ii) the petrophysical properties of the rock, and (iii) the adsorption characteristics of the reservoir rock. Thus, during production there are three main processes at play. First, the initial rate of gas or oil production may be dominated by the depletion of the gas or liquid from the fracture network. This form of production declines rapidly due to limited storage capacity. Second, after the initial decline rate of production stabilizes, the depletion of gas or oil stored in the matrix becomes the primary process involved in the production of the resource. The amount of gas held in the matrix is dependent on the particular properties of the shale reservoir which can be hard to estimate. Third, but secondary to the depletion process, is desorption whereby adsorbed gas or oil is released from the rock as pressure in the reservoir declines.

At that point, the rate of resource production by means of the desorption process is highly dependent on there being a significant drop in reservoir pressure. In addition, pressure changes and any effects on the rate of depletion typically advance through the reservoir rock at a very slow rate due to low permeability. Tight well spacing can therefore be required to lower the reservoir pressure enough to cause significant amounts of adsorbed gas to be desorbed. These overlapping production processes result in the characteristic hyperbolic production profile that can decline very sharply (by a reduction in the production rate on the order of 60%–80%) within a year (or two) after commencement of production.

Due to these particular properties, the ultimate recovery of the gas or oil in place surrounding a particular well can be on the order of 28–40% v/v whereas the recovery per conventional well may be as high as 60–80% v/v. Thus, the development of shale plays and tight plays differs significantly from the development of conventional resources. With a conventional reservoir, each well is capable of draining natural gas or crude oil over a relatively large area (dependent on reservoir properties). As such, only a few wells (normally vertical wells) are required to produce commercial volumes from the field. With shale and tight formation projects, a large number of relatively closely spaced wells are required to produce sufficiently large volumes to make the plays economic propositions. As a result, many wells must be drilled in a shale play to drain the reservoir sufficiently; for example, in the Barnett shale play (Texas, United States), the drilling density can exceed one well per 60 acres.

In 2014, the United States increased crude oil production by 1.6 million barrels per day (1.6×10^6 bbls/day) and became the first country ever to increase production by at least 1 million barrels per day (1.0×10^6 bbls/day) for three consecutive years (BP, 2015). This was due, in no small part, to the production of crude oil from tight formations. As a result, the United States has replaced Saudi Arabia as the largest oil producer in the world and the United States has also overtaken Russia as the largest producer of crude oil and natural gas in the world.

In terms of the future, the most significant development on the supply side of natural gas and crude oil is the continuing development of resources held in shale formation and in tight formations in the United States. However, the development of natural gas and crude oil fields will unfortunately, contribute to environmental pollution, including acid rain, the greenhouse effect, and *allegedly* global warming (global climate change).

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CHAPTER

3

Reservoirs and reservoir fluids

1. Introduction

The term *reservoir fluid* is used in this text to collectively include any fluid that exists in a reservoir, which includes gases, liquids, and solids − water may also be included in this terminology and is an important aspect of the reservoir fluid category. Nevertheless, water notwithstanding, the specific types of fluids of interest are (i) natural gas, (ii) crude oil, which includes gas condensate and paraffin wax, (iii) heavy oil, and (iv) tar sand bitumen. However, the focus of this text is predominantly on the first three categories of fluids. More specifically, the water that occurs in natural gas and crude oil reservoirs is usually a *brine* which consists of dissolved sodium chloride (NaCl) as well as salts (minerals) which include calcium (Ca), magnesium (Mg), sulfate (SO_4), bicarbonate (HCO_3), iodide (I), and bromide (Br). Under reservoir conditions, the brine that is sharing pore space with hydrocarbon derivatives always contains a limited amount of solution gas (predominantly methane) but increasing salinity decreases gas in solution. Reservoir brines exhibit only slight shrinkage (<5% v/v) when produced to the surface.

In addition, paraffin wax when occurring naturally (and not as part of crude oil) may also be classed as a reservoir fluid. The pure material is a white or colorless soft solid that consists of a mixture of hydrocarbon derivatives containing between twenty and forty carbon atoms (Gruse and Stevens, 1960; Wollrab and Streibl, 1969; Musser and Kilpatrick, 1998; Huang et al., 2003; Speight, 2014). Paraffin wax is solid at room temperature and begins to melt above approximately 37 °C (99 °F) with a boiling range in excess of >370 °C (698 °F). While naturally-occurring paraffin wax is of particular interest in some conventional crude oil reservoirs, it occurs in shale as part of the crude oil (with perhaps not the same molecular range as in conventional crude oil) and becomes of interest when the crude oil from shale formations is blended with other paraffinic liquids (such as paraffinic naphtha) that can lead to deposition of the wax during transportation and refining from which fouling can occur (Speight, 2014, 2015).

The fluids, particularly natural gas and crude oil as well as heavy oil, which exist in a reservoir (and which vary widely in properties) (Tables 3.1, 3.2, and 3.3) must be determined very early after the discovery of the reservoir. Fluid type is a critical consideration in the decisions that must be made related to production of the fluids. Furthermore, fluid properties play a key role in the design and optimization of injection/production strategies and surface

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TABLE 3.1 Constituents of natural gas.

Name	Formula	% v/v
Methane	CH_4	85+
Ethane	C_2H_6	4
Propane	C_3H_8	1–5
Butane	C_4H_{10}	1–2
Pentane$^+$	C_5H_{12}	1–5
Carbon dioxide	CO_2	1–2
Hydrogen sulfide	H_2S	1–2
Nitrogen	N_2	1–5
Helium	He	<0.5

Pentane$^+$: pentane and higher molecular weight hydrocarbon derivatives up to approximately octane (C_8H_{18}), including benzene and toluene.

TABLE 3.2 Selected crude oils showing the differences in API gravity and sulfur content.

Country	Crude oil	API	Sulfur % w/w
Abu Dhabi (UAE)	Abu Al Bu Khoosh	31.6	2.00
Abu Dhabi (UAE)	Murban	40.5	0.78
Angola	Cabinda	31.7	0.17
Angola	Palanca	40.1	0.11
Australia	Barrow Island	37.3	0.05
Australia	Griffin	55.0	0.03
Brazil	Garoupa	30.0	0.68
Brazil	Sergipano Platforma	38.4	0.19
Brunei	Champion Export	23.9	0.12
Brunei	Seria	40.5	0.06
Cameroon	Lokele	20.7	0.46
Cameroon	Kole Marine	32.6	0.33
Canada (Alberta)	Wainwright-Kinsella	23.1	2.58
Canada (Alberta)	Rainbow	40.7	0.50
China	Shengli	24.2	1.00
China	Nanhai Light	40.6	0.06
Dubai (UAE)	Fateh	31.1	2.00

TABLE 3.2 Selected crude oils showing the differences in API gravity and sulfur content.—cont'd

Country	Crude oil	API	Sulfur % w/w
Dubai (UAE)	Margham Light	50.3	0.04
Egypt	Ras Gharib	21.5	3.64
Egypt	Gulf of Suez	31.9	1.52
Gabon	Gamba	31.4	0.09
Gabon	Rabi-Kounga	33.5	0.07
Indonesia	Bima	21.1	0.25
Indonesia	Kakap	51.5	0.05
Iran	Aboozar (Ardeshir)	26.9	2.48
Iran	Rostam	35.9	1.55
Iraq	Basrah Heavy	24.7	3.50
Iraq	Basrah Light	33.7	1.95
Libya	Buri	26.2	1.76
Libya	Bu Attifel	43.3	0.04
Malaysia	Bintulu	28.1	0.08
Malaysia	Dulang	39.0	0.12
Mexico	Maya	22.2	3.30
Mexico	Olmeca	39.8	0.80
Nigeria	Bonny Medium	25.2	0.23
Nigeria	Brass River	42.8	0.06
North Sea (Norway)	Emerald	22.0	0.75
North Sea (UK)	Innes	45.7	0.13
Qatar	Qatar Marine	36.0	1.42
Qatar	Dukhan (Qatar Land)	40.9	1.27
Saudi Arabia	Arab Heavy (Safaniya)	27.4	2.80
Saudi Arabia	Arab Extra Light (Berri)	37.2	1.15
USA (California)	Huntington Beach	20.7	1.38
USA (Michigan)	Lakehead Sweet	47.0	0.31
Venezeula	Leona	24.4	1.51
Venezuela	Oficina	33.3	0.78

TABLE 3.3 API gravity and sulfur content of selected heavy oils.

Country	Crude oil	API	Sulfur % w/w
Canada (Alberta)	Athabasca	8.0	4.8
Canada (Alberta)	Cold Lake	13.2	4.11
Canada (Alberta)	Lloydminster	16.0	2.60
Canada (Alberta)	Wabasca	19.6	3.90
Chad	Bolobo	16.8	0.14
Chad	Kome	18.5	0.20
China	Qinhuangdao	16.0	0.26
China	Zhao Dong	18.4	0.25
Colombia	Castilla	13.3	0.22
Colombia	Chichimene	19.8	1.12
Ecuador	Ecuador Heavy	18.2	2.23
Ecuador	Napo	19.2	1.98
USA (California)	Midway Sunset	11.0	1.55
USA (California)	Wilmington	18.6	1.59
Venezuela	Boscan	10.1	5.50
Venezuela	Tremblador	19.0	0.80

facilities for efficient reservoir management and longevity. Inaccurate fluid characterization will lead to uncertainty in the amount of the resource that is in-place as well as predictions of recovery efficiency. Prior to production (Chapter 4), determination of the fluid properties may only represent laboratory (hence, ex-situ) properties but once production commences, variations in fluid composition because of pressure changes and flow throughout the reservoir will become apparent from which the in-place properties can be assessed accurately as well as a measure of reservoir longevity can be assessed.

Moreover, reservoir fluids vary greatly in composition – in some fields, the fluid is in the gaseous state and in others it is in the liquid state but generally gases and liquids frequently coexist in a reservoir – in some reservoirs (or deposits) solids may exist as a wax or as a *tar mat* (Wilhelms and Larter, 1994a,b; Zhang and Zhang, 1999; Speight, 2014). The rocks which contain these reservoir fluids also vary considerably in composition and can influence the physical properties and the flow properties. Other factors, such as producing area, height of the fluid column, natural fracturing, or faulting, and water production also serve to distinguish one reservoir from another and which also affect the choice of the production method.

In fact, in keeping with understanding the nature of the reservoir fluids, understanding the elastic properties of reservoir rocks is crucial for exploration and successful production of

TABLE 3.4 General types of clay minerals.

Group	Minerals in group
Kaolin	Kaolinite
	Dickite
	Halloysite
	Nacrite (polymorphs of $Al_2Si_2O_5(OH)_4$)
Smectite	Montmorillite
	Nontronite
	Beidellite
	Saponite
Illite	Illite
	Clay-micas
Chlorite	Considerable chemical variation throughout this group

TABLE 3.5 Chemical formulas of clay minerals.

Group	Layer type	Layer charge	Chemical formula
Kaolinite	1:1	<0.01	$[Si_4]Al_4O_{10}(OH)_8 \cdot nH_2O$ ($n = 0$ or 4)
Illite	2:1	1.4–2.0	$M_x[Si_{6.8}Al_{1.2}]Al_3Fe.025Mg_{0.75}O_{20}(OH)_4$
Vermiculite	2:1	1.2–1.8	$M_x[Si_7Al]AlFe0.5Mg0.5O_{20}(OH)_4$
Smectite	2:1	0.5–1.2	$M_x[Si_8]Al_{3.2}Fe_{0.2}Mg_{0.6}O_20(OH)_4$
Chlorite	2:1:1	Variable	$(Al(OH)_{2.55})4[Si_{6.8}Al0_{1.2}\}Al_{3.4}Mg_{0.6})_{20}(OH)_4$

natural gas and crude oil from tight shale and tight formation reservoirs. In the case of the static and dynamic elastic properties of shale from Barnett, Haynesville, Eagle Ford, and Fort St. John shale formations, the matter is not so straight-forward since the elastic properties of these rocks vary significantly between reservoirs (and even within a reservoir) due to the wide variety of minerals that form the reservoir rock as well as the microstructures exhibited by these shale reservoirs and tight reservoirs. For example, the static (Young's modulus) and dynamic (P- and S-wave moduli) elastic parameters generally decrease monotonically with the content of the clay minerals plus any kerogen. However, the elastic properties of the shale formations are strongly anisotropic (the properties are not identical in all directions) since the degree of anisotropy correlates with the organic content of the shale as well as the minerals that constitute the amount and type of clay minerals that constitute the shale (Tables 3.4 and 3.5) (Hillier, 2003; Bergaya et al., 2011). This is not (and should not be) uprising considering the complex and varying composition of clay minerals (Sone and Zoback, 2013a,b).

More generally, the production of natural gas and crude oil occurs form two classes of rock: (1) source rock and (ii) reservoir rock, although it is generally believed that crude oils have, at some time during the history of the formation of the crude oil, there has been migration of the crude oil (or a precursor to the crude oil) from the source rock to the reservoir rock (Speight, 2014) this differentiating between the original and final maturation state of the crude oil. The same rationale can be applied to natural gas. Typically, source rocks are sedimentary rocks in which natural gas and crude oil commences formation from organic debris. After forming in the source rock, the protopetroleum and any formed hydrocarbon derivatives as well as any potential hydrocarbon-forming constituents, which can vary from simple structures such as methane (Table 3.1) to more complex structures, such as those constituents of conventional crude oil heavy oil (as determined from the variation in properties), can migrate to the reservoir rock after which further maturation processes can take place (Speight, 2014).

Geologic formations that contain natural gas and crude oil include clastic or detrital rocks (pertaining to rock or rocks composed of fragments of older rocks or minerals), chemical rocks (formed by chemical precipitation of minerals), and organic rocks (formed by biological debris from shells, plant material, and skeletons). The three most common sedimentary rock types encountered in oil and gas fields are (i) shale, (ii) sandstone, and (iii) carbonate. Classifying these rock types primarily depends on characteristics such as grain size and composition, porosity (pore space within and between grains), and cementitious character (the manner in which the rock grains are held together), each of which can influence oil and gas production (Bustin et al., 2008). Historically, the majority of the crude oil and natural gas produced in the United States were withdrawn from conventional sandstone and carbonate reservoirs.

In fact, during the last decade of the 20th Century and the first decade of the 21st Century, the production of natural gas and crude oil from shale formations and other tight rock formations has increased dramatically. However, each of the geologic basins is different and each has its unique set of exploration criteria and operational challenges. Because of these differences, the development of shale gas resources in each of these areas poses potential challenges to the surrounding communities and ecosystems. For example the Antrim and New Albany Shale formations are shallower shale formations which produce significant volumes of formation water unlike most of the other shale formations.

2. Sediments

Sediments (sedimentary rocks) are types of rock that are formed by the deposition of material within bodies of water and sedimentation is the process in which mineral matter and/or organic particles (detritus) to settle and accumulate or which causes mineral matter to precipitate from a solution. In most cases, before being deposited, the sediment was formed by weathering and erosion in a source area, and then transported to the place of deposition by natural forces such as water, wind, ice, mass movement, or glaciers.

The sedimentary rock cover of the continents of the crust of the Earth is extensive, but the total contribution of sedimentary rocks is estimated to be only 8% w/w of the total volume of

TABLE 3.6 The geologic timescale.[a]

Era	Period	Epoch	Duration (10^6 years)	Years ago (10^6 years)
Cenozoic	Quaternary	Holocene	10,000—present	
		Pleistocene	2	0.01
	Tertiary	Pliocene	11	2
		Miocene	12	13
		Oligocene	11	25
		Eocene	22	36
		Paleocene	71	58
Mesozoic	Cretaceous		71	65
	Jurassic		54	136
	Triassic		35	190
Paleozoic	Permian		55	225
	Carboniferous		65	280
	Devonian		60	345
	Silurian		20	405
	Ordovician		75	425
	Cambrian		100	500
Precambrian			3380	600

[a] *The numbers are approximate (±5%) due to variability of the data in literature sources; nevertheless, the numbers do give an indication of the extent of geologic time.*

the crust. Sedimentary rocks are deposited in layers (strata) and form a bedding structure and can provide information related to the subsurface leading to discovery and development of natural resources, such as (in the context of this book) crude oil, natural gas, and coal seams as sources of coalbed methane.

The geologic age of any sediment is an important determinant of the potential of the sediment to contain crude oil and natural gas. While many rocks of different ages produce oil and natural gas, the areas of prolific production include formations that are from several different geologic periods: (i) the Devonian period, approximately 405 to 345 million years ago, (ii) the Carboniferous period, approximately 345 to 280 million years ago, (iii) the Permian, approximately 280 to 225 million years ago, and (iv) the Cretaceous period, approximately 136 to 71 million years ago (Table 3.6). During these periods, organic-rich materials accumulated with the sediments and, over geologic time (millions of years), chemical changes (induced by pressure from the overlying sediments and any resulting heat from increasing pressure) changed the original organic detritus thereby (eventually) producing natural gas and crude oil.

2.1 Rock types

Sandstone is the second most abundant clastic sedimentary rock and is the most commonly encountered reservoir rock for natural gas and crude oil and sandstone formations are created by larger sediment particles, and are typically deposited in river channels, deltas, and shallow sea environments. A clast is a fragment of geological detritus, chunks and smaller grains of rock broken off other rocks by physical weathering and clastic rocks are composed of fragments (clasts) of pre-existing minerals and rock. The term clastic is used with reference to sedimentary rocks as well as to particles in sediment transport whether in suspension or as bed load, and in sedimentary deposits (Marshak, 2012). The predominant clastic sedimentary rocks are: (i) *conglomerate*, in which the grains are predominately rounded and on the order of 64 mm to >256 mm in size, (ii) breccia, in which the angular grains on the order of 2−64 mm in size, and (iii) sandstone in which the grains range from 2 to 1/16 mm (c.f., shale formations are composed of particles less than 1/16 mm in size).

Conglomerate formations are the least abundant sediment type and are typically consolidated gravel deposits with variable amounts of sand and mud between the particles (sometimes referred to as *pebbles*). Conglomerates accumulate in stream channels, along the margins of mountain ranges, and on beaches and are composed largely of angular pebbles (*breccias*) and some (*tillites*) are formed in glacial deposits. On the other hand, *sandstone formations* are composed essentially of cemented sand and comprise approximately one-third of all sedimentary rocks. The most abundant mineral in sandstone is quartz (SiO_2), along with lesser amounts of calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), and various iron compounds. These formations tend to be more porous than shale formations, and consequently make excellent reservoir rocks − as long as impermeable basement rocks and cap rocks (such as shale formation) are present. The third most abundant formations, *carbonate formations*, are created by the accumulation of shells and skeletal remains of water-dwelling organisms in marine environments.

Chemical and organic sedimentary rocks are the other main group of sediments (besides clastic sediments) and are formed by weathered material in solution precipitating from water or as biochemical rocks made of dead marine organisms and special conditions (such as high temperature, high evaporation, and high organic activity) are required for the formation of these rocks. Some chemical sediment is deposited directly from the water in which the material is dissolved − for example, upon evaporation of seawater. Such deposits are generally referred to as *inorganic chemical sediments.* Chemical sediments that have been deposited by or with the assistance of plants or animals are classed as *organic sediments* or *biochemical sediments.*

Sedimentary rocks formed from sediments created by inorganic processes include (i) limestone, (ii) dolomite, and (iii) evaporites. *Limestone* ($CaCO_3$, calcite) is precipitated by organisms usually to form a shell or other skeletal structure. Accumulation of these skeletal remains results in the most common type of chemical sediment, limestone, which may also form by inorganic precipitation as well as by organic activity. *Dolomite* (magnesium limestone, $CaCO_3 \cdot MgCO_3$) occurs in the same settings as limestone and is formed when some of the calcium in limestone is replaced by magnesium. *Evaporite minerals* are sedimentary rocks (true chemical sediments) that are derived from minerals precipitated from seawater. There are two types of evaporite deposits: marine, which can also be described as ocean deposits, and non-marine, which are found in standing bodies of water such as lakes. Rock salt, which is composed of halite (NaCl), and rock gypsum ($CaSO_4 \cdot 2H_2O$), are the most common types of evaporite minerals. High evaporation rates cause concentration of solids to increase due to water loss by evaporation.

Biochemical sedimentary rocks consist of sediments formed from the remains or secretions of organisms and are formed by the accumulation and subsequent consolidation of sediments into various types of rock. They include *fossiliferous limestone, coquina* (limestone composed of shells and coarse shell fragments), *chalk* (porous, fine-textured variety of limestone composed of calcareous shells), *lignite* (brown coal), and *bituminous* (soft) *coal.*

2.2 Characteristics

Sedimentary rocks possess definite physical characteristics and display certain features that make them readily distinguishable from igneous rocks (rocks formed through the cooling and solidification of magma or lava) or metamorphic rocks (rocks have been modified by heat, pressure, and chemical processes, usually while buried deep below surface of the Earth). Some of the most important sedimentary characteristics include the following: (i) stratification, (ii) cross-bedding, (iii) graded bedding, (iv) texture, (v) ripple marks, (vi) mud cracks, (vii) concretions, (viii) fossils, and (ix) color.

Stratification, probably the most characteristic feature of sedimentary rocks, is their tendency of the rocks to occur in *beds* (*strata*), which are formed when geological agents such as wind, water, or ice gradually deposit sediment. *Cross-bedding* (*cross-stratification*) occurs to sets of beds that are inclined relative to one another. The beds are inclined in the direction that the wind or water was moving at the time of deposition and nay boundaries between sets of cross beds usually represent an erosional surface. The cross-bed are common in beach deposits, sand dunes, and river-deposited sediment and enable determinations to be made related to the origin and formation of ancient sediments. *Graded bedding* occurs as a result of a reduction in velocity (typically in a stream bed) and (i) larger or denser particles are deposited followed by (ii) deposition of smaller particles. This results in the bedding showing a decrease in grain size from the bottom of the bed to the top of the bed (fine sediment particles at the top of the bed and coarse sediment particles at the bottom of the bed).

Fossils are the remains of once-living organisms that have been preserved in the crust of the Earth. Because life has evolved, fossils give clues to the relative age of the sediment and can be important indicators of past climates. In addition, to such information, the totality of fossils, both discovered and undiscovered, and their placement in *fossiliferous* (fossil-containing) rock formations and sedimentary layers (strata) is known as the *fossil record*.

Finally, the minerals in some sediments impart color to the sediment. However, color is one of the first noticed and most obvious characteristics of a rock, but it is also one of the most difficult to interpret. With the exception of gray and black, which mostly results from partially decayed organic matter, most rock colors are the result of iron staining. Ferric iron (Fe^{3+}) produces red, purple, and yellow colors − minerals such as hematite (iron oxide, Fe_2O_3, also spelled *haematite*) and limonite (an iron ore consisting of a mixture of hydrated iron(III) oxide-hydroxides in varying composition) produce a pink or red color. Ferrous iron (Fe^{2+}) produces greenish colors in sediments. Typically, a red color can be interpreted as a well-oxygenated environment, such as river channels, some flood plains, and very shallow sea water. Green colors mean an environment low in, or lacking, oxygen, often associated with marine environments. Dark gray to black colors mean anoxic conditions, which may mean deep water, but could also be a swamp environment. The conclusion is, environmental interpretations can only be made in relation to the other evidence present with the rock. When and how these colors originate in sedimentary rocks is still subject to speculation and, thus, the meaning of the color as it related to the environment in which the sediment was formed must viewed with caution and any conclusion must be confirmed with independent evidence.

2.3 Composition

A sediment is composed of three basic components (i) grains, (ii) matrix, and (iii) cementitious materials. Grains (sometimes referred to as *framework grains*) refer to the larger, solid components in the sediment which form the basic small-scale units of sandstone reservoirs. The original grain composition is controlled by the composition of the sediment source (origin and history) as well as the physical and chemical processes under which the sediments are created and transported to the geologic basin. Often referred to as detrital grains, the grain composition of most sandstone reservoirs consists primarily of quartz, feldspars, and rock fragments (Berg, 1986).

Following deposition and burial, the framework grains (typically referred to as *authigenic grains*) are often altered by the physical effects of compaction as well as various chemical processes (diagenesis). The original grain composition governs the type and severity of diagenesis (Rushing et al., 2008). For example, some minerals are more brittle and may be more susceptible to compaction and/or failure during burial and the associated increase in stresses. Other minerals may be more reactive to natural fluids within the pores and may be altered (sometimes significantly) by adverse chemical reactions.

2.3.1 Inorganic constituents

The matrix component in a sediment refers to the finer materials deposited between the larger grains and typically includes both clay minerals and shale minerals. Clay minerals may also be classified as either detrital or authigenic: (i) detrital clay minerals originate either from the sediment source material during deposition, or may form from biogenic processes shortly after deposition, (ii) authigenic clay minerals are formed by a chemical process, either by precipitation from formation fluids or regeneration of detrital clays. Clay regeneration refers to processes in which clay minerals develop by alteration of precursor clays (Wilson, 1982; Rushing et al., 2008). The principal clay minerals observed in sandstone reservoirs are kaolinite, smectite, illite, and chlorite.

Shale formations consist of different types of clay minerals which may be present in sandstone either as a detrital matrix or as authigenic cement. Since clay minerals recrystallize and alter during burial, this distinction is always not easy to make. The presence of clay minerals in a reservoir has an adverse effect on the porosity and permeability of the reservoir.

While the mineralogy of clay minerals is complex, there are three groups to consider: (i) kaolinite clays minerals, (ii) illite clay minerals, and (iii) montmorillonite clay minerals which each have different effects on reservoirs and different sources of formation (Selley, 1998). Kaolinite generally occurs as well-formed, blocky crystals within the pore spaces which diminishes the porosity of the reservoir, but may have only a minor effect on permeability. Kaolinite is stable in the presence of acid solutions and, therefore, occurs as detrital clay in continental deposits, and as authigenic cement in sands that have been flushed by acidic waters, such as those of meteoric origin.

Illite clay minerals are quite different from the kaolin clay minerals. Authigenic illite grows as fibrous crystals, which typically occur as furlike jackets on the detrital grains. These structures often bridge over the throat passages between pores in a tangled mass. Thus, the content of illite cement may have a significant adverse effect on the permeability of the formation. Also, illite clay minerals are the dominant detrital clay of most marine sediments and occur as authigenic clay in sand formations through which alkaline connate water has moved (Selley, 1998).

The montmorillonite clay minerals (sometime referred to as smectite clay minerals) are formed from the alteration of volcanic glass and are occur in continental or deep marine deposits. These minerals have the ability to swell in presence of water and thus, reservoirs that contain montmorillonite are susceptible to formation damage if drilled with a conventional water based mud − drilling using an oil-based mud is recommended! When production begins, water displaces the crude oil thereby causing the montmorillonite to expand and destroy the permeability of the lower part of the reservoir.

Kaolinite, illite and montmorillonite may all be found in shallow reservoirs, depending on the source material and the diagenetic history. With the increasing burial the kaolinites and montmorillonite undergo metamorphosis to illite, the collapse of montmorillonite being a possible cause of overpressure, and related to the expulsion of crude oil (Selley, 1998).

Thus, clay minerals vary widely in the structure or morphology of both the individual and aggregate particles and the presence of these minerals in the pore of sediments and can significantly reduce both permeability and primary porosity (Table 3.7) (Neasham, 1977a,b; Wilson and Pittman, 1977). This potential (and real) effect of clay minerals m reinforces the importance of a comprehensive pore-scale program to identify clay type, origin, and the factors controlling its occurrence.

In terms of tight sand formations, a major component common for many tight gas sands is the grain cement (cementitious material) which typically refers to any mineral that forms during diagenesis and is precipitated after deposition of both grains and matrix components (Berg, 1986). As the name implies, the cement binds the minerals together in a competent mass in the rock and fills the pore system, thus reducing both permeability and porosity. The most common cement compositions are silica minerals and carbonate minerals. Silica minerals are precipitated as overgrowths or layers on quartz grains. Silica overgrowth cements may form soon after deposition but often continue to develop with increased pressure and temperature during burial. Carbonate cements are often precipitated early after deposition and tend to fill pore spaces between framework grains. Authigenic clay minerals may also act as cements by helping to bind rock particles together.

One aspect of reservoir properties that requires evaluation is an estimation of the total organic carbon in the formation. Crude oil accumulations such as (in the current context) as the Bakken formation in the Williston Basin of North Dakota have recently been recognized as being important in the future development of energy resources. There are several features that these crude oil systems have in common insofar as they typically include the

TABLE 3.7 Types of porosity (listed alphabetically).

Type	Description
Dual porosity	Refers to the conceptual idea that there are two overlapping reservoirs which interact. In fractured rock aquifers, the rock mass and fractures are often simulated as being two overlapping but distinct bodies.
Effective porosity	Also called *open porosity*; refers to the fraction of the total volume in which fluid flow is effectively taking place and includes catenary and dead-end (as these pores cannot be flushed, but they can cause fluid movement by release of pressure like gas expansion) pores and excludes closed pores (or non-connected cavities). This is very important for groundwater and petroleum flow, as well as for solute transport.
Fracture porosity	Porosity associated with a fracture system or faulting; can create secondary porosity in rocks that otherwise would not be reservoirs for hydrocarbons due to their primary porosity being destroyed (for example due to depth of burial) or of a rock type not normally considered a reservoir (for example igneous intrusions or meta-sediments).
Ineffective porosity	Also called *closed porosity*; refers to the fraction of the total volume in which fluids or gases are present but in which fluid flow cannot effectively take place and includes the closed pores.
Macroporosity	Refers to pores greater than 50 nm in diameter in solids (i.e. excluding aggregated materials such as soils). Flow through macropores is described by bulk diffusion.
Mesoporosity	Refers to pores greater than 2 nm and less than 50 nm in diameter in solids (i.e. excluding aggregated materials such as soils).
Microporosity	Refers to pores smaller than 2 nm in diameter in solids (i.e. excluding aggregated materials such as soils).
Primary porosity	The main or original porosity system in a rock or unconfined alluvial deposit.
Secondary porosity	A subsequent or separate porosity system in a rock, often enhancing overall porosity of a rock; can be a result of chemical leaching of minerals or the generation of a fracture system; can replace the primary porosity or coexist with it (see dual porosity).
Vuggy porosity	Secondary porosity generated by dissolution of large features (such as macrofossils in carbonate rocks leaving large holes, vugs, or caves).

deposition of organic-rich rocks that form the core of the crude oil system when subjected to elevated temperatures for sufficient periods of time. This allows for the source rock to evolve (or mature) to the point where crude oil is generated. Once a sufficient amount of generation has occurred the crude oil is expelled into neighboring rocks and, in instances when these rocks are poorly permeable, the oil accumulates under high pressures.

The most important properties in shale gas plays are the mineralogical content and its pore size distribution. For many years, shale formations were viewed as a hydrocarbon cap rock. Due to this traditional point of view, up to date only geochemical analysis has been routinely performed on the shale layers. However, for sweet spot mapping of shale gas plays, it is very important to have as much information as possible know related to petrophysical properties. Shale gas, which is mostly methane can be found in any sedimentary basin, but special methods of extraction is needed. Shale gas can be more expensive than conventional gas to extract (Hamada et al., 2018). In addition to the aforementioned properties, the three interconnected processes of (i) deposition, (ii) maturation, and (iii) expulsion may all be studied using various types of geochemical analyses.

Deposition of a potential source rock involves a tightly constrained set of circumstances. These include high rates of biological activity that produce organic carbon compounds that following floral death accumulate, are buried, and preserved. High levels of organic productivity are associated with many environments. However, the efficient preservation of organic matter produced in these environments is limited to only a few depositional settings. In general these settings contain low levels of free oxygen that prevent the deposited organic matter from being destroyed by biological activity or chemical processes. Environments that meet these criteria include lakes, seas, and marshes in which water depth, bottom topography, and the absence of currents prevents near-surface oxygenated waters from mixing with bottom waters.

When large amounts of organic debris are added to stagnant water, bottom waters become depleted in dissolved oxygen and under extreme conditions may become oxygen-free (anoxic). In this environment, proteins, carbohydrates, and other organic compounds accumulate and may be buried as the depositional environment subsides and sediment is added. Following burial, organic compounds deteriorate and reform into large, complex organic molecules that are insoluble in organic solvents. This material undergoes a continuous series of temperature-driven and pressure-driven chemical reactions that remove hydrogen, oxygen, sulfur, and nitrogen organic material. Over time, and with sufficient chemical changes, these reactions *mature* the organic material to the point that oil and gas is generated. At this stage, newly formed oil and gas expel water contained in the source-rock and with sufficient maturation, possibly in conjunction with source rock compaction, natural gas or crude oil is injected into the pore space of the surrounding non-source rock units (expulsion stage). If there are no permeable routes for the escape this gas and oil. The gas and oil collect close to the source bed, frequently under high pressure, and form (what is often termed) an unconventional resource. Throughout this process, changes in the composition of the organic material occur.

2.3.2 Organic constituents

The most important aspect of evaluating a potential source rock involves determining the amount and character of organic matter that could have been available, given the proper conditions, to generate oil and gas. One of the first things to consider is just how much organic carbon is currently present in the rock. Secondary concerns include evaluating the organic carbon with respect to the likely products that may be generated, as well as the subsurface conditions for the generation of oil and gas. Understanding these aspects of a source rock provides a basis for evaluating the resource potential of individual formations on a basin-wide basis.

The amount of total organic carbon (TOC) present in a potential source rock is one of the first analyses that need to be made. When a method is chosen, it is important to select a method that can differentiate between organic carbon and inorganic carbon using samples that weigh less than a gram. One of the important aspect that inorganic carbon compounds, mostly carbonate minerals, are removed with acid prior to analysis. The remaining organic carbon is combusted in an oxygen atmosphere releasing the organically bound carbon in the form of carbon dioxide. The mass of carbon dioxide measured is converted into a percent

(% w/w of the total organic carbon) using the dry weight of the original sample. In the absence of other information, the richness of a source rock may be classified by total organic carbon (% w/w) as:

Poor: 0–1% w/w
Fair: >1–2.5% w/w
Good: >2.5–5% w/w
Excellent: >5% w/w

The total organic carbon measured includes carbon compounds capable of generating natural gas or crude oil (*live carbon*) as well as carbon compounds that are not capable of generating natural gas or crude oil (*dead carbon*). Not all methods can be used to distinguish between *live organic carbon* and *dead organic carbon*. And, therefore, the total organic carbon content of a source rock must be combined with a method of determining how much of the total organic carbon consists of *live organic carbon*.

One of the least complicated methods of analyzing live organic carbon makes use of a programmed pyrolysis method (rock-eval analysis) which artificially matures source rock organic material by subjecting it to elevated temperatures. At high temperatures (400–500 °C, 750–930 °F) the chemical reactions that produce natural gas or crude oil (or crude oil-like products) are greatly accelerated – hopefully without changing the chemistry of the process that, under natural circumstances, would take millions of years to achieve. In the rock-eval method, a small sample (approximately 0.1 g) is placed in an oven and heated. During heating, free oil and live organic matter are converted to hydrocarbon vapors that are collected by a carrier stream of chemically inert helium or, in older units, nitrogen gas.

In most rock-eval systems the carrier stream is split into a stream that feeds a flame ionization detector and a second stream that flows to a detector that measures the mass of oxygen-bound carbon (carbon monoxide, CO, carbon dioxide, CO2). The stream passed to the flame ionization detector flows into an oxygen-hydrogen flame that burns (ionizes) the hydrocarbon derivatives and results in a voltage that is calibrated to the mass of the hydrocarbon derivatives that are present in the carrier gas stream. The method consists of two heating periods which are (i) the first period during which the temperatures are held constant at 300 °C (570 °F) and at this temperature, free oil vaporizes and is recorded, and (ii) the second heating phase during which the sample is heated from 300 to 650 °C (570–1,110 °F) at a rate of 25 °C (45 °F) per minute. Between these temperatures, live organic material decomposes into hydrocarbon vapor, which is collected and recorded.

The use of the rock-eval data is capable of providing essential information that may be used to evaluate the oil generation potential of source rocks. These data include the means to estimate the type and quantity of organic matter present in a source bed as well as data that bear on the degree of oil generation that has occurred. The inclusion of these data with other indicators of accumulated oil, such as high shale resistivities and overpressured formation pressures, are the building blocks needed to construct and calibrate a predictive three-dimensional model of oil and gas generation.

2.4 Texture

Sediment texture is another important aspect of sandstone reservoirs include grain size, sorting, packing, shape, and grain orientation since it not only affects properties of the sediment at deposition but also can impact the rate, magnitude, and severity of diagenesis. *Sediment texture* refers to the size, shape, and arrangement of materials that is derived from processes of weathering, transportation, deposition, and diagenesis.

The texture in sediment and sedimentary rocks is dependent on the processes that occur during each stage of formation which also includes (i) the nature of the source materials, (ii) the nature of wind and water currents present, (iii) the distance that materials were transported as well as the timer spent in the transportation process, (iv) any biological activity, and (v) exposure to various chemical environments.

Grain size and distribution, sorting, shape and packing also govern the type and magnitude of the original porosity present following sediment deposition, but before significant diagenesis has occurred. Generally, clean coarse-grained materials will have larger, better connected pores, while small-grained sands will have smaller and less well connected pores. Depending on the type and morphology, the presence of smaller matrix materials (i.e., clay minerals and shale minerals) in clean coarse-grained sands will tend to reduce both permeability and primary porosity. Other textural traits include grain shape and orientation. Grain shape is usually expressed as sphericity (a measure of the deviation of a grain from a spherical shape) and roundness (a measure of the roundness of the grain edges) (Berg, 1986). On the other hand, grain orientation refers to the preferred direction of the long axes of the grain.

2.5 Structure

Sediment structure (including identification of bed geometry, bedding planes, contacts between beds, and bedding plane orientation) is an important element of the depositional process since the type of structure may help in identifying the original depositional environment. Understanding sedimentary structure is also an important component in optimizing field development activities since bed geometry and dimensions may impact both vertical and lateral continuity which would, in turn, dictate well spacing and the type of wellbore architecture. For example, significant vertical heterogeneity may determine how effectively horizontal wellbores will recover the natural gas or the crude oil.

Other aspects of sediment structure, insofar as the outcome is differences to the surface structure (appearance) of the sediment are (i) ripple marks, (ii) mud cracks. *Ripple marks* in a sediment are characteristic of deposition of the inorganic materials in shallow water and are caused by forces such as wave-related forces or wind-related forces that leave ripples of sand as typified by the marks seen on beach sand or on the bottom of a shallow stream. Thus, ripples of this type can provide information related to the conditions of deposition when the sediment was originally deposited. *Mud cracks* provide other signs that are a guide to the environment in which the sediment was formed. Mud cracks which result from the drying out of wet sediment on the bottom of dried-up lakes, ponds, or stream beds. Mud cracks may be many-sided (polygonal) shapes that present a honeycomb-type appearance on the surface of the bch or stream sand. If these marks are preserved in sedimentary rocks, there is the suggestion that the original material was subjected to alternating periods of flooding and drying. *Concretions* are spherical or flattened masses of rock enclosed in some (but not all) shale formations or in some limestone formations and which are generally harder than the rock enclosing them. Concretions are typically an indication that the softer environmentally-prone rock was eroded away leaving the harder concretions intact.

Thus, understanding the depositional history of the reservoir is important in terms of predicting the long-term production behavior.

3. Reservoirs and reservoir evaluation

The organic-rich shale formations (shale gas formations) have become an attractive target in the United States and Canada (Table 3.8) because they represent a huge resource of natural gas and, in some cases, natural gas liquids. Multiple operators are currently leasing and evaluating gas shale properties throughout the United States. If the prospective gas shale formation s can be economically developed, many thousands of wells will be drilled in these regions during the next decade.

TABLE 3.8 Shale gas formations in the United States and Canada.

Formation	Period	Location
Antrim shale	Late Devonian	Michigan basin, Michigan
Baxter shale	Late Cretaceous	Vermillion basin, Colorado, Wyoming
Barnett shale	Mississippian	Fort Worth and Permian basins, Texas
Bend shale	Pennsylvanian	Palo Duro basin, Texas
Cane Creek shale	Pennsylvanian	Paradox basin, Utah
Caney shale	Mississippian	Arkoma basin, Oklahoma
Chattanooga shale	Late Devonian	Alabama, Arkansas, Kentucky, Tennessee
Chimney rock shale	Pennsylvanian	Paradox basin, Colorado, Utah
Cleveland shale	Devonian	Eastern Kentucky
Clinton shale	Early Silurian	Eastern Kentucky
Cody shale	Cretaceous	Oklahoma, Texas
Colorado shale	Cretaceous	Central Alberta, Saskatchewan
Conasauga shale	Middle Cambrian	Black Warrior basin, Alabama
Dunkirk shale	Upper Devonian	Western New York
Duvernay shale	Late Devonian	West central Alberta
Eagle Ford shale	Late Cretaceous	Maverick basin, Texas
Ellsworth shale	Late Devonian	Michigan basin, Michigan
Excello shale	Pennsylvanian	Kansas, Oklahoma
Exshaw shale	Devonian-Mississippian	Alberta, northeast British Columbia
Fayetteville shale	Mississippian	Arkoma basin, Arkansas
Fernie shale	Jurassic	West central Alberta, northeast British Columbia

TABLE 3.8 Shale gas formations in the United States and Canada.—cont'd

Formation	Period	Location
Floyd/Neal shale	Late Mississippian	Black Warrior basin, Alabama, Mississippi
Frederick Brook shale	Mississippian	New Brunswick, Nova Scotia
Gammon shale	Late Cretaceous	Williston basin, Montana
Gordondale shale	Early Jurassic	Northeast British Columbia
Gothic shale	Pennsylvanian	Paradox basin, Colorado, Utah
Green River shale	Eocene	Colorado, Utah
Haynesville/Bossier shale	Late Jurassic	Louisiana, east Texas
Horn River shale	Middle Devonian	Northeast British Columbia
Horton Bluff shale	Early Mississippian	Nova Scotia
Hovenweep shale	Pennsylvanian	Paradox basin, Colorado, Utah
Huron shale	Devonian	East Kentucky, Ohio, Virginia, West Virginia
Klua/Evie shale	Middle Devonian	Northeast British Columbia
Lewis shale	Late Cretaceous	Colorado, New Mexico
Mancos shale	Cretaceous	San Juan basin, New Mexico, Uinta basin, Utah
Manning Canyon shale	Mississippian	Central Utah
Marcellus shale	Devonian	New York, Ohio, Pennsylvania, West Virginia
McClure shale	Miocene	San Joaquin basin, California
Monterey shale	Miocene	Santa Maria basin, California
Montney-Doig shale	Triassic	Alberta, northeast British Columbia
Moorefield shale	Mississippian	Arkoma basin, Arkansas
Mowry shale	Cretaceous	Bighorn and Powder River basins, Wyoming
Muskwa shale	Late Devonian	Northeast British Columbia
New Albany shale	Devonian-Mississippian	Illinois basin, Illinois, Indiana
Niobrara shale	Late Cretaceous	Denver basin, Colorado
Nordegg/Gordondale shale	Late Jurassic	Alberta, northeast British Columbia
Ohio shale	Devonian	East Kentucky, Ohio, West Virginia
Pearsall shale	Cretaceous	Maverick basin, Texas
Percha shale	Devonian-Mississippian	West Texas
Pierre shale	Cretaceous	Raton basin, Colorado
Poker Chip shale	Jurassic	West central Alberta, northeast British Columbia

(*Continued*)

TABLE 3.8 Shale gas formations in the United States and Canada.—cont'd

Formation	Period	Location
Queenston shale	Ordovician	New York
Rhinestreet shale	Devonian	Appalachian basin
Second White Speckled shale	Late Cretaceous	Southern Alberta
Sunbury shale	Mississippian	Appalachian basin
Utica shale	Ordovician	New York, Ohio, Pennsylvania, West Virginia, Quebec
Wilrich/Buckinghorse/ Garbutt/Moosebar shale	Early Cretaceous	West central Alberta, northeast British Columbia
Woodford shale	Devonian-Mississippian	Oklahoma, Texas

Shale gas resources are now important energy sources for meeting rising energy demands in the future. Development of horizontal drilling and hydraulic fracturing (Chapter 5) is crucial for the economic production of shale gas reservoirs. Commercial successes in the Barnett shale, which is currently the largest producing natural gas field, and other shale plays in the United States have made shale gas exploration possible and development has begun to spread all around the world. Massive hydraulic fractures are created to effectively connect a huge reservoir area to the wellbore when the wellbore is drilled in the direction of minimum horizontal stress. Maximizing the total stimulated reservoir volume (SRV) plays a major role in successful economic gas production (Yu and Sepehrnoori, 2013). Despite the success of shale gas development recently, it is difficult to predict well performance and evaluate economic viability for other shale plays with certainty because it involves high risk and uncertainties.

Hydraulic fracture complexity (Chapter 5) is the key to unlocking the potential of shale plays. Microseismic monitoring suggests that complex fracture network can be developed in some shale plays. Microseismic monitoring is a proven technology and has been widely used to monitor and evaluate the effectiveness of hydraulic fracture treatments in various formations, including shale. Theoretically, in shale plays, a complex fracture should produce better compared to bi-wing planer fractures as a result of increased fracture surface area. The value of the microseismic data is that it provides operators with 3D visualization of where the hydraulic fracture process is impacting the rock in the reservoir. When real-time monitoring is used, the micro-seismic information can be used to prevent fracture growth out of zone. Micro-seismic hydraulic fracture monitoring is another of these new technologies. One of the principal costs in extracting natural gas is the hydraulic fracture process. The rock must undergo extensive fracturing to create the permeability required to allow gas to flow into the wellbore. Micro-seismic methodologies arguably offer industry the best method to determine the efficiency of the fracture stimulation process, as it applies to making contact with the gas resource locked in the rock.

Because of this interest, natural gas and crude oil production in the United States has grown significantly in recent years as improvements in horizontal drilling and hydraulic fracturing technologies have made it commercially viable to recover gas trapped in tight formations, such as shale and coal. The United States is now the number one natural gas producer in the world and, together with Canada, accounts for more than 25% v/v of global natural gas production. Shale gas will play an ever-increasing role in this resource base and economic outlook of the United States. Furthermore, production of shale gas is projected to increase to 49% v/v of total natural gas production in the United States by 2035, up from 23% v/v in 2010, highlighting the significance of shale gas in the future energy mix in the United States. Lower and less volatile prices for natural gas in the recent past reflect these new realities, with benefits for American consumers and the competitive and strategic interests of the united States, including the revitalization of several domestic industries.

Production of crude oil and natural gas occurs in two classes of rock: source rocks and reservoir rocks. Source rocks are sedimentary rocks in which hydrocarbon derivatives (organic chemical compounds of hydrogen and carbon) form. Reservoir rocks are both porous, meaning that there are open spaces, or voids, within the rock, and permeable, meaning fluids are able to flow within them. After forming in the source rock, hydrocarbon derivatives, which can vary from simple structures, like methane (a constituent of natural gas), to very complex structures, like bitumen (contained in formation such as tar sand formations), can migrate to the reservoir rock.

Historically, nearly all hydrocarbon derivatives produced domestically were withdrawn from carbonate and sandstone reservoirs. However, over the past decade, production from shale and other tight rock formations, spurred by advances in exploration and production technology, has grown dramatically. Geologic formations that contain oil and gas include clastic or detrital rocks (formed from pieces of pre-existing rocks or minerals), chemical rocks (formed by chemical precipitation of minerals), and organic rocks (formed by biological debris from shells, plant material, and skeletons). The three most common sedimentary rock types encountered in oil and gas fields are shales, sandstones, and carbonates. Classifying these rock types primarily depends on characteristics such as grain size and composition, porosity (pore space within and between grains), and cement (a chemically formed material that holds the grains together), each of which can influence oil and gas production.

The critical elements of a crude oil system are: (i) the source rock, which is the rock containing the organic precursors which were converted into crude oil reservoir fluid, (ii) the migration path, which is the path taken by the crude oil – or immature crude oil that is not fully matured – from the source rock to the reservoir, (iii) the reservoir, which is a rock formation – such as sandstone, limestone, or dolomite – that has sufficient porosity to store the fluid and sufficient permeability for fluid mobility, (iv) the seal, which is impermeable basement rock and cap rock that prevent the escape of the crude oil. For the purpose of this test, the critical part of the crude oil and/or natural gas system is the reservoir.

Crude oil (conventional crude or heavy oil) cannot be retained as an accumulation unless there is a trap, and this requires that the boundary between the cap rock or other sealing agent but the exact form of the boundary varies widely. The simplest forms are the flat-lying convex lens, the anticline, and the dome, each of which has a convex upper surface. Many oil and gas accumulations are trapped in anticlines or domes, structures that are generally more easily detected than some other types of traps, such as fault traps and salt dome traps (Hunt, 1996; Dandekar, 2013; Speight, 2014). Thus, reservoir evaluation is an important aspect of oil and gas production. A reservoir is a subsurface porous permeable rock body or formation that has been created by the sequential steps of deposition, conversion, migration, and entrapment and has the ability to store fluids, such as natural gas, crude oil, and water. As such, each reservoir will exhibit individual properties that are specific to that reservoir (site specific properties). Indeed, within a reservoir, these properties may even change with longitudinal extent and with vertical height of the reservoir.

Typically, reservoir rocks exhibit porosity – a measure of the openings in a rock in which crude oil and natural gas can exist. Another characteristic of reservoir rock is that it must be permeable – the pores of the rock must be inter-connected thereby allowing so that crude oil and/or natural gas mobility within the reservoir and thence flow to a production well. A reservoir with high porosity but low permeable is a general indication of immobility of the gas and/or oil within the reservoir. In such a case, variations in gas composition and crude oil composition from different locations within the reservoir might be expected. Thus, reservoirs that are to be developed for crude oil and/or natural gas production are characteristically large and extensive in volume with a good fluid-holding capacity (high porosity) and also have the capability to transmit fluids once penetrated by geological disturbances (such as earthquakes) or anthropological disturbances, such as drilling a well into the reservoir.

As a result, effective resource exploitation requires a comprehensive reservoir description and characterization program to quantify gas-in-place and to identify those reservoir properties which control production. In terms of reservoir evaluation, reservoirs are generally evaluated on the basis of (i) rock types, (ii) structural types, (iii) heterogeneity, and (iv) porosity and permeability, which are obtained through core analysis.

In addtion, since different shale gas reservoirs have different properties, it is imperative to study them before any exploitation plan is put in place. Geophysical methods can help in characterizing the shale gas resource plays. However, the methodology adopted is in general quite different from methodologies applied to conventional reservoirs. In addition, the characterization of each shale reservoir could require particular types of tools and have to be applied with care. The choice of such methods would continue to evolve to meet the growing challenges and expectations.

A comparison of some of the factors for a shale gas reservoir is essential. Another important point to consider is that the necessary properties can be determined at the location of the wells where the well log and core data are available. A discussion of the relevant properties is presented in the following sections.

3.1 Rock identification

Fundamental to the process of reservoir evaluation is the identification and comparison of three different rock types: (i) *depositional rock types*, (ii) *petrographic rock types*, and (iii) *hydraulic rock types* (Rushing et al., 2008).

Depositional rock types that are rock types that are derived from *core-based descriptions* of genetic units which are collections of rocks grouped according to similarities in composition, texture, sedimentary structure, and stratigraphic sequence as influenced by the environment at the time of deposition. These rock types also represent original large-scale rock properties present at deposition. The *original* rock properties will vary depending on many factors, including the depositional environments, sediment source and depositional flow regimes, sand grain size and distribution, and the type and volume of clay deposited. Thus, depositional rock types are an aid in defining the geological architecture and to describe large-scale reservoir compartments. Mapping the distribution of depositional rock types should also define the extent of the reservoir as well as the natural gas and/or crude oil in-place.

Petrographic rock types re also described within the context of the geological framework, but the rock type criteria are based on pore-scale, microscopic imaging of the *current* pore structure, as well as the rock texture and composition, clay mineralogy, and diagenesis. *Hydraulic rock types* are rock types that are also defined at the pore scale and are the rock types that quantify the physical flow and storage properties of the rock relative to the native fluid(s) as controlled by the dimensions, geometry, and distribution of the current pore and pore throat structure (Rushing et al., 2008). The hydraulic rock type classification provides a physical measure of the rock flow and storage properties at current conditions. The size, geometry, and distribution of pore throats, as determined by capillary pressure measurements, control the magnitude of porosity and permeability for a given rock.

In addition, all three rock types should be similar if the rocks have been subjected to little or no diagenesis (Rushing et al., 2008). For example, the permeability-porosity relationships for depositional rock types would be expected to be applicable to petrographic and hydraulic rock types. However, as diagenetic effects increase in severity and occurrence, the original rock texture and composition, pore geometry, and physical rock properties are modified. Under these conditions, we would expect to see no or very poor correlations among the permeability-porosity relationships derived for each of the different rock types (Rushing et al., 2008).

Each rock type represents different physical and chemical processes affecting rock properties during the depositional and paragenetic cycles. Since most tight gas sands have been subjected to post-depositional diagenesis, a comparison of all three rock types will allow us to assess the impact of diagenesis on rock properties. If diagenesis is minor, the depositional environment (and depositional rock types) as well as the expected rock properties derived from those depositional conditions will be good predictors of rock quality. However, if the reservoir rock has been subjected to significant diagenesis, the original rock properties present at deposition will be quite different than the current properties. More specifically, use of the depositional environment and the associated rock types (in isolation) to guide field development activities may result in ineffective exploitation.

A natural gas and/or a crude oil reservoir is a subsurface collection (sometime referred to as a pool which leaves open the possibility of misinterpretation) of hydrocarbon derivatives and hydrocarbonaceous derivatives in porous or fractured rock formations. However, natural gas and crude oil reservoirs are typically classified as (i) conventional reservoirs and (ii) unconventional reservoirs. In the former type of reservoir − the conventional reservoir − the natural gas and crude oil are trapped by an underlying rock formation (the basement rock) and by an overlying rock formation (the cap rock) with lower permeability than the reservoir rock. In the second type of reservoir − the unconventional reservoir − the reservoir rock typically has high porosity and low permeability in which the natural gas and crude oil are trapped in place without the need for a cap rock or basement rock.

Conventional natural gas reservoirs and crude oil contain free gas or crude oil in interconnected pore spaces that can flow easily to the wellbore i.e. natural flow is possible. In conventional natural gas reservoirs and crude oil reservoirs, the gas or oil is often sourced from organic-rich shales which has migrated to these nearby sandstone or carbonate reservoirs, over geologic time. On the other hand, unconventional reservoirs produce from low permeability (tight and now ultra-tight) formations. The gas or oil is often sourced from the reservoir rock itself, adsorbed onto the matrix. Due to the low permeability of these formations, it is necessary to stimulate the reservoir by creating a fracture network to give enough surface area to allow sufficient production from the additional enhanced permeability of the reservoir. Thus, in a conventional natural gas and crude oil reservoirs (Speight, 2007; GAO, 2012; Speight, 2014), oil and gas are fairly mobile and easily move through the permeable formation because of buoyancy (they have a lower density than the water in the same formation and therefore rise) until they are trapped against an impermeable rock (i.e. a seal) that prevents further movement. This leads to localized pools of oil and gas while the rest of the formation is filled with water.

However, both biogenic and thermogenic shale gas, remains where it was first generated and can be found in three forms: (i) free gas in the pore spaces and fractures, (ii) adsorbed gas, where the gas is electrically stuck to the organic matter and clay, and (iii) a small amount of dissolved gas that is dissolved in the organic matter. In such reservoirs, typically an impermeable shale formation is either the basement rock or the cap rock of a sandstone formation thereby preventing any fluids within the sandstone from escaping or migrating to other formations. When a significant amount of organic matter has been deposited with the sediments, the shale rock can contain organic solid material (kerogen). The properties and composition of shale place it in the category of sedimentary rocks known as *mudstones*. Shale is distinguished from other mudstones because it is laminated and fissile − the shale is composed of many thin layers and readily splits into thin pieces along the laminations.

As a result of the depositional history, shale reservoirs consist of matrix and natural fracture systems and also have also layered structures. The natural gas and crude oil in shale reservoirs is stored in the pore spaces of shale matrix and natural fractures. Moreover, the gas or oil may be stored as an adsorbed phase on the surface of shale matrix, especially on the organic materials (kerogen) and clay minerals (Lancaster et al., 1993; Pashin et al., 2010; Salman and Wattenbarger, 2011). The total organic carbon (TOC) content increases adsorption capacity as does the clay content of the shale (Ross and Bustin, 2008).

Also, a shale reservoir may have a dual porosity due to the porosity of the rock matrix and due to the porosity of the natural fractures. However, due to overburden pressure, the natural fractures are generally closed (Sunjay and Kothari, 2011) and, hence, shale reservoirs typically have allow-to-no porosity. Also, shale reservoirs have an extremely low matrix permeability values typically ranging from 10 to 100 nanodarcies (Cipolla et al., 2010) − a reservoir with a permeability value greater than 0.1 millidarcy is defined as conventional reservoirs. Hence, shale reservoirs are in the classification of unconventional reservoirs.

Due to the extremely low permeability of shale, hydraulic fracturing and horizontal drilling operations are essential for the production of natural gas and crude oil (Sunjay and Kothari, 2011). However, before conducting hydraulic fracturing and horizontal drilling activities, reservoir management studies are necessarily made to investigate the feasibility of operations and this must be a multi-disciplinary approach with involvement not only of petroleum engineers but also drilling engineers, reservoir engineers, geologists, geochemists, and chemists, as well as any other disciplines so that nothing is missed in the evaluation of the reservoir and the surrounding formations. Hence, thermal maturity, reservoir thickness, total organic carbon content (TOC), adsorbed gas fraction, porosity, gas content, oil saturation, water saturation, permeability are key parameters for the reservoir management studies in shale gas reservoirs (Gutierrez et al., 2009).

Thus, the evaluation of any reservoir, including reservoirs formed from shale formations and tight formations, should always begin with a thorough understanding of the geologic characteristics of the formation. The important geologic parameters for a trend or basin are: (i) the structural and tectonic regime, (ii) the regional thermal gradients, and (iii) the regional pressure gradients, (iv) the depositional system, (v) the genetic facies, (vi) textural maturity, (vii) mineralogy, (viii) diagenetic processes, (ix) reservoir dimensions, and (x) the presence of natural fractures, all of which can affect drilling, evaluation, completion, and stimulation. Without understanding the above-listed factors can lead to guesswork in determining reservoir behavior, performance, and longevity.

One of the most difficult parameters to evaluate in tight gas reservoirs is the drainage area size and shape of a typical well. In tight reservoirs, months or years of production are normally required before the pressure transients are affected by reservoir boundaries or well-to-well interference. As such, it may be necessary to estimate the drainage area size and shape for a typical well in order to estimate reserves. Knowledge of the depositional system and the effects of diagenesis on the rock are needed to estimate the drainage area size and shape for a specific well. In blanket, tight gas reservoirs, the average drainage area of a well largely depends on the number of wells drilled, the size of the fracture treatments pumped on the wells, and the time frame being considered. In lenticular or compartmentalized tight gas reservoirs, the average drainage area is likely a function of the average sand-lens size or compartment size, and may not be a strong function of the size of the fracture treatment.

A main factor controlling the continuity of the reservoir is the depositional system. Generally, reservoir drainage per well is small in continental deposits and larger in marine deposits. Fluvial systems tend to be more lenticular whereas barrier-strand-plain systems tend to be more blanket and continuous. To date, most of the more successful tight gas plays are those in which the formation is a thick, continuous, marine deposit.

Thus, an understanding of the geology of a reservoir is essential to reservoir development, oil and gas production, and management, including reservoir longevity and environmental management. Furthermore, reservoir evaluation includes both the external geology of the reservoir (the forces responsible for the formation of the reservoir) and the internal geology of the reservoir (the nature of the rocks that constitute the reservoir). These aspects are even more important when hydraulic fracturing methodology is to be applied to the reservoir. In addition, the efficient extraction of crude oil and natural gas requires that the reservoir be visualized in three dimensions which can only be adequately provided through a variety of scientific and geological studies (Solano et al., 2013).

An important geologic aspect of the reservoir is the external geometry of the reservoir, defined by seals that inhibit the further migration of the natural gas and crude oil.

Migration will cease, and a hydrocarbon reservoir will form, only where hydrocarbon derivatives encounter a trap, which are composed of a suitable gas-holding or oil-holding rock with the following types of seals: (i) top, (ii) lateral, and (iii) bottom seals. In addition, the geometry of traps can be: (i) structural, (ii) sedimentary, and (iii) diagenetic (Hunt, 1996; Dandekar, 2013; Speight, 2014).

Another important geologic aspect of the reservoir is the internal architecture which involves the lateral distribution of depositional textures is related to depositional environments, and the vertical stacking of textures is described by stratigraphy, which is the geological study of the following aspects of rock strata: (i) form, (ii) arrangement, (iii) geographic distribution, and (iv) chronologic succession. Diagenesis, which refers to changes that happen to the sediment after deposition, can also control the lateral continuity and vertical stacking of reservoir rock types. This phenomenon is an important aspect of carbonate reservoirs, in which the conversion of limestone to dolostone and the dissolution of carbonate have a large effect on internal reservoir architecture (Tucker and Wright, 1990; Blatt and Tracy, 1996).

Briefly, dolostone or dolomite rock is a sedimentary carbonate-rich rock that contains a high proportion of dolomite ($CaCO_3 \cdot MgCO_3$), which has also been referred to as *magnesian limestone*. Most dolostone is formed as by magnesium replacement of calcium in limestone ($CaCO_3$) prior to lithification – the process in which sediments compact under pressure, expel connate fluids, and gradually become solid rock. Dolostone is resistant to erosion and can act as an oil and natural gas reservoir.

3.2 Structural types

Reservoirs are created by structural deformation of the geological strata and there are three basic forms of a structural trap in petroleum geology: (i) anticline trap, (ii) fault trap, and (iii) salt dome trap (Hunt, 1996; Dandekar, 2013; Speight, 2014). The *anticline trap* is a typical *structural trap* that is produced by compressional folding, by uplift and by drape over older tectonically created features. An anticline is an example of rocks which were previously flat, but have been bent into an arch. The rocks have been folded or bucked into the form of a dome and hydrocarbon derivatives accumulate in the hinge area of an anticline. The *fault trap* is formed by the movement of permeable and impermeable layers of rock along a fault line. The permeable reservoir rock faults such that it is now adjacent to an impermeable rock, preventing hydrocarbon derivatives from further migration. In some cases, there can be an impermeable substance smeared along the fault line (such as clay) that also acts to prevent migration. Another form of trap is the *stratigraphic trap* that is formed when other geologic formations seal a reservoir or when the permeability changes through a change in lithology, i.e. a change due to the presence of rock with characteristics different from those of the reservoir rock. *Salt domes* are formed by flow of salt or removal of salt deposits.

Reservoir rocks tend to show greater variations in permeability than in porosity and in addition, these two properties, as measured on core samples from reservoir rocks, are not always identical with the values indicated for the bulk rock in the underground formation because of the non-representative nature of many core sample. Generally, porosity is on the order of 5–30% v/v while permeability falls between 0.005 Darcy (5 milliDarcys) and several Darcys (several thousand milliDarcys) (Kovscek, 2002).

3.3 Heterogeneity

In addition to understanding the petrophysics of the reservoir, oil recovery requires an understanding of displacement and flow through porous media – however, flow through porous media is complicated (Dawe, 2004; Maxwell and Norton, 2012). Within the reservoir there can be displacements and miscible and/or immiscible flow, with one, two, or sometimes three mobile phases (oil, gas and water) (Grattoni and Dawe, 2003). Furthermore, heterogeneity in the form of layers, lenses, cross-beds and quadrants can have a significant effect on fluid displacement patterns.

Low-permeability crude oil and natural gas reservoirs exhibit a high degree of bodily heterogeneity encompassing different scales within the hosting geological formation. Local variations of porosity, permeability, and pore geometry are variably affected by the compositional nature of the sediments and the depositional environment in which they formed, as well as the evolving diagenetic and tectonic history of the reservoir rocks.

Physically, natural gas and crude oil reservoirs are not the homogeneous porous media that is often envisaged on paper and used in calculations using data from laboratory simulations. Heterogeneity means that a specific property of interest will vary vertically and longitudinally within the reservoir (Dawe, 2004) much like the coal in a seam that varies in composition from one part of the seam to another (Speight, 2013). For example, well log and core analysis reports show that all reservoirs are heterogeneous with rock properties (such porosity and pore saturation) varying within the reservoir. In addition, permeability heterogeneity causes variations in the fluid movements compared to a homogeneous system (Dawe, 2004). Furthermore, reservoir heterogeneity can arise from variations in permeability or variations in wettability. In fact, wettability of the reservoir rock by the crude oil (particularly adsorption of the polar constituents in heavy oil) can have significant effects on crude oil recovery (Anderson, 1986; Caruana and Dawe, 1996a,b; Dawe, 2004).

The *wettability* of reservoirs rocks refers to the tendency of the fluid (e.g., crude oil) to spread on or adhere to a solid surface in the presence of other immiscible fluids and is determined by complex *interface boundary conditions* acting within pore space of sedimentary rocks. The term *oil wet* refers reservoir rock that which is preferentially in contact with crude oil, which occupies the small pores and contacts the majority of the rock surface. Conversely, the term *water wet* refers to reservoir rock that is preferentially in contact with water. The minerals present in reservoir rocks are generally known as being intrinsically *hydrophilic* (i.e. preferentially water-wet) or *oleophilic* (i.e. preferentially oil-wet).

3.4 Porosity and permeability

Porosity and permeability are related properties of any rock or loose sediment. Most oil and gas has been produced from sandstones which usually have high porosity, and are usually high permeability. Porosity and permeability are necessary to make a productive oil or gas well and are the result of both depositional and diagenetic factors (Alreshedan and Kantzas, 2015). Although a relationship between porosity and permeability is often difficult to interpret (Speight, 2014), there are trends that show a very general relationship between the two properties (Fig. 3.1).

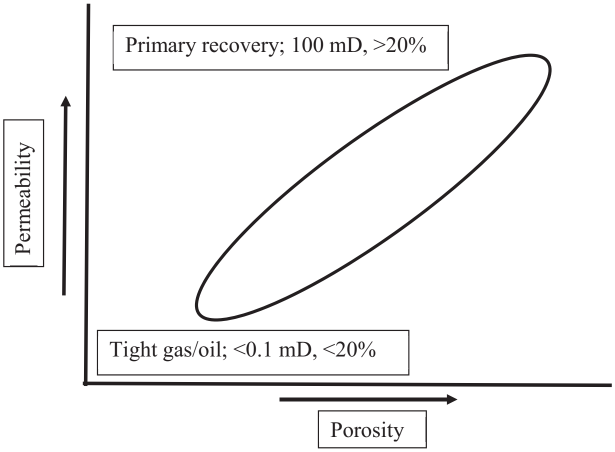

FIG. 3.1 General trends in the relationship between porosity and permeability.

In conventional reservoirs, hydrocarbon derivatives move easily through the formation until they are trapped against an impermeable rock that prevents further flow downward (basement rock) or upward (cap rock). This leads to localized pools of oil and natural gas that can be accessed with a vertical well drilled directly into the reservoir. In reservoirs that consists of tight formations, the natural gas and crude oil are often found within the same rocks they were generated in, trapped in their pore spaces, natural fractures, and within the organic matter itself (inside its pores and stuck to pore walls). Otherwise, hydrocarbon derivatives in tight reservoirs can be found in the pore spaces and natural fractures of any tight rocks into which they migrated. Shale formations, tight sandstone formations, and tight carbonate formations, and the resources contained therein, tend to be widely distributed over extensive areas rather than concentrated in specific locations.

In conventional reservoirs, pore space (pore volume, porosity) can vary from fairly large, visible openings to microscopic pores, and generally comprises less than 30% v/v of the reservoir rock volume. In tight reservoirs, porosity is commonly less than 10% v/v of the reservoir rock. However, regardless of the total porosity volume, if these pores are not efficiently connected one to the other (to give permeability), natural gas and crude oil cannot migrate. Thus, the higher the permeability, the greater the amount of fluid that can flow through the rock. Conventional reservoirs may have a permeability in the range of tens to hundreds of milliDarcys. Tight reservoirs usually have permeability from 0.1 to 0.001 milliDarcy, and shale reservoirs are even less permeable – in the 0.001 to 0.0001 microDarcy range (Fig. 3.2). In tight reservoirs, the typical permeability is usually too small to allow commercial production unless unconventional completion techniques (horizontal drilling and hydraulic fracturing) are used.

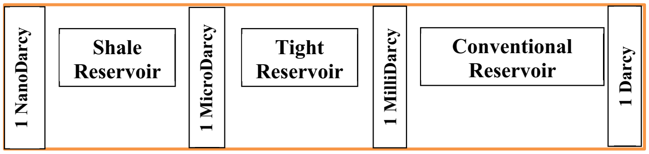

FIG. 3.2 Representation of differences in permeability of shale reservoirs, tight reservoirs, and conventional reservoirs.

The characterization of porosity and permeability is of fundamental importance for the proper evaluation of a reservoir. At the microscopic scale, porosity and permeability are highly dependent on the geometry of the pores and pore throats within volumetrically finite homogeneous systems. These microscopic, locally homogeneous domains are usually found as layered sediments and/or clusters which confer different degrees of heterogeneity to the reservoir (Radlinski et al., 2004). Thus, porosity is the proportion of void space to the total volume of rock and is a measure of the ability of the rock to hold fluids (including gas). Mathematically, porosity is the open space in a rock divided by the total rock volume and is normally expressed as a percent of the total rock which is taken up by pore space. For example, sandstone may have 8% v/v porosity − the other 92% v/v consists of solid space-filling rock. In newly deposited sand formations and poorly consolidated sandstone formations, grain size correlates well with pore size and hence is a primary control on permeability.

In 1978, the US government defined reservoirs with a permeability of less than 0.1 mD as *tight reservoirs*. However, several studies since have shown that permeability is not, in fact, the only aspect that can identify tight gas reservoirs (Shanley et al., 2004; Aguilera and Harding, 2008). Several researches characterized tight gas reservoirs by high capillary entry pressures, high irreducible water saturations, low to moderate porosity, and low permeability (Thomas and Ward, 1972; Dutton, 1993; Byrnes, 1997, 2003) as well as pore geometry (Soeder and Randolph, 1987) which was subdivided into three categories: (i) grain supported pores, (ii) slot and solution pores, and (iii) matrix-supported grains and emphasized that the most common pore structure of tight gas reservoirs consists of secondary solution pores connected to each other through narrow tortuous slots (or fractures) known as a dual porosity model. These slots have an important effect on permeability, as well as on gas flow through tight porous media, but they may not have significant contribution to porosity (Soeder and Randolph, 1987; Aguilera, 2008; Byrnes et al., 2009). Thus, the pore topology/structure of unconventional reservoirs is not only heterogeneous but also unlike conventional reservoirs. It has been found in coal, shale and tight gas reservoirs that the liquid permeability is lower than measured gas permeability (Bloomfield and Williams, 1995; Byrnes, 1997; Cui et al., 2009; Cluff and Byrnes, 2010; Ziarani and Aguilera, 2012; Ghanizadeh et al., 2014). Throat radius is the accounted parameter for this variation (Bloomfield and Williams, 1995; Mehmani and Prodanović, 2014). The Knudsen number (K_n) is being used as a dimensionless correction factor to quantify the amount different gas flow regimes (slip flow, transition and free molecular) as a function of pore−throat radius (Knudsen, 1909; Javadpour et al., 2007).

Moreover, pore structure controls both the natural gas in place and the crude oil in place and long-term deliverability in tight formations. This is controlled by mineralogy, which is dependent on depositional environment and post-depositional diagenetic processes (Hamada et al., 2018). Understanding the means by which the mineral composition controls rock fabric, natural gas in place, crude oil in place, and the mechanical properties of the formation is critical to accurately assessing its potential. Pore throat size controls permeability of the rock, affecting the gas flow rate and porosity controls the distribution of the natural gas and crude oil in the formation. In formations with smaller pores, a larger amount of surface area is available for the constituents of the natural gas or crude oil to be adsorbed, and a larger fraction of the gas or oil may be present in the adsorbed state than in the free state.

Laboratory measurements for tight porous media are costly and time-consuming. Also, studying the effect of a certain parameter in such complex pore structures is difficult due to the complexity associated with the experimental setup. As an alternative approach, pore network modeling can be used to construct physically sound models of a real porous media. Pore network modeling gives a reasonable prediction of fluid flow properties at pore scale, and offers the flexibility of studying macroscopic properties relationship with pore structure and geometry.

In pore network modeling, the complex pore structure in a rock is represented by a network of pore bodies (void spaces) and pore—throats (narrow paths that connect pore bodies) with simplified geometries. When this is successfully established, then single and multiphase flow calculations can be performed (Okabe and Blunt, 2005). Detailed physics and productive capabilities for pore-scale modeling of multiphase flow at the pore scale have been reviewed in several studies (Blunt, 2001; Blunt et al., 2002). At the early stages of network modeling, capillary pressure and relative permeability curves of drainage using two-dimensional (2D) regular lattice networks where the radii were randomly assigned were predicted (Fatt, 1956) and later illustrated (Chatzis and Dullien, 1977) that 3D pore network models represent the real porous media more realistically than 2D pore network models. Following this early work, extensive studies on the importance of topology, pore bodies and throats size distribution and their spatial correlations were performed (Chatzis and Dullien, 1977; Jerauld and Salter, 1990; Grattoni and Dawe, 1994). However, most of these studies were based on regular lattice networks which are limited in reflecting the real topology and geometry of a rock. The capabilities of network modeling were enormously improved and have been applied to make many successful predictions of single and multiphase flow and transport properties including two- and three-phase relative permeability and capillary pressure of conventional formations (Øren et al., 1998; Patzek, 2001; Øren and Bakke, 2002, 2003; Valvatne and Blunt, 2003; Piri and Blunt, 2005a, 2005b).

In complex sandstones, it is recommended to create first a 3D image-based representation of the pore space that should capture the statistics of the real rock. This can be generated using a direct imaging technique such as micro-CT scanning (Okabe and Blunt, 2005), or by various process/object-based modeling approaches (Bakke and Øren, 1997; Øren et al., 1998; Øren and Bakke, 2002, 2003). Subsequently, using various image-based network extraction techniques (Al-Kharusi and Blunt, 2007; Dong and Blunt, 2009), an equivalent pore network is then extracted from the 3D image to estimate the single and multiphase fluid flow properties.

Permeability and formation factor are physical properties of the rock. Permeability is defined by Darcy's law and formation factor is defined by Archie's law. Permeability plays a critical role in determining the potential of hydrocarbon flow in a porous medium. Further, formation factor gives an indication of the availability of pathways for transport. Both properties are sensitive to pore and throat size, connectivity and geometries.

Permeability values for tight formations usually fall into a range from the sub-microdarcy ($<10^{-3}$ mD) up to the one hundred of milliDarcys. Permeability is usually measured either with core plugs or full-diameter core samples using unconfined, unsteady-state techniques. For the measurements of ultra-low permeability samples, crushed rock pressure decay techniques are used instead.

The porosity of rock samples is traditionally calculated from helium pycnometer measurements — as used for crude oil coke and other solids (ASTM D2638) — from which an accurate value of grain density is obtained. The relatively small size of helium molecules ensures that even sub-nanometer sized pores and pore throats are probed. In addition, the low adsorptive capacity of these molecules reduces the errors that might be introduced due to the absorption processes during the measurements. However, helium may be accessible to finer pores than crude oil and natural gas constituents in shale formations thereby overestimating accessible porosity (Cui et al., 2009).

On the other hand, permeability is the ability of fluid to move through the pores and is a measure of the ease with which fluids (including gas) pass through a rock. Thus, it is extremely important to know the values of formation permeability in every rock layer. The values of permeability control everything from gas flow rate to fracture fluid leak-off. It is impossible to optimize the location of the perforations, the length of the hydraulic fracture, the conductivity of the hydraulic fracture, and the well spacing, if one does not know the values of formation permeability in every rock layer. In addition, one must know the formation permeability to forecast gas reserves and to analyze post-fracture pressure buildup tests. To determine the values of formation permeability, one can use data from logs, cores, production tests, and pre-fracture pressure buildup tests or injection falloff tests (Ahmed et al., 1991).

Permeability in crude oil-producing rocks is usually expressed in milliDarcys and most oil and gas reservoirs have permeability in the range up to several hundred milliDarcys (Fig. 3.2). The extremely low permeability of shale formations determines the effectiveness of basement rock and cap rock seals for many conventional reservoirs. However, grain-size combinations are the key in determining these seal and leakage characteristics. Although well-compacted clay-rich formations are generally considered as good seals, certain combinations with larger grains, such as silt grains, can reduce the seal quality. Clay-poor formations are generally considered to be poor seals, but recent studies have shown that certain combinations of large and smaller grains can contribute to improving their seal characteristics. Therefore, it is important to understand the effect of texture on seal quality and develop field methods to detect these characteristics. This understanding is also essential for predicting and detecting possible leakage mechanisms in rocks that are thought to be good seals.

Accumulations of crude oil and natural gas can only occur if all of the essential elements (source rock, reservoir rock, seal rock, and overburden rock) and processes (generation-migration-accumulation-trap formation) have operated adequately and in the proper time space framework (Magoon and Dow, 1994; Speight, 2014). Absence or inadequacy of even one of the elements or processes eliminates any chance of economic success. Thus, reservoir parameters (reservoir size, porosity, and permeability) are among the geologic controls that have to be included in the consideration of risk factors for reservoir development (Berg, 1970; Ahmed et al., 1991; Rose, 1992; White, 1993; Ramm and Bjørlykke, 1994; Yao and Holditch, 1996). The quantification and predictability of three major causes of anomalously high porosity: (i) grain coats and grain rims, (ii) early emplacement of hydrocarbon derivatives, and (iii) shallow development of fluid overpressure.

Grain coats are the result of authigenic processes and form subsequent to burial by growth outward from framework grain surfaces, except at points of grain-to-grain contact (Wilson and Pittman, 1977). Grain coats include clay minerals and microcrystalline quartz.

Grain coats and grain rims retard quartz cementation and concomitant porosity and/or permeability reduction by blocking potential nucleation sites for quartz overgrowths on detrital-quartz seed grains. The effectiveness of grain coats or grain rims in preserving porosity is a function of the thermal history, grain size, and the abundance of quartz grains (Walderhaug, 1996; Bonnell et al., 1998). Grain coats and grain rims have no effect on porosity where the primary control of reservoir quality is the occurrence of cements such as carbonate minerals, sulfate minerals, or zeolites (Pittman et al., 1992).

Porosity and permeability generally decrease with increasing depth (thermal exposure and effective pressure); however, a significant number of deep (approximately 13,000 feet) sandstone reservoirs worldwide are characterized by anomalously high porosity and permeability (Bloch et al., 2002). Anomalous porosity and permeability can be defined as being statistically higher than the porosity and permeability values occurring in typical sandstone reservoirs of a given lithology (composition and texture), age, and burial/temperature history.

In tight gas (shale) reservoirs, areas where the reservoir quality and completion are high (*sweet spots*) are confined to areas that have high clay rim coverages but relatively low volume of clay minerals. By contrast, interstratified clay-free and coarse-grained non-reservoir rock is tightly cemented by quartz overgrowth (Wescott, 1983; Weimer and Sonnenberg, 1994). Furthermore, drilling success in any reservoir is dependent on finding the most prospective areas, or the *sweet spots*, and aligning the wellbore for maximum borehole exposure to these zones. In shale reservoirs this means placing the well in the zones most conducive to fracturing. This requires a thorough understanding of the shale gas reservoir characteristics. Aiming for a middle-of-the-road operation is rarely a successful strategy – shale formations can have significant variance in thickness and composition.

The thickness of a tight formation is one of the primary reasons, along with a large surface area of fine-grained sediment and organic matter for adsorption of gas, that resource evaluations in tight formations yield such high values for total organics carbon content and potential producibility of the natural gas or crude oil. A general rule-of-thumb is that a thicker formation is a more attractive (producible and economic) shale. Shale targets such as the Bakken formation (Williston Basin), however, are less than one hundred and fifty feet thick in many areas but are yielding economic rates of gas flow and recovery. The required thickness to economically develop a tight formation may decrease as drilling and completion techniques improve, as porosity and permeability detection techniques progress in unconventional targets and, perhaps, as the price of gas increases.

In summary, the success or failure of a hydraulic fracture treatment will depend on the quality of the candidate well selected for the treatment. Evaluation and selection of a suitable candidate reservoir for stimulation is a move in the depiction of success, while choosing a poor candidate normally results in failure. To select the best candidate for stimulation, the design engineer must consider many variables of which the most critical parameters for hydraulic fracturing are: (i) formation permeability, (ii) the in-situ stress distribution, (iii) viscosity of the reservoir fluid, (iv) reservoir pressure, (v) reservoir depth, (vi) the condition of the wellbore, and (vii) prior stimulation of, or damage to, the reservoir.

The best candidate wells for hydraulic fracturing treatments have a substantial volume of oil and gas in place and need to increase the productivity index. The characteristics of such reservoirs include: (i) a thick pay zone, (ii) medium to high pressure, (iii) in-situ stress barriers to minimize vertical height growth, and (iv) either a low-permeability zone or a zone that has been damaged. On the other hands, reservoirs that are poor candidates for hydraulic fracturing are those with little oil or gas in place because of thinness (lack of thickness or depth) as well as low reservoir pressure and small areal extent. Reservoirs with extremely low permeability may not produce enough hydrocarbon derivatives to pay all the drilling and completion costs, even if successfully stimulated; thus, such reservoirs would not be good candidates for stimulation.

3.5 Reservoir morphology

Finally, reservoir morphology defines the sand-body dimensions, geometry, orientation, heterogeneity, and continuity as developed by depositional and post-depositional processes. Both sand quality and quantity are controlled by primary and secondary depositional environments and processes. Quantification of the morphology helps define the reservoir architecture and compartments, and ultimately, to determine the original reservoir volume or "container." For example, the gas-in-place volumes and producing characteristics for a "blanket" sand will be much different than for a reservoir characterized by lenticular sands. Reservoir morphology will also affect the optimum well spacing to for field development. Depositional environment and post-depositional diagenesis both have a significant bearing on morphology, including reservoir compartmentalization and heterogeneity. Reservoir compartments refer to intervals or sections of the sand deposits that are mostly or completely isolated (i.e., not in pressure communication) from other parts of the reservoir. Compartments may be created by significant changes in the depositional environment or by post-depositional processes (such as diagenesis and/or tectonic activity creating sand pinch-outs, and no-flow barriers). Reservoir heterogeneities, which are typically manifested by lateral and vertical variability in permeability and porosity within the same sand body, are mostly caused by post-depositional diagenesis. Most diagenetic processes do not cause completely isolated reservoir compartments — but such processes may yield complex and/or poor quality flow paths, which may result in low productivity for a given reservoir system.

4. Tight formations

Geologic age is an important determinant of hydrocarbon potential, beyond the characteristics of source and reservoir rocks. Identifying fossils, other chemical markers, and correlating rocks across different formations allows earth scientists to determine the age of the rock and to understand the processes that influenced the sediments and organic material over time. While many rocks of different ages produce oil and natural gas, domestic areas of prolific production include formations from several different geologic periods: (i) Devonian period − 416 to 359 million years ago, (ii) Carboniferous period − 359 to 299 million years ago, (iii) Permian period − 299 to 251 million years ago, and (iv) Cretaceous period − 145 to 65 million years ago. During these periods, organic-rich materials accumulated and, over time, heat and pressure chemically altered originally organic chemicals into natural gas and oil.

Unconventional natural gas resources and crude oil and crude oil resources found in shale formations and in tight formations (Ma et al., 2016; Moore et al., 2016) comprise a significant percentage of the North American natural gas and crude oil resource base and these systems represent an important source for future reserve growth and production. Similar to conventional natural gas and crude oil systems, unconventional reservoirs are characterized by complex geological and petrophysical systems as well as reservoir heterogeneity. In fact, low-permeability oil reservoirs exhibit a high degree of heterogeneity. Local variations of porosity, permeability, and pore geometry are variably affected by the compositional nature of the sediments and the depositional environment in which they formed, as well as the evolving diagenetic and tectonic history of the reservoir rocks (Solano et al., 2013). In addition, and unlike conventional reservoirs, unconventional reservoirs typically exhibit storage and flow characteristics which are uniquely tied to depositional and diagenetic processes.

Tight formations such as shale formations are complex reservoirs insofar as they represent significant variety in reservoir characteristics (i.e., mineralogy, porosity, permeability, gas content, and pressure) (Fig. 3.2). Thus:

Conventional Gas

- MilliDarcy Range (>1 mD)
- Fluid type varies
- Rock type varies

Tight Gas

- Micro Darcy Range
- Dry gas – wet gas
- Primarily Sandstone

Shale Gas

- NanoDarcy range
- Dry gas – wet gas
- Mostly free gas - some adsorbed gas
- Flow mostly through fractures (cleats)

The natural gas in shale reservoirs occurs both as a free phase within pores and fractures and as gas sorbed onto organic matter. Consolidated rocks (such as shale, sandstone, limestone, or granite) potentially have a more complex dual porosity when compared with alluvial sediment. This can be split into connected and unconnected porosity. Connected porosity is more easily measured through the volume of gas or liquid that can flow into the rock, whereas fluids cannot access unconnected pores. Shale formations containing gas typically have a low porosity and a total organic carbon content (TOC) of 4% w/w or higher (Curtis, 2002). Shale reservoirs containing represent a unique reservoir due to the very low permeability. Most shale reservoirs have a matrix permeability of 10^{-4} to 10^{-8} mD. The presence, density, and continuity of natural, open fractures are believed to be critical to enhance system permeability. Successful development generally entails hydraulic fracturing in order to connect these natural fractures to the wellbore.

The behavior and properties of each reservoir are symptomatic of the rock types that constituent the reservoir and each reservoir must be assessed differently according to the geochemical characteristics (Jarvie et al., 2011). For example, each rock type represents different physical and chemical processes affecting rock properties during the depositional and paragenetic cycles (equal equilibrium sequences of mineral phases). Since most tight gas sands have been subjected to post-depositional diagenesis, a comparison of the rock types allow an assessment of the impact of diagenesis on rock properties. If diagenesis is minor, the depositional environment (and depositional rock types) as well as the expected rock properties derived from those depositional conditions will be good predictors of rock quality. However, if the reservoir rock has been subjected to significant diagenesis the original rock properties present at deposition will be quite different than the current properties. Thus, it might be anticipated that use of the depositional environment and the associated rock types may not always result in effective exploitation of a formation or reservoir (Rushing et al., 2008).

Generally, a tight reservoir is a layered system and, in a clastic depositional system, the layers are composed of: (i) shale, (ii) mudstone, (iii) and siltstone while in a carbonate system the layers are composed predominantly of: (i) limestone, $CaCO_3$, (ii) dolomite, $CaCO_3 \cdot MgCO_3$, (iii), possibly halite, NaCl, or anhydride, $CaSO_4$, and some shale. Thus to optimize the development of a tight reservoir, a multi-disciplinary team consisting of (minimally) geoscientists, petrophysicists, and engineers must fully characterize all the layers of rock above, within, and below the pay zones in the reservoir.

Another key difference between conventional gas reservoirs and shale gas reservoirs is adsorbed gas. Adsorbed gas is gas molecules that are attached to the surface of the rock grains. The nature of the solid sorbent, temperature, and the rate of gas diffusion all affect the adsorption. Presently, the only method for accurately determining the adsorbed gas in a formation is through core sampling and analysis. Understanding the effects of adsorption on production data analysis increase the effectiveness of reservoir management in these challenging environments. They contain natural gas in both the pore spaces of the reservoir rock and on the surface of the rock grains themselves that is referred to as adsorbed gas. This is a complicated problem in that desorption time, desorption pressure, and volume of the adsorbed gas all play a role in how this gas affects the production of the total system. Adsorption can allow for significantly larger quantities of gas to be produced. Shale gas reservoirs present a unique problem for production data analysis.

The effects of the adsorbed gas are not clearly understood except that it tends to increase production and ultimate recovery. The phenomena of gas storage and flow in shale gas sediments are a combination of different controlling processes. Gas flows through a network of pores with different diameters ranging from nanometers ($nm = 10^{-9}$ m) to micrometers ($\mu m = 10^{-6}$ m). In shale gas systems, nanopores play two important roles. Petrophysical imaging employs first, second, and third generation wavelet to delve deep into complex shale gas reservoir. Nanoscale gas flow in Shale gas sediments has scope to cope with research on dry nanotechnology (smart fluid/nanofluid). Anisotropy in sediments may develop during deposition or post deposition. In clastic sediments, anisotropy can arise both during and after deposition. In carbonates, anisotropy is controlled mostly by fractures and diagenetic processes, and so tends to arise after deposition. For anisotropy to develop during deposition of clastic sediments, there needs to be an ordering of sediments-in essence, some degree of homogeneity, or uniformity from point to point.

If a rock were heterogeneous in the five fundamental properties of its grains-composition, size, shape, orientation and packing-anisotropy cannot develop because there would be no directionality intrinsic to the material. Anisotropy at the bedding scale that arises during deposition therefore may have two causes. One is a periodic layering, usually attributed to changes in sediment type, typically producing beds of varying material or grain size. Another results from the ordering of grains induced by the directionality of the transporting medium. Anisotropy is therefore governed not only by variation in the type of material but also by variation in its arrangement and grain size. The main cause of elastic anisotropy in shales appears to be layering of clay platelets on the micron (micrometer) scale due to geotropism -turning in the gravity field of the Earth — and compaction enhances the effect. Shale, with its inherent heterogeneity and anisotropy, has always been problematic in many operations ranging from seismic exploration, well-log data interpretation, well drilling and well-bore stability problems, to production. Research work focus at bridging the gap between invariant characteristics at nano scale of sedimentary rocks and their macroscopic properties. 3D seismic is becoming successful because of the ability to identify fracture and fault trends. Surface geochemistry cannot be used to identify in the subsurface where the fracture systems or fault systems will be intersected by the drill bit. Thus 3D is now being used aggressively and successfully.

4.1 Shale formations

In conventional reservoirs, natural gas and crude oil are fairly mobile and easily move through the permeable forma ion because of buoyancy (because of the lower density than the water in the same formation and therefore rise) until the gas and oil are trapped against an impermeable rock (i.e., a seal) that prevents further movement. This leads to localized pools (not really pools as might be generally understood but the collection of natural gas and/or crude oil in a specific area within the pores systems of the reservoir rock) of natural gas and crude oil and gas while the rest of the formation is filled with water.

The complexity of shale reservoirs makes the proper understanding of reservoir parameters very important. Typically, shale reservoirs possess the following characteristics: (i) they cover large area, (ii) they are thick/stacked reservoirs, (iii) they are complex and possess lateral heterogeneity dues to the methods of deposition and fractures, as well as diagenesis, (iv) the gas is stored by sorption and compression, (v) they have low matrix permeability, and are subject to rapid decline rates in during production. The most rigorous method to represent shale gas reservoirs is to grid the entire reservoir discretely, including the network fractures, hydraulic fracture, matrix blocks, and the un-simulated area. The purpose of hydraulic fracturing is to promote fracture complexity, by using a large amount of fracturing fluid (Chapter 5).

In shale reservoirs, there are two storage mechanisms: (i) adsorbed gas and (ii) free gas. Although adsorbed gas may form up to 50% v/v of the total gas in place, the ability to produce adsorbed gas is limited because of the tightness of matrix rock. Though the contribution of the adsorbed gas may become significant during the later life of the well, this delay, in many shale wells makes insignificant impact on the well economics. It is also important to account for reservoir length along with the total organic content and the reservoir pressure (Sondergeld et al., 2010). Above all, it must always be remembered that no two shale formations are alike. And there are even extreme variations even within the same shale block. However there are certain parameters that may be complete qualifiers or disqualifiers of shale formations, the most important being (i) the gas in place, (ii) the total organic content, (iii) the transformation ratio organic matter into hydrocarbon, (iv) maximum temperature obtained via rock-eval analyses and vitrinite reflectance which is a measure of thermal maturity.

However, shale gas, both biogenic and thermogenic, remains where it was first generated and can be found in three forms: (i) free gas in the pore spaces and fractures, (ii) adsorbed gas, where the gas is adsorbed on clay minerals and on the organic matter, and (iii) a small amount of dissolved gas that is dissolved in the organic matter. Because typical shale formations are a several dozen to hundreds of feet (even a mile or more) thick and extend over very wide geographic areas (resource plays), where natural gas resources are widely distributed over extensive areas rather than concentrated in specific locations. The volume of natural gas contained within a resource play increases as the thickness and areal extent of the deposit grows.

The amount and distribution of gas within the shale is determined by, among other things, the initial reservoir pressure, the petrophysical properties of the rock, and its adsorption characteristics. During production there are three main processes at play. Initial gas production is dominated by depletion of gas from the fracture network. This form of production declines rapidly due to limited storage capacity. After the initial decline rate stabilizes, the depletion of gas stored in the matrix becomes the primary process involved in production. The amount of gas held in the matrix is dependent on the particular properties of the shale reservoir which can be hard to estimate. Secondary to this depletion process is desorption whereby adsorbed gas is released from the rock as pressure in the reservoir declines. The rate of gas production via the desorption process depends on there being a significant drop in reservoir pressure. Pressure changes typically advance through the rock very slowly due to low permeability. Tight well spacing can therefore be required to lower the reservoir pressure enough to cause significant amounts of adsorbed gas to be desorbed.

Individual gas shales appear to have copious amounts (trillions of cubic feet, 10^{12} Tcf) of gas in place spread over hundreds to thousands of square miles. The difficulty lies in extracting even a small fraction of that gas. The pore spaces in shale, through which the natural gas must move if the gas is to flow into any well, are 1000 times smaller than pores in conventional sandstone reservoirs. The gaps that connect pores (the pore throats) are smaller still, only 20 times larger than a single methane molecule (Bowker, 2007). Therefore, shale has very low permeability. However, fractures, which can act as conduits for the movements for natural gas, may naturally exist in the shale and increase its permeability.

Shale is formed by the accumulation of very small sediments deposited in deep water, at the bottoms of rivers, lakes, and oceans. Shales are the most abundant clastic sedimentary rock, and because of their potential for a high organic content, shales are considered to be the primary source rocks for hydrocarbon derivatives. *Sandstone* is created by larger sediment, deposited in deserts, river channels, deltas, and shallow sea environments. These rocks tend to be more porous than shales, and consequently make excellent reservoir rocks. Sandstone is the second most abundant clastic sedimentary rock and is the most commonly encountered reservoir rock in hydrocarbon production. *Carbonate* is created by the accumulation of shells and skeletal remains of water-dwelling organisms in marine environments. The third most abundant sedimentary rock, carbonate (e.g., limestone) rocks are also very good reservoirs and are commonly encountered during hydrocarbon production.

On the other hand, a *shale reservoir* (*shale play*) is similar on a worldwide basis insofar as organic-rich, gas-prone shale is generally difficult to *discover*. Tight shale formations are heterogeneous and vary widely over relatively short distances. Thus, even in a single horizontal drill hole, the amount recovered may vary, as may recovery within a field or even between adjacent wells. This makes evaluation of plays and decisions regarding the profitability of wells on a particular lease difficult. However, the lack of a strict definition for shale causes an additional degree of difficulty for resource evaluation. Such a broad spectrum of lithology appears to form a transition with other resources, such as natural gas and crude oil, where the difference between the tight gas reservoir and gas shale may be the higher amount of sandstone (in the tight gas reservoir) and the tight gas reservoir may actually contain no organic matter. The properties and composition of shale place it in the category of sedimentary rocks known as *mudstones*. Shale is distinguished from other mudstones because it is laminated and fissile – the shale is composed of many thin layers and readily splits into thin pieces along the laminations.

Shale formations are a worldwide occurrence (Ma et al., 2016; Moore et al., 2016). Shale is a geological rock formation that is rich in clay, typically derived from fine sediments, deposited in fairly quiet environments at the bottom of seas or lakes, having then been buried over the course of millions of years. Shale formations can serve as pressure barriers in basins, as top seals, and as reservoirs in shale gas plays. More technically, shale is a fissile, terrigenous sedimentary rock in which particles are mostly of silt and clay size. In this definition, *fissile* refers to the ability of the shale to split into thin sheets along bedding and *terrigenous* refers to the origin of the sediment. In many basins, the fluid pressure of the aqueous system becomes significantly elevated, leading to the formation of a hydro-fracture, and fluid bleed-off. However, the occurrence of a natural hydro-fracture is an unlikely process in the circumstances that exist in most basins.

Shale is composed mainly of clay-size mineral grains, which are usually clay minerals such as illite, kaolinite and smectite. Shale usually contains other clay-size mineral particles such as quartz, chert, and feldspar. Other constituents can include organic particles, carbonate minerals, iron oxide minerals, sulfide minerals and heavy mineral grains and the presence of such minerals in shale is determined by the environment under which the shale constituents were.

Shale is formed by the accumulation of very small sediments deposited in deep water, at the bottoms of rivers, lakes, and oceans. Shale is, by definition, a sedimentary rock that is predominantly composed of consolidated clay sized particles but is separated from the more generally-recognized sedimentary rocks that typically constitute a natural gas or crude oil reservoir. Shale formations are deposited as muds in low-energy environments such as tidal flats and deep water basins where the fine-grained clay particles fall out of suspension in the quiet waters. During the deposition process, in addition to the fine-grained material that eventually forms the sediment, there can also be the deposition and accumulation of organic matter in the form of algae, plant, and animal derived organic debris that is eventually converted to natural gas and crude oil (Davis, 1992).

Shale formations and silt formations are the most abundant sedimentary rocks in the crust of the Earth. In crude oil geology, organic shale formations are source rocks as well as seal rocks that trap oil and gas (Speight, 2014). In reservoir engineering, shale formations are flow barriers. In drilling, the bit often encounters greater shale volumes than reservoir sands.

In seismic exploration, shale formations interfacing with other rocks often form good seismic reflectors. As a result, seismic and petrophysical properties of shale formations and the relationships among these properties are important for both exploration and reservoir management.

Shale is composed mainly of clay-size mineral grains, which are usually clay minerals such as illite, kaolinite and smectite. Shale usually contains other clay-size mineral particles such as quartz, chert, and feldspar. Other constituents might include organic particles, carbonate minerals, iron oxide minerals, sulfide minerals and heavy mineral grains and the presence of such minerals in shale is determined by the environment under which the shale constituents were. Shale formations consist of consolidated clay and other fine particles (mud) that have hardened into rock. These formations are the most abundant of all sedimentary rocks, comprising approximately two-thirds of the sedimentary rocks. Typically, these formations are fine-grained and thinly bedded and readily split along dividing (bedding) planes. Shale is classified or typed by composition; for example, shale containing large amounts of clay is referred to as *argillaceous shale,* and shale containing appreciable amounts of sand is known as *arenaceous shale*. Shale with a high content of organic matter (*carbonaceous shale*) is typically black in color. Shale that contains large amounts of lime (*calcareous shale*) is used in the manufacture of Portland cement. Another type of shale, *oil shale,* is currently of great interest worldwide because of the supply and demand and increasing cost of crude oil. Oil shale contains kerogen (Chapters 1 and 11), a fossilized insoluble organic material that is converted into synthetic crude oil from which a variety of crude oil-type products can be produced (Chapter 16).

The very fine-grained sheet-like clay mineral grains and any laminated layers of sediment result in a rock with permeability that is limited horizontally and even more limited when measured from samples taken from different vertical height within the formation. Such formations provide excellent cap rocks and basement rocks for conventional natural gas and crude oil (sandstone) reservoirs (Speight, 2014). However, in the current context, the low permeability of shale formations results in natural gas and crude oil that has originated in the shale remains trapped in the formation cannot move within (or migrate from) the rock except (in some instances) over geologic time (millions of years). Shale formations are the most abundant clastic sedimentary rock and, because of their potential for a high organic content, such formations are considered to be the primary source rocks for the formation of natural gas and crude oil.

Indeed, the variety of rock types observed in organic-rich shale formation confirms the implication that a range of different types of shale reservoirs exist. Each reservoir may have distinct geochemical and geological characteristics that may require equally unique methods of drilling, completion, production and resource and reserve evaluation (Cramer, 2008) − leading to further necessary considerations when the shale gas had to be processed (Chapter 8). Additionally, it must not be forgotten that a shale formation is often a seal or cap rock for a conventional (sandstone) crude oil or natural gas reservoir and that not all shale are necessarily reservoir rocks (Speight, 2007, 2014).

There is also the possibility (only assiduous geological studies will tell) of hybrid shale formations, where the originally deposited mud was rich in sand. These foreign minerals (sand, silt, clay minerals) result in a natural higher permeability for the shale formation and result in greater susceptibility of the shale to hydraulic fracturing.

More specific to this text, four general types of shale formation (shale plays) have been defined as being predominant in the shale formations investigated and developed and have been given the simple designations: Type 1, Type 2, Type 3, and Type 4, without any order of preference but more on the basis of composition and behavior. The *Type 1 shale* is a fractured organic mudstone with high carbonate content − an example is the Barnett Shale − and primary typically involves a mix of gas released from fractures and micropores through gas desorption from the organic material and clay minerals. On the other hand, the *Type 2 shale* has laminated sands embedded in organic-rich shale − an example is the Bakken Formation, which is primarily is an oil resource play. The *Type 3 shale* is an organic-rich black shale − the carbonaceous content is typically greater than 1% w/w, such as the Marcellus Shale, and production occurs through gas desorption − the gas has been observed to carry with it gas condensate. Finally, the *Type 4 shale* (such as the Niobrara Shale) is a combination of the other three type of shale formations and production is through desorption, matrix structures, and fractures.

A significant factor associated with tight gas reservoirs is the low productivity, which is emphasized in the case of gas condensate fluids, which exhibit complex phase behavior and complex flow behavior due to the appearance of condensate banking in the near-well region. This behavior differs essentially in their behavior from conventional gas reservoirs, especially for low permeability high yield condensate systems, which have more severe condensate banking problems. Thus, it is necessary to have a thorough understanding of the manner by which the condensate accumulation influences the productivity. Knowledge of the composition configuration in the liquid phase is very important to optimize the producing strategy for tight formations, to reduce the impact of condensate banking, and to improve the ultimate gas recovery.

A key factor that controls the gas-condensate well deliverability is the relative permeability, which is influenced directly by the condensate accumulation which not only reduces both the gas and liquid relative permeability but also changes the phase composition of the reservoir fluid, hence changes the phase diagram of reservoir fluid and varies the fluid properties (Wheaton and Zhang, 2000. Pedersen and Christensen, 2006). In addition, different producing strategies may impact the composition configuration of the condensate for both the flowing phase and the static phase and the amount of the liquid trapped in the reservoir, which in turn may influence the well productivity and hence the ultimate gas and liquid recovery from the reservoir. Changing the manner in which the well is brought into flowing condition can affect the liquid dropout composition and can therefore change the degree of productivity loss.

As might be expected (even predicted), shale plays that cover large subterranean areas show considerable variations in mineralogical composition, formation depth, and thermal maturity. An example of a large-area play is the Marcellus Shale, which covers portions of the states of Pennsylvania, New York, Ohio, West Virginia, Virginia, Tennessee and Maryland. Examples of plays confined to smaller areas include the Eagle Ford Shale, which covers a portion of south Texas, the Barnett Shale in central Texas and Haynesville Shale, which underlies parts of Arkansas, Louisiana and Texas. It must also be realized that the definitions given above are for convenience based on current investigations and it is likely (perhaps, even expected) that a wider variety of shale types exists and will be explored and developed in the future as technology improves.

On a more physical note, typical shale formations can be anywhere from twenty feet to a mile or so thick and extend over very wide geographic areas, a gas shale reservoir is often referred to as a *resource play*, where natural gas resources are widely distributed over extensive areas (perhaps several fields) rather than concentrated in a specific location. The volume of natural gas contained within a resource play increases as the thickness and areal extent of the deposit grows. Individual gas shale formations may have a billion cubic feet (1×10^9 ft^3) or even e a trillion cubic feet (1×10^{12} ft^3) of gas in place spread over hundreds to thousands of square miles. The difficulty lies in extracting even a small fraction of that gas.

Shale formations exhibit a wide range of mechanical properties and significant anisotropy reflecting their wide range of material composition and fabric anisotropy (Sone, 2012). The elastic properties of these shale rocks are successfully described by tracking the relative amount soft components (clay and solid organic materials) in the rock and also acknowledging the anisotropic distribution of the soft components. Gas shale formations also possess relatively stronger degree of anisotropy compared to other organic-rich shale formations, possibly due to the fact that these rocks come from peak-maturity source rocks. The deformational properties are influenced by the amount of soft components in the rock and exhibited mechanical anisotropy.

The pore spaces in shale, through which the natural gas must move if the gas is to flow into any well, are as much as one thousand times smaller than pores in conventional sandstone reservoirs. The gaps that connect pores (the pore throats) are smaller still, only twenty times larger than a single methane molecule. Therefore, shale has very low permeability but natural or induced fractures, which act as conduits for the movement for natural gas, will increase the permeability of the shale.

Shale comes in two general varieties based on organic content: (i) dark colored or (ii) light colored. Dark colored or black shale formations are organic-rich, whereas the lighter colored shale formations are organic-lean. Organic-rich shale formations were deposited under conditions of little or no oxygen in the water, which preserved the organic material from decay. The organic matter was mostly plant debris that had accumulated with the sediment. Black organic shale formations are the source rock for many of the oil and natural gas deposits of the world. These black shale formations obtain their black color from tiny particles of organic matter that were deposited with the mud from which the shale formed. As the mud was buried and warmed within the earth some of the organic material was transformed into oil and natural gas.

A black color in sedimentary rocks almost always indicates the presence of organic materials. Just one or two percent organic materials can impart a dark gray or black color to the rock. In addition, this black color almost always implies that the shale formed from sediment deposited in an oxygen-deficient environment. Any oxygen that entered the environment quickly reacted with the decaying organic debris. If a large amount of oxygen was present, the organic debris would all have decayed. An oxygen-poor environment also provides the proper conditions for the formation of sulfide minerals such as pyrite, another important mineral found in black shale sediments or formations.

The presence of organic debris in black shale formations makes them the candidates for oil and gas generation. If the organic material is preserved and properly heated after burial oil and natural gas might be produced. The Barnett Shale, Marcellus Shale, Haynesville Shale Fayetteville Shale and other gas producing rocks are all dark gray or black shale formations that yield natural gas.

The oil and natural gas migrated out of the shale and upwards through the sediment mass because of their low density. The oil and gas were often trapped within the pore spaces of an overlying rock unit such as a sandstone formation. These types of oil and gas deposits are known as *conventional reservoirs* because the fluids can easily flow through the pores of the rock and into the extraction well.

Shale formations are ubiquitous in sedimentary basins – they typically form approximately 80% of the formations through which a well will be drilled. As a result, the main organic-rich shale formations have already been identified in most regions of the world. Their depths vary from near surface to several thousand feet underground, while their thickness varies from a tens of feet to several hundred feet. Often, enough is known related to the geological history to infer which shale formations are likely to contain gas (or oil, or a mixture of both). In that sense there may appear to be no real need for a major exploration effort and expense required for shale gas. However, the amount of gas present and particularly the amount of gas that can be recovered technically and economically cannot be known until a number of wells have been drilled and tested.

Each shale formation has different geological characteristics that affect the way gas can be produced, the technologies needed and the economics of production. Different parts of the (generally large) shale deposits will also have different characteristics: *small sweet spots* or *core areas* may provide much better production than the remainder of the formation, often because of the presence of natural fractures that enhance permeability (Hunter and Young, 1953).

The amount of natural gas liquids (NGLs – hydrocarbon derivatives having a higher molecular weight than methane, such as propane, butane, pentane, hexane, heptane, and even octane) commonly associated with natural gas production present in the gas can also vary considerably, with important implications for the economics of production. While most dry gas plays in the United States are probably uneconomic at the current low natural gas prices, plays with significant liquid content can be produced for the value of the liquids only (the market value of natural gas liquids is correlated with oil prices, rather than gas prices), making gas an essentially free by-product.

The Barnett Shale of Texas was the first major natural gas field developed in a shale reservoir rock. Producing gas from the Barnett Shale was a challenge because the pore spaces in shale are so tiny that the gas has difficulty moving through the shale and into the well. Drillers discovered that the permeability of the shale could be increased by pumping water down the well under pressure that was high enough to fracture the shale. These fractures liberated some of the gas from the pore spaces and allowed that gas to flow to the well (hydraulic fracturing, hydrofracing).

Horizontal drilling and hydraulic fracturing revolutionized drilling technology and paved the way for developing several giant natural gas fields. These include the Marcellus Shale in the Appalachians, the Haynesville Shale in Louisiana and the Fayetteville Shale in Arkansas. These enormous shale reservoirs hold enough natural gas to serve all of the United States' needs for twenty years or more. Hydraulic properties are characteristics of a rock such as permeability and porosity that reflect its ability to hold and transmit fluids such as water, oil or natural gas. In this respect, shale has a very small particle size so the interstitial spaces are very small. In fact, they are so small that oil, natural gas and water have difficulty moving through the rock. Shale can therefore serve as a cap rock for oil and natural gas traps and it also is an aquiclude that blocks or limits the flow of underground water.

Although the interstitial spaces in a shale formation are very small they can take up a significant volume of the rock. This allows the shale to hold significant amounts of water, gas or oil but not be able to effectively transmit them because of the low permeability. The oil and gas industry overcomes these limitations of shale by using horizontal drilling and hydraulic fracturing to create artificial porosity and permeability within the rock.

Some of the clay minerals that occur in shale have the ability to absorb or adsorb large amounts of water, natural gas, ions or other substances. This property of shale can enable it to selectively and tenaciously hold or freely release fluids or ions.

Thus, this shale gas resource can be considered a technology-driven resource as achieving gas production out of otherwise unproductive rock requires technology-intensive processes. Maximizing gas recovery requires far more wells than would be the case in conventional natural gas operations. Furthermore, horizontal wells with horizontal legs up to one mile or more in length are widely used to access the reservoir to the greatest extent possible.

Multi-stage hydraulic fracturing (Chapter 5), where the shale is cracked under high pressures at several places along the horizontal section of the well, is used to create conduits through which gas can flow. Micro-seismic imaging allows operators to visualize where this fracture growth is occurring in the reservoir. However, as a technology-driven resource, the rate of development of shale gas may become limited by the availability of required resources, such as fresh water, fracture proppant, or drilling rigs capable of drilling wells several two miles or more in length.

As in shale formations, which are believed to be the source rocks in which oil and gas form during geological time, crude oil and gas are contained in the pore space of the formation — which can include sandstone formations, siltstone formations, and carbonate formations. While a conventional formation containing crude oil and/or natural gas can be relatively easily drilled and extracted from the ground, tight gas and tight oil (natural gas and crude oil in tight formations) requires more effort to extract from a tight reservoir. In such formations, the pores in the formation in which the gas is trapped are either irregularly distributed or interconnection of the pores is poor, which adversely affects permeability. Without secondary production methods, gas and/or oil from a tight formation would flow at very slow rates, making production uneconomical.

While vertical wells may be easier and less expensive to drill, they are not the most conducive to developing tight formations. In a tight formation, it is important to expose as much of the reservoir as possible, making horizontal and directional drilling a necessity. Here, the well can run along the formation, opening up more opportunities for the natural gas and/or tight crude oil to enter the wellbore. A more common technique for developing reserves in tight formations includes drilling more wells which enhances the ability of the oil and gas to leave the formation and enter the wellbore. This can be achieved through drilling several myriad directional wells (the number of wells is formation specific) from one location, which lessens the environmental footprint of the drilling operation. After seismic data has illuminated the best well locations, and the wells have been drilled, production stimulation (through both fracturing and acidizing) is employed on tight reservoirs to promote a greater rate of flow.

Fracturing involves breaking apart the rocks in the formation (Chapter 5). After the well has been drilled and completed, hydraulic fracturing is achieved by pumping the well full of fracturing fluids under high pressure to cause rock fracturing in the reservoir and improve permeability. Additionally, acidizing the well is employed to improve permeability and production rates of tight gas formations, which involves pumping the well with acids that dissolve the limestone, dolomite and calcite cement between the sediment grains of the reservoir rocks. This form of production stimulation helps to reinvigorate permeability by reestablishing the natural fissures that were present in the formation before compaction and cementation.

Typically, North American crude oil and natural gas formations that require fracturing are located one mile or more below the water table and below many layers of impermeable rock. These thousands of feet of rock overlying the tight gas formations, combined with the low permeability of the tight gas formations themselves, ensure that the natural gas and crude oil remain contained within the target formation and also help prevent migration of any hydraulic fracturing fluids that may be pumped into such formations. Drilling, casing, and cementing procedures must be designed to at least to meet (or even) exceed regulatory requirements to protect groundwater by isolating the well from any groundwater supplies.

The upper portions of the well, where the wellbore passes through the water table, should be reinforced to prevent either gas or oil (and any fracturing fluids) from escaping into the surrounding ground. Wells are lined with steel pipes and sealed in place with cement from the surface to below the level of drinking water supplies, typically to a depth of 1000 feet or more. These barriers help to contain the fracturing fluid and, along with the depth at which fracturing takes place, prevent the fluid from mingling with drinking water close to the surface. During and after hydraulic fracturing, wells are monitored with pressure sensors to check that they are firmly sealed which helps to make production as efficient as possible and protects the environment (Chapters 5 and 18).

The manner in which gas and oil are trapped within tight formations and shale formations requires advanced technology to access these resources. Horizontal and directional drilling techniques are used to access a large underground area from a single well pad and when followed by hydraulic fracturing technology stimulates the release of the encapsulated oil and gas to flow into the wellbore. One of the most difficult parameters to evaluate in tight reservoirs is the drainage area size and shape of a typical well. Knowledge of the depositional system and the effects of diagenesis on the rock are needed to estimate the drainage area size and shape for a specific well.

Finally, because of the properties of the shale formation (above) such as (i) the presence of *hard minerals*, and (ii) the *internal pressure* of the shale, it may be possible to isolate sections along the horizontal portion of the well, segments of the borehole for one-at-a-time fracking (multi-stage fraccing). By monitoring the process at the surface and in neighboring wells, it can be determined how far, how extensively, and in what directions the shale has cracked from the induced pressure. As has been discovered because of the natural gas and crude oil contents of shale formations, these formations can be re-fractured after production has declined, which may (i) allow the well to access to larger areas of the reservoir that may have been missed during the initial hydraulic fracturing or (ii) to reopen fractures that may have closed due to the decrease in pressure as the reservoir was drained. Even with hydraulic fracturing, wells drilled into low-permeability reservoirs have difficulty communicating far into the formation. As a result, additional wells must be drilled to access as much gas as possible, typically three or four, but up to eight, horizontal wells per section.

As a final note to this sub-section, there are also hybrid gas shales, where the originally deposited mud was rich in sand or silt, therefore having naturally higher permeability and greater susceptibility to hydraulic fracturing. Examples include the Triassic Montney Formation and the Cretaceous Second White Speckled Shale. The Montney is so rich in silt and sand that it is often referred to as tight gas, as it has been in many NEB publications. However, unlike typical tight-gas plays, the natural gas in the Montney is sourced from its own organic matter, more typical of shale gas. For simplicity and convenience most of the hybrid shale formations as often referred to by the term *shale gas formations*.

4.2 Sandstone and carbonate formations

The term *tight formation* refers to a formation consisting of extraordinarily impermeable, hard rock. Tight formations are relatively low permeability, non-shale, sedimentary formations that can contain oil and gas. When a significant amount of organic matter has been deposited with the sediments, the shale rock can contain organic solid material (kerogen). Reservoirs with estimated *in situ* permeability of 0.1 milliDarcy or less were recognized late 1970s and early 1980s as *tight reservoirs* (Moslow, 1993). Since that time, however, and for all practical purposes, a tight reservoir is generally recognized as any low permeability formation in which special well completion techniques (such as horizontal drilling and hydraulic fracturing) are required to stimulate production (Chapter 5).

The low permeability (and porosity) associated with tight sands are attributed to a large distribution of small to very small pores and/or a complex system of pore throats connecting those pores. Furthermore, both small pores and pore throat systems can result from several processes: (i) deposition of fine to very fine grained sediments, (ii) the presence of various types of dispersed shale minerals and clay minerals in the pores and/or (iii) post-depositional diagenesis that alter the original pore structure (Rushing et al., 2008). Therefore, successful exploitation of a tight gas sand reservoir requires a basic understanding of the rock pore structure and properties as well as the processes affecting those properties.

Geologically, tight reservoirs are reservoirs having a low permeability and are often associated with conventional reservoirs, which could be sandstone, siltstone, limestone, dolomite, sandy carbonate minerals and shale minerals having significant thickness. Tight reservoir sands are continuous and stacked sedimentary layers charged with hydrocarbon derivatives. Many tight gas sand formations (and shale formations) are naturally fractured and/or layered. Development of tightness and different geological complexities in sandstone reservoirs are due to different geological events. It is due to loss of porosity through diagenesis, occurrence of most porosity in secondary pore spaces. In comparison to the typical sandstone formation, tight sand formations have lesser void space and void connectivity.

Development of tight reservoirs includes two factors: (i) the provenance, mineralogy, grain size, its sorting, flow regime, sedimentary depositional environment and the lithification and (ii) diagenesis which involves compaction, cementation, and dissolution followed by tectonics and development of fractures. Regional and local tectonics plays a very important role in the evaluation of the tight sand reservoirs. Pressure and thermal gradient are affected by the tectonics and are also an important aspect of the evolution of this types of reservoir. The most common tight sand formations generally consist of highly altered primary porosity, with authigenic quartz growth, coupled with secondary pore developments.

As expected for any complex reservoir system, successful exploitation of a tight reservoir requires basic understanding of the rock pore structure and properties as well as processes affecting those properties. Core analysis is direct evidence of the reservoir composition and mineral relationships and will help in understanding nature of facies, the depositional environment, sand texture, digenetic alteration, reservoir morphology, sand distribution and its orientation. The different sedimentary structures control tightness of the reservoir as well. The thin section analysis of the rock infers detail mineralogy, texture, sorting of grains, matrix and cementing material and the type of porosity.

Low permeability formations occur in almost all sedimentary basins worldwide. In North America, the vast majority of tight gas reservoirs can be grouped into two main geological categories: (i) Devonian shales from eastern United States and Canada, and (ii) low permeability sandstones from throughout the United States and from the Western Canada Sedimentary basin. It has been estimated that in the United States alone, tight sandstone formations are likely to have recoverable reserves ranging from 100 to 400 tcf, and Devonian shales have recoverable reserves of up to 100 tcf (Rushing et al., 2008). The successful exploitation of tight gas resources in the future will depend in large part on advancements made in the proper geological evaluation of low permeability reservoirs.

A *tight reservoir* (*tight sands*) is a low-permeability sandstone reservoir – in some sedimentary basins tight reservoirs consist of mainly sandstone, silty sandstone, siltstone, argillaceous limestone and dolomites. A tight reservoir is one that cannot be produced at economic flow rates or recover economic volumes of gas unless the well is stimulated by a large hydraulic fracture treatment and/or produced using horizontal wellbores. This definition also applies to coalbed methane and tight carbonate reservoirs – shale gas reservoirs are also included by some observers (but not in this text). Typically, tight formations which formed under marine conditions contain less clay and are more brittle, and thus more suitable for hydraulic fracturing than formations formed in fresh water which may contain more clay. The formations become more brittle with an increase in quartz content (SiO_2) and carbonate content (such as calcium carbonate, $CaCO_3$, or dolomite, $CaCO_3 \cdot MgCO_3$).

Thus, a tight reservoir is an umbrella term often used to refer to low-permeability reservoirs that produce mainly dry natural gas and volatile crude oil. Many of the low-permeability reservoirs that have been developed in the past are sandstone, but significant quantities of gas are also produced from low permeability carbonate formations, shale formations, and coal seams (which is not included in this text). In tight reservoirs, the expected value of permeability is less than one milliDarcy (Fig. 3.2) whereas in shallow, thin, low-pressure reservoirs a permeability of several milliDarcys might be required to produce natural gas or crude oil at economic flow rates, even after successful fracture treatment. In this context, perhaps the best definition of a tight reservoir is a reservoir from which gas or liquids cannot be produced at economic flow rates nor recover economic volumes of natural gas unless the reservoir is stimulated by hydraulic fracture treatment or produced by use of a horizontal wellbore or multilateral wellbores. In fact, further to this definition, and remembering the role of economics in reservoir development, a typical tight reservoir does not exist – the reservoir can involve a range of physical parameters: (i) deep or shallow, (ii) high pressure or low pressure, (iii) high temperature or low temperature, (iv) blanket or lenticular, (v) homogeneous or heterogeneous, (vi) naturally fractured – which is unlikely – or require serious fracturing by hydraulic means, and (vii) composed of a single layer or multiple layers. Therefore, the optimum drilling, completion, and stimulation methods for each well in a specific reservoir are functions of reservoir characteristics.

In tight reservoirs, the typical drainage area of a well largely depends on (i) the number of wells drilled, (ii) the size of the fracture treatments, and (iii) the time frame being considered. In lenticular or compartmentalized tight reservoirs, the drainage area is usually a function of the sand-lens size or compartment size, and may not be a strong function of the size of the fracture treatment. A main factor controlling the continuity of the reservoir is the depositional system. Generally, reservoir drainage per well is small in continental deposits and larger in marine deposits. Fluvial systems tend to be more lenticular whereas barrier-strand plain systems tend to be more continuous.

Also, in tight reservoirs *diagenesis* (any post-depositional process causing changes in the initial rock properties) is very important aspect of reservoir geology since it is the principal cause of both low permeability and low porosity. The diagenesis process may be either a physical process or a chemical process, or a combination of several different types of processes. The initial digenetic process is directly attributable to the prevailing local depositional environment as well as the sediment composition. Subsequent diagenesis is typically more widespread, often crossing multiple facies boundaries as a result of regional fluid migration patterns (Stonecipher and May, 1990). Thus, diagenesis is frequently caused by interactions between the sediment minerals and pore fluids at the elevated pressure and temperature conditions prevalent in the reservoir. The primary diagenetic processes commonly observed in tight sands are: (i) mechanical compaction, (ii) chemical compaction, (iii) cementation, (iv) mineral dissolution, (v) mineral leaching, and (vi) clay genesis.

Mechanical compaction is caused by grain rearrangement, ductile and plastic rock deformation, and fracturing/shearing of brittle materials. This form of compaction may be mitigated by high pore pressure which tends to reduce stresses transferred to the grain materials. Chemical compaction refers to changes in grain size and geometry caused by physical and chemical reactions enhanced by pressure conditions, such as mineral solution. Generally, both mechanical and chemical compaction will reduce both permeability and porosity – permeability is reduced when the pore throats are partially or completed closed and porosity is reduced by a reduction in the primary pore volume. Cementation is a chemical process in which minerals are precipitated from pore fluids and bind with existing grains and rock fragments. The most common cement compositions in tight sands are composed of silica minerals and carbonate minerals. Silica minerals are precipitated as overgrowths or layers on quartz (SiO_2) grains which may form soon after deposition but often continue to develop with increased pressure and temperature during burial. Carbonate cements are often precipitated early after deposition and tend to fill pore spaces between minerals. Authigenic clay minerals (i.e. clay minerals that formed during sedimentation and were not transported from elsewhere – allogenic minerals – by water or wind) may also act as cementitious materials by helping to bind rock particles together. Most cements tend to reduce both permeability and porosity. However, the presence of authigenic grain coats and rims can retard quartz cementation and the associated reduction in permeability and porosity by blocking potential nucleation sites for quartz overgrowths on detrital quartz grains (Bloch et al., 2002).

Another type of chemical diagenesis is mineral dissolution. For example, quartz (silica, SiO_2) can become soluble by the application of pressure (pressure solution, which can only occur at higher temperatures) caused by stress concentrations at grain contacts which results in silica dissolution, diffusion, transport of silica for reprecipitation in adjacent pores, and an associated loss in porosity. Another type of mineral dissolution is mineral leaching which often results in an increase in primary porosity and/or the creation of secondary porosity. A common source of secondary porosity creation is dissolution of carbonate cements which are often precipitated early after deposition and tend to fill pore spaces between framework grains.

Clay genesis refers to authigenic clay minerals created or generated after deposition. Such minerals that are found in tight sands include chlorites, mixed-layer smectite/illite clay minerals, and illite clay minerals. Authigenic chlorite minerals typically develop under iron-rich conditions and commonly occur as pore linings (or coatings). Since these clay minerals often do not completely cover the detrital grain surfaces, quartz overgrowths may develop on many grains, thus reducing the original primary porosity. Smectite clay minerals have been observed in sandstones that contain significant amounts of volcanic rock fragments. Illite minerals may also form from kaolinite and can develop either through precursor detrital or authigenic clays. Illite crystals can occur either as fibrous, sheet-like or plate structures – the fibers tend to break easily and accumulate in pore throats, causing a reduction or loss of permeability. Illite sheets and plates may also reduce permeability by blocking pore throats.

Both reservoir pressure and temperature affect the type, magnitude and severity of diagenesis. Moreover, increasing temperatures increases the solubility of minerals and causes the pore waters to become saturated, thereby increasing precipitation and formation of cementitious materials.

Finally, rocks with interlaminated shale and siltstone is a shale gas target (e.g., Lewis Shale, New Mexico; Colorado Group, Alberta) that may require new techniques for detection in well logs, as well as new completion and drilling techniques. The silt laminations are too thin to be detected on well logs and to allow an accurate determination of how many laminations are in a given interval. Also, well logs are unable to accurately determine the percentage of porosity in shale or the laminations, the degree of water saturation in a reservoir or the relative degree of permeability in each lamination. Laminations both store gas (free gas) and are pathways of transport for diffusion of gas from shale to the well bore (Beaton et al., 2009). The laminations are also particularly difficult completion targets. Normally, induced fractures are meant to extend laterally rather than vertically in a reservoir, yet the laminations may span tens of hundreds of feet vertically. Therefore, a horizontal fracture may miss many productive shale and silt laminations. Induced fracturing techniques may have to be altered, or new techniques developed for this type of shale gas reservoir.

4.3 Development and production

As a part of the development and production activities in a tight reservoir, one of the most difficult parameters to evaluate is the drainage area size and shape of a typical well. Knowledge of the depositional system and the effects of diagenesis on the rock are needed to estimate the drainage area size and shape for a specific well. In continuous -type (blanket-type) tight reservoirs, the average drainage area of a well largely depends on the number of wells drilled, the size of the fracture treatments pumped on the wells, and the time frame being considered. In lenticular-type or compartmentalized tight gas reservoirs, the average drainage area is likely a function of the average sand-lens size or compartment size, and may not be a strong function of the size of the fracture treatment.

A main factor controlling the continuity of the reservoir is the depositional system. For example, reservoir drainage per well is small in continental deposits and larger in marine deposits while in fluvial systems the drainage area tends to be more lenticular. Tight reservoirs that have been more successfully developed, such as the Vicksburg in south Texas, the Cotton Valley Taylor in east Texas, the Mesa Verde in the San Juan Basin, and the Frontier in the Green River Basin, are tight sandstones that originated as marine deposits, which tend to be more continuous (blanket reservoirs). In fact, most of the more successful tight reservoirs are those in which the formation is a thick, continuous, marine deposit. However, there are other formations, such as the Travis Peak formation in east Texas, the Abo formation in the Permian Basin, and the Mesa Verde formation in parts of the Rocky Mountains that are fluvial systems and tend to be highly lenticular. The Wilcox Lobo formation in south Texas is highly compartmentalized because of faulting. In lenticular reservoirs (compartmentalized reservoirs) the drainage area is controlled by the geology and must be estimated by the geologist or engineer.

Whether the reservoir is a tight sandstone reservoir or a shale reservoir, development of the reservoir (Chapter 4) requires a vertical well drilled and completed in the must be successfully stimulated to produce at commercial gas flow rates and produce commercial gas volumes. Typically, hydraulic fracturing is required to produce natural gas and crude oil economically. In some naturally fractured tight reservoirs, horizontal wells and/or multilateral wells can be used to provide the stimulation required for commerciality. Moreover, to optimize the development of a tight reservoir, the number of wells drilled must be optimized along with the necessary drilling and completion procedures for each well. Often, more data and more engineering manpower are required to understand and develop tight gas reservoirs than are required for higher permeability, conventional reservoirs. This requires that more wells (or smaller well spacing) must be drilled into a tight reservoir to recover a large percentage of the original gas in place (OGIP) or original oil in place (OOIP) when compared to a conventional reservoir.

In all cases, a thorough understanding of the fundamental geochemical and geological attributes of tight formations and shale formations is essential for resource assessment, development and environmental stewardship. Four very pertinent properties that define the characteristics of a reservoir are: (i) the maturity of the organic matter, (ii) the type of gas generated and stored in the reservoir – biogenic gas or thermogenic gas, (iii) the total organic carbon content of the strata, and (iv) the permeability of the reservoir. Only when these characteristics are known can the reservoir be successfully developed and exploited.

Thus, tight reservoirs can be sub-divided into three rock types – (i) *depositional*, (ii) *petrographic*, and (iii) *hydraulic* (Newsham and Rushing, 2001; Rushing and Newsham, 2001; Rushing et al., 2008). Each rock type represents different physical and chemical processes affecting the rock properties during both depositional and paragenetic cycles. We define the tight gas sand rock types as follows:

Production from tight reservoirs usually requires enhancement due to problems associated with very low permeability (Akanji and Matthai, 2010; Akanji et al., 2013). The collection of the fundamental knowledge database needed to fully understand the key mechanisms affecting flow behavior in tight formation is still sparse. In this paper, we applied a new technique of measuring flow properties in porous media to characterize flow behavior in core samples of tight carbonate formations.

Moreover, the permeability of the samples is higher for the core samples obtained vertically through the parent rock. Tight formations are considered to be reservoirs with an absolute permeability of generally less than 10 milliDarcy and can range down to the micro-Darcy range, (10^6 Darcy) in many situations. These reservoirs could potentially serve as media for the storage of commercial accumulation of hydrocarbon. However, production and ultimate recovery are usually uneconomical due to a number of factors which include poor reservoir quality, unfavorable initial saturation condition, formation damage caused by drilling and completion operations, hydraulic or acid fracturing, kill or work-over treatments and other production-related problems.

Many tight reservoirs are extremely complex producing oil or gas from multiple layers with low permeability that often require enhancement by natural fractures. Despite the marginal economics and low productivity from these reservoirs, the soaring demands for energy has necessitated a devotion of technologies to optimize recovery. Description of the pore geometry of reservoirs plays a major role in understanding the degree of pore interconnectivity, pore shapes and sizes, capillary trapping potentials and flow behavior.

5. Core analyses

Obtaining and analyzing cores is crucial to the proper understanding of any layered, complex reservoir system. To obtain the data needed to understand the fluid flow properties, the mechanical properties and the depositional environment of a specific reservoir requires that cores be cut, handled correctly, and tested in the laboratory using modern and sophisticated laboratory methods. Of primary importance is measuring the rock properties under restored reservoir conditions. The effect of net overburden pressure (NOB) must be reproduced in the laboratory to obtain the most accurate quantitative information from the cores.

To provide all the data needed to characterize the reservoir and depositional system, a core should be cut in the pay interval and in the layers of rock above and below the pay interval. Core from the shales and mudstones above and below the pay interval help the geologist determine the environment of deposition. Having more information related to the deposition allows the reservoir engineer to better estimate the morphology and size of the gas-bearing reservoir layers. Also, mechanical property tests can be run on the shales to determine estimates of Poisson's ratio and Young's modulus. Additional tests can be run to measure the shale density and the sonic travel time in the shale to assist in the analyses of the density- and sonic-log data. In fact, the rock quality governs the hydrocarbon storage properties whereas completion quality depends on the elastic properties. Successful hydraulic fracturing of low permeability reservoirs requires identification of reservoir sections along the wellbore with good reservoir and completion qualities. Elastic properties govern in-situ stress field, stress concentration around wellbore and failure properties of the units, which leads to hydraulic fracture geometry and propagation behavior. Geomechanical modeling and characterization is one of the key components to get the desired fracturing results (Guha et al., 2013).

5.1 Handling and testing cores

After cutting the cores in the field, it is important to handle the core properly: (i) the core should not be hammered out of the barrel. It should be pumped out, (ii) once the core is laid out on the pipe racks, it should be wiped with rags to remove the mud (do not wash with water), then described as quickly as possible, (iii) bedding features, natural fractures, and lithology should be described foot by foot, (iv) permanent markers should be used to label the depth of the core and clearly mark the up direction on the core, (v) as quickly as feasible, the core should be wrapped in heat shrinking plastic, then sealed in paraffin for the trip to the core analysis laboratory, and (vi) precautions should be taken to minimize alteration of the core properties while retrieving and describing the core in the field.

Once in the laboratory, the core is unwrapped and slabbed, and plugs are cut for testing. Normally, a core plug should be cut every foot in the core, trying to properly sample all the rock—not just the cleaner pay zones. Routine core analyses can be run on these core plugs. Once the routine core analyses are completed, additional core plugs are cut for special core analyses. Sometimes samples of whole core are used for testing. Both the routine and the special core analyses are required to calibrate the open-hole logging data, and to prepare the data sets required to design the optimum completion. The core plugs must also be treated with care. For example, if a core plug from a shale-containing sand is placed in a standard oven, it is likely that the clays in the pores will be altered as they dry out. A more accurate core analysis can be achieved if the core plugs are dried in a humidity-controlled oven in which the free water is evaporated, but the treatment should not be so severe as to affect the bound clay water.

5.2 Routine core analyses

Routine core analyses should be run on core plugs cut every foot along the core. Routine core analyses should consist of measurements of: (i) grain density, (ii) porosity and permeability to air, both unstressed and stressed, (iii) cation exchange capacity, and (iv) fluid saturations analysis. In addition, each core plug should be described in detail to understand the lithology and grain size and to note any natural fractures and other details that could be of importance to the geologist, petrophysicist, or engineer.

The porosity is used to determine values of gas in place and to develop correlations with permeability. The grain density should be used to determine how to correlate the density log values and to validate any calculation of lithology from log data. The cation exchange capacity can be used to determine how much electric current can be transmitted by the rock rather than the fluid in the pore space. The cation exchange capacity must be measured in the laboratory, using samples of rock, and is a function of the amount and type of clay in the rock. Saturation analysis measures the amount of water, oil, and gas in the core plugs in the laboratory. Saturation analysis can be misleading in rocks that are cored with water based mud because of mud filtrate invasion during the coring process and problems that occur with core retrieval and handling prior to running the laboratory tests. However, the values of water saturation from the core analysis of cores cut with an oil-based mud can be used to calibrate the log data and to estimate values of gas in place in the reservoir.

The measurements of porosity and permeability are a function of the net stress applied to the rock when the measurements are taken. For low porosity rock, it is very important to take measurements at different values of net stress to fully understand how the reservoir will behave as the gas is produced and the reservoir pressure declines. In fact, a challenge in the development of resources from low permeability formations is the ability to accurately evaluate rock properties (such as permeability, porosity and capillary pressure). This information is necessary to quantify the resource potential of the formation and also to predict production behavior. However, due to the complex structure of the pore network, simple relationships relating permeability to porosity are not representative since the low permeability of tight formations renders the standard steady-state techniques, which are applicable in evaluating conventional natural gas and crude oil reservoirs, difficult to implement in terms of producing reliable and meaningful data.

Furthermore, the measurement of permeability and porosity of conventional, high permeability reservoirs are typically performed at low pressure in the laboratory and are not representative of in-situ conditions which means that the effect of the overburden stress is largely ignored. As stress is increased, the high aspect ratio of the pore structures dominating conductive pathways are compressed and ultimately closed off, restricting fluid flow and increasing tortuosity of flow pathways. Thus, after the values of porosity and permeability are measured in the laboratory, the values should be correlated to the conditions in the tight formation (Thomas and Ward, 1972; Jones and Owens, 1980; Soeder and Randolph, 1987; Guha et al., 2013). In addition, However, it should be remembered that these estimates are from routine core analyses, which means the core has been tested dry with no water in the core. If similar measurements are made at connate water saturation, the permeability in the core is further reduced, maybe by a factor of 2 or even an order of magnitude in some cases. As such, in tight gas reservoirs, it is often found that in-situ permeability to gas is 10–100 times lower than gas permeability measured at ambient conditions on dry core plugs cut from whole core. If cores come from a percussion sidewall device, the core plugs are typically altered, and the values of permeability under unstressed conditions can be even more optimistic.

5.3 Specialized analyses

To fully understand the properties of tight gas formations, special core analyses must be run on selected core plugs to measure values of gas permeability versus water saturation, resistivity index, formation factor, capillary pressure, acoustic velocity, and the rock mechanical properties. The values of resistivity index and formation factor are used to better analyze the porosity and resistivity logs. The acoustic velocity can be used to better estimate porosity and to determine how to estimate the mechanical properties of the rock from log data. The mechanical properties are measured and correlated to log measurements and lithology. The capillary pressure measurements and the gas permeability versus water saturation relative permeability measurements are required to properly simulate fluid flow in the reservoir and to design hydraulic fracture treatments.

It is important to choose the correct core samples for conducting the special core analyses. Special core analysis tests are expensive and require weeks or months of special laboratory measurements. As such, the core samples must be chosen with care to provide the optimum data for designing the well completion and the well stimulation treatment and forecasting future gas recovery. A good way to select the core samples for special core analysis testing is to: (i) form a team of geologists, engineers, and petrophysicists, (ii) lay out the core, (iii) have the routine core analysis and log analysis available, (iv) determine how many rock types or lithology types that are contained in the core are important to the completion and stimulation process, and (v) pick three to six locations for each rock type or lithology where core plugs are cut for testing.

In addition to the composition of the shale (i.e., shale type), the depth of the formation is a major parameter since depth also influences thermal maturity, bottomhole temperatures, formation pressure, and overall formation behavior. For example, the Haynesville play is relatively deep which is reflected in high-pressure and high-temperature conditions whereas the Marcellus play is relatively shallow and is only mildly over-pressured in the most productive areas. Pore pressure can also be used as an indicator of reservoir quality − higher pressures typically reflect a high degree of gas generation and storage. Furthermore, in order to better understand the effect of hydraulic stimulation, it is necessary to understand the stress state in conjunction with the elastic and strength properties of the rock mass. Such a study may commence with determination of the brittleness index of the rocks.

The *brittleness index* (BI), a measure of the ability of the rock to crack or fracture, also assists shale play developers when they evaluate a well and field and is primarily related to shale mineralogy and rock strength. A high brittleness index is typically associated with high quartz content or high carbonate (dolomite) content, as illustrated by the Barnett shale play and the Woodford shale play. On the other hand, the *brittleness index* decreases with increasing clay and organic matter, as is in the Marcellus shale play. Thus, the *brittleness index* serves as a guide for placement of perforations, isolation points and fracture stages (Wylie, 2012).

However, the brittleness index should be used according to the relevant definition (Herwanger et al., 2015) within which the brittleness of rocks is characterized from (i) the elastic properties, (ii) the petrophysical properties, and (iii) the strength properties. The definition that is predominant in the geophysical literature relates to a high brittleness for rocks that exhibit a high Young's modulus E and low Poisson's ratio, ν (Rickman et al., 2008). There is also a *brittleness index* that is related to a specific combination of Lamé parameters λ and μ (Goodway et al., 2010). Another category of definitions of *brittleness index* is based on mineral content of the rocks (Jarvie et al., 2007) while definition of brittleness index can also be based on strength parameters to derive a brittleness index from a combination of uniaxial compressive strength σ_c and tensile strength σ_t (Altindag, 2003). Whatever system is used, the brittleness index is essentially a lithology (or mineralogy) indicator and the user should make sure to provide the method employed to determine the index thereby mitigating any possible confusion.

Finally, specialized methods specialized methods to characterize pore structure, storage capacity and flow characteristics of tight reservoirs need further development. The techniques currently applied to assess the properties of tight formations are methods that were originally developed for conventional reservoir rocks and coal seams using the assumption that the same transport and storage mechanisms occur in tight reservoirs containing natural gas and crude oil. However, tight formations have a rock composition and structure that is different from coal and conventional reservoirs and many of the techniques employed to characterize porosity are not always suitable for tight formations. In addition, most methods for characterization require pre-drying of the samples which can cause the clay minerals to shrink and, hence, alter the rock structure. As a consequence, the sample and the properties determined therefrom may not to be representative of the in-situ formation. Whether or not the errors are small enough to be discounted, in reality small errors in porosity (which is related to gas storage capacity) can eventually lead to errors in the capacity of the reservoir to hold natural gas and crude oil because of the large areal extent of many tight reservoirs. Understanding the limitations of current characterization techniques and the adjustments that are required to calibrate these measurements to the realities of the tight formation important for accurate assessment of any natural gas or crude oil resource base.

6. US resources

Conventional resources of natural gas (or for that matter, any fossil fuel) exist in discrete, well-defined subsurface accumulations (reservoirs), with permeability values greater than a specified lower limit. Such conventional gas resources can usually be developed using vertical wells, and generally yield the high recovery factors. Briefly, permeability is a measure of the ability of a porous medium, such as that found in a hydrocarbon reservoir, to transmit fluids, such as gas, oil or water, in response to a pressure differential across the medium. In petroleum engineering, permeability is usually measured in units of millidarcies (mD).

By contrast, unconventional resources are found in accumulations where permeability is low (<0.1 mD). Such accumulations include *tight* sandstone formations, coal beds (coal bed methane, CBM) and shale formations (Fig. 3.3). Unconventional resource accumulations tend to be distributed over a larger area than conventional accumulations and usually require advanced technology such as horizontal wells or artificial stimulation in order to be economically productive; recovery factors are much lower — typically of the order of 15–30% v/v of the gas initially in place (GIIP). The mature, organic-rich shale formations that serve as sources for gas and which have received considerable interest, have become an attractive target because they represent a huge resource (500 to 780 × 10^{12} ft^3) and are distributed throughout the forty eight contiguous United States (Fig. 3.4) (Hill and Nelson, 2000).

Due to the unique nature of shale, every basin, play, well and pay zone may require a unique treatment. Briefly comparing the characteristics of some of the current hottest plays can help illustrate the impact of these differences throughout development. It is necessary to study and understand key reservoir parameters for gas shale deposits and these parameters include: (i) thermal maturity, (ii) reservoir thickness, (iii) total organic carbon (TOC) content, (iv) adsorbed gas fraction, (v) free gas within the pores and fractures, and (vi) permeability (Chapter 4) of which the first two parameters are measured as a matter of routine. Thermal maturity is commonly measured in core analysis and reservoir thickness is routinely measured with logs. The calculation of the final four parameters requires a novel approach.

Almost all (96% v/v) of the shale natural gas in proved reserves in 2010 came from the six largest shale plays in the United States (US EIA, 2012). The Barnett again ranked as the largest shale gas play in the United States, significantly higher increases over 2009 proved reserves were registered by the Haynesville/Bossier (which more than doubled 2009 volumes) and the

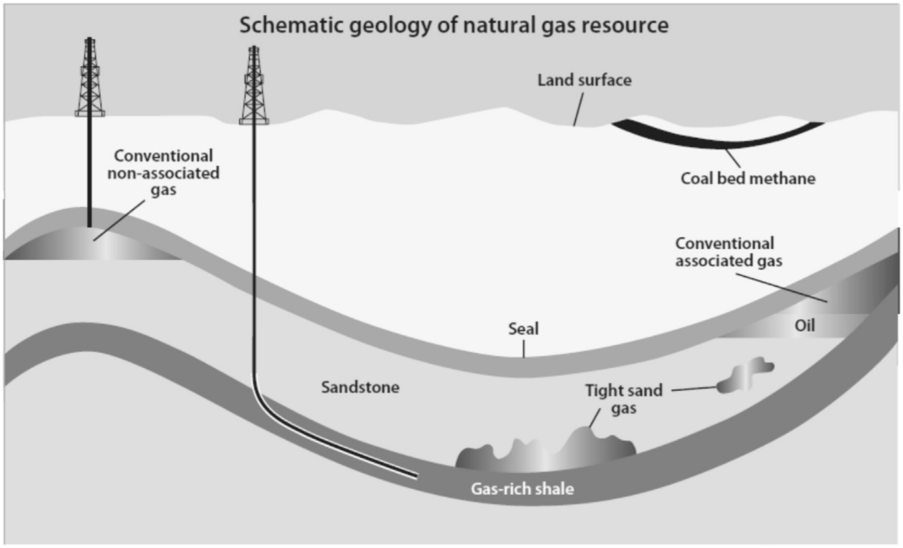

FIG. 3.3 Illustration of the conventional and unconventional gas reservoirs. *From: US EIA (2011). Energy Information Administration, United States Department of Energy, Washington, DC.*

Marcellus (which nearly tripled). Among these six shale plays, the only decline from 2009 volumes was in the Antrim of northern Michigan – a mature, shallow biogenic shale gas play discovered in 1986 that is no longer being developed at the same pace as the other leading shale resources.

However, there are other gas shale resources that are of increasing importance to the United States energy balance and economics. These must not be ignored and the predominant shale gas resources in the United states are listed below in *alphabetical order* and not in order of preference or importance.

6.1 Antrim shale

The Antrim Shale (Michigan Basin) is part of an extensive, organic-rich shale depositional system that covered large areas of the ancestral North American continent in the Middle-to-Late Devonian. The intracratonic Michigan basin was one of several depocenters situated along the Eastern Interior Seaway. The basin has been filled with more than 17,000 feet of sediment, 900 feet of which comprises the Antrim Shale and associated Devonian-Mississippian rocks. The base of the Antrim, near the center of the modern structural basin, is approximately 2400 feet below sea level (US EIA, 2011).

The Antrim shale is a black, organic rich bituminous shale which is divided into four members, from base to top: the Norwood, Paxton, Lachine, and upper members. The upper members are overlaid by the Greenish-gray Ellsworth Shale. The stratigraphy of the Antrim shale stratigraphy is relatively straightforward and wells are typically completed in the Lachine and Norwood members of the lower Antrim, whose aggregate thickness approaches 160 feet. The total organic carbon (TOC) content of the Lachine and Norwood ranges from 0.5

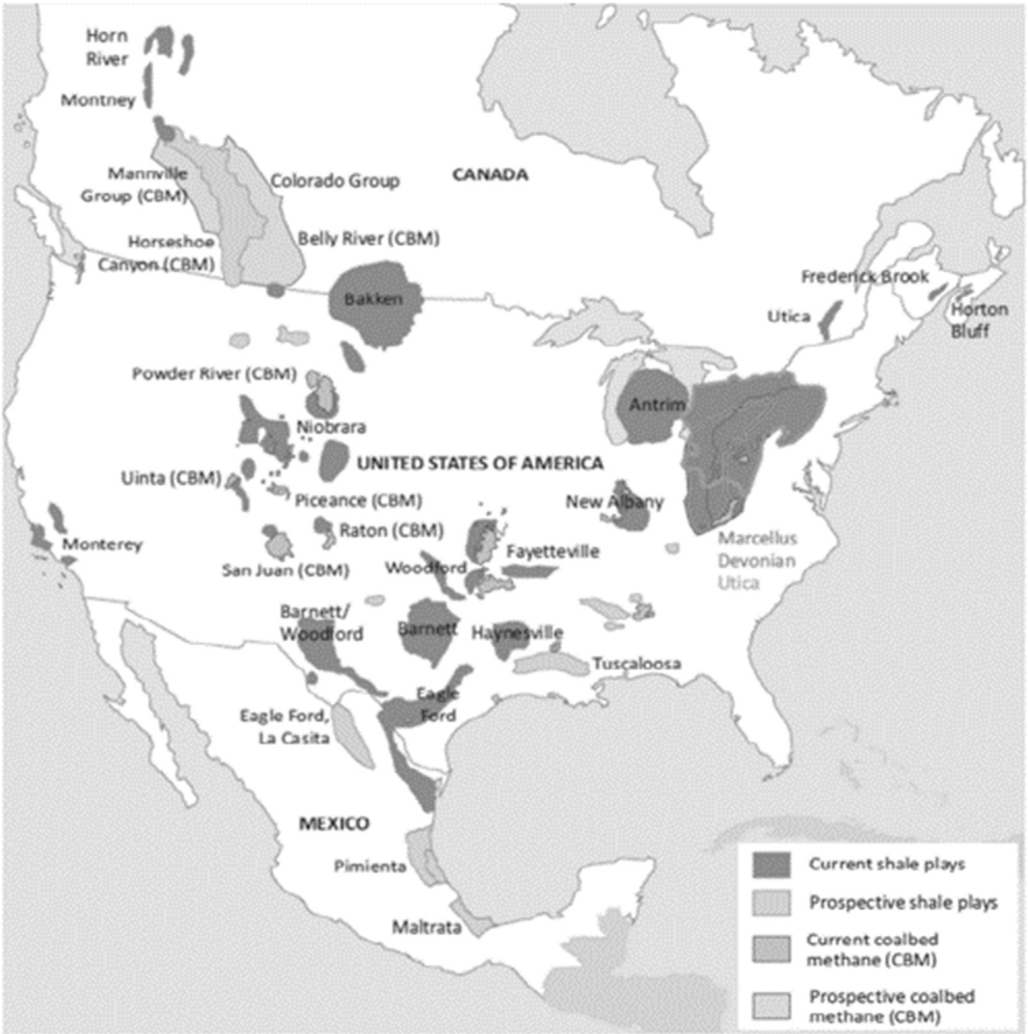

FIG. 3.4 Shale gas resources (shale gas plays) in the contiguous United States, Canada, and Mexico. *Adapted from US EIA (2012). Energy Information Administration, United States Department of Energy, Washington, DC.*

to 24% w/w. These black shale formations are silica rich (20–41% w/w microcrystalline quartz and wind-blown silt) and contain abundant dolomite and limestone concretions and carbonate, sulfide, and sulfate cements. The remaining lower Antrim unit, the Paxton, is a mixture of lime mudstone and gray shale lithology (Martini et al., 1998) containing 0.3–8% w/w total organic carbon and 7–30% w/w silica. Correlation of the fossil alga *Foerstia* has established time equivalence among the upper part of the Antrim Shale, the Huron Member of the Ohio Shale of the Appalachian basin, and the Clegg Creek Member of the New Albany Shale of the Illinois basin (Roen, 1993).

Typical depths for the entire Antrim shale unit range from 500 to 2300 feet and the areal extent is roughly approximately 30,000 square miles (US EIA, 2011). The entire area is overlain by Devonian and Mississippian sediments and hundreds of feet of glacial till. The Antrim mineralogy shows the shale to be laminated with very fine grains. The composition consists mainly of illite and quartz with small quantities of organic material and pyrite.

The Antrim Shale has an organic matter up to 20% w/w, and is mainly made up of algal material. The vitrinite reflectance is in the range of 0.4–0.6, indicating that the shale is thermally immature. The shale is also shallow and there is a high concentration of methane in the composition, which would lead one to assume the gas is of a microbial origin, but, $\delta^{13}C$ values indicate a more thermogenic origin (Martini et al., 1996). For shallow wells in the Antrim shale, the gas is of microbial origin. Deeper wells have a mix of thermogenic gas and microbial gas. For gas compositions with $C1/(C2+C3) < 100$ the gas origin is thermogenic, and this occurs for the gas present in the Niagaran formation which under lays the Antrim Shale. Since the Antrim has so many natural fractures, it is reasonable to assume there is migration of gas from the Niagaran formation in to the Antrim Shale.

The Antrim shale has two main ways of storing gas: absorption and free gas in the pore volume. The lower Norwood member has a higher adsorption capacity (approximately 115 ft^3 per ton) than the Lachine member (approximately 85 ft^3 per ton) (Kuuskraa et al., 1992). This is an important factor to consider when designing a fracture treatment because it would be more beneficial to have more of the proppant in the zone with the highest gas content. The free gas in the pore space can account for up to 10% v/v of the total gas in place, but it is still not clear on how dependant the free gas is on the water in place. The very low permeability of the matrix could make it very difficult if not impossible to remove a significant portion of the free gas.

Two dominant sets of natural fractures have been identified in the northern producing trend, one oriented toward the northwest and the other to the northeast and both exhibiting sub-vertical to vertical inclinations. These fractures, generally uncemented or lined by thin coatings of calcite, have been mapped for several meters in the vertical direction and tens of meters horizontally in surface exposures. Attempts to establish production in the Antrim outside this trend have commonly encountered organic, gas-rich shale but minimal natural fracturing and, hence, permeability (Hill and Nelson, 2000).

Thus, the Antrim Shale is highly fractured for a shale reservoir. Fracture spacing can be as close as 1–2 feet, compared to 10–20 feet for the Barnett shale. These fractures can create permeability-thicknesses in the range of 50–5000 md-ft, which increases gas production. But, it also helps water flow, and thus most wells produce large amounts of water which must be disposed.

6.2 Bakken shale

The Bakken Shale of the Williston Basin of Montana and North Dakota has seen a similar growth rate to the Barnett. The Bakken is another technical play in which the development of this unconventional resource has benefitted from the technological advances in horizontal wells and hydraulic fracturing. In April 2008, the United States Geological Survey (USGS) released an updated assessment of the undiscovered technically recoverable reserves for this shale play estimating there are 3.65 billion barrels (3.65×10^9 bbls) of oil, 1.85 trillion cubic feet (1.85×10^{12} ft^3) of associated natural gas, and 148 million barrels (148×10^6 bbls) of natural gas liquids in the play (USGS, 2008; US EIA, 2011, 2014).

The Bakken shale formation differs from other shale plays in that it is an oil reservoir, a dolomite layered between two shale formations, with depths ranging from around 8000 to 10,000 feet from which oil, gas and natural gas liquids are produced. Each succeeding member of the Bakken formation – lower shale, middle sandstone and upper shale member – is geographically larger than the one below. Both the upper and lower shale formations, which are the crude oil source rocks, present fairly consistent lithology, while the middle sandstone member varies in thickness, lithology and petrophysical properties.

The Bakken shale formation is not as naturally fractured as the Barnett shale formation and, therefore, requires more traditional fracture geometry with both longitudinal and transverse fractures. Diversion methods are used throughout hydraulic fracture treatments, which primarily use gelled water fracture fluids, although there is a growing trend toward the use of an intermediate strength proppant. Recently, the Bakken gas shale has seen an increase in activity, and the trend is toward longer laterals – up to 10,000 feet for single laterals in some cases. In addition, there is also a trend to drill below the lower Bakken shale and fracture upwards.

6.3 Barnett shale

The wedge-shaped Fort Worth basin covers approximately 15,000 square miles in North-Central Texas and is centered along the north-south direction, deepening to the north and outcropping at the Liano uplift in Liano County (Bowker, 2007; Jarvie et al., 2007; EISA, 2011, 2014). The Cambrian Riley and Hickory formations are overlaid by the Viola-Simpson and Ellenburger groups. The Viola-Simpson limestone group is found in Tarrant and Parker counties and acts as a barrier between the Barnett and the Ellenburger formation. The Ellenburger formation is a very porous, karst aquifer (Zuber et al., 2002) that if fractured will produce copious amounts of highly saline water, effectively shutting down a well with water disposal cost.

A karst aquifer is a topography that is formed from the dissolution of soluble rocks such as limestone ($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$), and gypsum ($CaSO_4$). It is characterized by underground drainage systems with sinkholes and cavers. It has also been documented for more weathering-resistant rocks, such as quartzite – a hard, non-foliated metamorphic rock which was originally pure quartz (SiO_2) sandstone. The sandstone is converted into quartzite through heating and pressure usually related to tectonic compression. Pure quartzite is usually white to gray, though quartzites often occur in various shades of pink and red due to varying amounts of iron oxide (Fe_2O_3). Other colors, such as yellow, green, blue and orange, are due to other minerals.

Subterranean drainage may limit surface water, with few to no rivers or lakes. However, in regions where the dissolved bedrock is covered (perhaps by debris) or confined by one or more superimposed non-soluble rock strata, distinctive karst features may occur only at subsurface levels and can be totally missing above ground.

Geochemical and reservoir parameters for the Barnett Shalein the Fort Worth basin differ markedly from those of other gas-productive shales, particularly with respect to gas in place. For example, Barnett shale gas is thermogenic in origin and hydrocarbon generation began in the Late Paleozoic, continued through the Mesozoic, and ceased with uplift and cooling during the Cretaceous (Jarvie et al., 2001, 2007). In addition, organic matter in the Barnett shale formation has generated liquid hydrocarbon derivatives and Barnett-sourced oils in other formations, ranging from Ordovician to Pennsylvanian in age, in the western Fort Worth basin (Jarvie et al., 2001, 2007) – cracking of this oil may have contributed to the gas-in-place resource.

The Mississippian-age Barnett Shale overlies the Viola-Simpson group. The Barnett shale is varies in thickness from 150 to 800 feet, and is the most productive gas shale in Texas. The permeability ranges from 7 to 50 nanodarcies and the porosity from 4 to 6% v/v (Montgomery et al., 2005; Cipolla et al., 2010). In addition, well performance of the Barnett Shale changes significantly with changing produced fluid type, depth and formation thickness (Hale and William, 2010) and on the type of completion method implemented and the large hydraulic fracture treatments (Ezisi et al., 2012).

The three most important production related structures in the basin include both major and minor faulting, fracturing, and karst-related collapse features (Franz et al., 2005). Fracturing is important to gas production because it provides a conduit for gas to flow from the pores to the wellbore, and it also increases exposure of the well to the formation. The Barnett shale formation exhibits complex fracture geometry which often creates difficulty in estimating fracture length and exposure to the formation due to the complex geometry. The fracturing is believed to be caused by the cracking of oil into gas. This cracking can cause a ten-fold increase in the hydrocarbon volume, increasing the pressure until the formation breaks. The precipitation of calcium carbonate in the fractures can cut down on the conductivity of the fractures. This precipitation is hard to detect on logs, and can cause a well location that appears to be good on seismic into an unproductive well. This precipitation is also hard to treat with acidization due to the long distances the acid is required to travel before making a noticeable impact on production.

Change in gas content with pressure occurs in the Barnett shale with a typical reservoir pressure in the range of 3000–4000 psi (Franz et al., 2005). In low permeability formations, pseudo radial flow can take over 100 years to be established. Thus, most gas flow in the reservoir is a linear flow from the near fracture area toward the nearest fracture face. Faulting and karst-related collapse features are important mainly in the Ellenburger formation.

In addition to drilling longer laterals, current trends in the Barnett are toward bigger hydraulic fracturing projects and more stages. Infills are being drilled and testing of spacing is down to 10 acres, while re-fracturing of the first horizontal wells from 2003 to 2004 has commenced; both infills and refracts are expected to improve the *estimated ultimate recovery* from 11 to 18% v/v. In addition, pad drilling (Chapter 4), especially in urban areas, and recycling of water are growing trends in the Barnett shale, as elsewhere.

6.4 Baxter shale

The Baxter Shale is stratigraphically equivalent to the Mancos, Cody, Steele, Hilliard, and Niobrara/Pierre formations (US EIA, 2011) and was deposited in hundreds of feet of water in the Western Interior Seaway from approximately ninety to eighty million years ago (Coniacean to lower Campanian) and consists of approximately two thousand five hundred feet of dominantly siliceous, illitic, and calcareous shale that contains regionally correlative coarsening-upward sequences of quartz-and carbonate-rich siltstones several tens of feet thick. The total organic carbon content ranges from 0.5 to 2.5% w/w in the shale and from 0.25 to 0.75% w/w in the siltstones. Measured porosities in both the shale and siltstones typically range from 3% to 6% with matrix permeability of 100−1500 nanodarcies. The resource area is defined by numerous wells with gas shows and over-pressuring in the Baxter shale with gradients ranging from 0.6 to 0.8 psi/ft at depths greater than ten thousand feet.

Gas production has been established from the Baxter Shale in twenty two vertical wells and three horizontal wells in the Vermillion Basin of northwestern Colorado and adjacent Wyoming. Production comes mainly from the silt-rich intervals as determined by production logs. The productive area in the Baxter Shale has vitrinite reflectance values approaching 2% and is in the dry gas generation window. A challenge within this reservoir is the ability to economically access this large unconventional gas accumulation. This is not a classic 100- to 300-foot-thick organic-rich shale gas reservoir. Instead it is a very large hydrocarbon resource stored in two thousand five hundred feet of shale with interbedded siltstone intervals. 3-D seismic data have proved useful in helping define potential fracture networks in the Baxter shale that can be targeted with horizontal wells.

6.5 Caney shale

The Caney Shale (Arkoma Basin, Oklahoma) is the stratigraphic equivalent of the Barnett Shale in the Ft. Worth Basin. The formation has become a gas producer since the large success of the Barnett shale formation. The Caney Shale, Chesterian age, was deposited in the Oklahoma part of the Arkoma Basin one of a series of foreland basins that formed progressively westward along the Ouachita Fold Belt from the Black Warrior Basin in Mississippi to basins in southwest Texas. The Arkoma Basin in Oklahoma is in the Southeast corner of the state north and northwest of the Ouachita Mountains. The Caney shale formation dips southward from a depth of three thousand feet in northern McIntosh County, Oklahoma to twelve thousand feet north of the Choctaw thrust. The Caney formation thickens toward the southeast from 90′ at its northwest edge to 220′ along the Choctaw fault in the south. It can be subdivided into six intervals based on characteristics of the density and resistivity logs.

Reported average total organic carbon values the Caney formation range from 5 to 8% w/w, which show a linear correlation with density. Mud log gas shows have a strong correlation with desorbed gas values that range from one hundred and twenty to one hundred and fifty cubic feet per ton of shale. Estimates of gas in place for the Caney range from thirty to forty billion cubic feet (30 to 40 $\times$ 10^9 ft^3).

6.6 Chattanooga shale

The Chattanooga Shale (Black Warrior Basin) and has been considered as a rich oil shale formation (Rheams and Neathery, 1988). The Chattanooga sits within the thermogenic gas window in much of the Black Warrior Basin and may thus contain significant prospects for natural gas. The Chattanooga disconformity overlies Ordovician through Devonian strata, and the time value of the disconformity increases northward (Thomas, 1988). The Chattanooga is overlain sharply by the Lower Mississippian Maury Shale, which is commonly thinner than 2 feet, and the Maury is in turn overlain by the micritic Fort Payne Chert. The Chattanooga Shale in Alabama was apparently deposited in dysoxic to anoxic subtidal environments and can be considered as a cratonic extension of the Acadian foreland basin (Ettensohn, 1985).

The thickness of the Chattanooga varies significantly within the Black Warrior Basin. The shale is thinner than 10 feet and is locally absent in much of Lamar, Fayette, and Pickens Counties, which is the principal area of conventional oil and gas production in the Black Warrior Basin. For this reason, the Chattanooga has not been considered to be the principal source rock for the conventional oil and gas reservoirs in this area. The shale is thicker than 30 feet in a belt that extends northwestward from Blount County into Franklin and Colbert Counties. A prominent depocenter is developed along the southwestern basin margin in Tuscaloosa and Greene Counties. Here, the shale is consistently thicker than 30 feet and is locally thicker than 90 feet.

The Chattanooga Shale is in some respects analogous to the Barnett Shale of the Fort Worth Basin in that it is an organic-rich black shale bounded by thick, mechanically stiff limestone units that may help confine induced hydrofractures within the shale (Hill and Jarvie, 2007; Gale et al., 2007). Because the Chattanooga is relatively thin, horizontal drilling combined with controlled hydrofracturing may maximize production rates.

6.7 Conasauga shale

The Conasauga shale gas formation (Conesauga shale gas formation, Alabama) continues to be developed primarily in northeast Alabama (US EIA, 2011, 2014). With the exception of one well in Etowah County and one well in Cullman County, all of the development has been in St. Clair County. Etowah and St. Clair Counties are located northeast of Birmingham in the Valley and Ridge Province of Alabama. Cullman County is north of Birmingham in the Cumberland Plateau Province.

This shale formation it represents the first commercial gas production from shale in Alabama, but because it is geologically the oldest and most structurally complex shale formation from which gas production has been established. The Conasauga differs from other gas shale formations in several respects. The productive lithology is thinly inter-bedded shale and micritic limestone that can contain more than 3% w/w total organic carbon.

The Conasauga shale is of Middle Cambrian age and can be characterized as a shoaling-upward succession in which shale passes vertically into a broad array of inner ramp carbonate facies. The shale was deposited on the outer ramp, and the shale is thickest in basement grabens that formed during late Precambrian to Cambrian Iapetan rifiting (Thomas et al., 2000). The shale facies of the Conasauga is part of the weak litho-tectonic unit that hosts the basal detachment of the Appalachian Thrust Belt in Alabama (Thomas, 2001; Thomas and Bayona, 2005). The shale has been thickened tectonically into anti-formal stacks that have been interpreted as giant shale duplexes, or mushwads (Thomas, 2001). In places, the shale is thicker than 8000 feet, and the shale is complexly folded and faulted at outcrop scale.

Surface mapping and seismic exploration reveal that at least three Conasauga anti-forms are preserved in the Alabama Appalachians. Exploration has focused primarily on the southeastern portion of the Gadsden anti-form, which is in St. Clair and Etowah Counties. The Palmerdale and Bessemer anti-forms constitute the core of the Birmingham anticlinorium. The Palmerdale and Bessemer structures are overlain by a thin roof of brittle Cambrian-Ordovician carbonate rocks, and Conasauga shale facies are exposed locally. The Palmerdale structure is in the heart of the Birmingham metropolitan area and thus may be difficult to develop, whereas the southwestern part of the Bessemer structure is in rural areas and may be a more attractive exploration target. Additional thick shale bodies may be concealed below the shallow Rome thrust sheet in Cherokee and northeastern Etowah Counties and perhaps in adjacent parts of Georgia (Mittenthal and Harry, 2004).

6.8 Eagle Ford shale

The Eagle Ford shale (discovered in 2008) is a sedimentary rock formation from the Late Cretaceous age underlying much of South Texas which covers three thousand square miles and consists of an organic-rich marine shale that also has been found to appear in outcrops (US EIA, 2011). This hydrocarbon-producing formation rich in oil and natural gas extends from the Texas-Mexico border in Webb and Maverick counties and extends 400 miles toward East Texas. The formation is fifty miles wide and an average of two hundred and fifty feet thick at a depth between four thousand and twelve thousand feet. The shale contains a high amount of carbonate which makes it brittle and easier to apply hydraulic fracturing to produce the oil or gas.

The Eagle Ford shale formation is estimated to have 20.81 trillion cubic feet (20.81 × 1012 ft^3) of natural gas and 3.351 billion barrels (3351 × 109 bbls) of oil.

6.9 Fayetteville shale

With productive wells penetrating the Fayetteville shale (Arkoma Basin) at depths between a few hundred and 7000 feet, this formation is somewhat shallower than the Barnett shale formation (US EIA, 2011). Mediocre production from early vertical wells stalled development in the vertically fractured Fayetteville, and only with recent introduction of horizontal drilling and hydraulic fracturing has drilling activity increased.

In the most active Central Fayetteville Shale, horizontal wells are drilled using oil-based mud in most cases, and water-based mud in others. In addition, 3-D seismic is gaining importance as longer laterals of 3000-plus feet are drilled and more stages are required for hydraulic fracturing. With growing numbers of wells and a need for more infrastructure – pad drilling is another trend emerging in the Fayetteville.

6.10 Floyd shale

The Upper Mississippian Floyd Shale is an equivalent of the prolific Barnett Shale of the Fort Worth Basin. The shale is an organic-rich interval in the lower part of the Floyd Shale that is informally called the Neal shale, which is an organic-rich, starved-basin deposit that is considered to be the principal source rock for conventional hydrocarbon derivatives in the Black Warrior basin.

The Floyd shale is a black marine shale located stratigraphically below the Mississippian Carter sandstone and above the Mississippian Lewis sandstone (US EIA, 2011, 2014). Although the Carter and Lewis sandstones have historically been the most prolific gas-producing zones in the Black Warrior Basin Region of Alabama, there has been no prior production history reported for the Floyd Shale. The Chattanooga Shale is located below the Floyd and is separated from it in most areas by the Tuscumbia Limestone and the Fort Payne Chert.

The Mississippian Floyd Shale is an equivalent of the prolific Barnett Shale of the Fort Worth Basin and the Fayetteville Shale of the Arkoma Basin and has thus been the subject of intense interest. The Floyd is a broadly defined formation that is dominated by shale and limestone and extends from the Appalachian Thrust Belt of Georgia to the Black Warrior Basin of Mississippi.

Usage of the term, Floyd, can be confusing. In Georgia, the type Floyd Shale includes strata equivalent to the Tuscumbia Limestone, and in Alabama and Mississippi, complex facies relationships place the Floyd above the Tuscumbia Limestone, Pride Mountain Formation, or Hartselle Sandstone and below the first sandstone in the Parkwood Formation. Importantly, not all Floyd facies are prospective as gas reservoirs. Drillers have long recognized a resistive, organic-rich shale interval in the lower part of the Floyd Shale that is called informally the Neal shale (Cleaves and Broussard, 1980; Pashin, 1994). In addition to being the probable source rock for conventional oil and gas in the Black Warrior Basin, the Neal has the greatest potential as a shale-gas reservoir in the Mississippian section of Alabama and Mississippi. Accordingly, usage of the term, Neal, helps specify the facies of the Floyd that contains prospective hydrocarbon source rocks and shale-gas reservoirs.

6.11 Haynesville shale

The Haynesville Shale (also known as the Haynesville/Bossier) is situated in the North Louisiana Salt Basin in northern Louisiana and eastern Texas with depths ranging from 10,500 to 13,500 feet (US EIA, 2011). The Haynesville is an Upper Jurassic-age shale bounded by sandstone (Cotton Valley Group) above and limestone (Smackover Formation) below.

The Haynesville Shale covers an area of approximately 9000 square miles with an average thickness of 200−300 feet. The thickness and areal extent of the Haynesville has allowed operators to evaluate a wider variety of spacing intervals ranging from 40 to 560 acres per well. Gas content estimates for the play are 100−330 scf/ton. The Haynesville formation has the potential to become a significant shale gas resource for the United States with original gas-in-place estimates of 717 trillion cubic feet (717×10^{12} ft^3) and technically recoverable resources estimated at 251 trillion cubic feet (251×10^{12} ft^3).

Compared to the Barnett shale, the Haynesville shale is extremely laminated, and the reservoir changes over intervals as small as four inches to one foot. In addition, at depths of 10,500 to 13,500 feet, this play is deeper than typical shale gas formations creating hostile conditions. Average well depths are 11,800 feet with bottomhole temperatures averaging

155 °C (300 °F) and wellhead treating pressures that exceed 10,000 psi. As a result, wells in the Haynesville require almost twice the amount of hydraulic horsepower, higher treating pressures and more advanced fluid chemistry than the Barnett and Woodford shale formations.

The high-temperature range, from 125 °C (260 °F) to 195 °C (380 °F), creates additional problems in horizontal wells, requiring rugged, high-temperature/high-pressure logging evaluation equipment. The formation depth and high-fracture gradient demand long pump times at pressures above 12,000 psi. In deep wells, there is also concern related to the ability to sustain production with adequate fracture conductivity. In large volumes of water for fracturing, making water conservation and disposal a primary issue.

The Bossier Shale, often linked with the Haynesville shale is a geological formation that produces hydrocarbon and delivers large amounts of natural gas when properly treated. While there is some confusion when distinguishing Haynesville shale from the Bossier Shale, it is a relatively simple comparison – the Bossier Shale lies directly above the Haynesville shale but lies under the Cotton Valley sandstones. However, some geologists still consider the Haynesville shale and the Bossier Shale one in the same.

The thickness of the Bossier Shale is approximately 1800 feet in the area of interest. The productive zone is located in the upper 500–600 feet of the shale. The Bossier shale is located in eastern Texas and northern Louisiana.

The Upper Jurassic (Kimmeridgian to Lower Tithonian) Haynesville and Bossier hale formations of East Texas and northwest Louisiana are currently one of the most important shale-gas plays in North America, exhibiting overpressure and high temperature, steep decline rates, and resources estimated together in the hundreds of trillions of cubic feet. These shale-gas resources have been studied extensively by companies and academic institutions within the last year, but to date the depositional setting, facies, diagenesis, pore evolution, petrophysics, best completion techniques, and geochemical characteristics of the Haynesville and Bossier shales are still poorly understood and new insights are required into Haynesville and Bossier Shale facies, the mechanism of deposition, geochemistry, petrophysics, reservoir quality, and stratigraphy in light of the paleographic setting and regional tectonics.

Haynesville and Bossier Shale deposition was influenced by basement structures, local carbonate platforms, and salt movement associated with the opening of the Gulf of Mexico basin. The deep basin was surrounded by carbonate shelves of the Smackover/Haynesville Lime Louark sequence in the north and east and local platforms within the basin. The basin periodically exhibited restricted environment and reducing anoxic conditions, as indicated by variably increased molybdenum content, presence of framboidal pyrite, and TOC-S-Fe relationships. These organic-rich intervals are concentrated along and between platforms and islands that provided restrictive and anoxic conditions during Haynesville and part of Bossier times.

The mudrock facies range from calcareous-dominated facies near the carbonate platforms and islands to siliceous-dominated lithologies in areas where deltas prograded into the basin and diluted organic matter (e.g., northern Louisiana and northeast Texas). These facies are a direct response to a second-order transgression that lasted from the early Kimmeridgian to the Berriasian. Haynesville and Bossier shales each compose three upward-coarsening cycles that probably represent third-order sequences within the larger second-order transgressive systems and early highstand systems tracts, respectively. Each Haynesville third-order cycle is characterized by unlaminated mudstone grading into laminated and bioturbated mudstone. Most of the three Bossier third-order cycles are dominated by varying amounts of siliciclastic mudstones and siltstones. However, the third Bossier cycle exhibits higher carbonate and an increase in organic productivity in a southern restricted area (beyond the basinward limits of Cotton Valley progradation), creating another productive gas-shale opportunity. This organic-rich Bossier cycle extends across the Sabine Island complex and the Mt. Enterprise Fault Zone in a narrow trough from Nacogdoches County, Texas, to Red River Parish, Louisiana. Similar to the organic-rich Haynesville cycles, each third-order cycle grades from unlaminated into laminated mudstone and is capped by bioturbated, carbonate-rich mudstone facies. Best reservoir properties are commonly found in facies with the highest TOC, lowest siliciclastics, highest level of maturity, and highest porosity. Most porosity in the Haynesville and Bossier is related to interparticle nano- and micropores and, to a minor degree, by porosity in organic matter.

Haynesville and Bossier gas shales are distinctive on wireline logs—high gamma ray, low density, low neutron porosity, high sonic travel time, moderately high resistivity.

6.12 Hermosa shale

The black shale of the Hermosa Group (Utah) consists of nearly equal portions of clay-sized quartz, dolomite and other carbonate minerals, and various clay minerals. The clay is mainly illite with minor amounts of chlorite and mixed layer chlorite-smectite (Hite et al., 1984).

The area of interest for the Hermosa Group black shale is the northeast half of the Paradox basin, the portion referred to as the fold and fault belt. This is the area of thick halite deposits in the Paradox Formation, and consequently narrow salt walls and broad interdome depressions. To the southwest of this stratigraphically controlled structural zone the black shale intervals are fewer and thinner, and they lack the excellent seals provided by the halite. The area encompasses eastern Wayne and Emery Counties, southern Grand County and the northeast third of San Juan County (Schamel, 2005, 2006). The kerogen in the shale is predominantly gas-prone humic type III and mixed type II–III (Nuccio and Condon, 1996).

Numerous factors favor the possible development of shale gas in the black shale intervals of the Hermosa Group. First, the shale are very organic-rich, on the whole the most carbonaceous shale in Utah, and they are inherently gas-prone. Second, they have reached relatively high degrees of thermal maturity across much of the basin. Third and perhaps most significant, the shale is encased in halite and anhydride which retard gas leakage, even by diffusion. Yet it is curious that the Paradox basin is largely an oil province (Morgan, 1992; Montgomery, 1992) in which gas production is historically secondary and associated gas, which relates to the concentration of crude oil development in the shallower targets on the southwest basin margin and in the salt-core anticlines.

6.13 Lewis shale

The Lewis Shale (San Juan Basin) is a quartz-rich mudstone that was deposited in a shallow, off-shore marine setting during an early Campanian transgression southwestward across shoreline deposits of the underlying pro-gradational Cliffhouse Sandstone Member of the Mancos Formation (Nummendal and Molenaar, 1995; US EIA, 2011, 2014). The gas resources of the Lewis Shale are currently being developed, principally through recompletions of existing wells targeting deeper, conventional sandstone gas reservoirs.

The 1000 to 1500 feet thick Lewis Shale is lowermost shore-face and pro-delta deposits composed of thinly laminated (locally bioturbated) siltstones, mudstones and shale. The average clay fraction is just 25% w/w, but quartz is present to the extent of 56% w/w. The rocks are very tight – the typical matrix gas porosity is on the order of 1.7% v/v and the typical gas permeability is on the order of 0.0001 mD. The rocks also are organically lean, with an average total organic carbon content is only 1.0% w/w with a general range of 0.5–1.6% w/w. The reservoir temperature is 46 °C (140 °F). Yet the adsorptive capacity of the rock is 13–38 scf/ton, or approximately 22 billion cubic feet (22×10^9 ft^3) per quarter section (i.e., per 160 acres) (Jennings et al., 1997).

Four intervals and a conspicuous, basin-wide bentonite marker are recognizable in the shale. The greatest permeability is found in the lowermost two-thirds of the section, which may be the result of an increase in grain size and micro-fracturing associated with the regional north-south/east-west fracture system (Hill and Nelson, 2000).

6.14 Mancos shale

The Mancos shale formation (Uintah Basin) is an emerging shale-gas resource (US EIA, 2011, 2014). The thickness of the Mancos (averaging four thousand feet in the Uinta Basin) and the variable lithology present drillers with a wide range of potential stimulation targets. The area of interest for the Mancos Shale is the southern two-thirds of the greater Uinta Basin, including the northern parts of the Wasatch Plateau. In the northern one-third of the basin there have been two few well penetrations of the Mancos Shale, and it is too deep to warrant commercial exploitation of a "low density" resource such as shale gas. The area is within Duchesne, Uintah, Grand, Carbon and the northern part of Emery Counties.

The Mancos Shale is dominated by mudrock that accumulated in offshore and open-marine environments of the Cretaceous Interior seaway. It is 3450 to 4150 feet thick where exposed in the southern part of the Piceance and Uinta Basins (Fisher et al., 1960), and geophysical logs indicate the Mancos to be approximately 5400 feet thick in the central part of the Uinta Basin. The upper part of the formation is inter-tongues with the Mesaverde Group – these tongues typically have sharp basal contacts and gradational upper contacts. Named tongues include the Buck and the Anchor Mine Tongues. An important hydrocarbon-producing unit in the middle part of the Mancos was referred to as the Mancos B Formation, which consists of thinly interbedded and interlaminated, very fine grained to fine-grained sandstone, siltstone, and clay that was interpreted to have accumulated as north-prograding fore slope sets within an open-marine environment. The Mancos B has been incorporated into a thicker stratigraphic unit identified as the Prairie Canyon Member of the Mancos, which is approximately 1200 feet thick (Hettinger and Kirschbaum, 2003).

At least four members of the Mancos have shale-gas potential: (i) the Prairie Canyon (Mancos B), (ii) the Lower Blue Gate Shale, (iii) the Juana Lopez, and (iv) the Tropic-Tununk Shale. Organic matter in the shale has a large fraction of Terrigenous material derived from the shorelines of the Sevier belt. The thickness of the organic-rich zones within individual system tracts exceeds twelve feet. Vitrinite reflectance values from a limited number of samples at the top of the Mancos range from 0.65% at the Uinta Basin margins to >1.5% in the central basin.

Across most of Utah the Mancos Shale has not been sufficiently buried to have attained the levels of organic maturity required for substantial generation of natural gas, even in the humic kerogen-dominant (type II–III) shale that characterize this group (Schamel 2005, 2006). However, vitrinite reflectance values beneath the central and southern Uinta Basin are well within the gas generation window at the level of the Tununk Shale, and even the higher members of the Mancos Shale. In addition to the *in situ* gas within the shale, it is likely that some of the gas reservoired in the silty shale intervals has migrated from deeper source units, such as the Tununk Shale or coals in the Dakota.

The Mancos Shale warrants consideration as the significant gas reservoir and improved methods for fracture stimulation tailored to the specific rock characteristics of the Mancos lithology are required. The well completion technologies used in the sandstones cannot be applied to the shale rocks without some reservoir damage.

6.15 Marcellus shale

The Marcellus Shale (Appalachian Basin), also referred to as the Marcellus Formation, is a Middle Devonian black, low density, carbonaceous (organic rich) shale that occurs in the subsurface beneath much of Ohio, West Virginia, Pennsylvania, and New York. Small areas of Maryland, Kentucky, Tennessee, and Virginia are also underlain by the Marcellus Shale (US EIA, 2011).

The Marcellus Shale formations are 400 million years in the making, stretching from western Maryland to New York, Pennsylvania and West Virginia and encompassing the Appalachian region of Ohio along the Ohio River. It has been estimate that the Marcellus shale formation could contain as much as 489 trillion cubic feet of natural gas, a level that would establish the Marcellus as the largest natural gas resource in North America and the second largest in the world.

Throughout most of its extent, the Marcellus is nearly a mile or more below the surface. These great depths make the Marcellus Formation a very expensive target. Successful wells must yield large volumes of gas to pay for the drilling costs that can easily exceed a million dollars for a traditional vertical well and much more for a horizontal well with hydraulic fracturing. There are areas where the thick Marcellus Shale can be drilled at minimum depths and tends to correlate with the heavy leasing activity that has occurred in parts of northern Pennsylvania and western New York.

Natural gas occurs within the Marcellus Shale in three ways: (i) within the pore spaces of the shale, (ii) within vertical fractures (joints) that break through the shale, and (iii) adsorbed on mineral grains and organic material. Most of the recoverable gas is contained in the pore spaces. However, the gas has difficulty escaping through the pore spaces because they are very tiny and poorly connected.

The gas in the Marcellus Shale is a result of its contained organic content. Logic therefore suggests that the more organic material there is contained in the rock the greater its ability to yield gas. The areas with the greatest production potential might be where the net thickness of organic-rich shale within the Marcellus Formation is greatest. Northeastern Pennsylvania is where the thick organic-rich shale intervals are located.

The Marcellus shale ranges in depth from 4000 to 8500 feet, with gas currently produced from hydraulically fractured horizontal wellbores. Horizontal lateral lengths exceed 2000 feet, and, typically, completions involve multistage fracturing with more than three stages per well.

Before 2000, many successful natural gas wells had been completed in the Marcellus shale. The yields of these wells were often unimpressive upon completion. However, many of these older wells in the Marcellus have a sustained production that decreases slowly over time and many of them continued to produce gas for decades. To exhibit the interest in this shale formation, The Pennsylvania Department of Environmental Protection reports that the number of drilled wells in the Marcellus Shale has been increasing rapidly. In 2007, 27 Marcellus Shale wells were drilled in the state, however, in 2011 the number of wells drilled had risen to more than 2000.

For new wells drilled with the new horizontal drilling and hydraulic fracturing technologies the initial production can be much higher than what was seen in the old wells. Early production rates from some of the new wells have been over one million cubic feet of natural gas per day. The technology is so new that long term production data is not available. As with most gas wells, production rates will decline over time, however, a second hydraulic fracturing treatment could stimulate further production.

6.16 Neal shale

The Neal shale is an organic-rich facies of the Upper Mississippian age Floyd shale formation. The Neal shale formation has long been recognized as the principal source rock that charged conventional sandstone reservoirs in the Black Warrior Basin (US EIA, 2011) and has been the subject of intensive shale-gas exploration in recent years.

The Neal shale is developed mainly in the southwestern part of the Black Warrior Basin and is in facies relationship with strata of the Pride Mountain Formation, Hartselle Sandstone, the Bangor Limestone, and the lower Parkwood Formation. The Pride Mountain-Bangor interval in the northeastern part of the basin constitutes a progradational parasequence set in which numerous stratigraphic markers can be traced southwestward into the Neal shale. Individual parasequences tend to thin southwestward and define a clinoform stratal geometry in which near-shore facies of the Pride Mountain-Bangor interval pass into condensed, starved-basin facies of the Neal shale.

The Neal formation maintains the resistivity pattern of the Pride Mountain-Bangor interval, which facilitates regional correlation and assessment of reservoir quality at the parasequence level. The Neal shale and equivalent strata were subdivided into three major intervals, and isopach maps were made to define the depositional framework and to illustrate the stratigraphic evolution of the Black Warrior Basin in Alabama. The first interval includes strata equivalent to the Pride Mountain Formation and the Hartselle Sandstone and thus shows the early configuration of the Neal basin. The Pride Mountain-Hartselle interval contains barrier-strand plain deposits. Isopach contours define the area of the barrier-strand plain system in the northeastern part of the basin, and closely spaced contours where the interval is between 25 and 225 feet thick define a southwestward slope that turns sharply and faces southeastward in western Marion County. The Neal starved basin is in the southwestern part of the map area, where this interval is thinner than 25 feet.

The second interval includes strata equivalent to the bulk of the Bangor Limestone. A generalized area of inner ramp carbonate sedimentation is defined in the northeastern part of the formation where the interval is thicker than 300 feet. Muddy, outer-ramp facies are concentrated where this interval thins from 300 to 100 feet, and the northeastern margin of the Neal starved basin is marked by the 100-foot contour. Importantly, this interval contains the vast majority of the prospective Neal reservoir facies, and the isopach pattern indicates that the slope had prograded more than 25 miles southwestward during Bangor deposition.

The final interval includes strata equivalent to the lower Parkwood Formation. The lower Parkwood separates the Neal shale and the main part of the Bangor Limestone from carbonate-dominated strata of the middle Parkwood Formation, which includes a tongue of the Bangor that is called the *Millerella* limestone. The Lower Parkwood is a succession of siliciclastic deltaic sediment that prograded onto the Bangor ramp in the northeastern part of the study area and into the Neal basin in the southern part and contains the most prolific conventional reservoirs in the Black Warrior Basin. The lower Parkwood is thinner than 25 feet above the inner Bangor ramp and includes a variegated shale interval containing abundant slickensides and calcareous nodules, which are suggestive of exposure and soil formation. The area of deltaic sedimentation is where the lower Parkwood is thicker than 50 feet and includes constructive deltaic facies in the Neal basin and destructive, shoal-water deltaic facies along the margin of the Bangor ramp. In the southern part of the study area, the 25-foot contour defines a remnant of the Neal basin that persisted through lower Parkwood deposition. In this area, condensation of lower Parkwood sediment brings middle Parkwood carbonate rocks within 25 feet of the resistive Neal shale.

6.17 New Albany shale

The New Albany Shale (Illinois Basin) is organic-rich shale located over a large area in southern Indiana and Illinois and in Northern Kentucky (US EIA, 2011). The depth of the producing interval varies from 500 feet to 2000 feet depth, with thicknesses of approximately 100 feet. The shale is generally sub-divided into four stratigraphic intervals: from top to bottom, these are (i) Clegg Creek, (ii) Camp Run/Morgan Trail, (iii) Selmier, and (iv) Blocher intervals.

The New Albany shale can be considered to be a *mixed source rock* in which some parts of the basin produced thermogenic gas, and other parts produced biogenic gas. This is indicated by the vitrinite reflectance in the basin, varying from 0.6 to 1.3. It is not known whether circulating ground waters recently generated this biogenic gas or whether it is original biogenic gas generated shortly after the time of deposition.

Most gas production from the New Albany comes from approximately sixty fields in northwestern Kentucky and adjacent southern Indiana. However, past and current production is substantially less than that from either the Antrim Shale or Ohio Shale.

Exploration and development of the New Albany Shale was spurred by the spectacular development of the Antrim Shale resource in Michigan, but results have not been as favorable.

Production of New Albany Shale gas, which is considered to be biogenic, is accompanied by large volumes of formation water. The presence of water would seem to indicate some level of formation permeability. The mechanisms that control gas occurrence and productivity are not as well understood as those for the Antrim and Ohio shale formations.

6.18 Niobrara shale

The Niobrara shale formation (Denver-Julesburg Basin, Colorado) is a shale rock formation located in Northeast Colorado. Northwest Kansas, Southwest Nebraska, and Southeast Wyoming. Oil and natural gas can be found deep below the surface of the Earth at depths of three thousand feet to fourteen thousand feet. Companies drill these wells vertically and even horizontally to get at the oil and natural gas in the Niobrara Formation.

The Niobrara Shale is located in the Denver-Julesburg basin which is often referred to as the DJ Basin. This resource exciting oil shale play is being compared to the Bakken shale resource, is located in North Dakota.

6.19 Ohio shale

The Devonian shale in the Appalachian Basin was the first produced in the 1820s. The resource extends from Central Tennessee to Southwestern New-York and also contains the Marcellus shale formation. The Middle and Upper Devonian shale formations underlie approximately 128,000 square miles and crop out around the rim of the basin. Subsurface formation thicknesses exceed 5000 feet and organic-rich black shale exceeds 500 feet (152 m) in net thickness.

The Ohio Shale (Appalachian Basin) differs in many respects from the Antrim Shale crude oil system. Locally, the stratigraphy is considerably more complex as a result of variations in depositional setting across the basin. The shale formations can be further subdivided into five cycles of alternating carbonaceous shale formations and coarser grained clastic materials. These five shale cycles developed in response to the dynamics of the Acadian orogeny and westward progradation of the Catskill delta.

The Ohio Shale, within the Devonian Shale, consists of two major stratigraphic intervals: (i) the Chagrin Shale and (ii) the underlying Lower Huron Shale.

The Chagrin Shale consists of 700—900 feet of gray shale (Curtis, 2002), which thins gradually from East to West. Within the lower 100—150 feet, a transition zone consisting of interbedded black and gray shale lithology announces the underlying Lower Huron formation. The Lower Huron shale is 200—275 feet of dominantly black shale, with moderate amounts of gray shale and minor siltstone. Essentially all the organic matter contained in the lower Huron is thermally mature for hydrocarbon generation, based on vitrinite reflectance studies.

The vitrinite reflectance of the Ohio Shale varies from 1 to 1.3%, which indicates that the rock is thermally mature for gas generation. The gas in the Ohio Shale is consequently of thermogenic origin. The productive capacity of the shale is a combination of gas storage and deliverability. Gas storage is associated with both classic matrix porosity as well as gas adsorption onto clay and non-volatile organic material. Deliverability is related to matrix permeability although highly limited (10^{-9} to 10^{-7} millidarcies) and a well-developed fracture system.

6.20 Pearsall shale

The Pearsall Shale is a gas bearing formation that garnered attention near the Texas-Mexico border in the Maverick Basin before development of the Eagle Ford shale truly commenced. The Pearsall Shale formation is found below the Eagle Ford formation at depths of seven thousand to twelve thousand feet with a thickness of six hundred to nine hundred feet.

The formation does have the potential to produce liquids east of the Maverick Basin. As of 2012, only a few wells had been drilled in the play outside of the Maverick Basin but early results indicate there is potential that has largely been overlooked.

6.21 Pierre shale

The Pierre Shale, located in Colorado, produced two million cubic feet of gas in 2008. Drilling operators are still developing this rock formation, which lies at depths that vary between 2500 and 5000 feet, and will not know its full potential until more wells provide greater information related to the limits of the formation.

The Pierre shale formation is a division of Upper Cretaceous rocks laid down from approximately one hundred and forty six million to sixty five million years ago and is named for exposures studied near old Fort Pierre, South Dakota. In addition to Colorado, the formation also occurs in South Dakota, Montana, Colorado, Minnesota, New Mexico, Wyoming, and Nebraska. The formation consists of approximately 2000 feet of dark gray shale, some sandstone, and many layers of bentonite (altered volcanic-ash falls that look and feel much like soapy clays). In some regions the Pierre Shale may be as little as seven hundred feet feet thick.

The lower Pierre Shale represents a time of significant changes in the Cretaceous Western Interior Seaway, resulting from complex interactions of tectonism and eustatic sea level changes. The recognition and redefinition of the units of the lower Pierre Shale has facilitated understanding of the dynamics of the basin. The Burning Brule Member of the Sharon Springs Formation is restricted to the northern part of the basin and represents tectonically influenced sequences. These sequences are a response to rapid subsidence of the axial basin and the Williston Basin corresponding to tectonic activity along the Absoroka Thrust in Wyoming. Unconformities associated with the Burning Brule Member record a migrating peripheral bulge in the Black Hills region corresponding to a single tectonic pulse on the Absoroka Thrust. Migration of deposition and unconformities supports an elastic model for the formation and migration of the peripheral bulge and its interaction with the Williston Basin.

6.22 Utah shale

There are five kerogen-rich shale units as having reasonable potential for commercial development as shale gas reservoirs. These are (i) four members of the Mancos Shale in northeast Utah - the Prairie Canyon, the Juana Lopez, the Lower Blue Gate, and the Tununk, and (ii) the black shale facies within the Hermosa Group in southeast Utah.

The Prairie Canyon and Juana Lopez Members are both detached mudstone-siltstone-sandstone successions embedded within the Mancos Shale in northeast Utah. The Prairie Canyon Member is up to 1200 feet thick, but the stratigraphically deeper Juana Lopez Member is less than 100 feet. Both are similar in lithology and basin setting to the gas-productive Lewis Shale in the San Juan basin. As in the Lewis Shale, the lean, dominantly humic, kerogen is contained in the shale interlaminated with the siltstone-sandstone. The high quartz content is likely to result in a higher degree of natural fracturing than the enclosing clay-mudstone rocks. Thus, they may respond well to hydraulic fracturing. Also the porosity of the sandstone interbeds averaging 5.4% v/v can enhance gas storage. Both units extend beneath the southeast Uinta basin reaching depths sufficient for gas generation and retention from the gas-prone kerogen. Although not known to be producing natural gas at present, both units are worthy of testing for add-on gas, especially in wells that are programmed to target Lower Cretaceous or Jurassic objectives.

The Lower Blue Gate and Tropic-Tununk shales generally lack the abundant siltstone-sandstone interbeds that would promote natural and induced fracturing, but they do have zones of observed organic richness in excess of 2.0% w/w organic material that might prove to be suitable places for shale gas where the rocks are sufficiently buried beneath the southern Uinta basin and perhaps parts of the Wasatch Plateau.

The black shale facies in the Hermosa Group of the Paradox basin is enigmatic. These shale formations contain mixed type II—III kerogen that should favor gas generation, yet oil with associated gas dominate current production. They are relatively thin, just a few tens of feet thick on average, yet they are encased in excellent sealing rocks, salt and anhydride. In the salt walls (anticlines) the shale formations are complexly deformed making them difficult to develop even with directional drilling methods, but where they are likely less deformed in the interdome areas (synclines) they are very deep. Yet in these deep areas one can expect peak gas generation. The shale formations are over-pressured, which suggests generation currently or in the recent past. Prospects are good that shale gas reservoirs can be developed in the Paradox basin, but it may prove to be technically and economically challenging.

6.23 Utica shale

The Utica shale is a rock unit located approximately four thousand to fourteen thousand feet below the Marcellus shale and has the potential to become an enormous natural gas resource. The boundaries of the deeper Utica Shale formation extend under the Marcellus Shale region and beyond. The Utica shale encompasses New York, Pennsylvania, West Virginia, Maryland and even Virginia. The Utica Shale is thicker than the Marcellus and has already proven its ability to support commercial gas production.

The geologic boundaries of the Utica Shale formation extend beyond those of the Marcellus Shale. The Utica formation, which was deposited 40–60 million years (40 to 60 × 10^6 years) before the Marcellus formation during the Paleozoic Era, is thousands of feet beneath the Marcellus formation. The depth of Utica Shale in the core production area of the Marcellus shale formation production area creates a more expensive environment in which to develop the Utica shale formations. However, in Ohio the Utica shale formation is as little as 3000 feet below the Marcellus Shale, whereas in sections of Pennsylvania the Utica formation is as deep as 7000 feet below the Marcellus formation creating a better economic environment to achieve production from the Utica shale formation in Ohio. Furthermore, the investments in the infrastructure to extract natural gas from the Marcellus shale formation also increase the economic efficiency of extracting natural gas from the Utica shale.

Although the Marcellus Shale is the current unconventional shale drilling target in Pennsylvania. Another rock unit with enormous potential is a few thousand feet below the Marcellus.

The potential source rock portion of the Utica Shale is extensive and underlies portions of Kentucky, Maryland, New York, Ohio, Pennsylvania, Tennessee, West Virginia and Virginia. It is also present beneath parts of Lake Ontario, Lake Erie and part of Ontario, Canada. This geographic extent of potential Utica Shale source rock along with the equivalent Antes Shale of central Pennsylvania and Point Pleasant Shale of. In keeping with this areal extent, the Utica Shale has been estimated to contain (at least) thirty eight trillion cubic feet (38 × 10^{12} $ft^{3)}$ of technically recoverable natural gas (at the mean estimate) according to the first assessment of this continuous (unconventional) natural gas accumulation by the US Geological Survey.

In addition to natural gas, the Utica Shale is also yielding significant amounts of natural gas liquids and oil in the western portion of its extent and has been estimated to contain on the order of nine hundred and forty million barrels (940 × 10^6 bbls) of unconventional oil resources and approximately two hundred and eight million barrels (208 × 10^6 bbls) of unconventional natural gas liquids. A wider estimate place gas resources of the Utica shale, from 2 trillion cubic feet to 69 trillion cubic feet (2 to 69 × 10^{12} ft^3), which put this shale on the same resource level as the Barnett shale, the Marcellus shale, and the Haynesville shale formations.

6.24 Woodford shale

The Woodford Shale, located in south-central Oklahoma, ranges in depth from 6000 to 11,000 feet (US EIA, 2011). This formation is a Devonian-age shale bounded by limestone (Osage Lime) above and undifferentiated strata below. Recent natural gas production in the Woodford Shale began in 2003 and 2004 with vertical well completions only. However, horizontal drilling has been adopted in the Woodford, as in other shale gas plays, due to its success in the Barnett Shale.

The Woodford Shale play encompasses an area of nearly 11,000 square miles. The Woodford play is in an early stage of development and is occurring at a spacing interval of 640 acres per well. The average thickness of the Woodford Shale varies from 120 to 220 feet across the play. The gas content in the Woodford Shale is higher on average than some of the other shale gas plays at 200–300 scf/ton. The original gas-in-place estimate for the Woodford Shale is similar to the Fayetteville Shale at 23 trillion cubic feet (23×10^{12} ft^3) while the technically recoverable resources are estimate at 11.4 trillion cubic feet (11.4×10^{12} ft^3).

Woodford shale stratigraphy and organic content are well understood, but due to their complexity compared to the Barnett shale, the formations are more difficult to drill and fracture. As in the Barnett, horizontal wells are drilled, although oil-based mud is used in the Woodford shale and the formation is harder to drill. In addition to containing chert and pyrite, the Woodford formation is more faulted, making it easy to drill out of the interval; sometimes crossing several faults in a single wellbore is required.

Like the Barnett shale, higher silica rocks are predominant in the best zones for fracturing in the Woodford formation, although the Woodford has deeper and higher fracture gradients. Due to heavy faulting, 3-D seismic is extremely important, as the Woodford formation trends toward longer laterals exceeding 3000 feet with bigger fracture projects and more stages. Pad drilling also will increase as the Woodford shale formation continues expanding to the Ardmore Basin and to West Central Oklahoma in Canadian County.

7. World resources

Significant amounts of shale gas occur outside of the United States in other countries. The initial estimate of technically recoverable shale gas resources in the 32 countries 5760 trillion cubic feet (5760×10^{12} ft^3) (US EIA, 2011). Adding the US estimate of the shale gas technically recoverable resources of 862 trillion cubic feet (862×10^{12} ft^3) results in a total shale gas resource base estimate of 6622 trillion cubic feet (6622×10^{12} ft^3) for the United States and the other 32 countries assessed. To put this shale gas resource estimate in context, the technically recoverable gas resources worldwide are approximately 16,000 trillion cubic feet ($16{,}000 \times 10^{12}$ ft^3), largely excluding shale gas (US EIA, 2011). Thus, adding the identified shale gas resources to other gas resources increases total world technically recoverable gas resources by more than 40% to 22,600 trillion cubic feet ($22{,}600 \times 10^{12}$ ft^3) (US EIA, 2011).

At a country level, there are two country groupings that emerge where shale gas development appears most attractive. The first group consists of countries that are currently highly dependent upon natural gas imports, have at least some gas production infrastructure, and their estimated shale gas resources are substantial relative to their current gas consumption. For these countries, shale gas development could significantly alter their future gas balance, which may motivate development. The second group consists of those countries where the shale gas resource estimate is large (>200 trillion cubic feet, $>200 \times 10^{12}$ ft^3) and there already exists a significant natural gas production infrastructure for internal use or for export. Existing infrastructure would aid in the timely conversion of the resource into production, but could also lead to competition with other natural gas supply sources. For an individual country the situation could be more complex.

The predominant shale gas resources are found in countries (listed alphabetically below).

7.1 Argentina (Neuquén basin)

Argentina has 774 trillion cubic feet (774×10^{12} ft^3) of technically recoverable shale gas, making it the third-largest resource in the world, behind the United States and China. Located on the border of Argentina with Chile, the Neuquén Basin is the largest source of hydrocarbon derivatives, holding 47% v/v of the natural gas reserves 35% v/v of the crude oil reserves of Argentina. Within the basin, the Vaca Muerta Shale formation may hold as much as 240 trillion cubic feet (240×10^{12} ft^3) of exploitable gas.

The largest energy company in Argentina – YPF – has found unconventional tight natural gas and crude oil in the Mendoza province, confirming the extension of the massive Vaca Muerta area. Exploration at the Payun Oeste and Valle del Rio Grande blocks pointed to an estimated one billion barrels (1×10^9 bbls) of oil equivalent (boe) in unconventional oil and gas in Mendoza. Energy resources and reserves in the province, which border the Andes mountain range in western Argentina, currently stand at 685 million (685×10^6) barrels of oil equivalent.

7.2 Canada

Recent estimates (NEB, 2009) in indicate that there is the potential for one quadrillion cubic feet (1×10^{15} ft^3) of gas in place in shale formation in Canada located in different areas but predominantly in the Western Canada Sedimentary basin (WCSB) (Fig. 3.5). However, high uncertainty, because gas shale formations are still in the initial stages of evaluation across Canada, precludes calculating more rigorous resource estimates for Canada at the current time (NEB, 2009).

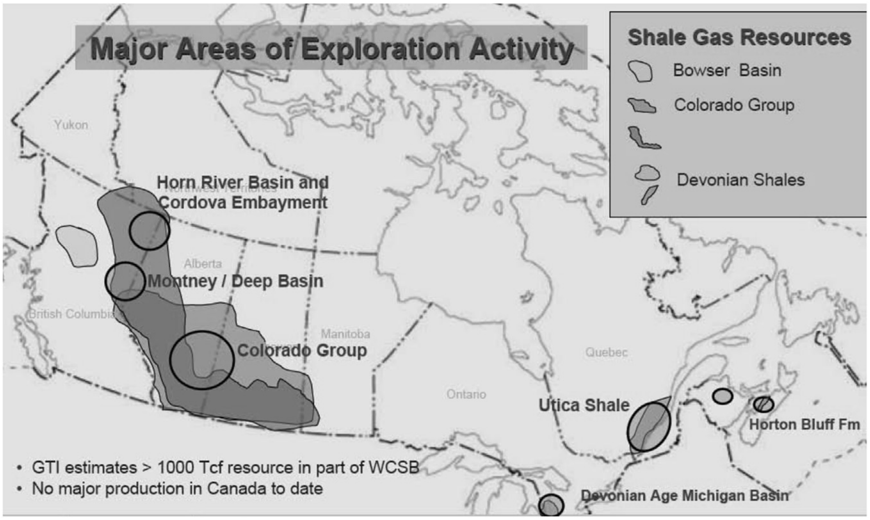

FIG. 3.5 Occurrence of shale gas in Canada, especially the Western Canada Sedimentary basin (WCSB). *Adapted from NEB (2009). A Primer for Understanding Canadian Shale Gas. National Energy Board, Calgary, Alberta, Canada. November.*

7.2.1 Colorado Group

The Colorado Group consists of various shale-containing horizons deposited throughout southern Alberta and Saskatchewan during globally high sea levels of the middle Cretaceous, including the Medicine Hat and Milk River shale-containing sandstones, which have been producing natural gas for over 100 years, and the Second White Speckled Shale, which has been producing natural gas for decades (Beaton et al., 2009).

In the Wildmere area of Alberta, the Colorado Shale is approximately six hundred and fifty feet thick, from which natural gas has potential to produce from five intervals. Unlike shale formations from the Horn River Basin and the Utica Group of Quebec, shale from the Colorado Group produces through thin sand beds and lamina, making it a hybrid gas shale like the Montney shale. Furthermore, the gas produced in the Colorado has biogenic rather than thermogenic origins. This would suggest very low potential for natural gas liquids and an under-pressured reservoir, which is more difficult to hydraulically fracture. Colorado Group shale formations are sensitive to water, which makes them sensitive to fluids used during hydraulic fracturing.

The total volume of gas in the Colorado Group is very difficult to estimate given the wide lateral extent of the shale and variability of the reservoir and the absence of independent and publicly available analyses. However, there could be at least one hundred trillion cubic feet (100×10^{12} ft^3) of gas in place.

7.2.2 Duvernay shale

The Devonian Duvernay shale is an oil and natural gas field located in Alberta, Canada (in the Kaybob area) which extends into British Columbia. The Duvernay Formation (Devonian-Frasnian) of Alberta, Canada is a Type II marine, proven source rock which has yielded much of the oil and gas to the adjacent classical Devonian, conventional fields in carbonate reefs and platform carbonates. Production in these conventional fields is in decline and exploration and development has now shifted to their source, the Duvernay shale. The Devonian is considered the source rock for the light oil resources of the Leduc (Alberta, Canada) reefs, discovery of which in 1947 was one of the defining moments in the past-present-and-future Western Canadian natural gas and crude oil industry.

The Duvernay shale, which can be found just north of the Montney shale is distributed over most of central Alberta and absent in areas of Leduc reef growth, except beneath the Duhamel reef, where it may be represented by a thin development of calcilutite (a dolomite or limestone formed of calcareous rock flour that is typically non-siliceous). At its type section in the East Shale Basin it is the shale formation is 174 fee) thick – it thickens to (246 feet east and southeastward toward the Southern Alberta Shelf. Northeastward the formation reaches 394 feet at its truncation in the subsurface at the pre-Cretaceous unconformity. In the West Shale Basin it averages 197 feet thick and thickens northward, attaining over 820 feet to the east of Lesser Slave Lake.

The formation consists of interbedded dark brown bituminous shale sediments, dark brown, black and occasionally gray-green calcareous shale sediments and dense argillaceous limestone sediments. The shale formations are characteristically petroliferous and exhibit plane parallel millimeter lamination. The addition of minor constituents can alter the color of shale rock. When carbonaceous content of shale is greater than 1% w/w, the shale rock appears to be black in color. Brown, red, and green colors indicate the presence of iron oxide. Clay minerals form the major part of shale rocks and these minerals such as montmorillonite, kaolinite, and illite can be present in shale rocks. At the extreme level, mudrocks and shale rocks contain approximately 95% w/w organic matter.

Based on petrophysics calibrated to core and cuttings samples, the Duvernay formation is characterized by a porosity on the order of 6.0–7.5%, v/v a permeability on the order of 236–805 nD (nanodarcies), and a total organic carbon content on the order of 2.0–7.5% w/w. X-ray diffraction results from core and cuttings samples indicate that the formation is likely very brittle with a low content of clay minerals (26% w/w), amorphous biogenic silica (47% w/w), and a calcite and dolomite matrix on the order of 20% w/w (Switzer, 1994; Fowler et al., 2003).

7.2.3 Horn River basin

Devonian Horn River Basin shale formations were deposited in deep waters at the foot of the Slave Point carbonate platform in northeast British Columbia, which has been producing conventional natural gas for many decades. Horn River Basin shale formations are silica-rich (approximately 55% w/w silica) and approximately four hundred and fifty feet thick. The total organic content is one to six per cent. The rocks are mature, having been heated far into the thermogenic gas window. The Horn River Shale Formation located in British Columbia, is the largest shale gas field in Canada and part of Canadian deposits that amount to as much as 250 trillion cubic feet (250×10^{12} ft^3) of natural gas (Ross and Bustin, 2008).

It should be noted that the Horn River Basin shale gas play also includes the Cordova Embayment and the whole formation extends into both the Yukon Territory and the Northwest Territories, although its northward extent beyond provincial/territorial borders is poorly defined.

7.2.4 Horton Bluff Group

Lacustrine muds of the Horton Bluff Group of the Canadian Maritime Provinces were deposited in the Early Mississippian (approximately three hundred and sixty million years ago) during regional subsidence. The silica content in the Frederick Brook Shale of the Horton Bluff Group in New Brunswick averages 38% w/w but the clay content is also high, on the order of 42% w/w. There are indications that organic content of the Frederick Brook member in Nova Scotia are significantly higher than other Canadian gas shale formations, at 10% w/w, and the pay zone appears to be over five hundred feet thick, sometimes exceeding two thousand five hundred feet in New Brunswick.

There are also indications that most of the gas is adsorbed onto clay and organic matter, and it will take very effective reservoir stimulation to achieve significant production from Nova Scotia shale formations. It is unclear at this time at what proportion of gas is adsorbed onto clay and organic matter in the New Brunswick shale formations.

Analysis indicates that sixty seven trillion cubic feet (67×10^{12} ft^3) of free gas in place is present in the Frederick Brook shale of the Sussex/Elgin sub-basins of southern New Brunswick and sixty nine trillion cubic feet (69×10^{12} ft^3) of gas is present on the Windsor land block in Nova Scotia.

7.2.5 *Montney shale*

The Montney Shale formation is a shale rock deposit located deep below British Columbia, Canada and is located in the Dawson Creek area just south of the Horn Rover shale formation as well as the Duvernay shale formation. Natural gas can be found in large quantities trapped in this tight shale formation.

The formation is a hybrid between a tight gas and shale gas resource and the sandy mudstone formation dates back to the Triassic period and is located beneath the Doig formation at depths ranging from 5500−13,500 feet and is up to 1000 feet thick in places. As such, the Montney shale is poised to become one of the most significant shale gas resources in Canada. However, complicating reservoir characterization is the upper and lower Montney zones in the same area have different mineralogy which affects the formation evaluation data. The lower Montney is especially difficult as conventional open hole logs have historically caused people to believe that the lower Montney to be very tight. While the lower Montney has less porosity than the upper Montney formation, core data over the lower zone has porosity higher than expected.

The gas shale formation play is estimated to contain up to fifty trillion cubic feet (50×10^{12} ft^3) of natural gas trapped within poor permeability shale and siltstone. Horizontal wells are drilled at depths from 5500 13,500 feet and hydraulic fracturing enables the gas to flow more easily. Microseismic monitoring techniques can be used to assess fracture stimulations by locating events along each stage of the fracture and calculating the dimensions, geometry and effective fracture volume. The Montney shale is a unique resource play in that it is a hybrid between tight gas and traditional shale.

The Montney formation is rich in silt and sand (characteristics similar to tight gas) but the source of the natural gas originated from its own organic matter like shale plays. Due to the presence of siltstone and sand, the Montney formation has extremely low permeability and requires higher levels of fracture stimulation.

7.2.6 *Utica Group*

The Upper Ordovician Utica Shale is located between Montreal and Quebec City and was deposited in deep waters at the foot of the Trenton carbonate platform. Later, the shale was caught up in early Appalachian Mountain growth and became faulted and folded on its southeastern side. The Utica is approximately five hundred feet thick and has a total organic content of one to three per cent and has been known for decades as a crude oil source rock for associated conventional reservoirs.

However, unlike other Canadian gas shale formations, the Utica has higher concentrations of calcite, which occur at the expense of some silica. While calcite is still brittle, hydraulic fractures do not transmit as well through it.

7.3 China (Sichuan and Tarim basin)

In 2011, China was estimated that to have 1275 trillion cubic feet (1275×10^{12} ft^3) of technically recoverable shale gas. Since then a government geological survey confirmed a total of 882 trillion cubic feet (882×10^{12} ft^3) of technically recoverable shale gas, excluding Tibet. The Sichuan Basin, located in south central China, accounts for 40% of the tight shale resources of China.

7.4 Poland

Eastern Europe may hold as much as 250 trillion cubic feet (250×10^{12} ft^3) of shale gas, with the Silurian shale gas resource holding as much as 187 trillion cubic feet (187×10^{12} ft^3) of that total. These shale gas resources could reduce the dependence of European countries (i.e. the countries of the European Union) on imports of natural gas and will give Poland (Baltic-Podlasie-Lublin Basins) a strong claim to energy independence because the projected reserves of these basins equate to approximately 300 years of domestic consumption.

7.5 South Africa

In addition to being an area fertile in fossil remains, the Karoo Supergroup (South Africa) might also be one of the most plentiful sources of shale gas in the world. The area is constituted mainly of shale and sandstone and underlies more than two-thirds of the entire area of South Africa and contains an estimated 485 trillion cubic feet (485×10^{12} ft^3) of technically recoverable gas. Shale gas could reduce the dependence of South Africa on coal (currently considered with or without justification as the *bad boy* of fossil fuels) to fuel 85% of the energy needs.

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CHAPTER

4

Development and production

1. Introduction

Reservoir development involves the key scientific problems of reservoir connectivity, flow ability, time variability, and focuses on the forming mechanism and distribution model of geological factors controlling the reservoir development, the control mechanism of geological factors to oil and gas production, the rule of reservoir dynamic evolution during development, and the reservoir characterization and modeling technology (Li et al., 2017). Important progress has been made on theory and technology of reservoir development geology in high water-cut reservoirs, low permeability and tight shale reservoirs, fracture-cavity reservoirs, which makes the reservoir development geology grow as an independent academic subject already. With the development expansion in areas of deep-strata, deep-water, and unconventional hydrocarbon reservoirs (i.e., tight reservoirs), and the increasing difficulties of high water-cut reservoir development, the theory and technology of reservoir development geology remain to be developed in order to support efficient and economic development of tight gas and tight oil reservoirs with a sustainable growth.

The volumes of natural gas and crude oil gas in place in tight reservoirs have been given various estimates and while production is underway in the United States and Canada, production of these resources by other countries has not yet searched the same level of activity. In fact, outside North America, only the few companies proficient in the complex techniques required to produce this gas have shown an active interest in the resources in tight reservoirs. For this reason, improving the recovery factor of any reservoir and driving down operating costs pose strategic challenges for developers and, as such, constitute the main targets of their efforts. The resources of natural gas and crude oil in tight formations have the potential to expand and facilitate the current wave of growth in the natural gas and crude oil gas industries. However, this is not to be taken from granted and issues arise when producing and refining these two resources but nevertheless, the future for the development and production of tight reservoirs holds much promise and may even help to discourage the continuing myths of peak energy (i.e., peak oil and gas) (Islam and Speight, 2016).

Although tight reservoirs world, sometimes associated with conventional natural gas and crude resources, they were long considered a secondary target because of the difficulty of producing natural gas and crude oil from these reservoirs. In the case of the United States, not until conventional resources began to decline did operators – spurred on by fiscal

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incentives − turn to the potential of tight gas and tight oil. Currently, the United States produces approximately 40% v/v of its gas from unconventional tight reservoirs. Elsewhere, the volumes of natural gas and crude oil in place, coupled with improvements in production techniques (such as horizontal drilling and hydraulic fracturing) (Chapter 5), have made it economically feasible to produce other natural gas and crude oil from other tight reservoirs (Chapter 3).

Briefly, hydraulic fracturing is a process that results in the creation of fractures in rocks, the goal of which is to increase the output of a well or a formation (Kundert and Mullen, 2009). The hydraulic fracturing is used to increase or restore the rate of fluid flow within the tight reservoir and horizontal drilling creates maximum borehole surface area in contact with the shale. Hydraulic fracture complexity is the key to unlocking the potential of shale plays.

In the present context, a tight gas reservoir and a tight oil reservoir (collectively, they are unconventional reservoirs) are the terms commonly used to refer to low permeability formations (i.e., low permeability reservoirs) that produce dry natural gas or light tight oil (Chapters 1 and 2). Many of the low permeability reservoirs that have been developed in the past are sandstone, but significant quantities of gas are also produced from low permeability carbonates, shales, and coal seams.

Unconventional reservoirs require some form of stimulation to obtain commercial production. Tight gas and tight oil reservoirs require fracture stimulation to unlock gas from extremely low-permeability formations (Chapter 5). As fracture stimulation is an important aspect of well completions, production companies need to know basic information related to fractures such as whether they will open (and stay open), direction of fracture propagation, dimensions and type of fracture, and whether they will stay in zone. Increasingly, seismic is utilized to provide such information, and to guide drillings and completions. A clear understanding of the geomechanical properties and their distribution explains the reservoir heterogeneity and thus the variation in economic ultimate recovery (EUR) between wells.

Production of gas from coal seams is not the focus of this book but needs to be acknowledged as another unconventional source of natural gas (coalbed methane) (Chapter 1). Also, natural fractures affect both the overall level of permeability in a reservoir. If a reservoir is naturally fractured, it is possible that a horizontal well or multilateral wellbores will be more effective in producing gas than a vertical well with a hydraulic fracture. If a hydraulic fracturing is performed in a reservoir containing an abundance of natural fractures, problems with multiple hydraulic fractures near wellbore, issues related to tortuosity, and excessive fluid leak-off can occur during the fracturing treatment.

Tight formation reservoirs have a common feature insofar as recovery of the gas or oil requires that a well drilled and completed in the tight reservoir must be successfully stimulated to produce at commercial gas flow rates and produce commercial gas volumes. In addition, a vertical well is not always the most effective type of well to drill into a tight formation to recover the gas or fluid resource and other actions are required to commercial development of the resource. Thus, in order to sustain a ready supply of energy, unconventional sources of natural gas and crude oil are being continually investigated and developed.

Recent development of new technologies of formation evaluation and simulating by horizontal drilling and hydraulic fracturing (Chapter 5), especially in the United States Canada has made low productive unconventional tight shale formations and other tight formations (including tight sandstone formations and tight carbonate formations) as well as coalbed

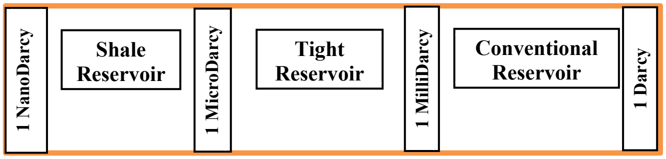

FIG. 4.1 Representation of the differences in permeability of shale reservoirs, tight reservoirs, and conventional reservoirs.

methane formations (Chapter 1) as attractive resources for production of natural gas, gas condensate, and crude oil. However, economic production of tight natural gas and tight crude oil reservoirs is challenging since the permeability of these reservoirs is in the micro-Darcy range (Fig. 4.1) – although shale reservoirs and tight sandstone (or carbonate) reservoirs could have a permeability on the same order of magnitude. Nevertheless, in spite of the shortcoming of low permeability and the inability of the fluids to be mobile within the reservoir system, these reservoirs and their natural gas and or crude oil content do offer a huge potential for current and future energy production.

Unlike conventional natural gas and crude oil reservoirs (Chapter 2), shale formations and tight sandstone or carbonate formations are considered to be the source rock in which the organic material evolved and also, because of the low permeability, became the reservoir rock.

The source rock is important for all hydrocarbon resource accumulations. For tight gas sands, the source rock should be in proximity to the relatively porous deposit so that the expulsion can drive the gas into the porous formation and form the reservoir (Meckel and Thomasson, 2008). The total organic carbon of the source rock should be large enough for generation of a significant amount of hydrocarbon derivatives. Moreover, the source rock should be subjected to heat transformation within the gas-generation window under burial history. Therefore, it is good practice to select exploration targets proximal to organically rich intervals (Coleman, 2008).

Thus, it is considered likely that the natural gas and crude oil remained in the formation in which they were originally produced. Both the shale reservoir system and the tight sandstone (or carbonate) reservoir systems have free gas stored within the pores of the rock matrix, although the tight reservoir system can differ from the conventional reservoir system in possessing the characteristic of gas or oil adsorption on the surface areas associated with organic content and clay (Chapter 2). The relative importance of adsorbed versus free gas and/or oil varies as a function of (i) the amount of organic matter present, (ii) the mineralogy, (iii) the pore size distribution, (iv) processes that contribute to diagenesis, (v) the rock texture as well as (vi) the reservoir pressure and the reservoir temperature (Bustin et al., 2008).

Geologically shale is a sedimentary rock that is predominantly comprised of very fine-grained clay particles deposited in a thinly laminated texture while the term *tight formation* refers to a formation consisting of extraordinarily impermeable, hard sandstone or carbonate rock. Like the shale formations, tight sandstone and carbonate formations are relatively low permeability, sedimentary formations that can contain natural gas and crude oil. When a significant amount of organic matter has been deposited with the sediments, the shale rock can contain organic solid material, which is referred to as *kerogen* (Scouten, 1990; Lee, 1991; Speight, 2008, 2012, 2014, 2016).

The shale formations and other tight formations were originally deposited as mud in low energy depositional environments, such as tidal flats and swamps, where the clay particles and other inorganic particle were deposited from the suspension. During the deposition of these sediments, organic matter was also deposited and deep burial of the sediment resulted in a multi-mineral layered rock (*shale*, *sandstone*, or *carbonate*) that contributed to the heterogeneous nature and laminar nature of the sediment and which can differ significantly between shale formations.

2. Tight reservoirs and conventional reservoirs

Briefly, *conventional gas reservoirs* and conventional crude oil reservoirs contain *free* gas and crude oil, respectively, in interconnected pore spaces that can flow easily to the wellbore i.e., natural flow is possible (Chapters 1 and 2). These reservoirs are identified by distinguishing between the porous rock that contains the natural gas or crude oil and the cap rock as well as the basement rock that constitute a permeability barrier.

On the other hand, *unconventional gas reservoirs* (i.e., shale gas reservoirs) produce from low permeability (tight and now ultra-tight) formations (Chapters 1 and 2). The gas is often sourced from the reservoir rock itself, adsorbed onto the matrix. Although shale gas plays have been in the spotlight recently, natural gas in tight sandstones is actually also an important hydrocarbon resource.

Tight gas sandstone reservoirs are natural extensions of conventional sandstone reservoirs, but with lower permeability and generally lower effective porosity. Hydrocarbons have traditionally been produced from sandstone and carbonate reservoirs with high porosity and permeability. Sandstone reservoirs with permeability lower than 0.1 milliDarcy (mD) were historically not economically producible, but advances in stimulation technology have enabled production from these tight formations. There is some confusion regarding the definition of tight gas sandstone reservoirs; they are sometimes referred to as deep-basin, basin-centered gas accumulation, or pervasive sandstone reservoirs (Meckel and Thomasson, 2008).

The United States Gas Policy Act of 1978 classified tight gas formations as those that have in situ permeability less than 0.1 mD. Thus, sandstone gas reservoir in which the formation has average permeability lower than 0.1 mD is a tight gas play regardless of its depositional environment. These reservoirs can occur in numerous settings, including channelized fluvial systems, such as in the Greater Green River basin (Law, 2002; Shanley, 2004; Ma et al., 2011), alluvial fans, delta fan, slope and submarine fan channels deposits, such as Granite Wash (Wei and Xu, 2015), or shelf margin, such as Bossier sand (Rushing et al., 2008). Some tight gas sandstones contain different depositional facies; the Cotton Valley formation, for example, includes stacked shoreface/barrier bar deposits, tidal channel, tidal delta, inner shelf, and back-barrier deposits. Because of the variety of depositional environments for sandstones and other variations, there is no typical tight gas sandstone reservoir (Holditch, 2006). While drilling, well design, and completion techniques for producing a tight sandstone reservoir are often similar to producing a shale gas reservoir, exploration and resource evaluation for them generally are quite different (Kennedy et al., 2012).

In many cases, tight gas sandstone resources can be developed more easily than shale gas reservoirs as the rocks generally have higher quartz content, and are more brittle and easier to complete for production. More generally, the low productivity typical of tight gas reservoirs is usually insufficient to ensure the economic viability of their development. The solution is to connect as much of the reservoir volume as possible to the well (provided this can be done cost-effectively), thereby limiting the number of boreholes needed to produce the reserves of natural gas and/or crude oil. The best well design (economic optimum) can be determined based on the identification and appraisal of the reservoirs. Due to the low permeability of these formations, it is necessary to stimulate the reservoir by creating a fracture network to give enough surface area to allow sufficient production from the additional *enhanced* reservoir permeability. Options include vertical wells with single or multiple hydraulic fractures, horizontal or sharply deviated wells, multilateral drains, and multiple fractures in multilateral completions (Chapter 5).

Because of the uncertainties related to the identification of tight reservoirs and the differences that exist between such reservoirs, development of a natural gas field or a crude oil field always poses challenges. For example, meandering formation that are the reservoirs may overlap to varying extents and may also be interconnected to varying degrees. As a result, drilling a well to produce a natural gas or crude oil reservoir with limited or no connections to other zones will yield only a small volume of gas. The key is to site the wells in zones known to have extensive connections to other reservoirs in order for each well to produce enough gas to be economically viable. Meeting this challenge requires comprehensive imaging of the spatial distribution of the reservoir system. The analysis of productivity test data provided valuable information concerning the extent of the sandstone lenses. Based on these data, the geologists and reservoir engineers can replicate the reservoir system in the form of a reservoir model and highlight the differences in well productivity according to the spatial configuration and interconnection of the reservoirs.

Thus, the analysis of any reservoir, including a tight reservoir, should always begin with a thorough understanding of the geologic characteristics of the formation (Chapter 2). The important geologic parameters for a play or basin are: (i) the structural and tectonic regime, (ii) the regional thermal gradients, and (iii) the regional pressure gradients. Furthermore, knowing the stratigraphy in a basin is an important aspect of resource development and can affect drilling evaluation, completion and stimulation operations. For example, important (if not, essential) geologic parameters that should be studied for each stratigraphic unit are: (i) the depositional system, (ii) the genetic facies, (iii) the textural maturity, (iv) the mineralogy, (v) any diagenetic processes, (vi) reservoir dimensions, and last, but certainly not least, (vii) the presence of natural fractures. When most sandstone sediments are deposited, the pores and pore throats are connected, thereby resulting in high permeability of the sediment. The original porosity and permeability of a sandstone is determined by characteristics such as mineral composition, pore type, grain size, and texture. After deposition and burial, the grains and matrix are commonly altered by the physical effects of compaction and by chemical changes (diagenesis).

To complete, fracture, and produce a natural gas or crude oil from a tight reservoir, each layer of the formation and the formations above and below the gas-containing or oil-containing formation must be thoroughly evaluated in term of: (i) formation thickness, (ii) porosity, (iii) permeability, (iv) water saturation, (v) pressure, (vi) in-situ stress, and (vii)

Young's modulus using data from: logs, cores, well tests, and any drilling records. In as much as tight reservoirs are normally also low porosity reservoirs, the importance of detailed log analyses becomes critical to understanding the reservoir.

One of the most difficult parameters to evaluate in tight gas reservoirs is the drainage area size and shape of a typical well. In tight reservoirs, months or years of production are normally required before the pressure transients are affected by reservoir boundaries or well-to-well interference. As such, an estimation of the drainage area size and shape for a typical well has to be made in order to estimate reserves. Furthermore, knowledge of the depositional system and the effects of diagenesis on the rock are needed to estimate the drainage area size and shape for a specific well. In tight reservoirs, the typical drainage area of a well largely depends on the number of wells drilled, the size of the fracture treatments pumped on the wells, and the time frame being considered. In lenticular or compartmentalized tight gas or oil reservoirs, the average drainage area is likely a function of the average size of the sand lens or the average size of the compartment and may not be a strong function of the size of the fracture treatment.

Generally, reservoir drainage per well is small in continental deposits and larger in marine deposits. Fluvial systems tend to be more lenticular. Barrier-strand-plain systems tend to be more blanket and continuous. Marine deposits tend to be more blanket and continuous. Most of the more successful tight gas plays are those in which the formation is a thick, continuous, marine deposit. By way of explanation, a strand plain (strandplain) is a broad belt of sand along a shoreline with a surface exhibiting well-defined parallel or semi-parallel sand ridges separated by shallow swales. A strand plain differs from a barrier island in that it lacks either the lagoons or tidal marshes that separate a barrier island from the shoreline to which the strand plain is directly attached. Also, the tidal channels and inlets which cut through barrier islands are absent. Strand plains typically are created by the redistribution by waves and longshore currents of coarse sediment on either side of a river mouth.

The best way to determine the depositional system is to cut and analyze cores (Chapter 2). Taking cores from the tight formations and from the non-reservoir rock above and below the main pay interval is recommended. From the test data, important information related to the depositional system become available and the core analyses can be correlated with open-hole logging data to determine the various depositional environments. Once these correlations are made, logs from additional wells can be analyzed to generate maps of the depositional patterns in a specific area from which field optimization plans can be developed.

Natural gas and crude oil from shale formations and from other tight formations are becoming an increasingly important energy source for meeting rising energy demands in the next several decades. Development of horizontal drilling and hydraulic fracturing is crucial for economic production of tight reservoirs, but it must be performed with caution and as a multi-disciplinary approach (King, 2010; Speight, 2016). The success of the Barnett shale in the United States has illustrated that gas can be produced economically from rock that was previously thought to be source rock and/or cap rock, not reservoir rock, leading to the development of many other tight reservoirs, including (alphabetically but not by preferences) the Fayetteville formation, Haynesville formation, Marcellus formation, and the Woodford formation. These commercial successes in the Barnett shale, which is currently the largest producing natural gas field, and other shale plays in the United States have made exploration of tight reservoirs not only possible but also economic and development has begun to spread all around the world. In most cases, economic production is possible only if a very complex, highly nonlinear fracture network can be created that effectively connects a large reservoir surface area to the wellbore (Upolla et al., 2009).

However, the economic viability of many unconventional gas developments requires effective stimulation of the extremely low-permeability rock by means of horizontal drilling followed by hydraulic fracturing (Chapter 5). In the process, the drill path is, at first, vertical and then the drill stem is caused to deviate (hence the alternate name of deviated drilling) and into the reservoir. Once reservoir penetration is achieved satisfactorily, hydraulic fractures are created in the reservoir to effectively connect a large gas-bearing or oil-bearing area to the wellbore when the wellbore is drilled in the direction of minimum horizontal stress. Maximizing the total stimulated reservoir volume (SRV) plays a major role in successful economic gas production (Yu and Sepehrnoori, 2013). Despite the success of recent tight reservoir development recently, it is difficult to predict well performance and evaluate economic viability for other shale resources with certainty because it involves high risk and uncertainties.

Thus, the uncertainties of reservoir properties and fracture parameters have significant effect on production of natural gas and crude oil from tight shales and tight formations, making the process of the design of the hydraulic fracturing process and optimization of the process, for economic gas production of gas or oil, much more complex. Thus, it is extremely important to identify the necessary and important process parameters and also to evaluate the effects of these parameters on well performance. As part of the optimization procedure, the detailed reservoir properties that affect each wellbore should be assessed by a multi-disciplinary team of scientists and engineers. For example, the optimization of critical hydraulic fracture parameters such as (i) fracture spacing, (ii) fracture half-length, and (iii) fracture conductivity, which control well performance, is important to obtain the most economical scenario. The cost of hydraulic fracturing of horizontal wells is expensive. Therefore, the development of a method quantifying uncertainties and optimization of natural gas and crude oil production with economic analysis in an efficient and practical way is clearly desirable (Zhang et al., 2007).

In general, the ultra-low permeability of tight formations ranges from as low as one nanoDarcy (10^{-6} Darcy) to 1 milliDarcy, illustrating that tight reservoirs require to be artificially fractured in order to make low permeability formations produce economically. Typically, the Barnett Shale reservoir exhibits a net thickness of 50–600 feet, porosity of 2–8% v/v, total organic carbon (TOC) of 1%–14% found at depths ranging from 1000 to 13,000 feet (Cipolla et al., 2010). Furthermore, reported that fracture spacing varied in the range from 100 feet to 700 feet in actual hydraulic fracturing operations in three Barnett Shale wells (Grieser et al., 2009) and well performance of Barnett Shale changes significantly with (i) the changing properties of the produced fluid, (ii) the type of fluid, (iii) the depth of the formation, and (iv) the thickness of the formation (Hale and William, 2010). Also, to add further complications, the productivity of wells in the Barnett Shale is highly dependent on (i) the type of completion method implemented and (ii) the large hydraulic fracture treatments (Ezisi et al., 2012). To optimize the development of a tight gas reservoir, the scientists and engineers must optimize the number of wells drilled, as well as the drilling and completion procedures for each well. To further complicate matters, it does not follow that each well will be equal to or equivalent to an adjacent well in terms of behavior and productivity. Often, more data and more scientific and engineering data required to understand and develop tight reservoirs than are required for the higher permeability, conventional reservoirs. For example, on an individual basis, a well in a tight gas reservoir will produce less gas over a longer period of time than can be expected from a well completed in a higher permeability, conventional reservoir. As such, many more wells (with smaller well spacing between wells) must be drilled into a tight shale reservoir or into another form of tight reservoir (sandstone or carbonate) to recover an effective amount of the original gas in place (OGIP) or the original oil in place (OOIP), when compared to a conventional reservoir. In summary, the optimum drilling, completion and stimulation methods for each well are a function of the reservoir characteristics as well as economic parameters. The costs to drill, complete and stimulate the wells, plus the gas price or oil price and the gas market or oil market serve to affect how tight reservoirs are developed.

Recall, shale is a sedimentary rock that is predominantly comprised of very fine-grained clay particles deposited in a thinly laminated texture (Chapter 1). These formations were originally deposited as mud in low energy depositional environments, such as tidal flats and swamps, where the clay particles fall out of suspension. During the deposition of these sediments, organic matter is also deposited. Deep burial of this mud results in a layered rock (*shale*), which actually describes the very fine grains and laminar nature of the sediment, not rock composition, which can differ significantly between shale formations.

Shale gas resources are becoming an important energy source for meeting rising energy demands in the next several decades. Development of horizontal drilling and hydraulic fracturing is crucial for economic production of shale gas reservoirs, but it must be performed with caution and as a multi-disciplinary approach (King, 2010). Commercial successes in the Barnett shale, which is currently the largest producing natural gas field, and other shale plays in the United States have made shale gas exploration possible and development has begun to spread all around the world. In the United States, production of shale gas began in the Barnett play of eastern Texas in the late 1990s and early 2000s. With the widespread application of horizontal drilling and hydraulic fracturing (“fracking”) beginning in 2003, production grew rapidly. The Haynesville play of Louisiana and east Texas was unknown as recently at 2007, and became the largest shale play in the US at its peak in late 2011, although production has subsequently declined.

Massive hydraulic fractures are created to effectively connect a huge reservoir area to the wellbore when the wellbore is drilled in the direction of minimum horizontal stress. Maximizing the total stimulated reservoir volume (SRV) plays a major role in successful economic gas production (Yu and Sepehrnoori, 2013). Despite the success of shale gas development recently, it is difficult to predict well performance and evaluate economic viability for other shale resources with certainty because it involves high risk and uncertainties.

Briefly, *conventional gas reservoirs* contain *free* gas in interconnected pore spaces that can flow easily to the wellbore i.e., natural flow is possible (Chapter 1). On the other hand, *unconventional gas reservoirs* (i.e., shale gas reservoirs) produce from low permeability (tight and now ultra-tight) formations (Chapter 1). The gas is often sourced from the reservoir rock itself, adsorbed onto the matrix. Due to the low permeability of these formations, it is necessary to stimulate the reservoir by creating a fracture network to give enough surface area to allow sufficient production from the additional *enhanced* reservoir permeability.

Thus, the uncertainties of reservoir properties and fracture parameters have significant effect on shale gas production, making the process of optimization of hydraulic fracturing treatment design for economic gas production much more complex. It is extremely important to identify reasonable ranges for these uncertainty parameters and evaluate their effects on well performance, because the detailed reservoir properties for each wellbore are difficult to obtain.

The optimization of critical hydraulic fracture parameters, such as fracture spacing, fracture half-length and fracture conductivity, which control well performance, is important to obtain the most economical scenario. The cost of hydraulic fracturing of horizontal wells is expensive. Therefore, the development of a method quantifying uncertainties and optimization of shale gas production with economic analysis in an efficient and practical way is clearly desirable (Zhang et al., 2007).

In reality, the ultra-low permeability of shale ranges from 10 to 100 nano-Darcy (10^{-6} mD), illustrating that shale gas reservoirs require to be artificially fractured in order to make low permeability formations produce economically. Typical the Barnett Shale reservoir exhibits a net thickness of 50–600 ft, porosity of 2%–8%, total organic carbon (TOC) of 1%–14% found at depths ranging from 1000 to 13,000 feet (Cipolla et al., 2010). Furthermore, reported that fracture spacing varied in the range from 100 feet to 700 feet in actual hydraulic fracturing operations in three Barnett Shale wells (Grieser et al., 2009) and well performance of Barnett Shale changes significantly with changing produced fluid type, depth and formation thickness (Hale and William, 2010). Also, well productivity in the Barnett Shale is highly dependent on the type of completion method implemented and the large hydraulic fracture treatments (Ezisi et al., 2012).

As stated earlier (Chapter 1), shale has very low permeability (measured in nanodarcies). As a result, many wells are required to deplete the reservoir and special well design and well stimulation techniques are required to deliver production rates of sufficient levels to make a development economic (Schweitzer and Bilgesu, 2009). Horizontal drilling and fracture stimulation have both been crucial in the development of the shale gas industry (Houston et al., 2009).

Natural gas will not readily flow to vertical wells because of the low permeability of shale. This can be overcome by drilling horizontal wells where the drill bit is steered from its downward trajectory to follow a horizontal trajectory for one to two miles, thereby exposing the wellbore to as much of the reservoir as possible.

The use of horizontal drilling in conjunction with hydraulic fracturing has greatly expanded the ability of producers to profitably recover natural gas and oil from low-permeability geologic plays, particularly, shale resources (US EIA, 2011). Application of fracturing techniques to stimulate oil and gas production began to grow rapidly in the 1950s, although experimentation dates back to the 19th century. Starting in the mid-1970s, a partnership of private operators, the US Department of Energy (US DOE) and predecessor agencies, and the Gas Research Institute (GRI) endeavored to develop technologies for the commercial production of natural gas from the relatively shallow Devonian (Huron) shale in the eastern United States. This partnership helped foster technologies that eventually became crucial to the production of natural gas from shale rock, including horizontal wells, multi-stage fracturing, and slick-water fracturing. The practical application of horizontal drilling to oil production began in the early 1980s, by which time the advent of improved downhole drilling motors and the invention of other necessary supporting equipment, materials, and technologies (particularly, downhole telemetry equipment) had brought some applications within the realm of commercial viability (US EIA, 2011).

All shale gas reservoirs require *fracture stimulation* to connect the natural fracture network to the well bore (Gale et al., 2007). As drilling is completed, multiple layers of metal casing and cement are placed around the wellbore. After the well is completed, a fluid composed of water, sand and chemicals is injected under high pressure to crack the shale, increasing the permeability of the rock and easing the flow of natural gas. A portion of the fracturing fluid will return through the well to the surface (*flow back*) due to the subsurface pressures. The volume of fluid will steadily reduce and be replaced by natural gas production.

The fissures created in the fracking process are held open by the sand particles so that natural gas from within the shale can flow up through the well. Once released through the well, the natural gas is captured, stored and transported to the relevant site processing. Furthermore, each gas shale basins is different and each has a unique set of exploration criteria and operational challenges. The technology was primarily developed in the Texas Barnett Shale and applied to other shale lay resources, often with a one-method-fits-all approach. However, there is now a realization that the Barnett shale technology needs to be adapted to other shale gas resources in a scientifically technologically structured.

For example, shale formations in the United States that presently produce gas commercially exhibit an unexpectedly wide variation in the values of five key parameters: (i) thermal maturity, expressed as vitrinite reflectance, (ii) the fraction of gas that is adsorbed, (iii) reservoir thickness, (iv) total organic carbon content, and (v) the volume of gas in place (Curtis, 2002). The degree of natural fracture development in an otherwise low-matrix-permeability shale reservoir is a controlling factor in gas producibility. To date, unstimulated commercial production has been achievable in only a small proportion of shale wells, those that intercept natural fracture networks. In most other cases, a successful shale-gas well requires hydraulic stimulation.

While it might be a rule-of-thumb that unconventional resources need unconventional techniques, it is clear that the poorer the reservoir the better the technology and accuracy of data needed to be able to fully characterize and develop each reservoir (resource) (Grieser and Bray, 2007). In fact, as shale gas resources have emerged as a viable energy source, their characterization using geophysical methods has gained significance (Chopra et al., 2012). The organic content in these shale formations which are measured by the total organic carbon content, influence the compressional and shear velocities as well as the density and anisotropy in these formations. Consequently, detecting changes in the total organic carbon content from the surface seismic response is a necessary step in reservoir characterization. And, in addition to the total organic carbon content, different shale formations have different properties in terms of maturation, gas-in-place, permeability, and brittleness. The realization is that typical shale reservoirs are more expensive and labor intensive than conventional reservoirs and the expertize needed to characterize reservoir and stimulation treatments is highly specialized.

Prior to recovery proper, a number of vertical wells (perhaps only two or three) are drilled and fractured to determine if shale gas is present and can be extracted. This exploration stage may include an appraisal phase where more wells (perhaps 10–15) are drilled and fractured to characterize the shale; examine how fractures will tend to propagate; and establish if the shale could produce gas economically. Further wells may be drilled (perhaps reaching a total of 30) to ascertain the long-term economic viability of the shale.

Once the reservoir properties and contents have been defined, the drilling program and recovery operations will commence.

3. Well drilling and completion

As stated earlier (Chapter 1), shale formations and tight formations have very low permeability (measured in nanoDarcys or, at best, milliDarcys) (Fig. 4.1). In addition, natural gas and crude oil in tight formations will not flow readily to vertical wells because of the low permeability of the formation. This can be overcome by drilling horizontal wells where the drill bit is steered from its downward trajectory to follow a horizontal trajectory for the necessary distance − often one to two miles - thereby exposing the wellbore to as much of the reservoir as possible. As a result, many wells are required to create acceptable and efficient well productivity and special well design and well stimulation techniques are required to deliver production rates of sufficient levels to make a development economic (Schweitzer and Bilgesu, 2009). Thus, it is not surprising that horizontal drilling and stimulation by hydraulic fracturing have both been crucial in the development of the resources in tight reservoirs (Houston et al., 2009).

Natural gas and crude oil in tight formations will not readily flow to any vertical well drilled through it because of the low permeability of the shale. This can be overcome to some extent by drilling horizontal wells, where the drill bit is steered from its downward trajectory to follow a horizontal trajectory for one mile or more to thereby exposing the wellbore to as much reservoir as possible. By drilling horizontally, the wellbore may intersect a greater number of naturally existing fractures in the reservoir − the direction of the drill path is chosen based on the known fracture trends in each area. However, some shale formations can only be drilled with vertical wells because of the risk of the borehole collapsing.

Thus, production in of gas from shale formations is a multi-scale and multi-mechanism process. Fractures provide the permeability for gas to flow, but contribute little to the overall gas storage capacity. The porosity of the matrix provides most of the storage capacity, but the matrix has very low permeability. Gas flow in the fractures occurs in a different flow regime than gas flow in the matrix. Because of these differing flow regimes, the modeling of production performance in fractured shale formations is far more complex than for conventional reservoirs, and scaling modeling results up to the field level is very challenging. This in turn makes it difficult to confidently predict production performance and devise optimal depletion strategies for shale resources.

Thus, in order to ensure the optimal development of shale gas resources it is necessary to build a comprehensive understanding of geochemistry, geological history, multiphase flow characteristics, fracture properties (including an understanding of the fracture network) and production behavior across a variety of shale plays. It is also important to develop knowledge that can enable the scaling up of pore-level physics to reservoir-scale performance prediction, and make efforts to improve core analysis techniques to allow accurate determination of the recoverable resource.

For example, unconventional resources require a high well density for full development. Technology that can reduce well costs and increase wellbore contact with the reservoir can make a significant impact on costs, production rates and ultimate recovery. Multi-lateral drilling, whereby a number of horizontal sections can be created from a single vertical wellbore, and coiled tubing drilling to decrease costs represent potential options for future unconventional gas development. A combination of steel casing and cement in the well provides an essential barrier to ensure that high-pressure gas or liquids from deeper down cannot escape into shallower rock formations or water aquifers. This barrier has to be designed to withstand the cycles of stress it will endure during the subsequent hydraulic fracturing, without suffering any cracks.

Hydraulic fracturing (commonly referred to as *fraccing*, *fracking*, or *fracing*) is already widely used by the oil and gas industry to improve low permeability reservoirs. Fluid (often water, carbon dioxide, nitrogen gas, or propane) is pumped down the well until the pressure surpasses the rock strength and causes the reservoir to crack. The fracturing fluid pumped down the well is loaded with proppant (often 100 tons or more of ceramic beads or sand) that infiltrate the formation and help to prop the fractures open, which are at risk of closing once the pressure is released. The choice of the fluid used in a fracturing operation depends on many factors, including whether clay in the reservoir is sensitive to water (some clays swell in the presence of fresh water, such as in the Colorado Shale) or whether the reservoir happens to respond better to particular fluids, usually only determined through experimentation. Two factors increase the ability of shale to fracture. The first factor relates to the presence of hard minerals like silica and to a lesser extent calcite, which break like glass. Clay, however, tends to absorb more of the pressure and often bends under applied hydraulic pressure without breaking. Therefore, silica-rich shales like those found in the Horn River Basin are excellent candidates for fraccing.

The second factor is the internal pressure of the shale formation. Over pressured shales develop during the generation of natural gas: because of the low permeability, much of the gas cannot escape and builds in place, increasing the internal pressure of the rock. Therefore, the artificially created fracture network can penetrate further into the formation because the shale is already closer to the breaking point than in normally pressured shales. The Horn River, Montney, and Utica shale formations are all considered to be over pressured whereas the Colorado Shale formation is under pressured. Furthermore, by isolating sections along the horizontal portion of the well, segments of the borehole can be fracked one at a time in a technique called multi-stage fracturing. By listening at the surface and in neighboring wells, it can be determined how far, how extensively, and in what directions the shale has cracked from the induced pressure. Finally, shale formations can be re-fractured years later − after production has declined − which may allow the well to access more of the reservoir that may have been missed during the initial hydraulic fracturing or to reopen fractures that may have closed due to the decrease in pressure as the reservoir was drained.

However, even with hydraulic fracturing, wells drilled into low-permeability reservoirs have difficulty communicating in the formation. As a result, additional wells must be drilled to access as much gas as possible, typically three or four, but up to eight, horizontal wells per section. In comparison, only one well per section is typically drilled for conventional natural gas reservoirs. However, this does not necessarily mean that there will be a heavier land use footprint versus conventional drilling. Several shale gas wells with horizontal lengths of up to a mile can be drilled from a single site one hectare in size, reducing the footprint to one well site or less per section. In conventional reservoirs, as much as 95% v/v of the natural gas can be recovered. For shale formation, the recovery are expected to be on the order of 20% v/v because of low permeabilities despite high-density horizontal drilling and extensive hydraulic fracturing.

The design aspects that are most important to ensure a leak-free well include the drilling of the well bore to specification (without additional twists, turns or cavities), the positioning of the casing in the center of the well bore before it is cemented in place (this is done with centralizers placed at regular intervals along the casing as it is run in the hole, to keep it away from the rock face) and the correct choice of cement. The cement design needs to be studied both for its liquid properties during pumping (to ensure that it gets to the right place) and then for its mechanical strength and flexibility, so that it remains intact. The setting time of the cement is also a critical factor − cement that takes too long to set may have reduced strength; equally, cement that sets before it has been fully pumped into place requires difficult remedial action.

Most shale gas resources are located at depths of 6000 feet or more below ground level, and can be relatively thin (for example, the Marcellus shale formation is between fifty and two hundred feet thick depending on location). The efficient extraction of gas from such a thin layer of rock requires drilling horizontally through the shale, which is accomplished by drilling vertically downward until the drill bit reaches a distance of around 900 feet from the shale formation. At this point, a directional drill is used to create a gradual 90-degree curve, so that the *wellbore* becomes horizontal as it reaches optimal depth within the shale. The wellbore then follows the shale formation horizontally for 5000 feet or more. Multiple horizontal wells accessing different parts of the shale formation can be drilled from a single pad. Thus, horizontal drilling reduces the footprint of these operations by enabling a large area of shale to be accessed from a single pad.

Thus, in the process, a large number of fractures are created mechanically in the rock, thus allowing the natural gas and/or crude oil trapped in subsurface formations to move through those fractures to the wellbore from where it can then flow to the surface. Fracking can both increase production rates and increase the total amount of gas that can be recovered from a given volume of shale. Pump pressure causes the rock to fracture, and water carries sand (*proppant*) into the hydraulic fracture to prop it open allowing the flow of gas. While water and sand are the main components of hydraulic fracture fluid, chemical additives are often added in small concentrations to improve fracturing performance.

At various stages in the drilling process, drilling is stopped and steel casing pipe is installed in the wellbore. Cement is pumped into the *annulus*, or void space between the casing and the surrounding mineral formation. After the wellbore reaches a depth below the deepest freshwater aquifer, casing and cement are installed to protect the water from contamination due to the drilling process. Additional casing and cementing along the entire wellbore occurs after the well has reached its full horizontal length. This process is intended to prevent leakage of natural gas from the well to the rock layers between the shale formation and the surface, as well as to prevent the escape of natural gas to the surface through the annulus. The casing surrounding the horizontal section of the well through the shale formation is then perforated using small explosives to enable the flow of hydraulic fracturing fluids out of the well into the shale and the eventual flow of natural gas out of the shale into the well.

3.1 Reservoir character

Before any drilling is initiated there must be a serious consideration of the reservoir character. This is obtained through investigation and consideration of (i) reservoir geology, (ii) reservoir continuity, (iii) regional tectonics, (iv) reservoir layers, (v) log data, and (vi) core data.

The analysis of a tight reservoir should always begin with a thorough understanding of the geologic characteristics of the formation. The important geologic parameters for a trend or basin are the structural and tectonic regime, the regional thermal gradients, and the regional pressure gradients. Knowing the stratigraphy in a basin is very important and can affect the drilling, evaluation, completion, and stimulation activities. Important geologic parameters that should be studied for each stratigraphic unit are the depositional system, the genetic facies, textural maturity, mineralogy, diagenetic processes, cements, reservoir dimensions, and presence of natural fractures (Berg, 1986). One of the most difficult parameters to evaluate in tight gas reservoirs is the drainage-area size and shape. In tight reservoirs, months or years of production normally are required before the pressure transients are affected by reservoir boundaries or well-to-well interference. As such, the engineer often has to estimate the drainage-area size and shape for a typical well to estimate reserves.

Knowledge of the depositional system is also necessary as well as the effects of diagenesis on the rock to estimate the drainage area size and shape for a specific well. Oblong (or noncircular) drainage volumes are likely caused by depositional or fracture trends and the orientation of hydraulic fractures. In blanket-type tight reservoirs, the average drainage area of a well largely depends on the number of wells drilled, the size of the fracture treatments pumped into the wells, and the time frame being considered. In lenticular or compartmentalized tight gas reservoirs, the average drainage area is likely a function of the average size of the sand lens or compartment and may not be a strong function of the size of the fracture treatment.

Tectonic activity during deposition can affect reservoir continuity and morphology. In addition, regional tectonics affect the horizontal stresses in all rock layers. The horizontal stresses, in turn, affect faulting, rock strength, drilling parameters, hydraulic-fracture propagation, natural fracturing, and borehole stability. The main concerns for tight gas reservoirs are the effects of regional tectonics on hydraulic-fracture propagation and natural fracturing in the formation.

Typically, a tight reservoir can be described as a layered system. In a clastic depositional system, the layers are composed of sandstone, siltstone, mudstone, and shale. To optimize the development of a tight gas reservoir, the reservoir must be fully characterized in terms of all the layers of rock above, within, and below the pay zones in the reservoir. Data concerning gross pay thickness, net pay thickness, permeability, porosity, water saturation, pressure, in-situ stress, and Young's modulus for all layers are required to use three-dimensional (3D) reservoir and fracture propagation models to evaluate the formation, design the fracture treatment, and forecast production rates and ultimate recovery. The raw data used to estimate values for these parameters come from logs, cores, well tests, drilling records, and production from offset wells.

In terms of log data, open-hole logs provide the most economical and complete source of data for evaluating layered, low-porosity, tight gas reservoirs. The minimal logging suite for a tight reservoir comprises spontaneous potential, gamma ray, formation density, neutron, sonic, and dual (or array) induction logs. Other logs, such as wellbore-image logs or nuclear-magnetic-resonance logs, may also provide useful information in some reservoirs. All open-hole logging data should be preprocessed before the data are used in any detailed computations. The steps required to preprocess the logs are as follows (Howard and Hunt, 1986).

Finally, obtaining and analyzing cores are crucial to proper understanding of any layered complex reservoir system. To obtain data needed to understand the fluid-flow properties, mechanical properties, and depositional environment of a specific reservoir requires that cores be cut, handled correctly, and tested in the laboratory with modern and sophisticated laboratory methods. Of primary importance is the measuring of rock properties under restored reservoir conditions. The effect of net overburden (NOB) pressure must be reproduced in the laboratory to obtain the most accurate quantitative information from the cores.

3.2 Drilling

The most important part of drilling a well in a tight gas reservoir or a tight oil reservoir is to drill a gauge hole, which is required to obtain an adequate suite of open-hole logs and to obtain an adequate primary cement job. In low porosity, shale reservoirs, the analyses of gamma ray (GR), spontaneous potential (SP), porosity, and resistivity logs to determine accurate estimates of shale content, porosity, and water saturation can be difficult. If the borehole is washed out (*out of gauge*), the log readings will be affected, and it will be even more difficult to differentiate the pay from the non-pay portions of the formation. If the borehole is washed out, obtaining a primary cement seal is difficult, which could affect zonal isolation and cause the well to have to be cement squeezed prior to running tests or pumping stimulation treatments.

Formation damage and drilling speed should be a secondary concern. Some wells are drilled underbalanced to increase the bit penetration rate or to minimize mud filtrate invasion. However, if the wellbore is severely washed out because the well was drilled underbalanced, it is probable that a lot of money will be wasted because the logs are not accurate and the primary cement job might not be adequate. It is best to drill a tight gas well near balanced to minimize borehole washouts and mud filtrate invasion.

Natural gas and crude oil in tight formations will not flow readily to a vertical well drilled through it because of the low permeability of the shale. This can be overcome to some extent by drilling horizontal wells, where the drill bit is steered from its downward trajectory to follow a horizontal trajectory for one mile or more to thereby exposing the wellbore to as much reservoir as possible. By drilling horizontally, the wellbore may intersect a greater number of naturally existing fractures in the reservoir — the direction of the drill path is chosen based on the known fracture trends in each area. However, some shale formations can only be drilled with vertical wells because of the risk of the borehole collapsing.

The use of horizontal drilling in conjunction with hydraulic fracturing has greatly expanded the ability of producers to recover natural gas and crude oil efficiently from low-permeability geologic plays, particularly, shale resources (US EIA, 2011). This history of the application hydraulic fracturing techniques to stimulate crude oil and natural gas production goes back well into the 20th Century and even into the 19th Century but began to grow rapidly in the 1950s. Since this time, the oil and gas industry has been completing and fracture treating low permeability wells in the United States. However, it was the natural-gas price increase in the 1970s that spurred significant activity in low permeability gas reservoirs and since then sustained increases in natural gas prices and in crude oil prices along with advances in evaluation, completion and stimulation technology, have led to substantial development of tight formations containing natural gas and crude oil.

Furthermore, commencing in the mid-1970s, a partnership of private operators with the United States Department of Energy (US DOE) and predecessor agencies and with the Gas Research Institute (GRI) endeavored to develop technologies for the commercial production of natural gas from the relatively shallow Upper Devonian (Huron) shale (which lies just above the Marcellus Shale – the Marcellus is part of the Middle Devonian formation), in the eastern United States. This partnership greatly assisted in the development of technologies that eventually became crucial to the production of natural gas from shale formations, including drilling horizontal wells as well as multi-stage hydraulic fracturing and slick-water fracturing (Chapter 5). Following from this development, the practical application of horizontal drilling to production of crude oil from tight formations began in the early 1980s by which time the advent of improved downhole drilling motors and the development of other necessary supporting equipment, materials, and new technologies (particularly, downhole telemetry equipment) had opened the path to bringing brought some applications into the realm of commercial operations (US EIA, 2011). By this time, it had been recognized that tight reservoirs require *fracture stimulation* to connect any natural fracture network to the well bore (Gale et al., 2007). The fissures created by the hydraulic fracturing process are held open by the sand particles so that the reservoir fluids from within the tight (but fractured) formation can flow up through the well. Once released through the well, the natural gas, crude oil, and water are captured, stored and transported to the relevant on-site processing operations.

The recovery technology was primarily developed in the Texas Barnett Shale and applied to other shale lay resources, often with a one-method-fits-all approach. However, the tight formations encountered in any operation to produce natural gas or crude oil are different and each has a unique set of exploration criteria and operational challenges and there is now a realization that the Barnett shale technology needs to be adapted to other tight resources in a scientifically technologically structured manner. Thus, while it might be thought that there is a rule-of-thumb that unconventional resources (resources in tight formations) need the application of unconventional recovery techniques, it is clear that a poorer quality the reservoir needs improved technology as well as highly accurate data to be able to fully characterize and develop each reservoir (resource) in an efficient and effective manner (Grieser and Bray, 2007).

In fact, over the past decade, resources from tight formations have emerged as a viable energy source and the accurate characterization of the whole resource (the reservoir plus the reservoir fluids) using geophysical methods has gained high significance (Chopra et al., 2012). The natural gas and crude oil reserves contained in these formations, which are estimated from the total organic carbon content of the formation, influence the compressional and shear velocity as well as the density and anisotropy in the formation. Consequently, detecting changes in the total organic carbon content from the surface seismic response is a necessary step in reservoir (and resource) characterization (Chapter 2). And, in addition to the total organic carbon content, different shale formations have different properties in terms of maturation, gas-in-place, permeability, and brittleness. Thus, there has also been the realization is that typical tight reservoirs (if there are such reservoirs) are more expensive and labor intensive than conventional reservoirs and the expertize needed to characterize reservoir and stimulation treatments is much more specialized.

In the process of reservoir characterization and prior to the onset of recovery operations, a number of vertical wells (perhaps two or three exploratory wells) are drilled and the hydraulic fracturing process applied to the formation to determine if natural gas or crude oil is present and can be extracted. This exploration stage may include an appraisal phase where more wells (perhaps 10—15) are drilled and fractured to characterize the formation. At this time, there is (or should be) an examination of the means in which the fracture pattern develops and the means by which the fractures will propagate and whether or not the natural gas or crude oil can be produced economically. As a final step, more wells may be drilled (perhaps reaching a total of 30 wells) to ascertain the long-term producibility and economic viability of the shale. Once the reservoir properties and contents have been defined, the drilling program and recovery operations can commence with a relatively high degree of success.

The leader and prime mover in the development of natural gas and crude oil recovery from tight formations has been the Barnett Shale formation with the results that, as of the current time, the focus of tight resource development has shifted to other tight reservoirs in the United States and Canada such as (alphabetically and not by timing or preference) (i) Fayetteville shale (in Arkansas) (ii) the Haynesville (on the Texas-Louisiana border), (iii) the Horn River Basin shale (in British Columbia, Canada), and (iv) Marcellus shale (in the northeastern United States). The physical and geophysical properties vary significantly both among and within tight shale gas plays as well as in other tight formations.

Furthermore, insofar as tight formations (especially shale plays) cover large areas, they also require that more wells are drilled more closely together than during the development of those of conventional reservoirs which leads to a much larger surface area being affected by the drilling and production operations. For example, some areas may require that well s be drilled have been drilled with wells every fifteen-to-twenty acres. In many cases, twenty-to-thirty wells are often drilled from a single surface location and long-reach horizontal wellbores of up to one-to-two miles are drilled to reduce the environmental impact on the surface. Future technological breakthroughs that further reduce the surface environmental impact would facilitate the development of more tight formations, especially in the more densely populated or environmentally sensitive areas and this will be a key factor in resource development in many countries.

3.2.1 Horizontal drilling

During the hundred years or so of the existence of the natural gas industry and the crude oil industry, drilling technology has progressed to the point of allowing the driller to turn corners by making the drill bit progress on a horizontal track while accurately staying within a narrow directional and vertical window. Because the horizontal portion is easily controlled, the well is able to drain shale gas resources from a geographical area that is much larger than a single vertical well in the same shale formation.

The primary differences between modern shale gas development and conventional natural gas development are the extensive uses of horizontal drilling and high-volume hydraulic fracturing. The use of horizontal drilling has not introduced any new environmental concerns. In fact, the reduced number of horizontal wells needed coupled with the ability to drill multiple wells from a single pad has significantly reduced surface disturbances and associated impacts to wildlife, dust, noise, and traffic. Where shale gas development has intersected with urban and industrial settings, regulators and industry have developed special practices to alleviate nuisance impacts, impacts to sensitive environmental resources, and interference with existing businesses.

Using the Marcellus shale resource in Pennsylvania as an example, a vertical well may only drain a cylinder of shale 1320 feet in diameter and as little as 50 feet high. By comparison, a horizontal well may extend from 2000 to 6000 feet in length and drain a volume up to 6000 feet by 1320 feet by 50 feet in thickness, an area approximately 4000 times greater than that drained by a vertical well. The increase in drainage creates a number of important advantages for horizontal wells over vertical wells, particularly with respect of associated environmental issues.

Thus, horizontal drilling is a technique that allows the wellbore to come into contact with significantly larger areas of hydrocarbon bearing rock than in a vertical well. As a result of this increased contact, production rates and recovery factors can be increased. As the technology for horizontal drilling and fracking has improved, the use of horizontal drilling has increased significantly. An important role that horizontal drilling has played is in development of the natural gas shale resources. These low permeability rock units contain significant amounts of gas and are present beneath very large parts of North America.

In general, a vertical well drilled and completed in a tight gas reservoir must be successfully stimulated to produce at commercial gas-flow rates and produce commercial gas volumes. Typically, hydraulic-fracture treatment is required to produce gas economically. Furthermore, in some naturally fractured tight gas reservoirs, horizontal wells can be drilled, but these wells also need to be stimulated. To optimize development of a tight gas reservoir, the number and locations of wells to be drilled must be optimized in addition to optimization of the drilling and completion procedures for each well. On an individual-well basis, a well in a tight gas reservoir will produce less gas over a longer period of time than one expects from a well completed in a higher-permeability conventional reservoir. As such, many more wells (closer well spacing) must be drilled in a tight gas reservoir to recover a large percentage of the original gas in place compared with a conventional reservoir.

Most horizontal wells begin at the surface as a vertical well. Drilling progresses until the drill bit is a few hundred feet above the target rock unit. At that point the pipe is pulled from the well and a hydraulic motor is attached between the drill bit and the drill pipe. The hydraulic motor is powered by a flow of drilling mud down the drill pipe. It can rotate the drill bit without rotating the entire length of drill pipe between the bit and the surface. This allows the bit to drill a path that deviates from the orientation of the drill pipe. After the motor is installed the bit and pipe are lowered back down the well and the bit drills a path that steers the well bore from vertical to horizontal over a distance of a few hundred feet. Once the well has been steered to the desired angle, straight-ahead drilling resumes and the well follows the target rock unit. Keeping the well in a thin rock unit requires careful navigation. Downhole instruments are used determine the azimuth and orientation of the drilling. This information is used to steer the drill bit.

The Barnett Shale of Texas, the Fayetteville Shale of Arkansas, the Haynesville Shale of Louisiana and Texas and the Marcellus Shale of the Appalachian Basin are examples of shale gas resources (Chapter 2). In these rock units the challenge is to recover gas from very tiny pore spaces in a low permeability rock unit (Gubelin, 2004). To stimulate the productivity of wells in organic-rich shale, companies drill horizontally through the rock unit and then use hydraulic fracturing to produce artificial permeability. Done together, horizontal drilling and hydraulic fracturing can make a productive well where a vertical well would have produced only a small amount of gas.

In fact, the productive potential of the Haynesville Shale was not fully realized until horizontal drilling and hydrofracturing technologies were demonstrated in other unconventional shale reservoirs. The hydrofracturing process − which is accomplished by sealing off a portion of the well and injecting water or gel under very high pressure into the isolated portion of the hole creating high pressure to fracture the rock open the fractures − helps liberate gas from the shale and horizontal drilling allows a single well to drain a much larger volume of rock than a traditional vertical well. In some geological settings, it is more appropriate to directionally drill s-shaped wells from a single pad to minimize surface disturbance. S-shaped wells are drilled vertically several thousand feet, then extend in arcs beneath the surface of the Earth.

During drilling, mobile drilling units are moved between wells on a single pad. This avoids dismantling and reassembling drilling equipment for each well, making the process quicker and saving resources.

3.2.2 Pad drilling

When multiple wells are drilled from the same pad, it is often referred to as *pad drilling* − as many as six to eight horizontal wells can originate from the same pad.

Typically the well pad drains an area that is rectangular (spacing unit, unit or pool), which is usually approximately one-half mile wide by two miles long with the pad itself positioned at the center of the rectangle. The majority of the surface area in the rectangle is not required for the well pad and will be left completely undisturbed. The well pad is generally on the order of four to five acres that is cleared, leveled and surfaced over for siting the drilling rig, trucks and various other equipment required for drilling and completion activities. The approach allows a drilling company to develop two separate formations on two separate spacing units simultaneously, thereby increasing production efficiency. It also allows the company to recover more of the available resources in a reservoir.

Pad drilling may be accomplished through the use of a movable flex or suitable-for-the-purpose drilling rigs with the intent to drill as many wells on a pad as are economically feasible. Drilling more wells on a pad is considered to help minimize the environmental impact (*environmental footprint*) of the drilling operation.

In shale drilling it is becoming increasingly common to use a single drill pad to develop as large an area of the subsurface as possible. One surface location may be used to drill multiple wells. Pad drilling increases the operational efficiency of gas production and reduces infrastructure costs and land use. Any negative impact upon the surface environment is therefore mitigated. Such technologies and practices developed by industry serve to reduce environmental impacts from shale gas operations.

3.2.3 Stacked wells

Drilling stacked horizontal wells may be possible where the shale is sufficiently thick or multiple shale rock strata are found layered on top of each other. One vertical well bore can be used to produce gas from horizontal wells at different depths. As in pad drilling, the environmental impact on the surface is mitigated as a result of reduced land use. This technology can be particularly beneficial in the thicker shale.

One area where this technology is being employed is in the Pearsall and Eagle Ford plays in southern Texas. Higher efficiency can be achieved as surface facilities are shared. As in pad drilling, the environmental impact on the surface is mitigated as a result of reduced land use.

3.2.4 Multilateral drilling

Multilateral drilling is similar to stacked drilling in that it involves the drilling of two or more horizontal wells from the same vertical well bore. With multilateral drilling, the horizontal wells access different areas of the shale at the same depth, but in different directions. Drilling multilateral wells makes it possible for production rates to be increased significantly for a reduced incremental cost.

Unconventional drilling is a growing part of the global drilling activity. In the past several years directional, horizontal, extended reach horizontal and multilateral wells have been drilled successfully using unconventional drilling techniques. Unconventional drilling technologies play a key role today where conventional technologies are not fully efficient to keep development profitable. These technologies allow the operator to increase production per well but also to improve ultimate reservoir recovery factor (RF). Multilateral drilling as one of unconventional drilling techniques emerged at the beginning of nineties. The general definition of a multilateral well is one in which there is more than one horizontal or near horizontal lateral well drilled from a single side (mother bore) and connected back to a single bore.

During the 1980s, advances in horizontal technology were adopted quickly in the Middle East to bring about dramatic improvements in well productivity. Many operators in the Persian Gulf region considered multilateral looked at ML drilling technology as a next step from horizontal drilling technology. These operators started to drill multilateral wells after experiencing successful drilling of horizontal wells. Since 1992, the use of multilateral drilling technology in the Middle East has seen significant growth to the extent that Middle East is one of the most active areas in the world for ML applications. In 1996, it is estimated that more than 35 multilateral wells were drilled in the Middle East (Mirzaei Paiaman and Moghadasi, 2009; Mirzaei et al., 2009).

Benefits due to the use of multilateral wells include reducing environmental impacts since one of the major concerns in the oil and gas drilling industry is harmful impact of drilling fluids and generated cuttings on the environment, especially when oil based muds are used. The volume of consumed drilling fluids and the generated cuttings during drilling multilateral wells are less than the consumed drilling fluid and generated cuttings from separated wells. Thus, the impact of the multilateral wells on the environmental is reduced.

The use of multilateral wells also aids in spreading the geological risks. Geological problems such as salt dome structures and shale layers may be faces during each time of drilling the new well. But in drilling multilateral wells, the geological risk will be spread and reduced instead of facing these geological problems each time of drilling the new wells. Also, drilling several laterals in a single well will result in substantial time and cost saving in comparison with drilling several wells in the reservoir. Therefore, more wells could be drilled in the reservoir. There are also benefits due to long horizontal section of multilateral wells which could assist in producing gas and/or oil from uneconomical pools, thin sand zones and blind zones. In the cases where thin pools are targeted, vertical wells yield small contact with the reservoir.

Drilling several laterals in such thin reservoirs and increasing reservoir contact improves recovery and reserve. In addition, the position of the laterals within the producing formation provides enough distance to the water zone and to the gas zone. Therefore, gas/water conning can be prevented or reduced. Also in comparison with vertical wells which experience high pressure near the wellbore, ML horizontal laterals exhibit more uniform pressure distributed along the length of the lateral. Therefore, multilateral wells are producible at high rates without experiencing coning. In the other words, the critical rate is higher for multilateral wells.

With the help of ML wells, the sweep efficiency will be improved and the recovery can be increased due to the area covered by the production. This is accompanied by an acceleration of the recovery of gas or oil. The production in multilateral well system is higher than that in single vertical or even the horizontal wells; hence the reservoir contact is higher in multilateral well system. There is also an increase in the recoverable reserves since multilateral penetrations are commonly used to increase the effective drainage and depletion of a reservoir. By drilling several laterals in the reservoir considerable reservoir area comes to contact with laterals. Better control of injection and production is achieved with proper installation since multilateral wells provide better control of injection and production due to the high distribution of the laterals through the reservoir.

3.2.5 Water requirements

Drilling a well followed by hydraulically fracturing can be water-intensive procedures. For example, each well in the Barnett Shale of the Fort Worth Basin in Texas requires an estimated 3 million US gallons of fresh water. However, water is not necessarily required for all hydraulic fracturing in gas shales. For example, many fracturing operations in the Montney play use carbon dioxide as the fracturing fluid. Furthermore, water is not a good candidate for use as a frac fluid for the shallow shales of the Colorado Group of southeastern Alberta and southwestern Saskatchewan because of the sensitivity of the formations to water. Operators there appear to be using nitrogen or a mixture of propane and butane as the fracturing fluid.

Fracturing water often contains chemical additives to help carry the proppant and may become enriched in salts after being injected into shale formations. Therefore, fracturing water that is recovered during natural gas production must be either treated or disposed of in a safe manner. Fracturing water is typically disposed of by injection into deep, highly saline formations through one or more wells drilled specifically for that purpose. The practice is commonplace in some areas where wells often produce water in conjunction with conventional natural gas and crude oil and is governed by clearly defined regulations.

Flowback water is infrequently reused in other fracturing operations because of the potential for corrosion or scaling, where the dissolved salts may precipitate out of the water and clog parts of the well or the formation. Projects for treatment of flowback water from the

Barnett Shale include distillation, where the distilled water can then be reused in other fracs to reduce requirements for fresh water. Importantly, operators avoid releasing the recovered frac water into the watershed. Furthermore, the fractured reservoir is normally a mile or more at depth and the fractures, and frac fluids, cannot extend through such a thick section of rock to reach aquifers at shallow depths where drinking water is extracted. For shallower shales, such as those in southeastern Alberta and southwestern Saskatchewan, the fractures are of considerably decreased size and the soft nature of the shale will likely prevent extensive penetration of fractures, which may also have a negative impact on ultimate productivity.

Finally, the amount of saline formation water produced from gas shales varies widely, from none to hundreds of barrels per day. The water comes from the gas shale itself or from adjacent formations that are connected through the fracture-induced fracture network. The water, like flowback water, is normally highly saline and must be treated and/or disposed of, typically by injection into deep saline formations.

3.3 Well completion

The stimulation strategy and well completion strategy required for a tight shale reservoir or a tight sandstone (or carbonate) reservoir very much depends on the number of layers of net gas pay and the overall economic assessment of the reservoir. In almost every case, a well in a tight gas reservoir is not economic to produce unless the optimum fracture treatment is both designed and pumped into the formation. The well can be perfectly drilled, cased, and perforated, but will be uneconomic until the optimum fracture treatment is pumped. As such, the entire well prognosis should be focused on how to drill and complete the well so that it can be successfully fracture treated. The hole sizes, casing sizes, tubing sizes, wellhead, flowlines, and perforation scheme should be designed to accommodate the fracture treatment.

By drilling horizontally into the formation, the wellbore may intersect a greater number of naturally existing fractures in the reservoir − the direction of the drill path is chosen based on the known fracture trends in each area. However, some shale formations can only be drilled with vertical wells because of the risk of the borehole collapsing. Thus, as drilling is completed, multiple layers of metal casing and cement are placed around the wellbore. After the well is completed, a fluid composed of water, sand and chemicals is injected under high pressure to crack the shale, increasing the permeability of the rock and easing the flow of natural gas. A portion of the fracturing fluid will return through the well to the surface (*flow back*) due to the subsurface pressures. The volume of fluid will steadily reduce and be replaced by natural gas production.

Once the well has been drilled, the final casing cemented in place across the gas-bearing rock has to be perforated in order to establish communication between the rock and the well (Leonard et al., 2007; Britt and Smith, 2009; LeCompte et al., 2009). The pressure in the well is then lowered so that hydrocarbon derivatives can flow from the rock to the well, driven by the pressure differential. With tight reservoirs, the rate of the flow of fluids to the well is very low, because of the low permeability of the rock. And, since the rate of fluid flow through the reservoir is a direct determination of the economic viability of the well, low flow rates can mean there is insufficient revenue to pay for operating expenses and provide a return on the capital invested. Without additional measures to accelerate the flow of hydrocarbon derivatives to the well, the operation is then not economic.

Several technologies have been developed over the years to enhance the flow from low permeability reservoirs. Acid treatment, involving the injection of small amounts of strong acids into the reservoir to dissolve some of the rock minerals and enhance the permeability of the rock near the wellbore, is probably the oldest and is still widely practiced, particularly in carbonate reservoirs. Wells with long horizontal or lateral sections (horizontal wells) can increase dramatically the contact area between the reservoir rock and the wellbore, and are likewise effective in improving project economics. Hydraulic fracturing, developed initially in the late 1940s, is another effective and commonly-practiced technology for low-permeability reservoirs. When rock permeability is extremely low, as in the case of natural gas (shale gas) or crude oil from tight formations (light tight oil), it often takes the combination of horizontal wells and hydraulic fracturing to achieve commercial rates of production.

Even though the well casing is perforated, little natural gas will flow freely into the well from the shale. Fracture networks must be created in the shale to allow gas to escape from the pores and natural fractures where it is trapped in the rock. This is accomplished through the process of hydraulic fracturing. In this process, typically several million gallons of a fluid composed of 98−99% w/w water and *proppant* (usually sand) is pumped at high pressure into the well. The rest of the fracturing fluid (0.5%−2% by volume) is composed of a blend of chemicals, often proprietary, that enhance the properties of the fluid. These chemicals typically include acids to clean the shale to improve gas flow, *biocides* to prevent organisms from growing and clogging the formation fractures, corrosion and scale inhibitors to protect the integrity of the well, gels or gums that add viscosity to the fluid and suspend the proppant, and friction reducers that enhance flow and improve the ability of the fluid to infiltrate and carry the proppant into small fractures in the shale.

This fluid pushes through the *perforations* in the well casing and forces the fractures open in the formation − connecting pores and existing fractures and creating a pathway for natural gas to flow back to the well. The proppant lodges in the fractures and keeps them open once the pressure is reduced and the fluid flows back out of the well. Approximately 1000 feet of wellbore is hydraulically fractured at a time, so each well must be hydraulically fractured in multiple stages, beginning at the furthest end of the wellbore. Cement plugs isolate each hydraulic fracture stage and must be drilled out to enable the flow of natural gas up the well after all hydraulic fracturing is complete. Thus, production in of natural gas and crude oil from shale formations is a multi-scale and multi-mechanism process and, especially, a multi-disciplinary process that requires cross-cooperation of several scientist and engineering discipline. Without the cooperation, the project may be doomed to technical failure with the consequences of serious environmental issues (Chapter 18).

Once the pressure is released, fluid (commonly referred to as *flowback water*) flows back out the top of the well. The fluid that is recovered not only contains the proprietary blend of chemicals present in the hydraulic fracturing fluid, but may also contain chemicals naturally present in the reservoir, including hydrocarbon derivatives, salts, minerals, and naturally occurring radioactive materials (NORMs) that leach into the fluid from the shale or result from mixing of the hydraulic fracturing fluid with brine (e.g., salty water) already present in the formation. The chemical composition of the water produced from the well varies significantly according to the formation and the time after well completion, with early flowback water resembling the hydraulic fracturing fluid but later converging on properties more closely resembling the brine naturally present in the formation.

Briefly and by way of explanation, flowback is a water based solution that flows to the surface during and after the completion of the hydraulic fracturing process. The water consists of the fluid used to fracture the formation and contains clay minerals, chemical additives, dissolved metal ions, as well as dissolved solids (measured as total dissolved solids, TDS). Typically, flowback water recovery is on the order of 0–40% v/v of the volume that was initially injected into the well. In contrast, produced water is naturally occurring water found in shale formations that flows to the surface throughout the entire lifespan of the gas well. This water has high levels of total dissolved solids and leaches minerals from the formation such as minerals containing barium, calcium, iron, and magnesium. The produced water may also contain dissolved hydrocarbon derivatives such as methane, ethane and propane along with naturally occurring radioactive materials (NORMs) such as radium isotopes.

In many cases, flowback water can be reused in subsequent hydraulic fracturing operations; this depends upon the quality of the flowback water and the economics of other management alternatives. Flowback water that is not reused is managed through disposal. While past disposal options sometimes involved direct dumping into surface waters or deposit at ill-equipped wastewater treatment plants, most disposal now occurs at *Class II injection wells* as regulated by the US Environmental Protection Agency. These injection wells place the flowback water in underground formations isolated from drinking water sources.

The hydraulic fracturing operation (Chapter 5) provides the permeable channels in the formation for natural gas or crude oil to flow to the wellbore, but contribute little to the overall storage capacity for natural gas or crude oil. The porosity of the matrix provides most of the storage capacity but the matrix has very low permeability and gas or oil flow in the fractures occurs in a different flow regime than gas or oil flow in the matrix. Because of these differing flow regimes, the modeling of production performance in fractured tight formations is much more complex than modeling of production performance in conventional reservoirs and scaling any modeling results up to the field operations is not only challenging but can be extremely difficult in spite of many claims of success. This, in turn, makes it difficult (sometimes impossible) to confidently predict production performance and devise optimal depletion strategies for tight resources. The proof is in the outcome of the field operations the balance of the field data with the data predicted from the modeling ventures.

Thus, in order to ensure the optimal development of tight natural gas and crude oil resources it is necessary to build a comprehensive understanding of geochemistry, geological history, multiphase flow characteristics, fracture properties (including an understanding of the fracture network) and production behavior across a variety of shale plays. It is also important to develop knowledge that can enable the scaling up of pore-level physics to reservoir-scale performance prediction, and make efforts to improve core analysis techniques to allow accurate determination of the recoverable resource.

For example, unconventional resources require a high well density for full development. Technology that can reduce well costs and increase wellbore contact with the reservoir can make a significant impact on costs, production rates and ultimate recovery. Multi-lateral drilling, whereby a number of horizontal sections can be created from a single vertical wellbore, and coiled tubing drilling to decrease costs represent potential options for future unconventional gas development.

As already noted, a combination of steel casing and cement in the well provides an essential barrier to ensure that high-pressure natural gas or crude oil liquids recovered from the deeper tight formations cannot escape into shallower rock formations or water aquifers. The casing and the support barrier must be designed to withstand the various cycles of stress (without suffering any cracks or induced faults) that will undoubtedly arise endure during the subsequent hydraulic fracturing (Chapter 5). In this respect, the design aspects that are most important to ensure a leak-free well include (i) the drilling of the well bore to specification (without any additional twists, turns or cavities), (ii) the positioning of the casing in the center of the well bore before it is cemented in place, which is achieved by use of centralizers placed at regular intervals along the casing as it is run in the drill hole, to keep it away from the rock face, and, equally important, (iii) the correct choice of cement. The cement design needs to be suitable for both its liquid properties during pumping – which will ensure that the cement gets to the right place – and then for its mechanical strength and flexibility. It is essential that the cement remains intact. The setting time of the cement is also a critical factor – cement that takes too long to set may have reduced strength – and equally important, cement that sets before it has been fully pumped into place requires difficult remedial action.

Thus, the combination of horizontal wells and hydraulic fracturing technologies has helped in unlocking shale gas resources, albeit at high cost of completions. It is essential that the quality of information for the completion design should be sufficiently high to justify the cost, thus: (i) type of completion – open hole or cased hole, (ii) fracture initiation locations, (iii) sleeves or perforations, (iv) number of stages, (v) type/volume/rate of fluids (vi) size/strength/proppant selection, (vii) overall fracture design, and (viii) comparison of the results versus model for both frac design and production. These items are determined through the completion, stimulation and assessment of the production from the vertical exploration wells. Through this process the minimum reservoir conditions are determined and an understanding of the initial production rate and the decline curves is made. This information is carried to the horizontal appraisal wells and which then allows the determining of the number of frac stages and optimum lateral length.

A key consideration in the completion design is to select cased completion using explosive perforating guns and plugs or sliding sleeves as part of an open-hole completion. Other components of the completion are the production equipment, both downhole from tubing size and deliquefication/lift design and optimization to surface facilities for efficient well flow back, separation, pipelines, compression and water treatment. A successful frac job is dependent upon frac flow-back, which is critical to maximizing liquid recovery and aiding in gas production. Each of these components mentioned are selected after intensive analysis of the reservoir parameters and economics.

A recent innovation in completion technology has been the addition of 3% v/v hydrochloric acid to induced fracturing in the Barnett Shale, which appears to increase the daily flow rate by enhancing matrix permeability and may add to the estimated ultimate recovery as long as environmental constraints are satisfied (Grieser et al., 2007). In addition, refracturing the reservoir is an option that is becoming more and more commonplace (Cramer, 2008) and can yield additional recoverable reserves.

3.4 Well integrity

Any well drilled into the Earth creates a potential pathway for liquids and gases trapped underground to reach the surface. The same technologies that contribute to the recovery on unconventional natural gas and crude oil resources – horizontal drilling and hydraulic fracturing – also create challenges for maintaining well integrity. In terms of the recovery of natural gas and crude oil from tight formations, the wells are typically longer, must deviate from the vertical plane to the horizontal plane (i) to travel laterally, (ii) access substantially (at least, potentially) over-pressured reservoirs, (iii) withstand more intense hydraulic fracturing pressures and (iv) withstand larger water volumes than traditional conventional natural gas and crude oil wells. Thus, poor well integrity can have a serious impact human health and the environment (Chapter 18).

For example, as a result of well leakage, formation fluids (liquids or gases) and injected fluids can migrate through holes or defects in the steel casing, through joints between casing, and through defective mechanical seals or cement inside or outside the well. In fact, a buildup of pressure inside the well annulus (*sustained casing pressure*) can force fluids out of the wellbore and into the surrounding formations. As a result of such leaks, fluids escape between the tubing and the rock wall where cement is absent or incompletely applied and the leaking fluids can then reach shallow groundwater or the atmosphere. Furthermore, well operations and the passage of time can seriously affect well integrity. For example, perforations, hydraulic fracturing, and pressure-integrity testing can cause thermal and pressure changes that damage the bond between cement and the adjacent steel casing or rock or that can fracture the cement or surrounding cap rock. In addition, chemical wear and tear can also degrade steel and cement through reactions with brines or other fluids that form corrosive acids in water (such as carbonic or sulfuric acids derived from carbon dioxide or hydrogen sulfide):

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

$$SO_2 + O_2 \rightarrow SO_3$$

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

In the atmosphere, these acids (along with nitrous and nitric acids formed by the reaction of water with nitrogen oxides, NO and NO_2) contribute to the formation of the environmentally harmful acid rain.

3.5 Production, abandonment, and reclamation

Once wells are connected to processing facilities, the main production phase can begin. During production, wells will produce hydrocarbon derivatives and waste streams, which have to be managed. But the well site itself is now less visible insofar as a *Christmas tree* of valves, typically three-to-four feet high, is left on top of the well, with production being piped to processing facilities that usually serve several wells; the rest of the well site can be reclaimed (Speight, 2014).

Thus, a variety of waste fluids are generated on site at shale gas wells. During drilling, used mud and saturated cuttings are produced and must be managed. The volume of mud roughly correlates with the size of the well drilled, so a horizontal Marcellus well may generate twice as much drilling waste as a single vertical well; however, as discussed above, it will replace four such holes. Drilling wastes can be managed onsite either in pits or in steel tanks. Each pit is designed to keep liquids from infiltrating vulnerable water resources. On-site pits are a standard in the oil and gas industry but are not appropriate everywhere; they can be large and they disturb the land for an extended period of time. Steel tanks may be required to store drilling mud in some environments to minimize the size of the well site "footprint" or to provide extra protection for a sensitive environment. Steel tanks are not, of course, appropriate in every setting either. In rural areas or pits or ponds, steel tanks are usually not needed.

In some cases, the operator may decide to repeat the hydraulic fracturing procedure at later times in the life of the producing well, a procedure called re-fracturing. This was more frequent in vertical wells but is currently relatively rare in horizontal wells, occurring in less than 10% of the horizontal shale-gas wells drilled in the United States. The production phase is the longest phase of the lifecycle. For a conventional well, production might last 30 years or more. For an unconventional development, the productive life of a well is expected to be similar, but wells in tight shale typically exhibit a burst of initial production and then a steep decline, followed by a long period of relatively low production. Output typically declines by between 50% and 75% in the first year of production, and most recoverable gas is usually extracted after just a few years.

During production, gas that is recovered from the well is sent to small-diameter gathering pipelines that connect to larger pipelines that collect gas from a network of production wells. Because large-scale natural gas production and light tight oil production from tight formations has only been occurring within the past decade, the production lifetime of wells in the tight formations is not yet fully established.

Although there is substantial debate on the issue, it is generally observed that wells in tight formations experience quicker production declines than conventional natural gas production. In the Fayetteville play in north-central Arkansas, it has been estimated that half-life of a production well, or half of the estimated ultimate recovery, occurs within its first five years of the well. Once a well no longer produces at an economic rate, the wellhead is removed, the wellbore is filled with cement to prevent leakage of gas into the air, the surface is reclaimed (either to its pre-well state or to another condition agreed upon with the landowner), and the site is abandoned to the holder of the surface rights of the land.

Like any other well, a well drilled into a tight formation is abandoned once it reaches the end of the producing life when extraction is no longer economic or possible. As with any gas-producing wells, at the end of their economic life, wells need to be safely abandoned, facilities dismantled and land returned to its natural state or put to new appropriate productive use. Long-term prevention of leaks to aquifers or to the surface is particularly important − sections of the well are filled with cement to prevent residual gas or residual oil flowing into water-bearing zones or up to the surface.

Since much of the abandonment will not take place until production has ceased, the regulatory framework needs to ensure that the companies concerned make the necessary financial provisions and maintain technical capacity beyond the economic life of the reservoir to ensure that abandonment is completed satisfactorily, and well integrity maintained over the long term.

4. Hydraulic fracturing

Hydraulic fracturing has been a key technology in making shale gas an affordable addition to the national energy supply, and the technology has proved to be an effective stimulation technique (Arthur et al., 2009; Spellman, 2013). While some challenges exist with water availability and water management (Chapter 5), innovative regional solutions are emerging that allow shale gas development to continue while ensuring that the water needs of other users are not affected and that surface and ground water quality is protected.

Thus, the first stage in the completion process is then to perforate the well, which refers to explosively punching a hole in the casing or liner, to connect the wellbore to the reservoir. This final stage of the completion process involves running perforating guns (a length of shaped explosive charges) down to the desired depth and firing them to perforate the casing or liner at the required depth. The second stage is then to hydraulically fracture the well by pumping fluid and proppant as sufficiently high pressures.

Shale is a sedimentary rock that is predominantly comprised of very fine-grained clay particles deposited in a thinly laminated texture, which is fine-grained and laminar in and can differ significantly between shale formations. These rocks were originally deposited as mud in low energy depositional environments, such as tidal flats and swamps, where the clay particles fall out of suspension. During the deposition of these sediments, organic matter is also deposited, which is measured by the *total organic content* (TOC).

The permeability of typical shale formations (i.e., the ability of fluids to pass through the shale) is very low (in fact, *ultra-low*) compared to conventional oil and gas reservoirs (nanodarcy 10^{-9} Darcy in shale formations vs. millidarcy 10^{-2} in conventional sandstone formations). In effect, the hydrocarbon derivatives are trapped and unable to flow under normal circumstances in shale, and usually only able to migrate out over geologic time. The slow migration of hydrocarbon derivatives from shale formations into shallower sandstone reservoirs and carbonate reservoirs has been the source of most conventional oil and gas fields, hence shale formations have historically been thought of as source and seal rocks, rather than potential reservoirs, but much of the hydrocarbon still remains bound in the shale.

Historically, there has not been any real need or desire to try to develop low productivity shale reservoirs as they were not economically attractive, though the potentially huge resource has always been suspected. However, recently shale gas development in the United States has been aggressively pursued as was (even in times of plenty) a need to secure lower risk/cost future gas.

For stacked sandstone reservoirs, designing the hydraulic fracture treatment should be based on the formation evaluation, especially the lithofacies layering geometry as the completion is based on the producing zones that are separated by vertical flow barrier layers (Holditch, 2006). The number of stages, for example, can be determined based on the stacking pattern of the geometry of sand bodies and shaley barriers. Depending on the thickness of the sand and shale layers and formation in situ stress profile, a single fracture treatment can be sometimes used to stimulate multiple layers, the well can be completed and stimulated with a single stage, and gas will be produced by commingling the different layers. On the other hand, when a thick shale barrier separates two productive layers, multiple hydraulic fractures should be created, especially when the in situ stress contrast is high.

Briefly, hydraulic fracturing involves pumping a (fracturing) fluid into a formation at a calculated, pre-determined rate and pressure to be able to fracture (crack) the shale and create fractures in the formation. Shale gas development typically uses water or water-based fluids as the fracture fluids, mixed with a small amount of various additives (see later).

Sand is the usual *proppant* material and is needed to maintain open fractures once fluid pumping of fluids has been terminated and the fluids have passed into the formation. Initially fractures were considered to grow as relatively regularly and were identical in shape and size at any point in time. However, as knowledge of the fracturing technology has progressed it is now obvious that fracture growth is complicated and much more.

Hydraulic fracturing has been widely used for fifty years or so by the oil and gas industry to improve low permeability reservoirs. Fluid (often water, carbon dioxide, nitrogen gas, or propane) is pumped down the well until the pressure surpasses the rock strength and causes the reservoir to crack. The fluid pumped down the well is loaded with proppant (often 100 tons−200,000 lbs) or more of ceramic beads or sand that infiltrate the formation and help to prop the fractures open, which are at risk of closing once the pressure is released. The choice of the fluid used depends on many factors, including whether clay in the reservoir is sensitive to water (some clays swell in the presence of fresh water) or whether the reservoir happens to respond better to particular fluids, usually only determined through experimentation.

Two factors increase the ability of shale to fracture: (i) the presence of *hard minerals*, and (ii) the *internal pressure* of the shale.

The presence of hard minerals such as silica (and to a lesser extent calcite), which break like glass, induce fractures into the shale when under pressure. Clay, however, tends to absorb more of the pressure and often bends under applied hydraulic pressure without breaking. Therefore, silica-rich shale formations are good candidates for fracking. In terms of the internal pressure of the shale, over-pressured shale formations develop during the generation of natural gas − because of the low permeability, much of the gas cannot escape and builds in place, increasing the internal pressure of the rock. Therefore, the artificially created fracture network can penetrate further into the formation because the shale is already closer to the breaking point than in normally pressured shale formations.

4.1 General aspects

Hydraulic fracturing is one of the key drivers to shale gas development because of its low to ultra-low permeability. Also key to shale gas development is the presence of natural fractures and planes of weakness that can result in complex fracture geometries during stimulation (Reddy and Nair, 2012). Furthermore, the presence and ability to open and maintain flow in both primary and secondary natural fracture systems are critical to shale gas production (King, 2010).

Hydraulic fracturing is a technology that involves pumping water, sand and a small amount of chemical additives into the well to fracture the rock, freeing the natural gas. This is common in oil and natural gas development — the technology has been used since the 1940s in more than one million wells in the United States. In fact, 90% of oil and gas wells in the United States undergo hydraulic fracturing to enhance production flow rates.

The development of large-scale shale gas production is changing the US energy market, generating expanded interest in the usage of natural gas in sectors such as electricity generation and transportation. At the same time, there is much uncertainty of the environmental implications of hydraulic fracturing and the rapid expansion of natural gas production from shale formations.

Water for fracturing can come from surface water sources (such as rivers, lakes or the sea), or from local boreholes (which may draw from shallow or deep aquifers and which may already have been drilled to support production operations), or from further afield (which generally requires trucking). Transportation of water from its source and to disposal locations can be a large-scale activity.

In areas of water-scarcity, the extraction of water for drilling and hydraulic fracturing (or even the production of water, in the case of coalbed methane) can have broad and serious environmental effects. It can lower the water table, affect biodiversity and harm the local ecosystem. It can also reduce the availability of water for use by local communities and in other productive activities, such as agriculture.

Limited availability of water for hydraulic fracturing could become a significant constraint on the development of tight gas and shale gas in some water-stressed areas. In China, for example, the Tarim Basin in the Xinjiang Uyghur Autonomous Region holds some of the largest shale gas deposits in China, but the region also suffers from severe water scarcity. Although not on the same scale, in terms of either resource endowment or water stress, a number of other prospective deposits occur in regions that are already experiencing intense competition for water resources. The development of shale gas industry in China has, to date, focused on the Sichuan basin, in part because water is much more abundant in this region.

Hydraulic fracturing dominates the freshwater requirements for unconventional gas wells and the dominant choice of fracturing fluid for shale gas, “slick-water”, which is often available at the lowest cost and in some shale reservoirs may also bring some gas-production benefits, is actually the most demanding in terms of water needs. Much attention has accordingly been given to approaches which might reduce the amount of water used in fracturing. Total pumped volumes (and therefore water volumes required) can be decreased through the use of more traditional, high viscosity, fracturing fluids (using polymers or surfactants), but these require a complex cocktail of chemicals to be added.

Foamed fluids, in which water is foamed with nitrogen or carbon dioxide, with the help of surfactants (as used in dish washing liquids), can be attractive, as 90% of the fluid can be gas and this fluid has very good proppant-carrying properties. Water can, indeed, be eliminated altogether by using hydrocarbon-based fracturing fluids, such as propane or gelled hydrocarbon derivatives, but their flammability makes them more difficult to handle safely at the well site. The percentage of fracturing fluid that gets back-produced during the flowback phase varies with the type of fluid used (and the shale characteristics), so the optimum choice of fluid will depend on many factors: the availability of water, whether water recycling is included in the project, the properties of the shale reservoir being tapped, the desire to reduce the usage of chemicals and the economics (Blauch et al., 2009).

Unlike conventional mineral formations containing natural gas deposits, shale has low permeability, which naturally limits the flow of gas or water. In shale formations, natural gas is held in largely unconnected pores and natural fractures. Hydraulic fracturing is the method commonly used to connect these pores and allow the gas to flow. The process of producing natural gas from shale deposits involves many steps in addition to hydraulic fracturing, all of which involve potential environmental impacts. Hydraulic fracturing is often misused as an umbrella term to include all of the steps involved in shale gas production. These steps include road and well pad construction, drilling the well, *casing*, perforating, hydraulic fracturing, *completion*, production, abandonment, and reclamation.

A common issue encountered in hydraulic fracturing operations in gas shale formations is the variability and unpredictability of the outcome of hydraulic fracturing. Industry experiences show that injection pressures required to fracture the formation (fracture gradient) oftentimes vary significantly along a well, and there can be intervals where the formation cannot be fractured successfully by fluid injection. The use of real-time fracture mapping allows for on-the-fly changes in fracture design. Mapping also impacts the perforation strategy and re-stimulation designs to maximize the *effective stimulation volume* (ESV − the reservoir volume that has been effectively contacted by the stimulation treatment as determined by microseismic event locations and density). A correlation of microseismic activity with log data allows estimation of fracture geometry to be made after which the data can be used to design a stimulation that has the greatest chance of maximizing production (Fisher et al., 2004; Baihly et al., 2006; Daniels et al., 2007).

Shale gas reservoirs also respond to fluid injection in a variety of modes. As observed through microseismic monitoring, distribution of activated seismicity can be confined along a macroscopic fracture plane, but most time they are dispersed throughout a wide region in the reservoir reflecting the development of a complex fracture network (Waters et al., 2006; Cipolla et al., 2009; Das and Zoback, 2011; Maxwell, 2011).

In recent years, various attempts have been made to optimize the design of transverse fractures of horizontal wells for shale gas reservoirs (Britt and Smith, 2009; Marongiu-Porcu et al., 2009; Meyer et al., 2010; Bhattacharya and Nikolaou, 2011; Gorucu and Ertekin, 2011). In most cases, the optimum design is identified by local sensitivity analysis and usually one variable is varied while keeping all other variables fixed. However, these optimization methods may not provide sufficient insight for screening insignificant parameters and for considering parameter interactions to obtain the optimal design. Hence, the optimization of hydraulic fracturing treatment design for shale gas production remains a challenge.

An additional factor to consider is shale thickness. The substantial thickness of shale is one of the primary reasons, along with a large surface area of fine-grained sediment and organic matter for adsorption of gas, that shale resource evaluations yield such high values for total organics carbon content and potential gas producibility. Not surprisingly, a general rule-of-thumb is that thicker shale is a better target. Shale targets such as the Bakken oil play in the Williston Basin (itself a hybrid conventional-unconventional resource), however, are less than one hundred and fifty feet thick in many areas and are yielding apparently economic rates of gas flow and recovery. The required thickness to economically develop a shale gas target may decrease as drilling and completion techniques improve, as porosity and permeability detection techniques progress in unconventional targets and, perhaps, as the price of gas increases. Such a situation would add a substantial amount of resources and reserves to the shale gas formation.

An additional consideration is the desorption of the gaseous constituents as well as any crude oil constituents (Kok and Merey, 2014). A significant amount of gas or oil in shale reservoirs is stored as adsorbed or condensed phase. The amount adsorbed depends on reservoir temperature, pressure, particle size, and type. Total organic carbon content (TOC) and clay content of shale are also important parameters for adsorption (Lu et al., 1993).

Shale reservoirs have naturally fractured systems. Shale matrices are layered structures. Gas or low-boiling constituents of the oil are is adsorbed on the surface of micro-porous shale matrix. Some gas is stored as a free phase in the fractures and porous spaces of shale matrix. In the adsorption process, Van der Waals-type interactions at the shale-hydrocarbon interface increase the concentrations of gas molecules near the shale surface, where the density increases comparable to the density of the liquids. Thus, shale reservoirs can actually hold more gas than conventional gas reservoirs of comparable volumes (Song et al., 2011).

Desorption – the reverse process of adsorption – from shale reservoirs, occurs when the reservoir pressure decreases due to the production of the adsorbed material (Song et al., 2011). In shale reservoirs, desorption mechanism is very important for production and to provide desorption, pressure is an important parameter for shale reservoir systems. By lowering the reservoir pressure, desorption occurs in a shale reservoir. In order to decrease reservoir pressure, much free gas and/or water is produced from the shale gas reservoir and then adsorbed gas in pore spaces starts to desorb in a significant amount. When production starts in shale gas reservoirs, free gas in a matrix porous system and fracture system is produced (Song et al., 2011), which causes a decrease in pressure. Decreasing pressure causes gas desorption in matrix pores and desorbed gas and free gas is produced through fracture systems. However, for this mechanism, successful hydraulic fracturing operations are essential to provide the diffusivity of desorbed gas from shale matrix through fractures.

In tight gas and tight oil reservoirs, the key is to ensure the best as possible desorption of the gas and oil constituents from the reservoir rock (Chapter 1). The proportion of gas and oil constituents existing in tight reservoirs in an adsorption state is variable and depends upon several factors, such as such as (i) pressure, (ii) temperature, (iii) the composition of shale, (iv) moisture, (v) the composition of the shale gas, and the thermal maturity of the shale rock system (Chapter 1). The adsorbed constituents must desorb from the shale surface before entering macropores and fractures. In fact, desorption is the main source of exploitation of shale gas. In the early development period, free gas flows fast and results in a prolific period (Lewis and Hughes, 2008; Cipolla, 2009; Anderson, 2010). However, the yield falls rapidly and the production period becomes stable. In the stable production period, the yield is mainly from desorption and diffusion of adsorbed constituents. The desorption and diffusion rates are very slow due to the mechanism of pressure depletion. Hence, the stable production stage is very long, and the yield is very low. The production cycle is long and gas recovery is low and, therefore, it is crucial to accelerate desorption in order to maintain efficient development of shale reservoirs. Based on investigations of mechanisms and the factors influencing adsorption/desorption, high-temperature mixture gas injection technology was developed to accelerate the desorption process.

4.2 Fracturing fluids

Initially, the fluid is injected that does not contain any propping agent is injected to create a fracture that is multi-directional and spreads up, out and down. The pad creates a fracture that is wide enough to begin accepting a propping agent material. The pad is then followed by the proppant slurry – a mix of the carrier fluid and proppant material. The purpose of the propping agent is to *prop open* the fracture once the pumping operation ceases and the fracture closes.

In deep reservoirs, man-made beads are sometimes used to prop open the fractures but in shallow reservoirs, sand can be used and remains the most common proppant. Once the fracture has initiated, fluid is continually pumped into the wellbore to extend the created fracture and develop a fracture network. Each formation has different properties and in-situ stresses so that each hydraulic fracture job is unique and different and is specifically designed for that well by a hydraulic fracturing specialist. The process of designing hydraulic fracture treatments involves identifying properties of the target formation including estimating fracture treating pressure, amount of material and the desired length for optimal economics.

The fracturing fluid should have a number of properties that are and tailored to and optimized for each formation, i.e., the fluid should be (i) be compatible with the formation rock, (ii) compatible with the formation fluid, (iii) generate sufficient pressure drop down the fracture to create a wide enough fracture, (iv) have sufficient lower viscosity to allow clean-up after the treatment, and (v) be cost effective. Water-based fluid are commonly used and − *slickwater* is the most common fluid used for shale gas fracturing, where the major chemical added is a surfactant polymer to reduce the surface tension or friction, so that water can be pumped at lower treating pressures. Other fluids that have been used include oil-based fluids, energized fluids, foams and emulsions.

Environmental concerns have focused on the fluid used for hydraulic fracturing and the risk of water contamination through leaks of this fluid into groundwater. Water itself, together with sand or ceramic beads (the "proppant"), makes up over 99% of a typical fracturing fluid, but a mixture of chemical additives is also used to give the fluid the properties that are needed for fracturing. These properties vary according to the type of formation. Additives (not all of which would be used in all fracturing fluids) typically help to accomplish four tasks:

(1) To keep the proppant suspended in the fluid by gelling the fluid while it is being pumped into the well and to ensure that the proppant ends up in the fractures being created. Without this effect, the heavier proppant particles would tend to be distributed unevenly in the fluid under the influence of gravity and would, therefore, be less effective. Gelling polymers, such as guar or cellulose (similar to those used in food and cosmetics) are used at a concentration of approximately 1%. Cross-linking agents, such as borates or metallic salts, are also commonly used at very low concentration to form a stronger gel. They can be toxic at high concentrations, though they are often found at low natural concentrations in mineral water.

(2) To change the properties of the fluid over time. Characteristics that are needed to deliver the proppant deep into subsurface cracks are not desirable at other stages in the process, so there are additives that give time-dependent properties to the fluid, for example, to make the fluid less viscous after fracturing, so that the hydrocarbon derivatives flow more easily along the fractures to the well. Typically, small concentrations of chelants (such as those used to de-scale kettles) are used, as are small concentrations of oxidants or enzymes (used in a range of industrial processes) to break down the gelling polymer at the end of the process.

(3) To reduce friction and therefore reduce the power required to inject the fluid into the well. A typical drag-reducing polymer is polyacrylamide (widely used, for example, as an absorbent in baby diapers).

(4) To reduce the risk that naturally occurring bacteria in the water affect the performance of the fracturing fluid or proliferate in the reservoir, producing hydrogen sulfide; this is often achieved by using a disinfectant (biocide), similar to those commonly used in hospitals or cleaning supplies.

Until recently, the chemical composition of fracturing fluids was considered a trade secret and was not made public. This position has fallen increasingly out of step with public insistence that the community has the right to know what is being injected into the ground. Since 2010, voluntary disclosure has become the norm in most of the United States. The industry is also looking at ways to achieve the desired results without using potentially harmful chemicals. “Slick-water”, made up of water, proppant, simple drag reducing polymers and biocide, has become increasingly popular as a fracturing fluid in the United States, though it needs to be pumped at high rates and can carry only very fine proppant. Attention is also being focused on reducing accidental surface spills, which most experts regard as a more significant risk of contamination to groundwater.

Finally because of the properties of the shale formation (above) such as (i) the presence of *hard minerals*, and (ii) the *internal pressure* of the shale, it may be possible to isolate sections along the horizontal portion of the well, segments of the borehole for one-at-a-time fracking (multi-stage fraccing). By monitoring the process at the surface and in neighboring wells, it can be determined how far, how extensively, and in what directions the shale has cracked from the induced pressure.

Finally, shale formations can be re-fracked years later, after production has declined, which may (i) allow the well to access to larger areas of the reservoir that may have been missed during the initial hydraulic fracturing or (ii) to reopen fractures that may have closed due to the decrease in pressure as the reservoir was drained. Even with hydraulic fracturing, wells drilled into low-permeability reservoirs have difficulty communicating far into the formation. As a result, additional wells must be drilled to access as much gas as possible, typically three or four, but up to eight, horizontal wells per section.

4.3 Fracturing fluid additives

Possible additives for fracturing fluids are chosen according to the task at hand − i.e., the properties of the reservoir. These additives include: (i) polymers, which allow for an increase in the viscosity of the fluid, together with cross-linkers, (ii) cross-linkers, which increase the viscosity of the linear polymer base gel, (iii) breakers, which are used to break the polymers and cross-link sites at formation temperature, for better clean-up, (iv) biocides, which re used to kill bacteria in the mix water, (v) buffers, which are used to control the pH, (vi) fluid loss additives, which are used to control excessive fluid leak-off into the formation, and (vii) stabilizers, which are used to keep the fluid viscous at higher temperature.

However, it must be emphasized that additives are used for every site and in general as few additives as possible are added to avoid potential environmental contamination (use of the additives must be controlled) and production problems with the reservoir.

A recent innovation in completion technology has been the addition of 3% v/v hydrochloric acid to induced fracturing in the Barnett Shale, which appears to increase the daily flow rate by enhancing matrix permeability and may add to the estimated ultimate recovery (Grieser et al., 2007). In addition, refracturing the reservoir is an option that is becoming more and more commonplace (Cramer, 2008) and can yield additional recoverable reserves.

Rocks with interlaminated shale and siltstone is a shale gas target (e.g., Lewis Shale, New Mexico; Colorado Group, Alberta) that may require new techniques for detection in well logs, as well as new completion and drilling techniques. The silt laminations are too thin to be detected on well logs and to allow an accurate determination of how many laminations are in a given interval. Also, well logs are unable to accurately determine the percentage of porosity in shale or the laminations, the degree of water saturation in a reservoir or the relative degree of permeability in each lamination. Laminations both store gas (free gas) and are pathways of transport for diffusion of gas from shale to the well bore (Beaton et al., 2009; Pawlowicz et al., 2009; Rokosh et al., 2009).

The laminations are also particularly difficult completion targets. Normally, induced fractures are meant to extend laterally rather than vertically in a reservoir, yet the laminations may span tens of hundreds of feet vertically. Therefore, a horizontal fracture may miss many productive shale and silt laminations. Induced fracturing techniques may have to be altered, or new techniques developed for this type of shale gas reservoir.

4.4 Fracture diagnostics

Fracture diagnostics are the techniques used to analyze the created fractures and involve analyzing data before (pre-fracture analysis), during (real time) and after (post-fracture) hydraulic fracture treatment (Barree et al., 2002; Vulgamore et al., 2007). The *raison d-être* for the is determination of the dimensions of the created fractures and also whether or not the fractures are effectively maintained in an open mode (*propped*) fracture. The diagnostic techniques are generally sub-divided into three groups: (i) direct far-field techniques, (ii) direct near-wellbore techniques, and (iii) indirect fracture techniques.

4.4.1 Direct far-field techniques

The *direct far-field* techniques comprise tiltmeter (an instrument designed to measure very small changes from the horizontal level, either on the ground or in subterranean structures) and microseismic fracture mapping techniques which require delicate instrumentation to be placed in boreholes surrounding and near the well to be fracture treated. Microseismic fracture mapping typically relies on using a downhole receiver array of accelerometers, or geophones, to locate *micro-earthquakes* that are triggered by shear slippage in natural fractures surrounding the hydraulic fracture. As with all monitoring and data collection techniques, however, examination of wells that are typically considered marginal wells is often not justified until the resource has been proved. If the technology is used at the beginning of the development of a field, however, the data and knowledge gained may be worthwhile and effective development of the shale resource is warranted.

4.4.2 Direct near-wellbore techniques

Direct near-wellbore techniques – which consist of tracer logs, temperature logging, production logging, borehole image logging, downhole video logging, and caliper logging – are used in the well that is being fractured to locate the portion of fracture that is very near wellbore and In Shale gas reservoirs, where multiple fractures are likely to exist, the reliability of these direct near-wellbore techniques may be questionable. As such, very few of these direct near-wellbore techniques are used on a routine-without-question basis to evaluate hydraulic fracture patterns and if deployed the *direct near-wellbore techniques* are typically used in conjunction with other more reliable techniques.

4.4.3 Indirect fracture techniques

Indirect fracture techniques consist of hydraulic fracture modeling and matching of the net surface treating pressures, together with subsequent pressure transient test analyses and production data analyses. As fracture treatment data and the post-fracture production data are normally available on every well, indirect fracture diagnostic techniques are the most widely used methods to determine the shape and dimensions of both the created and the propped hydraulic fracture.

5. Production trends

Many of the low permeability reservoirs that have been developed in the past are sandstone reservoirs but, currently, significant quantities of natural gas and crude are also produced from low permeability shale reservoirs, carbonate reservoirs, and coal seams. The tight gas reservoirs have one thing in common: a vertical well drilled and completed in the tight gas reservoir must be successfully stimulated to produce at commercial volumes and flow rates. Typically, a large hydraulic fracture treatment is required to produce the natural gas or crude oil and horizontal wells and/or multilateral wells are used to provide the stimulation required for natural gas or crude oil recovery.

To optimize the development of a tight reservoir, the recovery team must optimize the number of wells drilled, as well as the drilling and completion procedures for each well. On an individual well basis, a well in a tight reservoir will produce less gas over a longer period of time than one expects from a well completed in a higher permeability, conventional reservoir. As such, many more wells (or smaller well spacing) must be drilled in a tight gas reservoir to recover a large percentage of the original gas in place (OGIP) or the original oil in place (OOIP), when compared to a conventional reservoir.

Thus, economic natural gas production from unconventional tight formation reservoirs is achieved by the combination of horizontal drilling and reservoir stimulation by multistage slick-water fracturing. Ideally, every fracture treatment at every stage of the well is successful, but experiences from the Barnett Shale and other shale gas reservoirs have shown that not all stages are stimulated equally. The regions of stimulated reservoir volume may be different between stages in size and shape, sometimes confined along a plane or sometimes dispersed widely in the reservoir (Waters et al., 2006; Maxwell, 2011).

Operators also have observed that the fracturing pressure (fracture gradient) can vary between stages, sometimes to a point where pump pressures cannot reach the fracturing pressure required to propagate a fracture (Daniels et al., 2007). These variations in the outcome of hydraulic fracturing are caused by the heterogeneity in the rock mechanical/deformation properties, presence of natural fractures, and/or the variations in in-situ stress within the reservoir.

However, the increasing participation of major oil companies in the exploitation of North American shale gas and tight oil resources has had positive implications for the use of best practices and technologies in drilling and processing. Continued development of shale gas and tight oil resources in North America and other countries with significant resources will have an impact on the global gas markets, however this impact is expected to remain moderate in the short to medium term, nothing comparable to what happened in the United States (LEGS, 2011).

The increasing use of shale gas and light tight oil will primarily impact power generation, transport fuels and the petrochemical industry. In fact, estimates of proven reserves of shale gas are increasing globally and will continue to do so as exploration continues. Furthermore, exploitation of the shale gas and light tight oil can affect natural gas and crude oil availability and prices, particularly in North America.

5.1 Technology

Optimizing the production from tight reservoirs calls for complex development geometries, sometimes requiring several dozen multi-drain or horizontal wells. Preserving the permeability of the reservoir in the vicinity of the wells – low by definition in tight reservoirs – is a necessity for drilling projects. One option is the use of *underbalanced drilling* which is a procedure used to drill oil and gas wells where the pressure in the wellbore is kept lower than the fluid pressure in the formation being drilled. As the well is being drilled, formation fluid flows into the wellbore and up to the surface, which is the opposite of the usual situation, where the wellbore is kept at a pressure above the formation to prevent formation fluid entering the well. In conventional *overbalanced drilling*, if the well is not shut-in it can lead to a blowout (gusher) which can be a hazardous situation. In underbalanced drilling, however, there is a rotating head at the surface, which is a seal that diverts produced fluids to a separator while allowing the drill string to continue rotating. If the formation pressure is relatively high, using a lower density mud will reduce the well bore pressure below the pore pressure of the formation. Sometimes an inert gas is injected into the drilling mud to reduce its equivalent density and hence the hydrostatic pressure throughout the well depth. This gas is commonly nitrogen, as it is non-combustible and readily available, but air, reduced oxygen air, processed flue gas, and natural gas have all been used. On the other hand, coiled tubing drilling uses the established concept of coiled tubing and combines it with directional drilling using a mud motor to create a system for drilling reservoirs which allows for continuous drilling and pumping and therefore underbalanced drilling can be utilized which can increase the rate of penetration (ROP).

Thus, in the underbalanced drilling technique, the mud pressure is kept lower than the formation pressure, thereby preventing invasive formation damage and the associated risk of clogging. This complex technique, implemented on the Hassi Yakour tight gas field in Algeria during the second half of 2006, demands expert skill: the mud properties must be constantly adjusted to accommodate pressure variations caused by differences in subsoil characteristics. Bringing the wells into production is another critical juncture. Tight matrices need to be stimulated by fracturing to ensure sufficient flow rates. Gas gathering is improved by high-pressure injection and pumping of an aqueous fluid to break up the rock. However, the capillary pressure of the fluid can modify reservoir permeability; the fracturing fluid can become trapped, preventing efficient flow of the gas. To get around this drawback, Total adds volatile agents such as methanol to the fracturing fluid, to help the liquid recede faster. The final step entails the injection of granular supporting agents (proppants, usually a material such as sand) to maintain the properties of the induced fractures that allow the natural gas or crude oil to pass to the production well(s).

The development of natural gas and crude oil resources in tight formations is a modern technologically driven process for the production of natural gas resources. Currently, the drilling and completion of wells in tight shale reservoirs and in other tight reservoirs includes both vertical and horizontal wells. In both kinds of wells, casing and cement are installed to protect fresh and treatable water aquifers. The emerging shale gas and tight oil basins are expected to follow a trend similar to the Barnett Shale play with increasing numbers of horizontal wells as the plays mature. Operators are increasingly relying on horizontal well completions to optimize recovery and well economics. Horizontal drilling provides more exposure to a formation than does a vertical well.

This increase in reservoir exposure creates a number of advantages over vertical wells drilling. Six to eight horizontal wells drilled from only one well pad can access the same reservoir volume as sixteen vertical wells. Using multi-well pads can also significantly reduce the overall number of well pads, access roads, pipeline routes, and production facilities required, thus minimizing habitat disturbance, impacts to the public, and the overall environmental footprint (Chapter 5).

The other technological key to the economic recovery of natural gas and crude oil from tight reservoirs is hydraulic fracturing, which involves the pumping of a fracturing fluid under high pressure into a shale formation to generate fractures or cracks in the target rock formation. This allows the natural gas to flow out of the shale to the well in economic quantities. Ground water is protected during the hydraulic fracturing process by a combination of the casing and cement that is installed when the well is drilled and the thousands of feet of rock between the fracture zone and any fresh or treatable aquifers. For development of natural gas and crude oil from tight reservoirs, fracture fluids are primarily water based fluids mixed with additives that help the water to carry sand proppant into the fractures. Water and sand make up over 98% of the fracture fluid, with the rest consisting of various chemical additives that improve the effectiveness of the fracture job. Each hydraulic fracture treatment is a highly controlled process that must be designed to the specific conditions of the target formation.

A combination of improved technology and shale-specific experience has also led to improvements in recovery factors and reductions in decline rates. Each shale resource requires its own specific completion techniques, which can be determined through careful analysis of rock properties. The correct selection of well orientation, stimulation equipment, fracture size and fracturing fluids can all affect the performance of a well. The initial production rate from a particular well is highly dependent on the quality of the fracture and the well completion. In the United States it has been seen that initial production rates have been augmented over time as the resource matures. Initial production rates can be increased by several techniques, in particular by increasing the number of fracture stages and increasing the number of perforations per fracture stage. The quality of the fracture is also improved as fluid properties are developed. Microseismic data can also be used to improve the efficiency of the hydraulic fracturing process.

The primary differences between modern natural gas and crude oil development from tight reservoirs and the development of natural gas and crude oil from conventional reservoirs is the extensive uses of horizontal drilling and high-volume hydraulic fracturing. The use of horizontal drilling has not introduced any new environmental concerns. In fact, the reduced number of horizontal wells needed coupled with the ability to drill multiple wells from a single pad has significantly reduced surface disturbances and associated impacts to wildlife, dust, noise, and traffic. Where shale gas and tight oil development has intersected with urban and industrial settings, regulators and industry have developed special practices to alleviate nuisance impacts, impacts to sensitive environmental resources, and interference with existing businesses.

Hydraulic fracturing has been a key technology in making shale gas and tight oil an affordable addition to the US energy supply, and the technology has proved to be an effective stimulation technique. While some challenges exist with water availability and water management, innovative regional solutions are emerging that allow shale gas and tight oil development to continue while ensuring that the water needs of other users are not affected and that surface and ground water quality is protected. Taken together, state and federal requirements along with the technologies and practices developed by industry serve to reduce environmental impacts from shale gas and tight oil operations.

5.2 Product stability

Analysis of the gas composition of Devonian shale wells indicates that the composition of produced gas shifts during the production history of the well (Schettler et al., 1989). These changes in composition indicate that different components of natural gas produced have different decline curves. Thus, the total decline curve is the sum of the decline curves of the individual gas components. The way to explain observed fractionation with such classic mechanisms is to assume that total flow has several sources within the wellbore, each with different characteristic compositions and decline curves. It can also be assumed that the gas composition changes observed at the wellbore reflect changing composition of gas from at least some of the sources themselves. This option necessitates that the production mechanism include the presence of adsorption, solution, and/or diffusion.

The occurrence of adsorption is associated with the presence of certain minerals in the reservoir, such as clays. Likewise, solution is associated with the presence of crude oil and the diffusion option is associated with diffusion through small pores, such as those present in microporous reservoirs. Because these factors are commonly present, this second alternative may he involved in explaining fractionation in many reservoirs.

5.3 The future

Development of shale gas and tight oil resources in Western Europe, Scandinavia and Poland has the potential to reduce the considerable dependence of western European countries on Russian resources, unless, of course, Russian companies gain control of these resources through company actions or through invasive actions. Furthermore, discoveries of tight resources in South America have the potential of realigning the energy relationships on the continent. Argentina, Brazil and Chile are likely beneficiaries decreasing their dependence on Bolivian gas.

Notwithstanding the environmental moratoriums in some countries, shale gas and tight oil will be used in many parts of the world. This will place downward pressure on prices of natural gas and lower natural gas prices may lead to significant shifting in power generation and transport fuels.

Finally, shale gas liquids are having a significant impact on the petrochemical industry in North America, which has spillover effects in Europe, the Middle East and Asia. Further, the liquids are making shale gas more profitable than many traditional dry gas reservoirs.

Despite the availability of proven production technologies, environmental impacts are still being queried; in particular, the impact on ground water resources and the possible methane releases associated with current production techniques. These issues are the subject of intense scrutiny at the moment. The supply and use of shale gas and tight crude oil is already showing an impact on the fossil fuels energy sector is not restricted to the global natural gas pricing outlook but its development has become entwined with the global energy mix and emerging nexus in energy-climate-water and its impact on the global energy supplies environment.

Finally, property and mineral rights differ across the world. In the United States, individuals can own the mineral rights for land they own. In many parts of Asia, Europe and South America this is not the case. Therefore, unresolved legal issues remain obstacles for shale gas and tight oil exploitation in many countries across the globe. Given the investment requirements needed to develop shale basins that presently have little to no infrastructure, the legal issues are important to attract the investment needed for exploration and exploitation.

In summary, the recovery of natural gas and crude oil from tight reservoirs have heterogeneous geological and geomechanical characteristics that pose challenges to accurate prediction of the response to hydraulic fracturing. Experience in tight formations that contain natural gas and light tight oil formations shows that stimulation often results in formation of a complex fracture structure, rather than the planar fracture aligned with the maximum principal stress. The fracture complexity arises from intact rock and rock mass textural characteristic and the in-situ stress and their interaction with applied loads. Open and mineralized joints and interfaces, and contact between rock units play an important role in fracture network complexity which affects the rock mass permeability and its evolution with time.

Currently, the mechanisms that generate these fracture systems are not completely understood, and can generally be attributed to lack of in-situ stresses within the reservoir rock, rock brittleness, shear reactivation of mineralized fractures, and textural heterogeneity. This clearly indicate the importance of linking the mineralogy, rock mechanics, and geomechanics to determine the prospectively of an unconventional shale resource.

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CHAPTER 5

Hydraulic fracturing

1. Introduction

Hydraulic fracturing (hydraulic fracture stimulation, fracking, fraccing) has been referenced in an earlier chapter (Chapter 4) and, because it is one of the key techniques that allow access to natural gas and crude oil from tight formations, it is presented here in more detail.

Extraction of natural gas and crude oil from conventional reservoirs involves drilling through impervious rock that traps concentrated underground reservoirs of natural gas and crude oil and may even involve a mining operation for heavy oil and tar sand bitumen (Chapter 3) (Speight, 2014, 2016a). With conventional crude oil, extraction occurs simply due to the change in pressure caused by the drilling. Conventional crude oil reservoirs depend on the pressure of their gas cap and oil-dissolved gas to lift the oil to the surface (i.e., *gas drive)* (Chapter 3). Water trapping the crude oil from below also exerts an upward hydraulic pressure (i.e., *water drive)*. The combined pressure in crude oil reservoirs produced by the natural gas and water drives is known as the *conventional drive.* As the production of a reservoir declines, lifting further amounts of crude oil to the surface, like the lifting of water, requires pumping, or *artificial lift.*

However, not all of the natural gas and crude oil is conveniently located in conventional and accessible reservoirs. Many oil and gas resources are trapped in the pore spaces and cracks within impermeable sedimentary rock formations – shale formations, tight sandstone formations, and tight carbonate formations are examples of such reservoirs (Chapters 1 and 2). These reservoirs can vary in thickness – the shale formations are relatively thin layers (albeit deep under the ground) but cover extensive horizontal areas and a vertically drilled well will only access a small area of the reservoir and, by inference due to the impermeable nature of the formation, a minimal part of the resource. However, when the drilling operation can deviate from the conventional vertical plane and move in the horizontal plane much more of the reservoir resource becomes accessible (Ely, 1985; Gidley et al., 1990).

In the past three-to-four decades, hydraulic fracturing (Table 5.1) has been increasingly used in formations that were known to be rich in natural gas that was locked so tightly in the rock that it was technologically and economically difficult to produce. Application of fracturing techniques to stimulate oil and gas production began to grow rapidly in the 1950s, although experimentation dates back to the 19th Century. Starting in the mid-1970s, partnerships of various private operators, the US Department of Energy (DOE) and predecessor

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TABLE 5.1 Highlights in the development of hydraulic fracturing.

Date	Comment
Early 1900s	Natural gas extracted from shale wells
	Vertical wells fractured with foam
1947	Klepper gas unit no. 1; first well to be fractured to increase productivity
1949	Stephens county, Oklahoma; first commercial fracturing treatment
1950	Fracturing with cement pumpers
1950s	Evolution of fracture geometry
	Increasing well productivity
1960s	Fracturing pumpers and blenders
1970s	Massive hydraulic fracturing
	Increase recoverable reserves
	Hydraulic fracturing in Europe
1983	First gas well drilled in Barnett shale in Texas
1980s	Evolution of proppant transport
	Fracture conductivity testing
	Cross-linked gel fracturing fluids developed; used in vertical wells
1990s	First horizontal well drilled in Barnett shale
	Orientation of induced fractures identified
	Foam fracturing
1996	Slickwater fracturing fluids introduced
1996	Microseismic post-fracturing mapping developed
1997	Hydraulic fracturing in Barnett shale
	Slickwater fracturing developed
1998	Slickwater refracturing of originally gel-fractured wells
2002	Multi-stage slickwater fracturing of horizontal wells
2003	First hydraulic fracturing of Marcellus shale
2004	Horizontal wells become dominant
2005	Increased emphasis on improving the recovery factor
2007	Use of multi-well pads and cluster drilling

agencies, and the Gas Research Institute (GRI) endeavored to develop technologies for the commercial production of natural gas from the relatively shallow Devonian (Huron) shale in the eastern United States. This partnership helped foster technologies that eventually became crucial to the production of natural gas from shale rock, including horizontal wells, multi-stage fracturing, and slick-water fracturing. Practical application of horizontal drilling to oil production began in the early 1980s, by which time the advent of improved downhole drilling motors and the invention of other necessary supporting equipment, materials, and technologies (particularly, downhole telemetry equipment) had brought some applications within the realm of commercial viability.

Also key to shale gas development is the presence of natural fractures and planes of weakness that can result in complex fracture geometries during stimulation (Reddy and Nair, 2012). Furthermore, the presence and ability to open and maintain flow in both primary and secondary natural fracture systems are critical to shale gas production (King, 2010). The technology involves pumping water, a proppant such as sand (Table 5.2) to keep the fractures open, and a small amount of one or more chemical additives into the well to assist the fracture process, by which the natural gas or crude oil is enabled to flow to the wellbore. In fact, the use of horizontal drilling in conjunction with hydraulic fracturing has greatly expanded the ability of producers to profitably recover natural gas and oil from low-permeability geologic plays – particularly, shale plays and other tight reservoirs (Speight, 2016b).

In the process, the pressure exceeds the rock strength and the fluid opens or enlarges fractures in the rock. As the formation is fractured, a propping agent, such as sand or ceramic beads, is pumped into the fractures to keep them from closing as the pumping pressure is released. The fracturing fluids (water and chemical additives) are then returned back to the surface. Natural gas and crude oil will then flow from pores and fractures in the rock into the well for subsequent extraction to the surface. Naturally occurring sand grains or artificial ceramic material are common proppants used. Nano-proppants are light, high-strength ceramic proppants which are typically uniform in size so that they pack uniformly and create porosity providing significant space for all and gas to flow. In contrast, if the proppant being used has particles of varying shapes and sizes, such as the grains in commonly used, relatively inexpensive sand, they pack tighter, and the rate at which oil and gas come out of the well is slower. Another consideration is downhole injection where fluid is pumped down the borehole with varying-sized proppant particulates, their tendency to aggregate will limit how far down they can be pumped.

TABLE 5.2 Proppant type definition.

Sand	Includes all raw sand types.
Resin-coated sand	Includes only resin-coated proppants for which the substrate is sand; does not include any double-counting with the “sand category” described above.
Ceramic	Any proppant for which the substrate is a ceramic or otherwise manufactured proppant, resin-coated ceramic proppant is included in this category.

The development of large-scale natural gas and crude oil production from tight formations is changing the energy market of the United States – as well as the energy markets in various other countries (Chapter 2) – by generating expanded interest in the usage of natural gas in sectors such as electricity generation and transportation. At the same time, there is much uncertainty of the environmental implications of hydraulic fracturing and the rapid expansion of natural gas production from shale formations. For example, water for the hydraulic fracturing process can come from surface water sources (such as rivers, lakes or the sea), or from local boreholes (which may draw from shallow or deep aquifers and which may already have been drilled to support production operations), or from further afield (which generally requires trucking). Transportation of water from its source and to disposal locations can be a large-scale activity. Nevertheless, hydraulic fracturing has been a key technology in making shale gas an affordable addition to the national energy supply, and the technology has proved to be an effective stimulation technique (Arthur et al., 2009; Spellman, 2013, 2016).

While some challenges exist with water availability and water management (Chapters 6 and 18), innovative regional solutions are emerging and continually being sought that allow natural gas and crude oil development to continue while ensuring that the water needs of other users are not affected and that surface and ground water quality is protected. In the late 1940s, drilling companies began inducing hydraulic pressure in wells to fracture the producing formation. This stimulated further production by effectively increasing the contact of a well with a formation. Moreover, advances in directional drilling technology have allowed wells to deviate from nearly vertical to extend horizontally into the reservoir formation, which further increases contact of a well with the reservoir. Directional drilling technology (sometimes referred to as *deviated drilling technology*) also enables drilling a number of wells from a single well pad, thus cutting costs while reducing environmental disturbance. Combining hydraulic fracturing with directional drilling has opened up the production of tight (less permeable) natural gas reservoirs and crude oil reservoirs, particularly unconventional gas shales such as the Marcellus Shale formation.

The application of hydraulic fracturing to tight sands revitalized old fields and allowed establishment of new fields. Subsequently, the application of hydraulic fracturing to shale opened up new areas to development, including the Marcellus Shale in the eastern United States, the Barnett Shale in Texas, and the Fayetteville Shale in Arkansas, among others. In fact, the rise in production of natural gas and crude oil from these and other shale plays has effects the move of natural gas and crude oil prices to lower (currently) more stable levels (Fisher, 2012; Scanlon et al., 2014; US EIA, 2014). In practice, the well is fractured in stages and a plug set between each stage. When all of the stages have been completed and plugged, the plugs are removed (drilled out), which allows the natural gas or crude oil to flow up through the well to begin production.

Briefly, the process involves use of a *perforating gun* which is lowered into a newly drilled well and lined up precisely within the target formation (a tight shale, sandstone, or carbonate formation) using seismic images, well logs, global positioning systems and other indicators to target the spots from which natural gas and crude oil are most likely to occur. When fired, the gun punches small holes into the well casing, cement, and rock after which the fracturing fluid is forced out of the perforations under high pressure. This creates fractures (small cracks) in the formation that allow the natural gas and crude oil to flow from the reservoir into the wellbore. The fracturing fluid contains proppants such as sand or other similarly sized materials in order to maintain the fractures created by the pressure treatment in the open position, thus preventing closure when the pressure treatment is terminated. Although the fracturing fluid (*slickwater*) is predominantly water, it does contain chemicals (in addition to the proppant) which can pose an environmental risk (Green, 2014, 2015).

Thus, hydraulic fracturing has become an essential part of natural gas production and crude oil production, especially, production of natural gas and crude oil that is trapped in low-permeability (shale, sandstone, and carbonate) formations (Agarwal et al., 1979). The procedure significantly improves the recovery from the reservoir by stimulating the movement of natural gas and crude oil. When used in conjunction with horizontal drilling, an advanced drilling technology, hydraulic fracturing has made it possible to develop vast unconventional resources.

Without hydraulic fracturing and horizontal drilling, resources contained in tight formations would remain largely undeveloped. In fact, many modern oil field production operations would not exist without hydraulic fracturing and as the global balance of supply and demand forces the natural gas and crude oil industries toward more unconventional resources including shale formations such as the Barnett, Haynesville, Bossier, and Marcellus plays, hydraulic fracturing will continue to play a major role in unlocking theses otherwise unobtainable reserves.

To stimulate gas and/or oil flow from tight sand formation or from shale formations, where gas is trapped in tiny pores in the rock (rather than accumulated in large pools or more porous rock), hydraulic fracturing is applied. In spite of the various negative attitudes to hydraulic fracturing, the technique is proven technique and has been used for decades in many kinds of natural gas and crude oil recovery operations. However, hydraulic fracturing must be applied with diligence and caution and use of multi-disciplinary team, like all reservoir management operations (Speight, 2016b). Starting the process on the basis that *one person knows all* is guaranteed to cause a multitude of problems and result in failure.

Finally, naturally fractured reservoirs contain secondary or induced porosity in addition to their original primary porosity. Induced porosity is formed by tension or shear stresses causing fractures in a competent or brittle formation. Fracture porosity is usually very small. Values between 0.0001 and 0.001 of rock volume are typical (0.01%–0.1%) Fracture-related porosity, such as solution porosity in granite or carbonate reservoirs, may attain much larger values, but the porosity in the actual fracture is still very small. There are, of course, exceptions to all rules of thumb. In rare cases, such as the cooling of intrusive minerals or surface lava flows, in which natural fracture porosity may exceed 10%. When buried and later filled with hydrocarbon derivatives, they form very interesting reservoirs.

2. Reservoir evaluation

Reservoir characteristics, as well as the characteristics of the surrounding formations, must always be considered when designing any hydraulic fracturing project (Veatch, 1983; Smith and Hannah, 1996; Reinicke et al., 2010). More specifically, in tight formations, fracture length is the overriding factor for increased productivity and recovery. Typical conventional natural gas and crude oil reservoirs have a permeability deposits boast a permeability level on the order of 0.01–1 Darcy, but the formations termed *tight formations* (*tight reservoirs*) typically have permeability levels on the order of milliDarcys (Darcy × 10^{-3}) or microdarcy (Darcy × 10^{-6}) even down to nanoDarcys (Darcy × 10^{-9}) (Fig. 5.1), although the permeability data given for shale reservoirs and tight sandstone or carbonate reservoirs are not always as sharp as this illustration would indicate. Furthermore, there is no true or regular relationship between porosity and permeability, specifically for shale rock although some general trends may appear when the two are compared (Fig. 5.2).

In addition, and from a reservoir-development standpoint, understanding the fracture geometry and orientation is crucial for determining well spacing (Holditch et al., 1978). Thus, field-development strategies designed to extract more hydrocarbon derivatives from crude oil or natural gas and, furthermore, natural fractures, which are often the primary means for fluid flow in low-permeability reservoirs, can (and often do) compromise the predictability of the geometry of hydraulic fractures and the effect on production and drainage.

Finally, success or failure of a hydraulic fracture treatment often depends on the quality of the candidate well selected for the treatment. Choosing an excellent candidate for stimulation often ensures success, while choosing a poor candidate normally results in economic failure. To select the best candidate for stimulation, the design engineer must consider many variables. The most critical reservoir parameters for hydraulic fracturing that need consideration are: (i) formation permeability, (ii) the in-situ stress distribution, (iii) reservoir fluid viscosity, (iv) reservoir pressure, (v) reservoir depth, (vi) the condition of the wellbore, and (vii) the skin factor, which refers to whether the reservoir is already stimulated or, perhaps, damaged. Typical values for the skin factor range from -6 for an infinite-conductivity massive hydraulic fracture to more than 100 for a poorly formed gravel pack.

Tight formations vary considerably and for this reason no single technique for hydraulic fracturing has universally worked. Each play has unique properties that need to be addressed through fracture treatment and fluid design. For example, numerous fracture technologies have been applied in the Appalachian basin alone, including the use of carbon dioxide, nitrogen, carbon dioxide foam, and slickwater fracturing. The composition of fracturing fluids must be altered to meet specific reservoir and operational conditions. Slickwater hydraulic fracturing, which is used extensively in shale basis of the United States and Canada, is suited for complex reservoirs that are brittle and naturally fractured and are tolerant of large volumes of water. Ductile reservoirs require more effective proppant placement to achieve the desired permeability. Other fracture techniques, including carbon

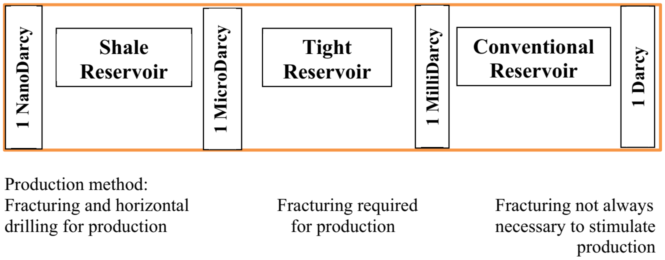

FIG. 5.1 Illustration of reservoir types based on permeability and production methods.

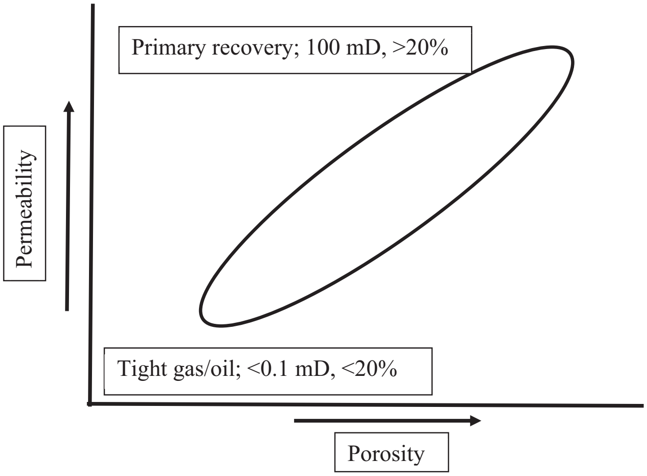

FIG. 5.2 General trends in the relationship between porosity and permeability.

dioxide polymer foam and nitrogen foam, are occasionally used in ductile rock (for instance, in the Montney Shale in Canada).

One of the most important aspects of drilling for any crude oil is predetermining the success rate of the operation. Operators do not just drill on a whim or a hunch and extensive seismic data is gathered and analyzed to determine where to drill and just what might be located below the surface of the Earth. These seismic surveys can help to pinpoint the best areas to tap tight gas reserves. A survey might be able to locate an area that portrays an improved porosity or permeability in the rock in which the gas is located. If drilling is sufficiently accurate to directly penetrate the best area to develop the reservoir, the cost of development and recovery can be minimized.

The changes in porosity and permeability of shale matrix occur when production starts. This variation in porosity and consequently permeability is because of two reasons; gas desorption from shale surface (unlike conventional reservoirs) and increasing effective stresses by pressure depletion. When gas molecules leave the surface of the shale rock and move toward the pore spaces, in fact the pore volume is increased as the matrix volume is decreased. This will result in an increase in porosity of the shale matrix. Unlike desorption effect, the porosity of shale tends to decrease with production as a result of increased net stress effect. The change in porosity and subsequent permeability of the shale has not been studied in the reservoir simulation while focusing on its effect on a long-term production outlook.

Generally, in early stages of production from shale formations as the reservoir pressure is considerably high, there is no significant desorption from shale surface to contribute to production. This means that up to some stages of production, reservoir is encountered with porosity reduction due to increased net stress and compaction. Once a critical lifetime of a shale reservoir is reached, the porosity changes due to desorption must be considered in which porosity will enhance due to increase of pore volume of shale and consequent reduction in rock volume. This critical life time of a shale reservoir depends on its isothermal desorption behavior that should be measured experimentally. After the critical period of shale production is passed, three different scenarios are possible. First, the compaction effect on porosity dominates the porosity change against desorption and the total effect tend to reduce shale porosity. Second, the two effects may not overcome each other that mean the porosity reduction due to compaction is balanced by its enhancement due to desorption. Last, porosity increases several orders of magnitude more than its reduction due to compaction.

Most tight gas and oil formations are found onshore, and land seismic techniques are undergoing transformations to better map out where drilling and development of these unconventional plays. Typical land seismic techniques include exploding dynamite and *vibroseis*, or measuring vibrations produced by purpose-built trucks. While these techniques can produce informational surveys, advancements in marine seismic technologies are now being applied to land seismic surveys, enhancing the information available related to the world below.

Fracturing a well involves breaking the rocks in the formation apart. Performed after the well has been drilled and completed, hydraulic fracturing is achieved by pumping the well full of fracturing fluids under high pressure to break the rocks in the reservoir apart and improve permeability, or the ability of the gas to flow through the formation. Additionally, acidizing the well is employed to improve permeability and production rates of tight gas formations, which involves pumping the well with acids that dissolve the limestone, dolomite and calcite cement between the sediment grains of the reservoir rocks. This form of production stimulation helps to reinvigorate permeability by reestablishing the natural fissures that were present in the formation before compaction and cementation.

While vertical wells may be easier and less expensive to drill, they are not the most conducive to developing tight gas. In a tight gas formation, it is important to expose as much of the reservoir as possible, making horizontal and directional drilling a necessity. Here, the well can run along the formation, opening up more opportunities for the natural gas to enter the wellbore. A more common technique for developing tight gas reserves includes drilling more wells. The more the formation is tapped, the more the gas will be able to escape the formation. This can be achieved through drilling myriad directional wells from one location, which lessens the drilling footprint and lowers the costs. After seismic data has illuminated the best well locations, and the wells have been drilled, production stimulation is employed on tight gas reservoirs to promote a greater rate of flow. Production stimulation can be achieved on tight gas reservoirs through both fracturing and acidizing the wells.

Formation evaluation is the process of interpreting a combination of measurements taken inside a wellbore to detect and quantify oil and gas reserves in the rock adjacent to the well. A formation consists of rock layers (strata) that have similar properties (Chapter 1) and, thus, formation evaluation is an important aspect of the fracturing process, especially in low permeability reservoirs because of the presence of alternating layers with various properties. Hence, it is necessary to define these properties, which include (but are not limited to): thickness, fluid saturation, porosity, Young's Modulus, in-situ stress, permeability, formation conductivity (Holditch et al., 1987).

Thus, formation evaluation is used to determine the ability of a well (borehole) to produce crude oil and/or natural gas. Typically, the well is drilled by a rotary drill which uses a heavy mud (drilling mud) as a lubricant and as a means of producing a confining pressure against the formation face in the borehole, preventing blowouts. A blowout is an uncontrolled release of fluids during the drilling, completion, or production of natural gas and crude oil. In former times, the blow out may have been referred to as a gusher which was spectacular but (Hollywood movies not withstanding) was a waste of crude oil and an environmental nightmare.

When a blowout occurs, it is typically when unexpectedly high pressures are encountered in the subsurface or due to valve failure or other type of mechanical failure. Blowouts may take place at the surface (wellhead or elsewhere) or subsurface (naturally high pressure, or may be artificially induced in the well bore during hydraulic fracturing during completion operations, but not during pumping). A high percentage of blowouts occur due to casing or cement failure, allowing high-pressure fluids to escape up the well bore and flow into subsurface formations. The potential environmental consequences of a blowout depend mostly on (i) the timing of the blowout relative to well activities, which determines the nature of the released fluid such as natural gas or pressurized fracturing fluid, (ii) the occurrence of the escape of containments through the surface casing or deep in a well, and (iii) the risk receptors, such as freshwater aquifers or water wells that are impacted.

Controlling a blowout can have disadvantages such as: (i) mud filtrate soaking into the formation in the near vicinity of the borehole and (ii) a mud cake plasters the sides of the hole. These factors obscure the possible presence of oil or gas in even very porous formations and further complications arise with the occurrence of small amounts of crude oil in the rocks of many sedimentary formations (sedimentary provinces). In fact, if a sedimentary formation does not exhibit any evidence for the presence of natural gas or crude oil, drilling operations will be terminated.

2.1 Geological and geotechnical evaluation

A primary step in the evaluation of feasibility of fracturing is characterization of the *geological parameters* by examination of at least one continuous core boring sample in order to characterize major and minor changes in lithology as well as an analysis of the geological cross sections which show sediment layering in the target zone, and the contaminant characteristics present in the target zone. Cores (cylinders of rock, approximately 3–4 inches in diameter and up to 60 feet long) collected during continuous and depth-specific sampling should also be examined for factors contributing to secondary permeability such as coarse-grained sediment inclusions and naturally occurring fractures. More specifically, the geologic parameters to be evaluated include: (i) the type of soil/rock, (ii) the type of deposition, (iii) the groundwater locale, including depth and dimensions of the aquifer, (iv) the possibility of pre-fracturing contamination, (v) the type of contamination, and (vi) the depth and extent of the contamination. The last three categories are necessary to establish the base-case condition of the area before fracturing commences and is the control by which the hydraulic fracturing process and any ensuing effects is measured.

Geotechnical characterization of the formations involves determining two general factors: (i) the lower limits for porosity, permeability, and upper limits for water saturation that permit profitable production from a particular formation or pay zone and (ii) whether or not the formations under consideration exceed these lower limits. Thus, target zone samples should be submitted for evaluation of (i) the grain size analysis, (ii) the liquid and plastic limits of the formations, (iii) the moisture content, and (iv) the unconfined compressive strength.

Grain size analysis recognizes that although fractures can be created in sediments and rock of variable grain size, the highest degree of permeability improvement can be expected from the finer grained materials. Grain size analysis can be performed by using the sieve analysis method and/or the hydrometer analysis method (ASTM D421; ASTM D422). The *liquid and plastic limits* of the formations (the Atterberg limits − a measure of the critical water contents of a fine-grained soil, such as its shrinkage limit, plastic limit, and liquid limit) and characterizes the plasticity of a formation (ASTM D4318). The *moisture content* (ASTM D2216) can influence the process insofar as permeability improvements are achievable with fracturing but vapor flow in particular is also controlled by the presence of moisture. Improvements in vapor flow through highly saturated formations (at or near capacity) will not always be achieved by fracturing alone and additional means of moisture removal may be required to obtain the desired effect through fracturing.

Data from measurement of the *unconfined compressive strength* (ASTM D2166) can be used for predicting the orientation and direction of propagation of fractures. Since hydraulic fracturing is generally applied at sites with characteristically low permeability, a baseline estimate of *permeability* (vapor and/or liquid) must be available, usually from testing concluded at the site during site investigations. This baseline estimate of permeability provides a basis for evaluating the necessity, benefit, and effectiveness of the fracturing process. In general, greater improvement of vapor or fluid flow and radial influence is observed in formations with lower initial permeability. In terms of cohesion, the more cohesive the soil is, more amenable it will be to fracturing. Longevity of the fractures, upon relaxation of fracture stress, is high in cohesive formations and fracturing in cohesive formations (such as silty clays) has been particularly successful.

2.2 Formation integrity

The formation integrity test is carried out to confirm the strength of formation and well casing shoe by increasing the bottomhole pressure to a design pressure. There is considerable confusion in industry nomenclature, as formation integrity tests (FITs) such as the use of leak-off tests (LOTs) (API RP 13M-4). The leak-off tests, also known as pressure integrity tests (PITs) are used to determine the fracture gradient of a formation (from stress estimates). Low leak-off (fluid loss) rate is the property that permits the fluid to physically open the fracture and one that controls its areal extent. The rate of leak-off to the formation is dependent upon the viscosity and the wall-building properties of the fluid (API RP 13M). Post-fracture breakdown is necessary such that the injected fluids do not hander the passage of oil and gas (clog) the formation. However, formation integrity tests are conducted to show that the formation below the casing shoe will not fail while drilling subsequent sections with a higher bottom hole pressure (Lee and Holditch, 1981). The test is generally conducted soon after drilling resumes after an intermediate casing string has been set and the purpose of the test is to determine the maximum pressures that may be safely applied without the risk of formation breakdown and the maximum well bore pressure does not exceed the least principal stress or was not sufficient to initiate a fracture of the well bore wall in an open hole test (Zoback, 2010).

2.3 Permeability and porosity

Permeability is of critical importance in determining wells applicable for hydraulic fracturing. Since the main reason fracturing is done, is to extract natural gas or crude oil that would not flow naturally to the well bore. The permeability of the formation also affects the formation breakdown pressure in hydraulically fractured wells and permeable rock typically has a lower breakdown pressure than impermeable rock under similar conditions (Postler, 1997).

The standard method of obtaining permeability in routine core analysis is by allowing dry gas, usually nitrogen, helium or air to flow through the samples. It has the following advantages over using liquid permeability: reduced fluid-rock interaction, easier to execute, faster and less expensive although the validity of the gas permeability method has been questioned (Unalmiser and Funk, 2008) Another shortcoming of using dry gas to obtain permeability is that it has to be corrected for gas slippage (the Klinkenberg effect), which arises with the type of gas used and the mean existing pressures in the core sample at the time of the measurement.

Porosity (the ratio of void volume to total) is obtained by measurement of either two of the three variables: pore volume (PV), bulk volume (BV) and grain volume (GV). It is important that calibration to standard temperature and barometric pressure is performed when measuring grain density for determination of the grain volume. The type of porosity test to be used out depends on the formation being sampled, for instance in vug formations (formations with small cavern or cavity within a reservoir rock, such as in carbonate formations) special procedures are required and, in addition, porosity measurement, like permeability measurement, is also sensitive to drying time.

As stated previously, there is no true or regular relationship between porosity and permeability, specifically for shale rock although some general trends may appear when the two are comparted graphically (Fig. 5.2). However, the porosity does tend to increase with the increase of clay minerals possibly because pore volumes in these formations mostly resides within the clay mineral aggregates and solid organics in the formation (Loucks et al., 2009; Sondergeld et al., 2010).

2.4 Residual fluid saturation and capillary pressure

Measurement of the *residual fluid saturation* was originally obtained by: (i) use of high powered vacuum distillation to recover oil and water or (ii) distillation extraction, which divides the extraction process into two parts in which the water was distilled and then the oil was extracted using suitable solvents for oil-solubility (Speight, 2015). Currently, fluid tracer studies, displaced-miscible fluid analyses (reducing damage to clays) and improved geochemical techniques are used to obtain saturation (Unalmiser and Funk, 2008). Fluid saturations are normally reported as a percent of the pore volume, and the accuracy of measurements is largely determined by conditions during sample recovery (Holditch et al., 1987).

A parameter of interest that influences most of the properties in the first phase is the wettability of the sample as it relates to fracture properties (Fernø et al., 2008). It is a measure of the preferred inclination of a fluid, i.e., water or oil to spread on the rock surface. It combines the interaction of the rock surface, fluid interfaces and pore shape. Another category of the analysis involves measurement of formation geomechanical properties like Poisson's ratio, Young's modulus, and fracture toughness (Holditch et al., 1987).

The *capillary pressure* is the difference in pressure across the interface between two phases. Relative permeability and capillary pressure relationships are used for estimating the amount of oil and gas in a reservoir and for predicting the capacity for flow of oil, water, and gas throughout the life of the reservoir. The relative permeability and capillary pressure are complex functions of the structure and chemistry of the fluids and solids in a producing reservoir and, as a result, will vary within a reservoir.

Thus, capillary pressure is used to characterize the reservoir by indicating water saturation, size of pore channels and differentiating productive from non-productive intervals (Keelan, 1982; Slattery, 2001).

2.5 Mechanical properties

Because of the high interest in producing natural gas and crude oil from unconventional tight reservoirs, and there is an increasing need to understand the petrophysical and mechanical properties of these rocks (Sone and Zoback, 2013a,b). In fact, there is a wide variation in the properties of the formations (between reservoirs and within a reservoir) and, as might be expected, the properties of these rocks are a strong function of their material composition. Furthermore, the general characterization of these organic-rich rocks (shale, sandstone, and carbonates) can be challenging because these rocks vary significantly.

For example, formations in the Barnett formation are silica-rich whereas the Ford Shale formation is carbonate-rich and contains relatively smaller amounts of silica minerals and clay minerals. In fact, many (tight) shale reservoirs typically have significant differences in lithology and petrophysical properties (Passey et al., 2010). Another source of complexity in these reservoirs is the mechanical anisotropy which is due to the organized distribution of presence of the clay minerals (Hornby et al., 1994; Johnston and Christensen, 1995; Sondergeld and Rai, 2011) and compliant organic materials (Vernik and Nur, 1992; Vernik and Liu, 1997; Vernik and Milovac, 2011). There are also indications that it is not only the amount of clay minerals or organic constituents, but also the maturity of the shale formations that may influence the various properties of these organic-rich shales (Vanorio et al., 2008; Ahmadov et al., 2009). Understanding the anisotropy and its causes is crucial because they strongly influence analyses/interpretations of seismic surveys, sonic logs, and microseismic monitoring (Sone and Zoback, 2013a,b).

Many tight gas reservoirs are thick, layered systems that must be hydraulically fracture treated to produce at commercial gas flow rates (Chapter 5) and to optimize production it is necessary to understand the mechanical properties of all the layers above, within, and below the natural gas or crude oil pay zones. Basic rock properties such as in-situ stress, Young's modulus and Poisson's ratio are needed to design a fracture treatment. The in-situ stress of each rock layer affects how much pressure is required to create and propagate a fracture within the layer. The values of Young's modulus relate to the stiffness of the rock and help determine the width of the hydraulic fracture. The values of Poisson's ratio relate to the lateral deformation of the rock when stressed. Poisson's ratio is a parameter required in several fracture design formulas.

The most important mechanical property is in-situ stress, often called the minimum compressive stress or the fracture closure pressure and to optimize gas or oil production it is very important to know the values of in-situ stress in the various strata. Generally, when the pressure inside the fracture is greater than the in-situ stress, the fracture is open but when the pressure inside the fracture is less than the in-situ stress, the fracture is closed. The necessary data can be obtained by using core sample, or injection tests.

3. The fracturing process

Hydraulic fracturing is a key technique that has enabled the economic production of natural gas from shale deposits, or *plays*. The development of large-scale shale gas production is changing the energy market of the United States, generating expanded interest in the usage of natural gas in sectors such as electricity generation and transportation. At the same time, there is much uncertainty of the environmental implications of hydraulic fracturing and the rapid expansion of natural gas production from shale plays (Speight, 2016b).

Unlike conventional mineral formations containing natural gas deposits, shale and other tight formations have a low permeability which naturally limits the flow of gas or water. In shale plays, natural gas is held in largely unconnected pores and natural fractures. Hydraulic fracturing is the method commonly used to connect these pores and allow the gas to flow. The process of producing natural gas from shale deposits involves many steps in addition to hydraulic fracturing, all of which involve potential environmental impacts. Hydraulic fracturing is often misused as an umbrella term to include all of the steps involved in shale gas production. These steps include road and well pad construction, drilling the well, casing, perforating, hydraulic fracturing, completion, production, abandonment, and reclamation.

Hydraulic fracturing is not a method for drilling or constructing a well but itis the process for creating a fracture or fracture system in a porous medium by injecting a fluid under pressure through a well bore in order to overcome the natural and inherent stresses in a formation. To fracture a formation, energy must be generated by injecting a fluid down a well and into the formation. The effectiveness of hydraulically created fractures is measured both by the orientation and areal extent of the fracture system and by the post-fracture enhancement of vapor or liquid recovery.

The process is applied after well completion to facilitate movement of the reservoir fluids to the well and thence to the surface. This process creates access to more natural gas and crude oil but requires the use of large quantities of water and fracturing fluids, which are injected underground at high volumes and pressure. Thus, the sequence of fracturing a particular formation typically consists of: (i) an acid stage, (ii) a pad stage, (iii) a prop sequence stage, and (iv) a flushing stage.

The *acid stage* consists of several thousand gallons of water mixed with a dilute acid, such as hydrochloric or muriatic acid, which serves to clear cement debris in the wellbore by dissolving carbonate minerals and opening fractures near the wellbore.

A well requires a prepared area on the surface (the pad) that provides a stable base for a drilling rig, retention ponds, water storage tanks, loading areas for water trucks, associated piping, and pumping and control trucks. After well completion, the pad serves as the location of the *wellhead* and other equipment. Preparing a pad involves clearing and leveling several acres of land. The size of the pad depends on the depth of the well and the number of wells to be drilled on the site. In addition to land disturbed for building the well pad, three to four acres are disturbed per pad for roads and utilities to service the pad.

The *pad stage* consists of use of approximately one hundred thousand gallons of water (or more) 100,000 gallons of slickwater without proppant material. In this slickwater pad stage, the slickwater solution fills the wellbore and opens the formation which and helps to facilitate the flow and placement of proppant material. The *prop sequence stage* may consist of several sub-stages of the use of water combined with proppant material, which consists of a fine mesh sand or ceramic material, and is intended to keep open (prop) the fractures created and/or enhanced during the fracturing operation after the pressure is reduced; this stage may collectively use several hundred thousand gallons of water. The proppant material may vary from a finer particle size to a coarser particle size throughout this sequence. The *flushing stage* consists of a volume of fresh water sufficient to flush the excess proppant from the wellbore; the amount of water used is dependent upon the site characteristics (including the character of the subterranean formations).

Most of the fluids used in hydraulic fracturing are water and chemicals (typically 1% v/v of the water). The formulas for fracturing fluids vary, partly depending on the composition of the gas-bearing or oil-bearing formations, remembering that all gas-bearing and oil-bearing formations are not the same even when the formations are composed of the same minerals (shale, sandstone, or carbonate). In addition, some of the chemical additives can be hazardous if not handled carefully (Table 5.3) and caution is advised since the amount of the chemical(s) must not exceed the amount specified in regulatory requirements related to handling hazardous materials. Even if the chemical is one that is indigenous to the sub-surface (and supposedly benign because it is found naturally), the amount used must not exceed the indigenous amount − in some case, exceeding the indigenous amount of a chemical can cause environmental problems.

Safe handling of all water and other fluids on the site, including any added chemicals, must be a high priority and compliance with all regulations regarding containment, transport and spill handling is essential. When it comes to disposal of the fracturing fluid, there are options. For example, the fluid, when possible without causing adverse effects to the environment, can be reused for additional wells in a single field − this reduces the overall use of fresh water and reduces the amount of recovered water and chemicals that must be sent for disposal. However, in such cases, recognition of the geological or mineralogical similarities or difference within a site must have been determined to assure minimal environmental damage. In addition, tanks (or *lined* storage pits) for the storage of recovered water are also a necessity until the water can be sent for disposal of in a permitted saltwater injection disposal well or taken to a treatment plant for processing. The linings of such pits must be in accordance with local environmental regulations.

All injection wells must be designed to meet the regulations set by the national agency (for example, the United States Environmental Protection Agency) or any local agency to protect the groundwater. In addition, production zones should have that have multiple confining

TABLE 5.3 Additives used in the hydraulic fracturing process.

Water and sand: approximately 98% v/v		
Water	Expand the fracture and delivers sand	Some remains in the formation; the remainder returns with natural formation water as produced water (amounts returned vary from well to well)
Sand (proppant)	Allows the fractures to remain open so that the oil and natural gas can escape	Stays in the formation, embedded in the fractures (used to keep the fractures open)
Other additives: approximately 2% v/v		
Acid	Helps dissolve minerals and initiate cracks in the rock	Reacts with the minerals present in the formation to create salts, water and carbon dioxide (neutralized)
Anti-bacterial agent	Eliminates bacteria in the water that produces corrosive by-products	Reacts with micro-organisms that may be present in the treatment fluid and formation
Breaker	Allows a delayed breakdown of the gel	Reacts with the crosslinker and gel in the formation making it easier for the fluid to flow to the borehole
Clay stabilizer	Prevents formation clays from swelling	Reacts with clays in the formation through a sodium-potassium ion exchange
Corrosion inhibitor	Prevents corrosion of the pipe	Bonds to the metal surfaces, such as pipe; any remaining product that is not bonded is broken down by micro-organisms
Crosslinker	Maintains fluid viscosity as temperature increases	Combines with the breaker in the formation to create salts that are returned to the surface in produced water
Friction reducer	Minimizes friction	Remains in the formation where temperature; exposure to the breaker allows it to be broken down and consumed by naturally occurring micro-organisms
Gelling agent	Thickens the water to suspend the sand	Combines with the breaker in the formation making it easier for the fluid to flow to the borehole
Iron control	Prevents precipitation of metal in pipe	Reacts with minerals in the formation to create simple salts, carbon dioxide and water
Non-emulsifier	Breaks or separates oil/water mixtures (emulsions)	Generally, returns to the surface with produced water; in some formations, may enter the gas stream and return to the surface in the produced oil and natural gas
pH adjusting agent	Maintains the effectiveness of other components, such as crosslinkers	Reacts with acidic agents in the treatment fluid to maintain a neutral (non-acidic, non-alkaline) pH

layers above the zone to keep the injected fluids within the target gas-bearing or oil-bearing formation. In addition, multiple layers of well casing and cement (similar to production wells) should be used with periodic mechanical integrity tests to verify that the casing and cement are holding the liquids. The amount and pressure of the injected fluid (specified in each well permit) should be monitored to maintain the fluids in the target zone and the pressure in the injection well and the spaces between the casing layers (also called the annuluses) should also be monitored check and verify the integrity of the injection well.

Finally, to be an aid in production, fractures must be connected to a reasonable hydrocarbon bearing reservoir with sufficient volume to warrant exploitation. If there is no reservoir volume, a lot of fractures won't help much unless there is sufficient fracture related solution porosity to hold an economic reserve. This can be determined by normal log analysis techniques. In reasonable non-fractured reservoirs, it is usually possible to estimate permeability, and hence productivity (Speight, 2014, 2016b), but this is not always possible in fractured reservoirs. Although both the presence of fractures and the presence of a reservoir can be determined from logs, a production test will be needed to determine whether economic production is possible. The test must be analyzed carefully to avoid over optimistic predictions based on the flush production rates associated with the fracture system. Local correlations between fracture intensity observed on logs and production rate are also used to predict well quality.

Sometimes the primary reservoir and the fracture system may be so poorly connected that they are saturated with different fluids. Production from fractures full of hydrocarbon derivatives in a water bearing formation may initially be very good but very short lived. A more desirable scenario is a primary reservoir with appreciable hydrocarbon saturation and a fracture system that is full of water close to the borehole, showing invasion and hence good permeability, but full of hydrocarbon in the uninvaded formation. There are several issues that must be taken into consideration during the fracturing process, these are: (i) equipment, (ii) well development, (iii) fracture patterns, (iv) fracture optimization, and (v) fracture monitoring.

3.1 Equipment

Conventional cement-pumping and acid-pumping equipment was used initially to execute fracturing treatments. One to three units equipped with one pressure pump delivering 75–125 hhp were adequate for the small volumes injected at the low rates. However, as treating volumes increased, accompanied by a demand for greater injection rates as well as special pumping and blending equipment was developed and development continues.

Initially, sand was added to the fracturing fluid by pouring it into a tank of fracturing fluid over the suction. More recently, with less-viscous fluid(s), a ribbon or paddle type of batch blender was used after which a continuous proportioning blender utilizing a screw to lift the sand into the blending tub was developed. As the procedure evolved, blending equipment has also had to evolve to meet the need for proportioning a large number of dry and liquid additives, then uniformly blending them into the base fluid and adding the various concentrations of sand or alternate propping agents. In fact, the hydraulic fracturing treatment follows the actual drilling and completion of the well (Hubbert and Willis, 1957; Hibbeler and Rae, 2005; Arthur et al., 2009).

In the initial stages of a fracturing project, the drilling may be the same as drilling a conventional reservoir. Thus, in the process, a borehole is drilled vertically, then a casing is put in place after which cement and mud is pumped into the annulus to form a barrier between the borehole and adjacent formations. Drilling is then continued, to an adequate depth adjacent (sometimes within) within the producing reservoir. From this point (the *kick-off point*), the well bore is deviated gradually until it curves into a horizontal plane and drilled a distance on the order of 1000 feet to more than 5000 feet (Arthur et al., 2009).

The hydraulic fracturing procedure is then initiated. The process involves fracturing at isolated intervals along the horizontal well since it is difficult (if not impossible) to apply pressure along the entire length of the well bore because of loss of pressure efficiency over the distance involved (1000−5000 feet). The fracturing areas are isolated using packers and perforations are created in the wellbore within the interval bounded by packers (Arthur et al., 2009). In some fracture treatments, acid is pushed through the perforated interval to help breakdown any barrier that might be due to the characteristics of the formation(s) surrounding the wellbore.

The design of fracture treatment is a complex task, which involves analysis, planning, experience and rigorous observation of different stages in the entire process. In order to develop a formation containing natural gas and/or crude oil, the wellbore is drilled in successive sections through the rock layers. Once the desired length of each wellbore section has been drilled, the drilling assembly is removed, and steel casing is inserted and cemented in place. As the well is constructed, concentric layers of steel casing and cement form the barrier to protect groundwater resources from the fluids that will later flow inside the well. In the next step, a section of casing within the formation is perforated at the desired location for gas or oil production.

At this stage, the well is ready for hydraulic fracturing process which involves pumping fluid through the perforations. The fracturing fluid exerts pressure against the rock, creating tiny cracks, or fractures, in the reservoir deep underground. The fluid is predominantly water, proppant (grains of sand or ceramic particles) and a small amount (on the order of 1% v/v) of chemical additives. Once fluid injection stops, pressure begins to dissipate, unless the necessary steps are token, the fractures previously held open by the fluid pressure begin to close. The necessary steps include the injection of proppants which act as wedges to hold open the narrow fractures, thereby creating pathways for the natural gas or crude oil and the fracturing fluids to flow more easily to the well. A plug is set inside the casing to isolate the stimulated section of the well and the perforate-inject-plug cycle is repeated at regular intervals along the targeted section of the reservoir. Finally, the plugs are drilled out, allowing the natural gas, crude oil, and other fluids to flow into the well casing and up to the surface. The natural gas/crude oil/fracturing fluid mixture is separated at the surface, and the fracturing fluid (also known as flowback water) is captured in tanks or lined pits. The fracturing fluids are then disposed of according to the regulatory-approved methods.

Briefly, several definitions exist for the terms *produced water* and *flowback water* and indicate the confusion in the use of the terminology. The common definitions are (i) *produced water* is any of the many types of water produced from oil and gas well and (ii) *flowback water* is the hydraulic fracturing fluid that returns that returns to the surface after a hydraulic fracture is completed.

Fractures from both horizontal and vertical wells can propagate vertically out of the intended zone thereby (i) reducing stimulation effectiveness, (ii) wasting proppant and fluids, and potentially connecting up with other hydraulic fracturing stages or unwanted water or gas intervals which can also lead to a variety of environmental issues (Chapter 18). The direction of lateral propagation is largely dictated by the horizontal stress regime, but in areas where there is low horizontal stress anisotropy or in reservoirs that are naturally fractured, fracture growth is not always easy to predict (Hammack et al., 2014). In shallow zones, horizontal hydraulic fractures can develop because the weight of the overburden − the vertical stress component −− is smallest. A horizontal hydraulic fracture reduces the effectiveness of the stimulation treatment because it most likely forms along horizontal areas of weakness − such as the areas between the formation strata − and is aligned preferentially to formation vertical permeability, which is typically much lower than horizontal permeability.

More specifically, after a hydraulic fracture is initiated, the degree to which the fracture grows laterally or vertically depends on numerous factors, such as confining stress, fluid leak from the fracture, fluid viscosity, fracture toughness and the number of natural fractures in the reservoir. Thus, prediction of the precise behavior of the fracture is difficult and, in many cases, may even be impossible because of incorrect information and assumptions used in planning the fracturing project.

The extent of a hydraulic fracture is a complex relationship between the strength of the rock and the pressure difference between the rock and the fracturing pressure. The extent is defined by the fracture dimensions - height, depth of penetration (wing length or fracture length), and aperture (width or opening). One measure of the strength of the rock is the Poisson Ratio. Thus, when a material is compressed in one direction, it usually tends to expand in the other two directions perpendicular to the direction of compression (the Poisson effect) and the Poisson's ratio (ν, the fraction or percent) of expansion divided by the fraction (or percent) of compression is a measure of this effect. The Poisson ratio is low (0.10−0.30) for most sandstone formations and carbonates − rocks that fracture relatively easily. On the other hand, the Poisson ratio is high (0.35−0.45) for shale, sandstone, and coal − rocks that are more elastic and are harder to fracture (Sone and Zoback, 2013a,b). Shale is often the upper and lower barrier to the height of a fracture in conventional sandstone.

One other aspect of equipment consideration relates to the inducement of fracturing by pneumatic methods. Pneumatic fractures can be generated in geologic formations if air or any other gas is injected at a pressure that exceeds the natural strength as well as the *in situ* stresses present in the formation. As noted earlier, pneumatic fracture propagation will be predominantly horizontal at over-consolidated formations. However, in shallow recent fills, some upward inclination of the fractures has been observed, the reason for which is attributed to the lack of stratification and consolidation in these formations. The amount of pressure required to initiate pneumatic fractures is dependent on the cohesive or tensile strength of the formation, as well as the overburden pressure (dependent upon the depth and density of the formation). The most important system parameter for efficient pneumatic fracturing is injection flow rate, as it largely determines the dimensions of a pneumatic fracture. Once a fracture has been initiated, it is the high volume airflow which propagates the fracture and supports the formation. The design goal of a pneumatic fracturing system therefore becomes one of providing the highest possible flow rate. Field observations indicate that pneumatic fractures reach their maximum dimension in less than 20 s, after which continued injection simply maintains the fracture network in a dilated state (in essence, the formation is “floating” on a cushion of injected air).4 Pneumatically induced fractures continue to propagate until they intersect a sufficient number of pores and existing discontinuities, so that leak-off (fluid loss) rate into the formation exactly equals the injection flow rate.

An individual pneumatic fracture is accomplished by (i) advancing a borehole to the desired depth of exploration and withdrawing the auger, (ii) positioning the injector at the desired fracture elevation, (iii) sealing off a discrete 1 or 2 feet interval by inflating the flexible packers on the injector with nitrogen gas, (iv) applying pressurized air for approximately 30 s, and (v) repositioning the injector to the next elevation and repeating the procedure. A typical fracture cycle takes approximately 15 min, and a production rate of 15–20 fractures per day is attainable with one rig.

The pneumatic fracturing procedure typically does not include the intentional deposition of foreign propping agents to maintain fracture stability. The created fractures are thought to be *self-propping*, which is attributed to both the asperities present along the fracture plane as well as the block shifting which takes place during injection. The aperture or thickness of a typical pneumatically induced fracture is approximately 0.5–1 mm. Testing to date has confirmed fracture viability in excess of 2 years, although the longevity is expected to be highly site-specific.

Without the carrier fluids used in hydraulic fracturing, there are no concerns with fluid breakdown characteristics for pneumatic fracturing. There is also the potential for higher permeability within the fractures formed pneumatically, in comparison to hydraulic fractures, as these are essentially air space and are devoid of propping agents. The open, self-propped fractures resulting from pneumatic fracturing are capable of transmitting significant amounts of fluid flow.

3.2 Well development and completion

Well development is an integral part of the hydraulic fracturing process and is typically divided into two stages: (i) the drilling stage and (ii) the completion stage. For a successful fracturing operation, it is important that drilling equipment are properly maintained and that their rated capacity is not exceeded.

Most of the tight gas and tight oil resources are located at depths of 6000 feet or more below ground level, and can be relatively thin (for example, the Marcellus shale formation is between 50 and 200 feet thick depending on location). The efficient extraction of gas from such a thin layer of rock requires drilling horizontally through the shale which is accomplished by drilling vertically downward until the drill bit reaches a distance of around 900 feet from the shale formation. At this point, a directional drill is used to create a gradual 90-degree curve, so that the *wellbore* becomes horizontal as it reaches optimal depth within the shale. The wellbore then follows the shale formation horizontally for 5000 feet or more. Multiple horizontal wells accessing different parts of the shale formation can be drilled from a single pad. Thus, horizontal drilling reduces the footprint of these operations by enabling a large area of shale to be accessed from a single pad.

The drilling rig is the most visible part of the drilling operation, however what is important is the underground activity and the main considerations in the selection of a rig are (King, 2012): (i) noise, which can be minimized by using electric rigs, (ii) dust − if air drilling is used, control of air and cuttings is required, (iii) appearance − most rigs for unconventional well drillings are from 50 feet to over 100 feet tall, which is visually undesirable and take more time to set up; lower profile rigs are preferred on shallower wells but the trade-off is that larger rigs are faster in operation, (iv) water and mud storage: requiring determination of size of pits or steel tanks − also storage considerations for chemicals that would be mixed with the mud, and (v) pressure control equipment − the equipment must undergo regular servicing and inspection. Completions involve the final stages of the well development process, which include casing and cementing design.

In terms of casing insertion, at various stages in the drilling process, drilling is stopped and steel casing pipe is installed in the wellbore. Cement is pumped into the *annulus*, or void space between the casing and the surrounding mineral formation. After the wellbore reaches a depth below the deepest freshwater aquifer, casing and cement are installed to protect the water from contamination due to the drilling process. Additional casing and cementing along the entire wellbore occurs after the well has reached its full horizontal length. This process is intended to prevent leakage of natural gas from the well to the rock layers between the shale formation and the surface, as well as to prevent the escape of natural gas to the surface through the annulus. The casing surrounding the horizontal section of the well through the shale formation is then perforated using small explosives to enable the flow of hydraulic fracturing fluids out of the well into the shale and the eventual flow of natural gas out of the shale into the well.

The rotary drilling process for a vertical well or for a directional well involves: (i) application of a force downward on a drill bit, (ii) rotation of the drill bit, and (iii) circulation of the drilling fluid from the surface through the tubular (drill string), and back to the surface through the annular space, which is the area between drill string and borehole wall or casing (Azar and Samuel, 2007). On the other hand, horizontal drilling involves directing the drill bit to follow a horizontal path, oriented at approximately 90° from the vertical, through the reservoir rock (Azar and Samuel, 2007). Over the years, hydraulic fracturing has been performed on vertical, deviated and horizontal wells. However, the coupling of horizontal wells and hydraulic fracturing have been proven to improve well performance in oil and gas reservoirs (Britt et al., 2010; Devereux, 2012) and enhances the recovery of natural gas or crude oil by reducing the number of vertical wells to develop fields of interest. In the current context, horizontal wells have found ready application in the Barnett shale, the Marcellus shale as well as in other shale plays.

Even though the well casing is perforated, little natural gas or crude oil will flow freely into the well from the shale. Fracture networks must be created in the shale to allow gas to escape from the pores and natural fractures where it is trapped in the rock. This is accomplished through the process of hydraulic fracturing. In this process, typically several million gallons of a fluid composed of 98−99.5% v/v water and *proppant* (usually sand) is pumped at high pressure into the well. The rest of the fracking fluid (0.5−2% v/v) is composed of a blend of chemicals, often proprietary, that enhance the properties of the fluid. These chemicals typically include acids to clean the shale to improve flow of the gas or oil, *biocides* to prevent organisms from growing and clogging the shale fractures, corrosion and scale inhibitors to protect the integrity of the well, gels or gums that add viscosity to the fluid and suspend the proppant, and friction reducers that enhance flow and improve the ability of the fluid to infiltrate and carry the proppant into small fractures in the shale (Speight, 2016b).

This fluid pushes through the perforations in the well casing and forces fractures open in the shale – connecting pores and existing fractures and creating a pathway for natural gas or oil to flow back to the well. The proppant lodges in the fractures and keeps them open once the pressure is reduced and the fluid flows back out of the well. Approximately 1000 feet of wellbore is hydraulically fractured at a time, so each well must be hydraulically fractured in multiple stages, beginning at the furthest end of the wellbore. Cement plugs isolate each hydraulic fracture stage and must be drilled out to enable the flow of natural gas up the well after all hydraulic fracturing is complete.

Once the pressure is released, fluid (commonly referred to as *flowback water*) flows back out the top of the well and is recovered not only contains the proprietary blend of chemicals present in the hydraulic fracturing fluid, but may also contain chemicals naturally present in the reservoir, including hydrocarbon derivatives, salts, minerals, and naturally occurring radioactive materials (NORMs) that leach into the fluid from the shale or result from mixing of the hydraulic fracturing fluid with brine (salty water) already present in the formation. The chemical composition of the water produced from the well varies significantly according to the formation and the time after well completion, with early flowback water resembling the hydraulic fracturing fluid but later converging on properties more closely resembling the brine naturally present in the formation.

In many cases, flowback water can be reused in subsequent hydraulic fracturing operations; this depends upon the quality of the flowback water and the economics of other management alternatives. Flowback water that is not reused is managed through regulated disposal.

Horizontal wellbores allow a far greater exposure to a formation than a conventional vertical wellbore which is particularly useful in tight formations that do not have a sufficiently high permeability to produce natural gas or crude oil economically from a vertically-drilled well. Furthermore, the type of wellbore completion used will influence the number of times that a formation is fractured and the locations along the horizontal section of the wellbore that fracturing is necessary. In North America, shale reservoirs such as the Bakken, Barnett, Montney, Haynesville, Marcellus, and (more recently) the Eagle Ford, Niobrara, and Utica shale formations have been drilled, completed, and fractured using this method. The method by which the fractures are placed along the wellbore is most commonly achieved by one of two methods: (i) as the *plug and perf* method and (ii) the *sliding sleeve* method.

The wellbore for the *plug and perf* method is generally composed of standard joints of steel casing, either cemented or uncemented, which is set in place at the conclusion of the drilling process. Once the drilling rig has been removed, a perforation is created near the end of the well, following which a fracturing stage is initiated. Once the fracturing stage is completed, a plug is set in the well to temporarily to seal off that section of the wellbore. Another stage is then pumped, and the process is repeated as necessary along the entire length of the horizontal part of the wellbore.

On the other hand, the wellbore for the *sliding sleeve* method is different insofar as the sliding sleeves are included at set distances (spacing) in the steel casing at the time the casing is set in place. The sliding sleeves are usually all closed at this time and when the well is ready for application of the fracturing process, the bottom sliding sleeve is opened and the first stage is pumped. Once finished, the next sleeve is opened which concurrently isolates the first stage, and the process is repeated. These completion techniques may allow more than thirty stages to be pumped into the horizontal section of a single well if required, which is many more stages than would typically be pumped into a vertical well (Mooney, 2011).

Finally, to optimize the completion, it is necessary to understand the mechanical properties of all the layers above, within, and below the gas pay intervals. Basic rock properties such as in-situ stress, Young's modulus and Poisson's ratio are needed to design a fracture treatment. The in-situ stress of each rock layer affects how much pressure is required to create and propagate a fracture within the layer. The values of Young's modulus relate to the stiffness of the rock and help determine the width of the hydraulic fracture. The values of Poisson's ratio relate to the lateral deformation of the rock when stressed. Poisson's ratio is a parameter required in several fracture design formulas.

The most important mechanical property is in-situ stress, often called the minimum compressive stress or the fracture closure pressure. When the pressure inside the fracture is greater than the in-situ stress, the fracture is open. When the pressure inside the fracture is less than the in-situ stress, the fracture is closed. To optimize the completion, it is very important to know the values of in-situ stress in every rock layer.

3.3 Fracturing fluids

Initially, the fluid is injected that does not contain any propping agent and is injected to create a fracture that is multi-directional and spreads in several directions. This creates a fracture that is sufficiently open for insertion of the proppant, which is injected as a slurry – a mix of the proppant and the carrier fluid and proppant material. In shallow reservoirs, sand is often used can be used and remains the most common proppant but in deep reservoirs, ceramic beads (in place of the usual sand proppant) may be used to prop open the fractures. Once the fracture has initiated, fluid is continually pumped into the wellbore to extend the created fracture and develop a fracture network. However, each formation has different properties and, therefore, diffident in-situ stress forces are operational es so that each hydraulic fracture project is unique and must be designed accordingly by identification of the properties of the target formation including estimating fracture treating pressure, amount of material and the desired length for optimal economics. Furthermore, the fracturing fluid should have a number of properties that are suited to the properties of the formation, such as: (i) compatibility with the formation rock, (ii) compatibility with the formation fluid, (iii) suitability to generate sufficient pressure drop down the fracture to create a wide enough fracture, and (iv) aa sufficiently low viscosity to allow clean-up after the treatment. Water-based fluids are commonly used – *slickwater* is the most common fluid used for shale gas fracturing, where the major chemical added is a surfactant polymer to reduce the surface tension or friction, so that water can be pumped at lower treating pressures. Other fluids that have been considered are oil-based fluids, foams, and emulsions but caution is advised when using non-aqueous fluids since these fluids must be allowable for injection (by regulation) and must not have any detrimental effect on the environment (Chapter 18).

Additives for fracturing fluids are chosen according to the properties of the reservoir and include (Table 5.3): (i) polymers, which allow for an increase in the viscosity of the fluid, together with cross-linkers, (ii) cross-linkers, which increase the viscosity of the linear polymer base gel, (iii) breakers, which are used to break the polymers and cross-link sites at formation temperature, for better clean-up, (iv) biocides, which re used to kill bacteria in the mix water, (v) buffers, which are used to control the pH, (vi) fluid loss additives, which are used to control excessive fluid leak-off into the formation, and (vii) stabilizers, which are used to keep the fluid viscous at higher temperature. However, it must be emphasized that additives are used for every site and in general as few additives as possible are added to avoid potential environmental contamination (use of the additives must be controlled) and production problems with the reservoir.

Environmental concerns have focused on the fluid used for hydraulic fracturing and the risk of water contamination through leaks of this fluid into groundwater (Chapters 6 and 18). Water, together with sand or ceramic beads (*proppant*), is the most common and acceptable (environmentally-acceptable and economically-acceptable) typical fracturing fluid, but a mixture of chemical additives is also used to give the fluid the properties that properties vary according to the type of formation. The additives (not all of which would be used in all fracturing fluids) (Table 5.3) typically assist in the accomplishment of four tasks: (i) to maintain the proppant in suspension, (ii) to allow a change in the properties of the hydraulic fracturing fluid over time, (iii) to reduce friction, and (iv) to reduce the risk of the effect of naturally occurring bacteria in the water.

In the first instance (to maintain the proppant in suspension in the fluid), this is accomplished by gelling the fluid while it is being pumped into the well and to ensure that the proppant ends up in the fractures being created. In the absence of this effect, the denser proppant particles would succumb to the influence of gravity and remain be unevenly distributed in the fluid, thereby losing some of the effectiveness. To ensure suspension of the proppant in the fluid, gelling polymers (such as guar or cellulose) are used at a concentration of approximately 1% while cross-linking agents, such as borates or metallic salts, may also be used (also at a very low concentration) to form a stronger gel.

In the second case, (to allow a change in the properties of the hydraulic fracturing fluid over time), the characteristics that are needed to deliver the proppant into subsurface cracks are not desirable at other stages in the injection process and the time-dependent properties that are imparted to the fluid can reduce the viscosity after fracturing, so that passage of the hydrocarbon derivatives (such natural gas liquids and as crude oil) will flow more easily along the fractures to the production well.

Reducing the fraction reduces the energy required to inject the fluid into the well; a typical drag-reducing polymer is polyacrylamide and, finally, to reduce the risk that naturally occurring bacteria in the water affect the performance of the fracturing fluid or proliferate in the reservoir, producing hydrogen sulfide is often achieved by using a disinfectant-type (biocide) additive.

3.4 Fracture patterns

Hydraulic fracturing may be performed on a single reservoir interval in a vertical well. Horizontal wells, however, by virtue of their significant wellbore length in the target formation, are generally isolated into several discrete intervals along the horizontal wellbore − there may be four-to-twenty intervals for each horizontal well, with each interval requiring its own fracturing stage. This is due to the difficulty in maintaining pressures sufficient to induce fractures over the complete length of the lateral leg.

The most important data for designing a fracture treatment and the resulting fracture patterns are (i) the in-situ stress profile, (ii) formation permeability, (iii) fluid-loss characteristics, (iv) total fluid volume pumped, (v) propping agent − type and amount, (vi) viscosity of the fracture fluid, (vii) injection rate, and (viii) formation modulus. The in-situ stress profile and the permeability profile of the zone to be stimulated must be quantified and identification of the layers of rock above and below the target zone must be identified since these formations will influence fracture height growth. In order to design the optimum treatment, the effect of fracture length and fracture conductivity on the productivity and the ultimate recovery from the well must be determined.

The selection of the fracture fluid for the treatment is a critical decision and selection of fracture fluid on the basis of factors such as (Economides and Nolte, 2000): (i) reservoir temperature, (ii) reservoir pressure, (iii) the expected value of fracture half-length, and (iv) any water sensitivity. The definition of what comprises a water-sensitive reservoir and what causes the damage is not always evident. Most reservoirs contain water, and most natural gas or crude oil reservoirs can be successfully water-flooded. Thus, most fracture treatments should be pumped with suitable water-base fracture fluids. Acid-base fluids can be used in carbonates but many deep carbonate reservoirs have been stimulated successfully with water-base fluids containing propping agents.

When selecting a propping agent, it is necessary to determine the maximum effective stress on the agent must be determined. The maximum effective stress depends on the minimum value of flowing bottomhole pressure expected during the life of the well. To confirm exactly which type of propping agent should be used during a specific fracture treatment, the designer should factor in the estimated values of formation permeability and optimum fracture half-length (Cinco-Ley et al., 1978). The treatment must be designed to create a fracture wide enough, and pump proppants at concentrations high enough, to achieve the conductivity required to optimize the treatment. There is a tendency to compromise fracture length and conductivity in an often unsuccessful attempt to prevent damage to the formation around the fracture and substantial damage to the formation around the fracture can be tolerated as long as the optimum fracture length and conductivity are achieved (Holditch, 1979). However, damage to the fracture or the propping agents can be very detrimental to the productivity of the fractured well. Ideally, the optimum fracture length and conductivity can be created while minimizing the damage to the formation.

Finally, in horizontal wells, transverse fractures are relatively more difficult to achieve than longitudinal fractures. However, for natural gas and crude oil formations typically characterized by low permeability, transverse fractures in horizontal wells have greater production benefits (Valko et al., 1998). Transverse vertical fractures move along the path of least resistance, which is normal to the minimum horizontal stress. In horizontal wells or deviated wells, there are effects in the immediate vicinity around the wellbore that lead to the transverse fractures taking unpredicted paths before eventually aligning normal to the horizontal stress. These effects are increased by the presence of natural fractures in the formation and the deviation of the horizontal well at an angle from the minimum horizontal stress.

In the design of a hydraulic fracturing procedure, most procedures to optimize well productivity begin with the fracture size. Limitations in the different hydraulic fracture design methods are inherent in their assumptions of (i) fracture geometry, (ii) dependence on fracture fluid properties, (iii) dependence on reservoir properties, (iv) dependence on whether or not the formations are layered, and (v) a variety of other factors, such as stress intensity. Challenges in fracture geometry when fracturing unconventional reservoirs include: fracture azimuth and dip, not creating expected length, brittle and ductile rocks − complex and simple networks, well bore axis (vertical or horizontal drilling) (Kennedy et al., 2012). In all cases however, knowledge of existing in-situ stress is essential to developing a fracture propagation model which describes the methods of obtaining a desired hydraulic fracture geometry definitely including the fracture (half) length, width, height and fracture complexity.

The ideal formation evaluation would be one where the value of the in-situ stress obtained from injection tests and those calculated from logs and core analysis all result in a consistent stress profile (Holditch et al., 1987). The hydraulic methods are also the most reliable for determining in-situ stress in deep (>160 feet) formations (Amadei and Stephansson, 1997).

Hydraulic fractures are formed in the direction perpendicular to the least stress. Typically, horizontal fractures will occur at depths less than approximately 2000 ft because the overburden at these depths provides the least principal stress. If pressure is applied to the center of a formation under these relatively shallow conditions, the fracture is most likely to occur in the horizontal plane, because it will be easier to part the rock in this direction than in any other. In general, therefore, these fractures are typically parallel to the bedding plane of the formation.

As depth increases beyond approximately 2000 feet, overburden stress increases by approximately 1 psi/foot, making the overburden stress the dominant stress. This means the horizontal confining stress is now the least principal stress and, since hydraulically induced fractures are formed in the direction perpendicular to the least stress, the resulting fractures at depths greater than approximately 2000 feet will be oriented in the vertical direction.

In the case where a fracture might cross over a boundary where the principal stress direction changes, the fracture would attempt to reorient itself perpendicular to the direction of least stress. Therefore, if a fracture propagated from deeper to shallower formations it would reorient itself from a vertical to a horizontal pathway and spread sideways along the bedding planes of the rock strata.

The extent that a created fracture will propagate is controlled by the upper confining zone or formation, and the volume, rate, and pressure of the fluid that is pumped. The confining zone will limit the vertical growth of a fracture because it either possesses sufficient strength or elasticity to contain the pressure of the injected fluids or an insufficient volume of fluid has been pumped. This is important because the greater the distance between the fractured formation and the underground source of drinking water, the more likely it will be that multiple formations possessing the qualities necessary to impede the fracture will occur. However, while it should be noted that the length of a fracture can also be influenced by natural fractures or faults, natural attenuation of the fracture will occur over relatively short distances due to the limited volume of fluid being pumped and dispersion of the pumping pressure regardless of intersecting migratory pathways.

3.5 Fracture optimization

Hydraulic communication is a key factor for determining hydrocarbon or thermal energy recovery sweep efficiency in an underground reservoir. Sweep efficiency is a measure of the effectiveness of heat, gas or oil recovery process that depends on the volume of the reservoir contacted by an injected fluid (Britt, 2012). Artificial (stimulated) hydraulic fractures are usually initiated by injecting fluids into the borehole to increase the pressure to the point where the minimal principal stress in the rock becomes tensile. Continued pumping at an elevated pressure causes tensile failure in the rock, forcing it to split and generate a fracture that grows in the direction normal to the least principal stress in the formation. Hydraulic fracturing activities often involve injection of a fracturing fluid with proppants in order to better propagate fractures and to keep them open (Britt, 2012). The design of fracturing treatment should involve the optimization of operational parameters, such as the viscosity of the fracturing fluid, injection rate and duration, as well as proppant concentration, so that a fracture geometry is created that favors increased sweep efficiency. The net present value is the economic criterion is usually used as an objective for optimal fracturing treatment design. Some studies have been reported to use a sensitivity-based optimization procedure coupled with a fracture propagation model and an economic model to optimize design parameters leading to maximum net present value (Hareland et al., 1993; Rueda et al., 1994; Aggour and Economides, 1998; Mohaghegh et al., 1999; Chen et al., 2013).

In summary, fracture geometry optimization involves defining the desired fracture half-length, width and conductivity for maximized production. While there are several optimization methods, all involve a relative comparison of the flow potential of the fracture to that of the reservoir. Thus, a fracture is often considered (or defined) as a high permeability path in a low permeability rock formation but if the fracture is filled with a cementing material, such as calcite (calcium carbonate, $CaCO_3$), resulting in a fracture with little or no permeability. Thus, in any evaluation of the reservoir, it is important to distinguish between open fractures and healed (plugged or filled) fractures. The total volume of fractures is often small compared to the total pore volume of the reservoir. Thus, natural fractures in reservoir rocks (especially in tight reservoir formations) contribute significantly to natural gas or crude oil production. Therefore, it is important to glean every scrap of information from open hole logs to locate the presence and intensity of fracturing. Even though some modern logs, such as the formation micro-scanner and televiewer, are the tools of choice for fracture indicators, many wells lack this data.

Most natural fractures are vertical − a horizontal fracture may exist for a short distance, propped open by bridging of the irregular surfaces. Most horizontal fractures, however, are sealed by overburden pressure. Both horizontal and semi-vertical fractures can be detected by various logging tools. The vertical extent of fractures is often controlled by thin layers of plastic material, such as shale beds or laminations, or by weak layers of rock, such as stylolites in carbonate sequences. The thickness of these beds may be too small to be seen on logs, so fractures may seem to start and stop for no apparent reason.

The nucleation and propagation of hydraulic rock fractures are chiefly controlled by the local *in situ* stress field, the strength of the rock (stress level needed to induce failure), and the pore fluid pressure. Temperature, elastic properties, pore water chemistry and the loading rate also have an influence (Secor, 1965; Phillips, 1972; Sone and Zoback, 2013a,b). Fractures in rock can be classified as tensile, shear or hybrid (a mixture of tensile and shear). If the dominant displacement of the wall rocks on either side of the fracture is perpendicular to the fracture surface, then the fracture is deemed tensile. New tensile fractures form when the pore fluid pressure in the rock exceeds the sum of the stress acting in a direction perpendicular to the fracture wall and the tensile strength of the rock. Note that any pre-existing fractures that are uncemented (i.e., have zero cohesion) can be opened at a lower value of pore fluid pressure, when it exceeds the stress acting in a direction perpendicular to the fracture wall.

The formation or reactivation of shear fractures depends on the shear stress, the normal stress, the pore fluid pressure and the coefficient of friction for the specific rock type. It is important to recognize that the hydraulic fracturing process of pumping large volumes of water into a borehole at a certain depth cannot control the type of fractures that are created or reactivated. The array of fractures created and/or reactivated or reopened depends on a complex interplay of the *in situ* stress, the physical properties of the local rock volume and any pre-existing fractures, and the pore fluid pressure (Phillips, 1972). This could have implications for the risk of ground water contamination by hydraulic fracturing operations, as the fracture network generated by the hydraulic fracturing fluid could be complex and difficult to predict in detail. The orientations, sizes and apertures of permeable rock fractures created by a hydraulic fracturing operation ultimately control the fate of the hydraulic fracturing fluid and the released shale gas, at least in the deep subsurface. Geomechanical models used to predict these fracture pattern attributes therefore need thorough testing/benchmarking, together with ongoing and future developments.

A common issue encountered in hydraulic fracturing operations in tight formations (especially in shale formations) is the variability and unpredictability of the outcome of the fracturing process. The injection pressure required to fracture the formation (fracture gradient) often varies significantly along a well, and there can be intervals where the formation cannot be fractured successfully by the injection of the fluid. The use of real-time fracture mapping allows real time observation of changes in fracture design and also allows changes in re-stimulation design to maximize the *effective stimulation volume* (ESV − the reservoir volume that has been effectively contacted by the stimulation treatment) A correlation of microseismic activity with log data allows estimation of fracture geometry to be made after which the data can be used to design a stimulation that has the greatest chance of maximizing production (Fisher et al., 2004; Baihly et al., 2006; Daniels et al., 2007). Shale gas reservoirs also respond to fluid injection in a variety of modes although distribution of activated seismicity can be confined along a macroscopic fracture plane, but most time they are dispersed throughout a wide region in the reservoir reflecting the development of a complex fracture network (Waters et al., 2006; Cipolla et al., 2009; Das and Zoback, 2011; Maxwell, 2011).

In recent years, various attempts have been made to optimize the design of transverse fractures of horizontal wells for shale gas reservoirs. However, these optimization methods may not provide the optimal design. Hence, the optimization of hydraulic fracturing treatment design for shale gas production remains a challenge.

Finally, earlier literature on fracture analysis suggested that fractures might contribute as much as a few to several percent porosity but more recent work using the fracture aperture (calculated from resistivity micro-scanner logs) indicates a much lower contribution to the porosity of the formation. The term *secondary porosity* also includes rock-volume shrinkage due to dolomitization, porosity increase due to solution or recrystallization, and other geological processes. *Secondary porosity* should not be confused with *fracture porosity* which can be determined by processing the formation micro-scanner curves for fracture aperture and fracture frequency (*fracture intensity*). The effect of fracture porosity on reservoir performance, however, is very large due to the substantial contribution to permeability. As a result, naturally fractured reservoirs behave differently than non-fractured reservoirs with similar porosity due to the relatively high flow rate and capacity of the secondary porosity system. This provides high initial production rates, which can lead to extremely optimistic production forecasts and sometimes, economic failures when the small reservoir volume is not properly taken into account.

3.6 Fracture monitoring

During the hydraulic fracturing process, fluid leak-off which is loss of fracturing fluid from the fracture channel into the surrounding permeable rock can (and often does) occur. If not controlled properly, the fluid loss can exceed 70% v/v of the injected volume which may result in formation matrix damage, adverse formation fluid interactions, or altered fracture geometry and thereby decreased production efficiency. Thus, fracture geometry and fracture monitoring are important aspects of the hydraulic fracturing process.

Monitoring technologies are used to map where fracturing occurs during a stimulation treatment and includes such techniques as microseismic fracture mapping, and tilt meter measurements (Arthur et al., 2008). These technologies can be used to define the success and orientation of the fractures created during a stimulation process. Measurements of the pressure and rate during the growth of a hydraulic fracture, as well as knowing the properties of the fluid and proppant being injected into the well provides the most common and simplest method of monitoring a hydraulic fracture treatment. This data, along with knowledge of the underground geology can be used to model information such as length, width and conductivity of a propped fracture.

Microseismic monitoring is the process by which the seismic waves generated during the fracturing of a rock formation are monitored and used to map the locations of the fractures generated. Monitoring is done using a similar technology to that used to monitor larger naturally occurring seismic events associated with earthquakes and other natural processes. Microseismic monitoring is an active monitoring process performed during a hydraulic fracture treatment. As an active monitoring process microseismic monitoring can be used to develop real time changes to a fracture program. Microseismic monitoring provides engineers the ability to manage the resource through intelligent placement of additional wells to take advantage of the natural conditions of the reservoir and expected fracture results in new wells.

Microseismic theory and mapping is based on earthquake seismology. Similar to earthquakes, but at a much higher frequency (200−2000 Hz), microseismic events emit elastic P waves (compressional) and S waves (shear waves) (Jones and Britt, 2009). During hydraulic fracture, there is an increase in formation stress proportional to the net fracturing pressure, and an increase in pore pressure due to fracturing fluid leak-off. The increase in stresses at the fracture tip and pore pressure increments causes shear slippages to occur. Microseismic technology thus uses earthquake seismology methodologies to detect and locate these hydraulic fracturing induced shear slippages, which resemble micro-earthquakes. Microseismic events or micro-earthquakes occur with fracture initiation and are observed with receivers placed on an offset wellbore like with the downhole tiltmeters.

Microseismic mapping technology involves installing an array of tri-axial geophone or accelerometer receivers into an offset well at approximately the depth of the fracture (like in downhole tiltmeters), orienting the receivers (geophones), recording seismic data, finding micro-earthquakes in the data and locating them. Locating the earthquake events requires the determination of compressional (P) and shear (S) wave arrivals and consequent acoustic interpretation of the velocity of the P-S waves (Davis et al., 2008; Jones and Britt, 2009). Standard microseismic mapping use P-S arrival time separation for distance location. Horizontal and vertical plane holograms are used to determine azimuth and inclination (Warpinski et al., 2005).

Tiltmeters are passive monitoring technologies which record the deformation of rocks that are induced by the hydraulic fracture process. Tiltmeters can be placed at the ground surface away from a well or downhole in a nearby wellbore tightly into the rock. Tiltmeters measure changes in inclination in two orthogonal directions, which can then be translated into the strain rotation that results from hydraulic fracturing. Engineers can then determine based on the strain rotation the location of the hydraulic fracturing event that caused the strain rotation.

Downhole tiltmeter mapping technology was developed to circumvent the limitations of the surface tiltmeter by giving estimates of the fracture dimensions. The downhole tiltmeters have the same operational principle as the surface tiltmeters, but instead of being at the surface, the tiltmeters are positioned by wireline in one or multiple offset wellbores at the depth of the hydraulic fracture. Typically, the array consists of 7–12 tiltmeters coupled to the borehole with standard oil-field centralizer springs (Wright et al., 1999). Downhole tiltmeters provide a map of the deformation of the Earth adjacent to the hydraulic fracture. Thus, what is obtained is an estimate of an ellipsoid that best approximates the fracture dimensions. The tiltmeters are located closer to the fracture than the surface tiltmeter and hence more sensitive to fracture dimensions (Cipolla and Wright, 2002). The closer the downhole tiltmeter to the fracture, the better the quality of data obtained to determine fracture height (Jones and Britt, 2009) which may be limited by the volume of the hydraulic fracturing fluid volume regardless of whether the fluid interacts with faults (Flewelling et al., 2013). The downhole array tilts in a continuous fashion, similar to surface tiltmeter records but the arrays span the same depth interval as the zone being fractured. The total interval covered by a downhole tilt array ranges from 300 feet to more than 1000 feet, depending on the design conditions. Conventionally, surface and downhole tiltmeter analysis are done separately but techniques have been proposed to combine them for evaluating fracture geometry during drill cuttings disposal.

The greatest advantage of both surface and downhole tiltmeter fracture mapping is that for a given fracture geometry, the induced deformation field is almost completely independent of formation properties. Also, the required degree of formation description is lower in tiltmeter mapping than microseismic mapping (such as velocity profiles and attenuation thresholds) as will be described in a later section. Complex fracture growth would yield independent fractures at different orientations or depths but in tiltmeter mapping a simpler analysis is required.

At the completion of the stimulation process, approximately 20−30% v/v of the water flows back up the wellbore, where it is collected and then recycled in a subsequent well completion operation. Over the productive life of the well, additional "produced" water slowly comes to the surface, where it is collected in on-site storage tanks and transported to permitted treatment facilities.

3.7 Fracture diagnostics

As part of the fracturing process, it is necessary that the fracture be analyzed through the various procedures known as *fracture diagnostics*, which are the techniques used to analyze the original state of the formation (pre-fracture analysis) and the created fractures and after hydraulic fracture treatment (post-fracture analysis) (Barree et al., 2002; Vulgamore et al., 2007). The data will allow the determination of the dimensions of the created fractures and also whether or not the fractures are effectively maintained in an open mode (*propped*). Thus, the fracture diagnostic techniques can be conveniently sub-divided into three groups: (i) direct far-field techniques, (ii) direct near-wellbore techniques, and (iii) indirect fracture techniques.

3.7.1 *Direct far-field techniques*

The *direct far-field* techniques require the use of a tiltmeter - an instrument designed to measure very small changes from the horizontal level, either on the ground or in subterranean structures − and microseismic fracture mapping techniques which require that the instrumentation is placed in boreholes surrounding, and near to, the well through which fracturing will occur. The microseismic fracture mapping technique relies on the use of a downhole receiver array of geophones, to locate any *micro-seismic events* that are triggered by movement in any natural fractures surrounding the hydraulic fracture.

3.7.2 *Direct near-wellbore techniques*

Direct near-wellbore techniques are used in the well that is being fractured to locate the portion of fracture that is very near wellbore. These techniques consist of tracer logs, temperature logging, production logging, borehole image logging, downhole video logging, and caliper logging. The caliper log provides a continuous measurement of the size and shape of a borehole along its depth and is commonly used when drilling wells to detect natural gas and crude oil formations. The measurements that are recorded can be an important indicator of cave ins or swelling in the borehole, which can affect the results of other well logs.

3.7.3 *Indirect fracture techniques*

Indirect fracture techniques consist of modeling the hydraulic fracturing process followed by matching of the net surface treating pressures, together with subsequent pressure transient test analyses and production data analyses. As fracture treatment data and the post-fracture production data are normally available on every well, the indirect fracture diagnostic techniques are widely used methods to determine (or estimate) the shape and dimensions of the created fractures and the propped hydraulic fracture.

3.8 Flowback

Flowback is a water based solution that flows back to the surface during and after the completion of hydraulic fracturing and consists of the fracturing fluid which contains clay minerals, chemical additives, dissolved metal ions and total dissolved solids (TDSs). The water has a murky appearance from high levels of suspended particles. Most of the flowback occurs in the first seven to ten days while the rest can occur over a three to four week time period. The volume of recovery is anywhere between 20% and 40% of the volume that was initially injected into the well. The rest of the fluid remains absorbed in the formation.

In contrast, produced water (which is not the same as flowback water) is naturally-occurring water found in shale formations that flows to the surface throughout the entire lifespan of the well. This water has high levels of total dissolved solids and leaches out minerals from the shale including barium, calcium, iron and magnesium. It also contains dissolved hydrocarbons such as methane, ethane and propane along with naturally occurring radioactive materials (NORMs) such as radium isotopes.

4. Proppants

Thus, hydraulic fracturing is a process through which a large number of fractures are created mechanically in the rock, thus allowing the natural gas and/or crude oil trapped in subsurface formations to move through those fractures to the wellbore from where it can then flow to the surface. Hydraulic fracturing can both increase production rates and increase the total amount of gas that can be recovered from a given volume of shale. Pump pressure causes the rock to fracture, and water carries sand ("proppant") into the hydraulic fracture to prop it open allowing the flow of gas. While water and sand are the main components of hydraulic fracture fluid, chemical additives are often added in small concentrations to improve fracturing performance.

A proppant is a solid material, typically sand, treated sand, or a manufactured ceramic material that is designed to prevent and keep an induced hydraulic fracture open during and after a fracturing treatment so that the fracture does not collapse and close (Veatch and Moschovidis, 1986; Mader, 1989). Proppants typically comprise sand or manufactured ceramics such as bauxite. Proppants can be resin-coated to improve packing, which helps the proppant stay in place and not flow back to the wellbore. Resin coatings also help provide better distribution of stress over the proppant pack.

Proppants are specified in grain diameter sizes of less than 1/16 of an inch. Some common mesh sizes are 16/20, 20/40, 30/50, 40/70, and 100. Treatments may use one size or a multitude of sizes during pumping. The smaller sizes are intended to reach closer to the fracture tip. A propped hydraulic fracture has a significantly greater fluid (hydraulic) conductivity than the surrounding lower permeability rock matrix. Challenges to stimulation treatments involve proper placement of proppant, prevention of crushing or embedment, plugging at restrictions, and potential flowback of proppant to the wellbore. In the process, the proppant is added to a fracturing fluid which may vary in composition depending on the type of fracturing used and can be water-based, foam-based, or gel-based, slickwater-based, or any of a number of alternate fluids.

In the process, the proppant is added to the fracturing fluid (which may vary in composition depending on the type of fracturing process) and can be gel, foam, or slickwater-based. In addition, there may be unconventional fracturing fluids. Other than proppant, slickwater fracturing fluids are predominantly water (typically 99% v/v) but gel-based fluids may use polymers and surfactants comprising as much as 7% v/v of the fracturing fluid. Other common additives include hydrochloric acid, friction reducers, biocides, emulsifiers, and emulsion breakers.

4.1 Types

Since propping agents are required to maintain the fracture in the open configuration once the pumps are shut down and the fracture begins to close, the ideal propping agent must be strong, resistant to crushing, resistant to corrosion, has a low density, and is readily available at low cost. The products that best meet these desired traits are silica sand, resin-coated sand (RCS), and ceramic proppants.

4.1.1 Silica sand

The term *sand* when applied to proppants has been used for many types of crushed minerals and may not be the true silica sand but may be composed of silica and other minerals and may not refer to a non-specific grain size. In fact, there are many varieties of sand in the world, each with their own unique composition and properties. For example, there are the white sands of many beaches that may consist primarily of limestone ($CaCO_3$) and there are also black sands which may consist of magnetite (Fe_3O_4 or $FeO \cdot Fe_2O_3$) or be volcanic in origin while yellow sands may have high levels of iron.

The type of sand used as a proppant is silica sand and which is the most commonly used type of proppant and is a natural resource than a manufactured product. Silica sand (industrial sand) is high-purity quartz (SiO_2) sand deposited by natural processes. In the petroleum industry, silica sand is used as hydraulic fracturing sand (also termed *frac sand*). In the process, the sand is pumped into the well during the fracturing operation. Since the sand is carried along with the fluid into the fracture, it will remain in the fracture when the pressure is removed, keeping the fracture propped open and allowing a good means by which the hydrocarbons can flow to the wellbore.

Ottawa white sand (which originates from Ottawa, Illinois near the center of St. Peters sandstone formation) is the one of the desired of sands due to the superior properties when used in hydraulic fracturing as a proppant. It is in highly demand for hydraulic fracturing because of the excellent properties of (i) roundness, (ii) spherical conformation, and (iii) 0 high crush strength which allow the sand to withstand the high pressures involved in the hydraulic fracturing process. The chemical purity of the sand makes it unreactive with the fluids used to transport it into the well, resulting in delivery of unchanged sand to the fracture points. Brown Sand is the second most sought after proppant − it is cost effective solution for the hydraulic fracturing of low depth wells. Brown sand is less desirable than Ottawa white sand in high stress applications but is considered high quality sand. Due to its limitations involving high pressure environments, Brown sand has a lower cost, but its properties allow it to be an effective proppant in the hydraulic fracturing of shallow wells.

4.1.2 *Resin-coated proppant*

Though sand is a common proppant, untreated sand is prone to significant fines generation; fines generation is often measured in wt% of initial feed. One way to maintain an ideal mesh size (i.e., permeability) while having sufficient strength is to choose proppants of sufficient strength; sand might be coated with resin, to form Curable resin-coated sand (CRCS) or pre-cured resin-coated sand (PRCS). In certain situations a different proppant material might be chosen altogether—popular alternatives include ceramic materials and sintered bauxite [predominantly gibbsite, $Al(OH)_3$, boehmite, γ-AlO(OH), and diaspore, α-AlO(OH)].

Thus, resin-coated proppant is typically silica sand coated with resin which is utilized for two main functions: (i) to spread the pressure load more uniformly that improves the resistance to crushing of the silica sand particles and (ii) to keep pieces together that were broken from high closure stress from down hole pressure and temperature which not only prevents broken pieces from flowing into the borehole but also prevents the broken pieces from returning to the surface during flowback production operation. Resin coated sand is dry silica sand that has been is coated with liquid resin in a batch mixing system in the presence of a with catalyst after which the coated sand is passed through a heating chamber for complete curing. The use of liquid resin gives a uniform coating on the sand grains and this.

There are two major types of resin-coated proppants (i) pre-cured resin-coated proppants and (ii) curable resin-coated proppants. The precured resin-coated proppant technology involves coating the resin on to the silica sand grains after which the resin is fully cured prior to injection into the fractures. The more recent curable resin-coated proppant technology involves incomplete curing of the resin prior to use and when the proppant is pumped downhole curing is completed in the fractures as a result of the downhole pressure and temperature. The advantage to the use of curable resin-coated proppant technology is that the individual proppant grains are allowed to bond together in the fracture, which results in the coated silica grains bonding together uniformly when temperature and pressure reach appropriate levels.

4.1.3 *Manufactured ceramic materials*

A third commonly-used type of proppant involves the use of manufactured ceramic materials − typically non-metallurgic bauxite or kaolin clay. In the manufacturing process, the ceramic proppant is prepared by sintering bauxite mixed with other additives, and the mineral composition of ceramic proppant is aluminum oxide, silicate and iron, with some titanium oxide. The proppant is generally uniform in round shape and character, which makes it owns much higher strength than quartz sand and resin-coated sand so that it is suitable for the fracturing of deep oil and gas stratum with high closure pressure. For middle and deep well operations, ceramic proppants can be used to enhance the conductivity as the trailing proppant. Compared to other proppant materials, ceramic proppants have superiority of smoother surface, higher fracturing strength, acid resistant, alkali resistant, and higher conductivity. Ceramic proppants are widely used to replace other proppant materials such as natural quartz sand, glass balls and metal balls.

The ceramic proppants exhibit high fracture strength and are mainly used for oil field downhole support to increase oil and gas production and an environmentally friendly products. This product uses high-quality bauxite and other raw materials, ceramic sintering is an alternative product of natural quartz sand, glass balls, metal balls and other low-strength proppants, has a positive effect to the oil and gas production. Ceramic proppants typically have (i) high crush resistance, (ii) lower acid solubility, (iii) high roundness and spherical conformation. Ceramic proppants tend to provide higher performance than other proppant type (Vincent, 2002).

Ceramic proppants are generally uniform in round shape and character, which gives the proppant much higher strength than quartz sand and resin-coated sand so that it is suitable for the fracturing of deep oil and gas stratum with high closure pressure. For the middle and deep well, ceramic proppants can be used to enhance the conductivity as the trailing proppant. Compared to other proppant materials, ceramic proppant has superiority of smoother surface, higher fracturing strength, acid proof and alkali proof, higher conductivity.

4.1.4 Other types

Recently, there has been a trend toward the usage of waste material – such as glass, metallurgical slag, and even rock cuttings produced to the surface during oil and gas drilling – has developed. The re-use of rock cuttings from gas drilling operations is especially attractive since not only does it re-use a common waste product in industry but it is also utilizing sources indigenous to the locality – which will cut down the amount of waste material as well as reducing any associated or ancillary costs.

Bauxite, an aluminum ore from which most aluminum is extracted, consists mostly of gibbsite [$Al(OH)_3$] boehmite [γ-AlO(OH)] and diaspore [α-AlO(OH)] mixed with the two iron oxides goethite (FeO(OH)) and hematite (Fe_2O_3), the clay mineral kaolinite [$Al_2Si_2O_5(OH)_4$], and small amounts of anatase (titanium dioxide, TiO_2). Kaolin clay is a name commonly applied to the clay mineral kaolinite [$Al_2Si_2O_5(OH)_4$]. Kaolin is one of the most common minerals, occurring in abundance from chemical weathering of rocks in hot, moist climatic soils like tropical rainforest areas.

Both bauxite and kaolin are utilized as proppants because of their superior strength characteristics which are further enhanced by sintering. The sintering process is conducted in high-temperature kilns that are used to bake the bauxite or kaolin powder after it has been made into specifically sized particles. The process decreases the water content in the bauxite and kaolin to make them more uniformly shaped for size roundness and spherical shape. The desired result of the sintering process is that the manufactured ceramic proppants can be engineered to withstand high levels of downhole pressure (closure stress).

The interest in *low-density proppants* is high because of the potential advantage for improving proppant transport and distribution in the fracture (Parker and Sanchez, 2012). These proppants require less viscosity for suspension, and the density of the base fluid can also be used to improve suspension. Various low-density materials have been investigated, such as walnut shells, hollow glass spheres, porous ceramics, and low-density plastics. Walnut shells and low-density plastics tend to continue to deform and lose width over time at stress. Glass spheres and porous ceramics are brittle materials, and they tend to fail catastrophically at a particular stress. Conventional proppants, such as natural sand and manmade proppants, are brittle and can also fail catastrophically. The nature of a packed bed with multiple contact points for each proppant grain tends to lower the chance of catastrophic failure, but broken grains, reduced width, and low conductivity still result. A new type of thermoplastic alloy (TPA) has been developed that is composed of a crystalline phase for excellent chemical stability and an amorphous phase for excellent dimensional strength and heat resistance.

4.2 Properties

Proppant properties and selection is crucial to optimizing well productivity. In spite of assiduous laboratory testing protocols, many proppants often do not perform as expected when subjected to real-world downhole conditions of pressure, temperature, and fluid (API RP 19C; API RP 19D). In terms of proppant hardness, if the proppant is unable to embed in the formation something referred to as point load occurs – which leads to higher flow capacity but the proppant will break easier. However, if the proppant is able to embed in the formation (embedment, which is also a function of particle size), the results is the load pressure spreading out over the proppant area, increasing the breaking point but also lowering flow capacity.

The relevant properties that are of importance when considering the suitability of proppants for a project are presented below – alphabetically rather than by preference since preference can change with the project and is site specific – and are (i) downhole scaling, (ii).

4.2.1 Downhole scaling

Scale is a deposit or coating formed on the surface of metal, rock or other material and is caused by a precipitation due to a chemical reaction with the surface, precipitation caused by chemical reactions, a change in pressure or temperature, or a change in the composition of a solution. Typical scales are calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$), barium sulfate ($BaSO_4$), strontium sulfate ($SrSO_4$), iron sulfide (FeS), iron oxides (FeO and Fe_2O_3), iron carbonate ($FeCO_3$), various silicates and phosphates, or any of a number of compounds insoluble or slightly soluble in water.

Scale is also a mineral salt deposit that may occur on wellbore tubulars and components as the saturation of produced water is affected by changing temperature and pressure conditions in the production conduit. In severe conditions, scale creates a significant restriction, or even a plug, in the production tubing. Scale removal is a common well-intervention operation, with a wide range of mechanical, chemical and scale inhibitor treatment options available (Sorbie and Laing, 2004).

Downhole proppant scaling is the result of a geochemical reaction (commonly known as proppant scaling or proppant diagenesis) which can occur downhole in the fracture in high-pressure/high-temperature wells, especially in a wet, hot downhole fracture environment. A crystalline material can form on uncoated ceramics and, acting like formation fines, plug the porosity and permeability of the proppant pack, thus reducing conductivity. The effects of scaling can occur slowly, but as long-term exposure increases, production decreases more rapidly because of the detrimental effects. A resin coating greatly reduces proppant scaling by providing a hydrophobic layer that prevents water from dissolving the prop-pant surface and forming scale. A wide variety of scale inhibitors is available, including phosphate esters and phosphonates (Table 5.4).

4.2.2 *Embedment*

Proppant embedment occurs as a result of the proppant embedding into the fracture face, especially in soft shale formations, leading to reduced fracture width and lower fracture flow capacity (Wen et al., 2007; Akrad et al., 2011; Zhang et al., 2015). In the embedment process, the proppant partially or completely sinks into a formation through displacement of the formation around the grain.

Embedment of the proppant is caused by an interaction between the formation and the proppant at the face of the fracture which causes a loss in conductivity. Embedment is usually considered to be a problem in partially consolidated to unconsolidated formations but it also can occur in hard rock formations (Jones and Britt, 2009). Another result of embedment is the creation of formation fines through spalling which can then migrate and further reduce conductivity (Terracina et al., 2010). Although often considered to be a disadvantage, an advantage of embedment is that can mitigate the potential for flowback.

Embedment pressure is a measure of the maximum pressure required to embed a steel ball to a given depth in rock (Rixe et al., 1963). This gives a direct indication of the resistance of the formation to embedment by a propping material and the effect of the rock on proppant deformation. It is a kind of indentation test and is a measure of the rock strength. A test procedure for determining the embedment pressure (Howard and Fast, 1970) uses a steel ball point 0.05 inches in diameter (which simulates the proppant) which is attached to the upper platen of a

TABLE 5.4 Examples of scale inhibitors.[a]

Acronym	Chemical name
ATMP	Amino-trimethylene phosphonic acid
CMI	Carboxy methyl inulin derivatives
HEDP	1-Hydroxyethylidene-1,1-diphosphonic acid
MAP	Maleic acid polymers.
MAT	Maleic acid terpolymer derivatives
PAA	Polyacrylic acid
PASP	Polyprotic acid
PBTC	Phosphonobutane-1,2,4-tricarboxylic acid
PCA	Polycarboxylic acid derivatives
PMA	Polymaleic acid derivatives
PPCA	Phosphinopolyacrylate derivatives
SPOCA	Sulfonated phosphonocarboxylic acid

[a] *Listed alphabetically rather than by any preference.*

hydraulic testing machine which moves, and loads the rock specimen (3.5 inches diameter) hydraulically. Where possible, the rock core should be obtained from the well to be hydraulically fractured. The steel ball point is embedded to a depth of 0.0125 in and a strain recorder is used to observe the results. The load at the target embedment, *Wp* is recorded and at least two more indentations are made on the test specimen, about 0.5 inches apart.

4.2.3 Flowback

Just as flowback can occur in the case of the injected fluids, proppant flowback is the movement (flow) of proppants back to the wellbore and the higher the pump velocity, the more the chance of flowback occurring. Furthermore, proppant flowback and pack re-arrangement is the main cause of well production decline, equipment damage as well as lock-down of the well for repairs. Thus, flowback reduces conductivity at the wellbore and decreases connectivity to the reservoir (Terracina et al., 2010).

Proppant flowback from fractured wells leads to high operational costs and can compromise safety. However, it can be prevented by the use of resin-coated proppants. Proppant flowback is a leading cause of well production decline, equipment damage, and wells shut in for repairs. Uncoated or precured resin coated proppants can flow back out of the fracture and into the wellbore as the well is produced. Proppant flowback can cause damage to downhole tools as well as surface equipment. In horizontal wells, flowback of uncoated proppant can deposit along the lateral fractures. All of these issues lead to expensive repairs and cleanouts. Proppant flowback can also cause loss of near-wellbore conductivity and reduced connectivity to the reservoir. Resin-coated proppants which have grain-to-grain bonding can eliminate proppant flowback, if applied properly, by forming a consolidated proppant pack in the fracture.

Post treatment proppant flowback is a leading cause of well production decline, equipment damage, and well shut-ins for repairs. Proppant flowback can also cause loss of near wellbore conductivity and reduced connectivity to the reservoir. Curable resin-coated proppants eliminate proppant flowback by forming a consolidated proppant pack in the fracture. This grain-to-grain bonding occurs under a combination of reservoir temperature and closure stress.

4.2.4 Fracture conductivity

The fracture conductivity (also referred to as *fracture capacity*) is a measure of proppant performance and proppant selection is deemed successful only when it can achieve substantial fracture conductivity. The fracture flow capacity (conductivity) depends on the fracture width, proppant distribution and proppant concentration. The post-fracture width is controlled by proppant size used for stimulation, while proppant concentration is controlled by spacers. Proppant distribution is not an easily controlled parameter (Howard and Fast, 1970).

4.2.5 Pack rearrangement

Proppant pack rearrangement in the fracture can cause a significant reduction in propped width which can also lead to reduced fracture flow capacity and connectivity to the wellbore. As a well is produced, high flow velocities in propped microfractures may cause uncoated or precured proppant packs to shift or rearrange, causing the microfractures to narrow or possibly close completely. Curable resin-coated proppants will prevent the proppant grains from shifting, keeping the microfractures propped open. This unique bonding technology provides additional proppant pack integrity, enhanced fracture flow capacity, and increased production during the life of the well (Terracina et al., 2010).

4.2.6 *Permeability*

The proppants employed for the fracturing process used should be permeable to gas under high pressures and the interstitial space between particles should be sufficiently large, yet have the mechanical strength to withstand closure stresses to hold fractures open after the fracturing pressure is withdrawn. However, increased strength often comes at a cost of increased density, which in turn demands higher flow rates, viscosity, or pressures during fracturing. Lightweight proppants conversely are designed to be lighter than sand (approximately 2.5 gm/cm^3) and thus allow pumping to be conducted at lower pressure or lower fluid velocity.

Light proppants are less likely to settle but porous materials can break the strength-density trend, or even afford greater gas permeability. Proppant geometry is also important; certain shapes or forms amplify stress on proppant particles making them especially vulnerable to crushing (a sharp discontinuity can classically allow infinite stresses in linear elastic materials).

4.2.7 *Production and migration of fines*

The word *fines* refers to the small particles that break off the surface of proppants as they are subjected to closure stress. The small broken pieces reduce pack porosity and permeability and cause major degradation in the conductivity of proppant packs. When proppant fines migrate down the proppant pack toward the well bore, they accumulate and reduce flow capacity. However, the proppant may be fully to blame for the presence of fines.

Fine-grained minerals are present in most sandstone formations as well as in some carbonate formations. The generation of fines from the proppant and the resulting migration in the fracture are considered to be one of the major contributors to poor treatment results and well performance. For example, the presence of just 5% fines can reduce conductivity by as much as 60%. The decrease in conductivity is made worse when the fines migrate to the wellbore. Generally, fines are unacceptable as they reduce fracture conductivity, the maximum tolerable fines for proppants is 1% (i.e., percentage that passes the #200 sieve) (Jones and Britt, 2009). It is recommended that classification of proppants can be done simply when 90% of the tested sample falls between the designated sieve sizes and fines tolerance limit should be observed.

4.2.8 *Shape, size, and concentration*

The definition of proppant shape consists of two main descriptions: (i) roundness and (ii) spherical conformation. The roundness is a measure of the smoothness of the proppant, while the spherical conformation is related to how well it resembles a sphere (Jones and Britt, 2009). At high stresses, the more spherical the proppant is, the more the permeability but at lower stresses, the more angular the proppant is the higher the permeability. Angular proppants tend to crush under conditions of high stress thus generating fines which lead to a reduction in conductivity.

Before use, proppant materials are carefully sorted for size and spherical conformation to provide an efficient conduit for production of fluid from the reservoir to the wellbore. Grain size is critical because a proppant must reliably fall within certain size ranges to coordinate with downhole conditions (such as fracture size and patterns) and completion design. Proppant shape and hardness qualities are also very important to the efficiency and effectiveness of a fracturing operation. A coarser proppant allows for higher flow capacity due to the larger pore spaces between grains but it may break down or crush more readily under high closure stress and rounder, smoother proppant shapes allow for better permeability.

Large-mesh proppants have greater permeability than small mesh proppants at low closure stresses, but will mechanically fail (i.e., get crushed) and produce very fine particulates (*fines*) at high closure stresses such that smaller-mesh proppants overtake large-mesh proppants in permeability after a certain threshold stress. Proppant mesh size also affects fracture length: proppants can be *bridged out* if the fracture width decreases to less than twice the size of the diameter of the proppant. As proppants are deposited in a fracture, proppants can resist further fluid flow or the flow of other proppants, inhibiting further growth of the fracture. In addition, closure stresses (once external fluid pressure is released) may cause proppants to reorganize or *squeeze out* proppants, even if no fines are generated, resulting in smaller effective width of the fracture and decreased permeability. Some companies try to cause weak bonding at rest between proppant particles in order to prevent such reorganization.

4.2.9 Size and concentration

The size and concentration of the proppants influences the placement of the proppant in several ways (Phatak et al., 2013). For example, larger proppants settle closer to the wellbore, due to their higher settling velocity and proppant bridging occurs more easily in large proppants. In addition, smaller proppants are transported a further distance and increase the chance of tip screen-out. However, for the smaller proppant size, the initial production is low but production decline is slower. The initial production is dependent on the pressure differential around the borehole caused by the conductivity (Phatak et al., 2013). In terms of production duration, the production rate of the larger proppant size depends only on the formation matrix permeability thus it declines faster. While that of the smaller proppant depends on both the formation matrix permeability and the conductivity of the fracture network, hence the longer it takes to decline. Proppant size can be gradually increased size during injection for a single treatment (Phatak et al., 2013).

Proppant concentration is achieved by using pelletized spacer materials. The spacers should have the following qualities: (i) similar specific gravity as the proppant, (ii) easily transportable, (iii) essentially insoluble in fracturing fluid, but soluble to post-fracturing injected solvents for easy removal, and (iv) resistant to breakage during pumping and ease of storage and handling in the field (Howard and Fast, 1970).

4.2.10 Stress

The stress to which a proppant is subjected is a critical factor to consider when selecting propping agents and proppants must be chosen so that they do not crush under field closure stress. When comparing proppants, one factor that must be considered is the performance of the proppant under closure stress changes.

The effective stress on the propping agent is the difference between the in-situ stress and the flowing pressure in the fracture. As the well is produced, the effective stress on the propping agent will normally increase because the value of the flowing bottomhole pressure will be decreasing. However, the in-situ stress tends to decrease with time as the reservoir pressure declines. As the effective stress increases to larger and larger values, then the higher-strength, more-expensive propping agents must be used to create a high conductivity fracture.

Related to stress is the strength of the proppant. Silica sand is must be tested to be sure it has the necessary compressive strength to be used in any specific situation. Generally, sand is used to prop open fractures in shallow formations. Sand is much less expensive per pound than resin-coated silica or ceramic proppants. Resin-coated silica is stronger than sand and is used where more compressive strength is required to minimize proppant crushing. Some resins can be used to form a consolidated pack in the fracture, which will help to eliminate proppant flow back into the wellbore. As expected, resin-coated silica is more expensive than sand but has an effective density that is less than sand. The strength of a ceramic proppant is proportional to its density and, furthermore, the higher-strength proppants, such as sintered bauxite, can be used to stimulate deep (>8000 ft) wells where high in-situ stresses will be responsible of large forces on the propping agent.

5. Hydraulic fracturing in tight reservoirs

Many tight reservoirs are thick, layered systems that must be hydraulically fracture treated to produce natural gas or crude oil at commercial flow rates. In tight reservoirs, as in conventional reservoirs, to create the fracture, a fluid is pumped into the wellbore at a high rate to increase the pressure in the wellbore. When the pressure reaches a value greater than the breakdown pressure (the sum of the in-situ stress and the tensile strength of the rock) of the formation the formation fractures. Once the fracture is created, the fracture can be extended using pressure (the *fracture-propagation pressure*) which is equal to the sum of: (i) the in-situ stress, (ii) the net pressure drop, and (iii) the near-wellbore pressure drop. The net pressure drop is equivalent to the pressure drop along the fracture as the result of viscous fluid flow in the fracture, plus any pressure increase caused by other effects. On the other hand, the near-wellbore pressure drop can be a combination of the pressure drop of the viscous fluid flowing through the perforations and/or the pressure drop resulting from tortuosity (such as twists and turns in the system) between the wellbore and the propagating fracture. This emphasizes the importance of the properties of the fracturing fluid in the creation and propagation of the fracture.

Overall, the hydraulic fracturing process is responsible for creating highly conductive channels and paths for the reservoir fluid to flow from the reservoir pay zone to the well bore provided the correct procedures are followed (Table 5.5). Moreover, stress-induced natural fractures open as a result of the hydraulic fracturing process thereby creating a secondary fracture network is created in addition to hydraulic fractures due to stress alterations during hydraulic fracturing (Cho et al., 2013). The main difference between primary fractures, which are hydraulic fractures, and secondary fractures is that the secondary fracture network does not contain proppants and is, therefore, unpropped. Therefore, since the natural

TABLE 5.5 Recommended practices and procedures to follow during hydraulic fracturing operations.[a]

- API Spec 4F, Drilling and Well Servicing Structures
- API RP 4G, Recommended Practice for Use and Procedures for Inspection, Maintenance, and Repair of Drilling Well Service Structures
- API RP 5A3, Recommended Practice on Thread Compounds for Casing, Tubing, and Line Pipe
- API RP 5A5, Field Inspection of New Casing, Tubing, and Plain-end Drill Pipe
- API Spec 5B, Specification for Threading, Gauging, and Thread Inspection of Casing, Tubing, and Line Pipe Threads
- API RP 5B1, Gauging and Inspection of Casing, Tubing, and Line Pipe Threads
- API RP 5C1, Recommended Practice for Case and Use of Casing and Tubing
- API TR 5C3, Technical Report on Equations and Calculations for Casing, Tubing, and Line Pipe Used as Casing or Tubing; and Performance Properties Tables for Casing and Tubing
- API RP 5C5, Recommended Practice on Procedures for Testing Casing and Tubing Connections
- API RP 5C6, Welding Connections to Pipe
- API Spec 5CT, Specification for Casing and Tubing
- API Spec 6A, Specification for Wellhead and Christmas Tree Equipment
- API Spec 7B-11C, Specification for Internal Combustion Reciprocating Engines for Oil-Field Service
- API RP 7C-11F, Recommended Practice for Installation, Maintenance, and Operation of Internal-Combustion Engines
- API Spec 10A, Specification for Cements and Materials for Well Cementing
- API RP 10B-2, Recommended Practice for Testing Well Cements
- API RP 10B-3, Recommended Practice on Testing of Deepwater Well Cement Formulations
- API RP 10B-4, Recommended Practice on Preparation and Testing of Foams and Cement Slurries at Atmospheric Pressure
- API RP 10B-5, Recommended Practice on Determination of Shrinkage and Expansion of Well Cement Formulations at Atmospheric Pressure
- API RP 10B-6, Recommended Practice on Determining the Static Gel Strength of Cement Formulations
- API Spec 10D, Specification for Bow Spring Casing Centralizers
- API RP 10D-2, Recommended Practice for Centralizer Placement and Stop Collar Testing
- API RP 10F, Recommended Practice for Performance Testing of Cementing Float Equipment
- API TR 10TR1, Cement Sheath Evaluation
- API TR 10TR2, Shrinkage and Expansion in Oilwell Cements
- API TR 10TR3, Temperatures for API Cement Operating Thickening Time Tests
- API TR 10TR4, Technical Report on Considerations Regarding Selection of Centralizers for Primary Cementing Operations
- API TR 10TR5, Technical Report on Methods for Testing of Solid and Rigid Centralizers
- API RP 11ER, Recommended Practice for Guarding of Pumping Units
- API Bulletin 11K, Data Sheet for Design of Air Exchange Coolers
- API Spec 11N, Specification for Lease Automatic Custody Transfer (LACT) Equipment
- API Spec 12B, Specification for Bolted Tanks for Storage of Production Liquids
- API Spec 12D, Specification for Field Welded Tanks for Storage of Production Liquids
- API Spec 12F, Specification for Shop Welded Tanks for Storage of Production Liquids
- API Spec 12J, Specification for Oil and Gas Separators
- API Spec 12K, Specification for Indirect Type Oilfield Heaters
- API Spec 12L, Specification for Vertical and Horizontal Emulsion Treaters
- API RP 12N, Recommended Practice for the Operation, Maintenance, and Testing of Flame Arresters
- API Spec 12P, Specification for Fiberglass Reinforced Plastic Tanks
- API RP 12R1, Recommended Practice for Setting, Maintenance, Inspection, Operation, and Repair of Tanks in Production Service
- API Spec 13A, Specification for Drilling Fluid Materials

(*Continued*)

TABLE 5.5 Recommended practices and procedures to follow during hydraulic fracturing operations.[a]—cont'd

- API RP 13B-1, Recommended Practice for Field Testing Water-based Drilling Fluids
- API RP 13B-2, Recommended Practice for Field Testing Oil-based Drilling Fluids
- API RP 13C, Recommended Practice on Drilling Fluid Processing Systems Evaluation
- API RP-13D, Recommended Practice on the Rheology and Hydraulics of Oil-well Drilling Fluids
- API RP 13I, Recommended Practice for Laboratory Testing Drilling Fluids
- API RP 13J, Testing of Heavy Brines
- API RP 13M, Recommended Practice for the Measurement of Viscous Properties of Completion Fluids
- API RP 13M-4, Recommended Practice for Measuring Simulation and Gravel-pack Fluid Leak-off Under Static
- API RP 19B, Evaluation of Well Perforators
- API RP 19C, Recommended Practice for Measurement of Properties of Proppants Used in Hydraulic Fracturing and Gravel-packing Operations
- API RP 19D, Recommended Practice for Measuring the Long-term Conductivity of Proppants
- API RP 49, Recommended Practice for Drilling and Well Servicing Operations Involving Hydrogen Sulfide
- API RP 53, Recommended Practices for Blowout Prevention Equipment Systems for Drilling Operations
- API RP 54, Occupational Safety for Oil and Gas Well Drilling and Servicing Operations
- API RP 55, Recommended Practices for Oil and Gas Producing and Gas Processing Operations Involving Hydrogen Sulfide
- API RP 65, Cementing Shallow Water Flow Zones in Deep Water Wells
- API RP 67, Recommended Practice for Oilfield Explosives Study
- API RP 74, Occupational Safety for Oil and Gas Well Drilling and Servicing Operations
- API RP 75L, Guidance Document for the Development of a Safety and Environmental Management System for Onshore Oil and Natural Gas Production Operation and Associated Activities
- API RP 76, Contractor Safety Management for Oil and Gas Drilling and Production Operations
- API RP 90, Annular Casing Pressure Management for Offshore Wells
- API RP 2350, Overfill Protection for Storage Tanks in Petroleum Facilities
- API Publication 4663, Remediation of Salt-Affected Soils at Oil and Gas Production Facilities
- API Bulletin E2, Bulletin on Management of Naturally Occurring Radioactive Waste Materials (NORM) in Oil and Gas Production
- API Bulletin E3, Environmental Guidance Document: Well Abandonment and Inactive Well Practices for U.S. Exploration and Production Operations
- API Environmental Guidance Document E5, Waste Management in Exploration and Production Operations
- API Guidelines for Commercial Exploration and Production Waste Management Facilities

These practices were created to meet or exceed federal requirements while remaining sufficiently flexible to accommodate the variations in regulatory frameworks that occur due to differences in regional geology and other factors.

[a] *American Petroleum Institute, Washington DC (www.api.org).*

fractures lack proppant, their conductivities are much more pressure dependent compared to hydraulic fractures (Cipolla et al., 2010; Eshkalak et al., 2014).

Physically, fractures appear in the rocks as narrow zones of structural discontinuity *(loss of cohesion)* that are the product of mechanical rupture. The term *brittle failure* refers to this mode of deformation while at higher temperatures and higher pressures, *ductile failure* (permanent deformation due to flow, but without loss of cohesion) may occur before the point of brittle failure is reached (Lei et al., 2015). Fractures may be dilational, *i.e., joints* (mode I fractures), or may exhibit shearing with components parallel (mode II) or perpendicular (mode III) to the direction of propagation of the fracture front. Shear fractures are also known as *faults*.

In carbonate rocks, natural fractures are more common than they are in sandstone rocks and some of the best fractured reservoirs occur in granite formation – often also referred to as unconventional reservoirs. Fractures occur in preferential directions, determined by the direction of regional stress, which is usually parallel to the direction of nearby faults or folds, but in the case of overthrust faults, they may be perpendicular to the fault or there may be two orthogonal directions. Induced fractures usually have a preferential direction, often perpendicular to the natural fractures.

5.1 Reservoir selection

The success or failure of a hydraulic fracture treatment often depends on the quality of the candidate reservoir selected for the treatment and the choice of an excellent candidate for stimulation often ensures success while the converse (i.e., choosing a poor candidate for hydraulic fracture treatment) typically results in technical and economic failure. To select the best candidate for stimulation, the design engineer must consider many variables – the most critical parameters for hydraulic fracturing are (i) formation permeability, (ii) the in-situ stress distribution, (iii) viscosity of the reservoir fluid, (iv) reservoir pressure, (v) reservoir depth, (vi) the condition of the wellbore, and (vii) the skin factor. As noted above, the skin factor refers to whether the reservoir is already stimulated or, perhaps, damaged and typical values for the skin factor range from -6 for an infinite-conductivity massive hydraulic fracture to more than 100 for a poorly-formed gravel pack. If the skin factor is positive, the reservoir is damaged and will likely be an excellent candidate for stimulation by hydraulic fracturing.

The best candidate wells for hydraulic fracturing treatment to recover natural gas or crude oil from a tight reservoir have a substantial volume of the original gas in place (OGIP) or the original oi in place (OOIP) and good barriers to vertical fracture growth above and below the net pay intervals. It is also understood that it is beneficial if a crude oil reservoir has gas in place to assist in the flow of oil to the wellbore. Such reservoirs have: (i) a thick pay zone, (ii) medium to high pressure, (iii) in-situ stress barriers to minimize vertical height growth, and (iv) substantial areal extent. In the case of tight gas reservoirs, the reservoirs that are not good candidates for hydraulic fracturing are those with: (i) a small volume of gas in place because of the thinness of the reservoir, (ii) low reservoir pressure, and (iii) small areal extent.

Also, reservoirs that do not have enough clean shale above or below the pay interval to suppress vertical fracture growth are considered to be poor candidates. Furthermore, reservoirs with extremely low permeability might not produce a sufficient amount of natural has or crude oil to pay for all the drilling and completion costs (recovery costs), even if the reservoirs is successfully stimulated; thus, such reservoirs are not considered to be good candidates for hydraulic fracture stimulation.

5.2 Fracture treatment optimization

The goal of the process design engineer is to design the optimum fracture treatment for each and every well by optimization of both the propped fracture length and the drainage area (well spacing) for low permeability natural gas and crude oil reservoirs (Holditch et al., 1978, 1987). As the propped length of a fracture increases, the cumulative production increased lead to profitability. However, as the fracture length increases, the incremental financial benefit (on the basis of $ of revenue per foot of additional propped fracture length) decreases. As the treatment volume increases, the propped fracture length increases. As the fracture length increases, the incremental cost of each foot of fracture (again, on the basis of $

of cost per foot of additional propped fracture length) increases. When the incremental cost of the treatment is compared to the incremental benefit of increasing the treatment volume, an optimum propped fracture length can be assessed found for every individual situation.

5.3 Design considerations and design procedures

The most important data for designing hydraulic fracturing treatment are: (i) the in-situ stress profile, (ii) the permeability of the formation, (iii) any fluid loss characteristics, (iv) the total fluid volume pumped, (v) the propping agent type, (vi) the amount of the propping agents, (vii) the pad volume, (viii) the viscosity of the fracture fluid, (ix) the injection rate, and (x) the formation modulus. If the modulus is large, the material is stiff. In hydraulic fracturing, a stiff rock results in more narrow fractures. If the modulus is low, the fractures are wider. The modulus of a rock is a function of the lithology, porosity, fluid type, and other variables. Thus, it is extremely important to quantify the in-situ stress profile and the permeability profile of the zone to be stimulated, plus the layers of rock above and below the target zone that influence fracture height growth.

To design the optimum treatment, it is essential to first determine the effect of fracture length and fracture conductivity upon the productivity and the ultimate recovery from the formation. As in all engineering problems, sensitivity runs must be made to evaluate uncertainties, such as estimates of formation permeability and drainage area. Then, a fracture treatment must be designed by using a fracture propagation model to achieve the desired length and conductivity at minimum cost. A hydraulic fracture propagation model should be developed to help in the determination of the material that needs to be mixed and pumped into the well to achieve the optimum values of propped fracture length and fracture conductivity – at the same time remembering that all wells may not be (are not) equal. This will help determine which variables are the most uncertain. For example, in many cases the values of in-situ stress, Young’s modulus, permeability, and fluid loss coefficient may not be known with any degree of certainty and have to be estimated, which can introduce elements of doubt. These uncertainties must be acknowledged and there is the necessity to determine the sensitivity of with the fracture propagation model in order note the effect of these uncertainties on the design process. As databases are developed and increase in terms of the data included, the number and magnitude of the uncertainties should diminish. This can only be achieved if there are numerous simulations of the hydraulic fracture treatment of the well which will assist in design improvement while also presenting indications of the means by which specific variables affect the dimensions of both the created fractures and the propped fractures.

5.4 Fracture fluid selection

A critical decision for any hydraulic fracturing project is the selection of the fracture fluid for the treatment by developing a flow chart that can be used to select the category of fracture fluid required to stimulate a natural gas or crude oil well on the basis of factors such as: (i) reservoir temperature, (ii) reservoir pressure, (iii) the expected value of fracture half-length, and (iv) a determination of whether the reservoir is water sensitive (Economides and Nolte, 2000).

The selection of the propping agent is based on the maximum effective stress that is applied to the propping agent during the life of the well. The maximum effective stress depends on the minimum value of flowing bottomhole pressure that one expects during the life of the well. For example, if the maximum effective stress is less than 6000 psi, sand is usually recommended as the propping agent but if the maximum effective stress is on the order of 6000—12,000 psi, either resin-coated sand or intermediate strength proppant is preferred for use, depending on the temperature. In cases in which the maximum effective stress is greater than 12,000 psi, high-strength bauxite should be used as the propping agent. But there will always be exceptions to these general *rules of thumb*.

For example, even if the maximum effective stress is less than 6000 psi, it may be preferable to choose to use resin-coated sand or other additives that effectively *lock* the proppant in place, especially when proppant flowback becomes an issue. Proppant flowback can result in significant nonproductive time. If a production operator chooses to pump a project with raw sand only, the proppant can flowback, requiring well intervention and causing significant production loss. Also, in high flow rate gas wells, intermediate strength proppants may be needed because of inertial flow. For fracture treatments in countries that do not mine sand (and thus the sand is not readily available for hydraulic fracturing) (projects), the largest cost for the proppant is may be the transportation costs. Thus, if it becomes necessary to import the propping agent, use of intermediate strength proppants may be the option, even for relatively shallow wells, but only if the cost differential between the intermediate strength proppants and sand is not always a significant factor.

Thus, the ideal properties of a fracturing fluid relate to its compatibility with the formation rock; its compatibility with the formation fluids; its ability to transfer enough pressure throughout the entire fracture to create a wide fracture, and be able to transport the proppant into the fracture, while breaking back down to a low viscosity fluid for cleanup after the treatment. Finally, and most importantly, the fracture treatment must meet necessary performance specifications.

5.5 Proppants

The proppant (fracking sand or propping agent) must have a series of properties that characterize it and thus determine a class. The main technical standards used in the characterization of proppant properties are: (i) size designation by sieves, (ii) format which is spherical conformation often referred to as sphericity and rounding, (iii) density, (iv) solubility in acidic solutions, (v) turbidity, which is the cloudiness or haziness of a fluid caused by large numbers of individual particles that are generally invisible to the naked eye, (vi) the crush test, which is an indicator of the propensity of the proppant to form small particles, and (vii) the conductivity test, which is related to the fratire conductivity of the proppant which, in turn, is dependent upon the proppant size and the pH. . In special applications, some different types of proppants as *tagged* that is a type of special ceramic proppant with a chemical marker to determine the source of reflux of the proppant it is in development. Traced ceramic proppants have been used to determine the location of the proppant.

The synthetic ceramic proppant is commonly made by the sintering of bauxite and/or kaolinite clays. Also, metakaolin, formed by the heat treatment at 700 °C (1,290 °F) of kaolin has been used with alkali agents to generate a geopolymer. According to the proportion of silicon and aluminum present in its formulation the geopolymer can be classified as polysialiate (ratio: 1), polysialatossiloxo (ratio: 2) and polysialatodisiloxane (ratio: 3).

The geopolymer activation reaction is exothermic and can be divided into the following phases:

Dissolution of the reactants:

$$Al_2O_3 + 3H_2O + 2OH^- \rightarrow 2[Al\ (OH)_4]$$

Transfer of the solids from the surface of the solid to a gel phase:

$$SiO_2 + H_2O + OH^- \rightarrow [SiO(OH)_3]$$

Polycondensation of the gel phase:

$$SiO_2 + 2OH^- \rightarrow [SiO_2(OH)_2]^2$$

The use of nanocarbons in cementitious matrixes has been carried out since 2004 and in some studies an increase of up to 50% in the compressive strength has been observed. In geopolymer matrices, increases on the order of 40% in flexural resistivity with the incorporation of CNT and, in some cases, an increase of up to three times was obtained for flexural strength.

5.5.1 Proppant selection

The most common completion in unconventional plays consists of a horizontal wellbore with multiple proppant fractures placed along it. In addition, to considerations of fracture conductivity, there are several other issues that must be addressed when selecting the appropriate proppant for use in multi-stage fractures, including flow convergence in transverse fractures, proppant transport when low-viscosity fluids are employed and proppant crush at typically low concentrations.

Production into a horizontal wellbore from an orthogonal fracture will exhibit linear flow in the far field as it travels down the fracture. However, as the fluids converge on the relatively small diameter of the wellbore, the fluid velocities in that region increase dramatically. Furthermore, the pressure drop in the transverse fracture could be significant compared to a fully connected vertical well. This leads to the conclusion that it is practically impossible to place enough conductivity near the wellbore in a transverse, horizontal well to be fully optimized. Generally, to fulfill such requirements, ceramic proppants are preferred because of the high conductivity as well as uniform size and shape. Resin-coated sand has medium strength but the shape and size can be irregular. Finally, sand has the lowest conductivity and as well as irregular size and shape. This will influence proppant choice along with the on-site needs of the project.

When choosing a propping agent, a proppant that will maintain enough conductivity after all crushing and embedment occurs must be chosen (Terracina et al., 2010). The effects of non-Darcy flow, multiphase flow, and gel residue damage should also be considered. Thus, the selection of the propping agent is based on the maximum effective stress that is applied to the propping agent during the life of the well. The maximum effective stress depends on the minimum value of flowing bottomhole pressure that one expects during the life of the well. If the maximum effective stress is less than 6000 psi, sand is usually recommended as the propping agent. If the maximum effective stress is between 6000 and 12,000 psi, one should use either resin-coated sand or intermediate strength proppant, depending on the temperature. For cases in which the maximum effective stress is greater than 12,000 psi, high-strength bauxite should be used as the propping agent.

Once the optimum fracture half-length has been determined and the fracture fluid and fracture propping agent have been selected, the design engineer needs to use model to determine the details of the design, such as the optimum injection rate, the optimum pad volume, the need for fluid loss additives, the proper location for the perforations, and other details. After designing the optimum treatment, the design engineer must compute the costs of the proposed treatment to be certain the costs are not too different from the costs assumed during the treatment optimization process. If the treatment costs are substantially different, the entire optimization loop should be retraced using the correct cost data.

Increased proppant strength often comes at a cost of increased density, which in turn demands higher flow rates, viscosities or pressures during fracturing, which translates to increased fracturing costs, both environmentally and economically. Lightweight proppants conversely are designed to be lighter than sand ($\sim 2.5\ \mathrm{g/cm^3}$) and thus allowing pumping at lower pressures or fluid velocities. Light proppants are less likely to settle. Porous materials can break the strength-density trend, or even afford greater gas permeability. Proppant geometry is also important; certain shapes or forms amplify stress on proppant particles making them especially vulnerable to crushing (a sharp discontinuity can classically allow infinite stresses in linear elastic materials).

Proppant mesh size also affects fracture length: proppants can be "bridged out" if the fracture width decreases to less than twice the size of the diameter of the proppant. As proppants are deposited in a fracture, proppants can resist further fluid flow or the flow of other proppants, inhibiting further growth of the fracture. In addition, closure stresses (once external fluid pressure is released) may cause proppants to reorganize or "squeeze out" proppants, even if no fines are generated, resulting in smaller effective width of the fracture and decreased permeability. Some companies try to cause weak bonding at rest between proppant particles in order to prevent such reorganization. The modeling of fluid dynamics and rheology of fracturing fluid and its carried proppants is a subject of active research by the industry.

Typically, in tight formations, proppant crushing can occur during the fracturing operation. Cracking and chipping of proppants can occur during the transportation of proppants pack from the manufacturing site to the place of final use which is the fracturing site. Efforts should be taken to minimize the exposure of proppant to chipping and cracking during the transportation process. The major source of proppant crushing is formation closure, particularly where the proppant is not well distributed. Conductivity examinations conducted on proppant pack indicates that crushing is most prevalent at the interface and less significant toward the center of the pack.

There are two primary sources of fines within a hydraulic fracture. Fines are generated either from the proppant pack or the reservoir itself. Reservoir fines can be generated due to spalling as proppant embeds into the fracture surface while proppant fines are generated due to proppant crushing. While all proppants experience crushing, the way they crush is dependent on their substrate. When sand based proppant crushes, it shatters similar to a drinking glass and it breaks into so many small fragments (Palisch et al., 2007; Weaver et al., 2007). On the other hand, most ceramic based proppant cleave like a brick. Fines generated falls into three size categories which includes: particles too large to penetrate the proppant pack, particles small enough to enter the proppant pack but large enough to subsequently plug the pore throat of the proppant pack, and lastly, particles small enough to flow through the proppant pack all the way to the wellbore.

The fines that are too large as well as those that are small enough to flow through the proppant pack are not damaging to the pack. However, particles small enough to enter the proppant pack but large enough to subsequently plug the pore throat of the proppant pack are detrimental to the proppant pack conductivity. When proppants are crushed and they produce fines that can plug the proppant pack, the porosity of the proppant pack is reduced which subsequently reduces the permeability of the proppant pack. Permeability reduction in the proppant pack will therefore reduce the fracture conductivity.

Finally, the typical low-proppant concentrations pumped in water-based fractures often designed for unconventional gas reservoirs can result in a low areal concentration of proppant in the fracture. These narrower fractures can have an impact on proppant crush. Inside a crush cell, interior grains are protected, due to their contact with six to twelve neighboring grains. However, exterior grains have fewer contact points, leading to greater stress at the points of contact, ultimately fracturing. Therefore, as proppant pack width and areal concentration decrease, the exterior grains comprise a larger percentage of the total grains in the pack, leading to higher proppant crush.

5.5.2 Proppant transport and placement

To create a hydraulic fracture, fluid is injected at high rate and pressure into a wellbore and into a formation that is open to the wellbore. Viscous fluid flow within the fracture as well as other effects creates the net pressure required to generate the created width profile and the created fracture height. The volume of fluid pumped will affect the created fracture length − however, without pumping a propping agent into the fracture, the created fracture will close once the pumping operation ceases. The flow of crude oil and natural gas from the formation into the fracture is dependent on the propped fracture dimensions. The really important characteristics of a fracture are the propped width, height, and length distributions; therefore, proppant transport considerations are very important in designing a hydraulic fracture treatment.

Proppant placement in the fractures is governed by a series of mechanisms involving the interaction between the fracturing fluid and proppant. For example, proppant density and size have a determining impact on proppant settling, which, in turn, impacts placement of the proppant in the fracture. The settling rate of the proppant is directly proportional to the difference in density between the fracturing fluid and proppant, and inversely proportional to the fluid viscosity. This condition makes settling an important consideration when pumping low-viscosity Newtonian fluids, as are typically used in horizontal multi-fracture treatments conducted in some shale formations. However, while much attention is typically given to density, diameter can actually be of greater importance in a fracturing treatment since settling velocity is proportional to particle diameter squared (Stoke's law, which is an expression for the frictional force − also called drag force − exerted on spherical objects with small Reynolds numbers i.e., very small particles) in a viscous fluid, thus having an exponentially larger effect on settling rate than fluid viscosity. This may not fully describe settling under dynamic conditions in a slurry situation but does illustrate that smaller and lighter proppant are easier to place.

The first fluid pumped into a well during a fracture treatment (the *prepad*) is used (i) to fill the casing and tubing, (ii) test the system for pressure, and (iii) break down the formation after which *the pad fluid* (the viscous fracturing fluid but without the propping agent) used during the treatment, is pumped into the well. The purpose of the pad is to create a tall, wide fracture that will accept the propping agent. Following the pad, the fluid containing propping agent (the *slurry*) is pumped and moves into the fracture. The propping agent particles move up, out, and down the fracture with the slurry and may settle in the fracture as a result of gravitational forces. The settling velocity increases as the diameter and density of the propping agent increase and as the density and viscosity of the fracturing fluid decrease. To minimize proppant settling, propping agents that are smaller in diameter and/or less dense, as well as a more viscous fluid, can be used.

There are other factors that must be included when trying to compute the propped fracture dimensions. For example, the type of fracture fluid affects transport of the proppant – a linear-structured fracture fluid will not transport proppants as well as fluids with structure, such as a cross-linked fracture fluid or a viscoelastic surfactant fluid. Geologic realities also must be considered; for example, no fracture is exactly vertical, and the walls of a fracture are rarely (if at all) smooth. If there are turns and ledges along the fracture walls, these geologic features tend to reduce proppant settling when compared with the theoretical equations for transport in smooth-wall, parallel-plate systems. Other issues such as (i) fracture height growth during and after pumping operations, (ii) fluid loss in layered formations, and (iii) slurry viscosity also affect the propped fracture dimensions (Gidley et al., 1989; Smith et al., 1997).

5.6 Post-fracture reservoir evaluation and production data

Analyzing post-fracture production and pressure data requires a thorough understanding of the flow patterns in the reservoir. The technique applied to analyze the data must be compatible with the flow regime that is occurring when the data are collected. For a well containing a finite conductivity hydraulic fracture, the flow regimes that occur consist of: (i) bilinear flow, (ii) linear flow, (iii) transitional flow, and (iv) pseudo-radial flow. These flow regimes can be defined in terms of dimensionless time.

The times that encompass bilinear flow, linear flow, and transitional flow can be termed *transient flow*. The pseudoradial flow data can be analyzed using semi-steady-state methods. In most tight gas reservoirs containing a finite conductivity hydraulic fracture, the flow rate and pressure data measured during well tests generally fall into the transient flow category. Seldom can semi-steady-state analyses techniques be used to successfully analyze well-test data in tight reservoirs containing a hydraulic fracture. As such, transient flow analyses methods are usually preferred to analyze such data. If long-term (years) production data are available, semi steady-state methods can be used successfully to analyze the production and pressure data.

In many cases, after a well is fracture treated (especially in the early days of application of the hydraulic fracturing technology), the well fluids were produced to a pit until the fracturing fluid was sufficiently clean to allow the well fluids to be suitable for sales. After the well has ceased to produce proppant and fracturing fluid, a test separator is usually installed to measure the flow rate of the sales fluid − natural gas or crude oil. The flow rate and the flow pressures are subsequently analyzed to estimate the value of the reservoir and fracture properties.

If a finite difference reservoir simulator is used to analyze field, it is clear that the production and pressure transient data, if measured accurately, can lead to a much better characterization of the reservoir and the hydraulic fracture. The very early flow-rate data are mostly affected by the fracture conductivity, often called bilinear flow. Later in the life of the well, during linear flow, the flow-rate data are most affected by the fracture half-length. If pseudoradial flow is reached, the flow-rate data are most affected by the formation permeability. As such, if the early time flow-rate and pressure data, during the first few days and weeks, are not measured accurately, it is possible to completely misunderstand the properties of the hydraulic fracture.

Finally, during production, gas or oil that is recovered from the well is sent to small-diameter gathering pipelines that connect to larger pipelines that collect gas or oil from a network of production wells. Because large-scale tight gas production and tight oil production has only been occurring very recently, the production lifetime of wells in tight formations is not fully established. However, it is generally observed that such wells experience quicker production declines than conventional natural gas production. For example, in the Fayetteville play in north-central Arkansas, it has been estimated that half of the lifetime production of a well, or estimated ultimate recovery, occurs within its first five years (Mason, 2011). Once a well no longer produces at an economic rate, the wellhead is removed, the wellbore is filled with cement to prevent leakage of gas into the air, the surface is reclaimed (either to its pre-well state or to another condition agreed upon with the landowner), and the site is abandoned to the holder of the surface rights to the land.

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CHAPTER

6

Fluids management

1. Introduction

For the purposes of this chapter, the term *fluids* refer to any fluid material that is either introduced into the formation to aid in the recovery of natural gas or crude oil as well as any fluid material that is recovered from the fractured formation (Table 6.1). Also, as a reminder and to avoid any confusion at this stage, the term *oil shale* refers to any source rock that contains solid insoluble hydrocarbonaceous material (kerogen) that is converted to synthetic fuel liquids when the rock is heated to temperatures in excess of 500 °C (930 °F) in the absence of oxygen (pyrolysis) (Chapter 11, Chapter 13) (Scouten, 1990; Lee et al., 2007; Speight, 2012, 2014a, 2016a).

In the various oil shale production processes (Chapter 14, Chapter 15) oil shale is heated to approximately 500 °C (930 °F) at which temperature the kerogen decomposes into oil vapor and gas. Cooling this vapor stream produces liquid oil and uncondensed, light hydrocarbon produces liquid oil and uncondensed, light hydrocarbon gases. Sub-surface retorting (in situ retorting) or surface retorting (ex situ retorting) is needed to produce valuable products from oil shale kerogen and but, however, most development work on oil shale recovery has been directed to mining the shale, bringing it to surface, and then processing it in surface facilities. Various surface retorting processes can be classified according to the method used to provide heat for the retorting reaction (Scouten, 1990; Lee, 1991; Lee et al., 2007; Speight, 2012, 2014a, 2016a).

In the present context, crude oil from tight shale formations (tight oil) is not shale oil since it is produced by a recovery process (hydraulic fracturing) rather than by a thermal conversion process that produces synthetic crude oil from kerogen (Chapter 13). It must be re-emphasized that crude oil from tight formations is not produced in the same manner as oil from the thermal decomposition of kerogen. As a result, the processes are different, especially since the crude oil (and natural gas) in tight formations (shale, sandstone, and carbonate exists in the formation in the form in which it (the natural gas or the crude oil) is recovered (Chapter 1). Therefore, water requirements and water usage to recover natural gas or crude oil cannot be considered to be the same as oil production by the conversion of kerogen (to oil) in situ or ex situ.

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TABLE 6.1 Typical properties of organic fluids occurring in tight formations and shale formations.

Constituents (%v/v)	Dry gas	Wet gas	Condensate	Volatile oil[a]
Methane, CH_4	86.12	92.46	73.19	57.60
Ethane, C_2H_6	5.91	3.18	7.80	7.35
Propane, C_3H_8	3.58	1.01	3.55	4.21
Butane derivatives (C_4H_{10})	1.72	0.52	2.16	2.84
Pentane derivatives (C_5H_{12})	0.50	0.21	1.32	1.48
Hexane derivatives (C_6H_{14})		0.14	1.09	1.92
Heptane derivatives (C_7H_{16})		0.82	8.21	22.57

[a] *Representative of Crude Oil from Tight Formations and Tight Shale Formations.*

Until recently the vast quantities of natural gas and crude oil in tight formations were unrecoverable using the older available technology. However, through the use of recently improved horizontal drilling techniques combined with hydraulic fracturing, have unlocked an abundance of natural gas and crude oil from deep tight formations in the United States. Indeed, given the density of the tight formations, hydraulically fracturing the wells is necessary to create pathways for oil and natural gas to flow to the production well (Chapter 5). Moreover, along with the rapid development of these resources, natural gas and crude oil production from tight formations is undergoing increased scrutiny due to various environmental consequences, not the least of which is the relatively large volume of water that is required to hydraulically fracture each tight formation. Innovation in horizontal drilling techniques hydraulic fracturing technology (Chapter 4, Chapter 5) is driving the rapid development of tight resources (which include shale gas, natural gas liquids, and tight oil) across the United States and Canada. In fact, the development of natural gas and crude oil from tight formations has significantly increased the volume of the natural gas and crude oil resources in the United States. On a worldwide scale, many governments (particular the government of Argentina, Canada, China, Mexico, Poland, South Africa, and the United Kingdom have started to explore the commercial viability of their shale reserves (Chapter 2). The potential for expansion is real since and newly discovered resources of natural gas and crude oil in tight formations continue to add to the known resources.

However, water is essential to the development of the resources of natural gas and crude oil in these tight formations but as developers escalate the exploration for suitable tight formations, the limited availability of water will (if it has not already become) a reality. Extracting these resources requires large amounts of water for not only for the drilling operations but particularly for the hydraulic fracturing operations (Chapter 5). In most cases, these demands are met by local freshwater − the financial aspects of shipping water to a remote site are not favorable. Nevertheless, the developers of tight resources are significant users and managers of water at local and regional levels and, as a result, water and energy have become interdependent. For example, improving the efficiency of water use reduces the need to develop, transport, pump, treat, and distribute additional water resources thereby reducing the amount of power or energy required for recovery of the resources. Alternatively, improving energy efficiency reduces the demand on electricity generation and fuel consumption for water transportation which, in turn, reduces the need for water resources for power generation cooling and fuel processing, along with reducing the water resources needed to extract the natural gas and crude oil.

Thus, the development of natural gas and crude oil resources in deep tight, low-permeability shale, sandstone, or carbonate formations, which are typically found thousands of feet below the surface of the Earth, requires copious amount of water than can floral and faunal communities, including human communities (Stillwell et al., 2010).

Finally, hydrological conditions vary spatially and seasonally across the regions where subterranean tight formations occur, with variation among not only between adjacent formation but within a single formation. This variability causes different demands on the water sources and makes the ability of the developers to meet the water demands for horizontal drilling and hydraulic fracturing highly unpredictable. Thus, estimates based on previous seasonal demands as well as demands by previously developed formations are not always transferable to new tight formations that are under investigation for the near-future development. Each formation becomes a development that must be considered to be site specific and subject not only to the depth and properties of the formation as well as the formation fluids (Chapter 3) but also to the seasonal availability of water. Furthermore, public concern over increased competition and impacts on freshwater availability for domestic purposes (with the guarantee of untarnished drinking water sources) can influence the awarding of a development license and ability of a developer to operate which, in turn, can lead to changes in government regulations that could impact both the short-term and long-term financial aspects of the development. Therefore, responsible water management practice is critical to a developer obtaining a license to operate at the site which is particularly true when a resources is located within a water-poor region, such as may be the case in certain regions Texas and North Dakota.

The quality of water used to in the hydraulic fracturing fluid and the effect and impact of the fluid on well production is a critical factor in developing a water management strategy (Vidic et al., 2013). Furthermore, regulatory requirements (mandated federal, state and local regulatory authorities) often dictate water management options. Also within the United States, multi-state and regional water permitting agencies may also be responsible for maintaining water quality and water supply. In fact, all authorities may dictate water withdrawal and/or disposal options that are available for consideration and use and injection wells that may be used for disposal of flowback water and other produced waters require state or federal permits which are subject to suitable analysis by standardized text methods (Blauch, 2009; Lest et al., 2015). The primary objective of any such program, whether administered at the state or federal level, is protection of underground sources of drinking water but, in many cases, the responsible authority is a function of the acquisition or disposal option chosen. For example, surface water discharge may be regulated by a different agency than subsurface injection. Therefore, regardless of the regulatory agency with program authority over subsurface injection, new injection wells will require a permit that meets the appropriate state or federal regulatory requirements.

Thus, it is the purpose of this chapter to introduce the reader to the various aspects of tight resource development and the necessity for water as part of the development of natural gas and crude oil resources in tight formations as well as the effects of this development on water use, water production, and water quality.

In addtion, it is also the purpose of this chapter to present the properties of crude oil and natural gas and to comment of the effects of these properties on recovery. In fact, the properties of reservoir fluids (particularly crude oil) are an important aspect of recovery operations. It is not just a matter of drilling a well into the reservoir (the producing formation) and the natural gas or crude oil ascends through the well to the surface. However, in the current context, the amounts of natural gas and crude oil that are recoverable is determined by a number of factors including the permeability of the rocks, the strength of natural drives (the gas present, pressure from adjacent water or gravity), and the viscosity of the crude oil. In conventional sandstone reservoirs that typically exhibit medium-to-high permeability, natural gas and crude oil flow freely to the well and thence to the surface.

2. Fluids evaluation

The proper management of production of fluids from a reservoir can maximize the recovery of the oil originally in the reservoir. Developing proper management strategies requires accurate knowledge of the characteristics of the reservoir fluid as long as fluid samples obtained from the reservoir fluid reflect the pertinent properties of the fluid, as determined by subsequent laboratory tests (Chapter 4).

Each reservoir has its own range of fluids which are usually identified by some distinguishing physical or chemical property. In order the understand the concept of reservoir fluids and the means of recovery − which typically specific to the reservoir − it is necessary to understand the different types of crude oil and heavy crude oil as well as tar sand bitumen. Tar sand formations require fracturing of the rock to create channels through which heated bitumen can move to the wellbore and it is the purpose of this section to describe the means by which reservoir fluids can be evaluated.

Reservoirs contain complex mixtures of fluids and the behavior of the fluids is strongly dependent on the chemical make-up of the fluid as well as the properties of the reservoir. Conventional crude oil is a complex mixture of hydrocarbons and non-hydrocarbons with molecular weight varying from 16 (methane) to several hundred and even into the thousands (resin and asphaltene constituents). More generally, reservoirs typically contain three main *fluids*: (1) natural gas, (ii) crude oil, and (iii) non-hydrocarbon fluids such as water with minor constituents being acid gases (carbon dioxide and hydrogen sulfide). For the purposes of the present text, near-solid and solid components of reservoirs (such as wax deposits and tar mats) are not discussed here. The focus is on the gaseous and liquid components of the reservoir which exhibit considerable variations in composition in combination and proportion within each reservoir.

The physical (bulk) composition of reservoir fluids is a subset of fluid characterization and evaluation and distribution within the reservoir which helps in defining reservoir continuity and communication among various zones. Interpretation of well-test data and the design of surface facilities and processing plants require accurate fluid information and its variation with time. In addition to initial reservoir-fluid samples, periodic sampling is necessary for reservoir surveillance.

Reservoir-fluid characterization consists of several key steps: (i) acquisition of representative samples, (ii) identification of reliable service laboratories to perform PVT measurements, (iii) implementation of QA/QC procedures to ensure data quality, and (iv) development of mathematical models to capture fluid-property changes accurately as functions of pressure, temperature, and composition. The fluid type and production processes dictate the type and the volume of required fluid data. This paper outlines recommended sampling techniques, PVT-data-acquisition strategies, and modeling methods and presents field examples covering a wide range of fluid types from heavy oils to lean gas condensates and production processes such as depletion, pressure maintenance, and miscible recovery.

Natural gas and crude oil − whether they are from conventional formations or tight formations − provides not only raw materials for the ubiquitous plastics and other products, but also fuel for energy, industry, heating, and transportation. From a chemical standpoint crude oil is an extremely complex mixture of hydrocarbon compounds, with minor amounts of nitrogen-, oxygen-, and sulfur-containing compounds as well as trace amounts of metal-containing compounds (Parkash, 2003; Gary et al., 2007; Mokhatab et al., 2016; Speight, 2014a, 2017; Hsu and Robinson, 2017, 2019). However, when the reservoir rocks exhibit low permeability such as in tight formations and shale formations, the natural gas and crude cannot flow (or can only flow with stimulation) to the well and the additional technique of hydraulic fracturing needs to be applied.

Tight formation and shale formations typically have permeability less than 1 mD and the reservoir rocks in such formations show a strong stress sensitivity of the fluid transport properties and a considerable productivity decline due to changing stress conditions during the production process. Furthermore, in a typical conventional the speed at which pressure transients move through porous media is not only a function of the formation permeability but also a function of (i) the fluid viscosity and (ii) the fluid compressibility, as well as other fluid properties. For example, in a high permeability gas reservoir (say, 100 md), a pressure transient will reach the reservoir boundary in a relatively short time (hours to days). However, in a low-permeability reservoir (ca. 0.1 mD), the pressure transients move much slower and it may require years of production before well-to-well interference or a boundary can be recognized by studying pressure transient or production data. Thus fluid (gas and liquid) properties can exert a considerable influence of the productivity of fluids from tight formations and shale formations.

To satisfy specific needs with regard to the recovery of natural gas and crude oil as well as the properties of the recovered product, various standard test methods are available from organizations, such as the ASTM International (Speight, 2014a, 2015). Thus, it is appropriate that in any discussion of the physical properties of reservoir fluids reference should be made to the corresponding test and, accordingly, the various test numbers have been included in the text. Application of standard test methods to reservoir fluids and inspection of the data provide indications of the most logical means of recovery. Indeed, careful evaluation from physical property data is a major part of the initial study of reservoir fluids and *proper* interpretation of the data resulting from the inspection of crude oil requires an understanding of the significance of the data (Speight, 2014a, 2015). But before any analysis occurs, it is necessary to ensure that the sample is consistent with (and a representative sample of) the fluid in the reservoir and that the data can be reproduced within the limits of accuracy (Speight, 2015, 2018, 2019).

2.1 Natural gas

Natural gas – whether it is from conventional reservoir or a tight reservoir – is a mixture of saturated gaseous hydrocarbon derivatives, predominantly C_1 to C_4, that may also contain hydrocarbon derivatives as high as C_{10}. Natural gas may also contain inorganic compounds, such as hydrogen, nitrogen, hydrogen sulfide, carbon monoxide and carbon dioxide. Separation and processing of natural-gas processing typically begins at the begins at the wellhead where the composition of the raw natural gas extracted from producing wells depends on the type, depth, as well as the geology and location of the underground reservoir (Chapter 7) (Mokhatab et al., 2006; Speight, 2008; 2014).

Raw natural gas varies greatly in composition and the constituents can be several of a group of hydrocarbons and non-hydrocarbons (Table 6.2). In addition, a natural gas stream typically has high proportions of *natural gas liquids* (NGLs) and is referred to as *rich gas*. Natural gas liquids are constituents such as ethane, propane, butane, and pentanes and higher molecular weight hydrocarbon constituents. The higher molecular weight constituents (i.e., the C_{5+} product) are commonly referred to as *natural gasoline*. Rich gas will have a high heating value and a high hydrocarbon dew point. When referring to natural gas liquids in the gas stream, the term *gallon* per *thousand cubic feet is* used as a measure of high molecular

TABLE 6.2 Composition of associated natural gas from a petroleum well.

Category	Component	Amount (%)
Paraffinic	Methane (CH_4)	70–98
	Ethane (C_2H_6)	1–10
	Propane (C_3H_8)	Trace-5
	Butane (C_4H_{10})	Trace-2
	Pentane (C_5H_{12})	Trace-1
	Hexane (C_6H_{14})	Trace-0.5
	Heptane and higher (C_7^+)	None-trace
Cyclic	Cyclopropane (C_3H_6)	Traces
	Cyclohexane (C_6H_{12})	Traces
Aromatic	Benzene (B_6H_6), others	Traces
Non-hydrocarbon	Nitrogen (N_2)	Trace-15
	Carbon dioxide (CO_2)	Trace-1
	Hydrogen sulfide (H_2S)	Trace occasionally
	Helium (He)	Trace-5
	Other sulfur and nitrogen compounds	Trace occasionally
	Water (H_2O)	Trace-5

weight hydrocarbon content. On the other hand, the composition of non-associated gas (sometimes called *well gas*) is deficient in natural gas liquids. The gas is produced from geological formations that typically do not contain much, if any, hydrocarbon liquids.

Gas production from unconventional shale gas reservoirs (such as tight shale formations) has become more common in the past decade. In terms of chemical makeup, shale gas is typically a dry gas composed primarily of methane (60%–95% v/v), but some formations do produce wet gas. The Antrim and New Albany plays have typically produced water and gas. Gas shale formations are organic-rich shale formations that were previously regarded only as source rocks and seals for gas accumulating in the strata near sandstone and carbonate reservoirs of traditional onshore gas.

Produced shale gas observed to date has shown a broad variation in compositional makeup, with some having wider component ranges, a wider span of minimum and maximum heating values, and higher levels of water vapor and other substances than pipeline tariffs or purchase contracts may typically allow. Indeed, because of these variations in gas composition, each shale gas formation can have unique processing requirements for the produced shale gas to be marketable.

Ethane can be removed by cryogenic extraction while carbon dioxide can be removed through a scrubbing process. However, it is not always necessary (or practical) to process shale gas to make its composition identical to *conventional* transmission-quality gases. Instead, the gas should be interchangeable with other sources of natural gas now provided to end-users. The interchangeability of shale gas with conventional gases is crucial to its acceptability and eventual widespread use in the United States.

Although not highly sour in the usual sense of having high hydrogen sulfide content, and with considerable variation from play to resource to resource and even from well to well within the same resource (due to extremely low permeability of the shale even after fracturing), shale gas often contains varying amounts of hydrogen sulfide with wide variability in the carbon dioxide content. The challenge in treating such gases is the low (or differing) hydrogen sulfide/carbon dioxide ratio and the need to meet pipeline specifications. In a traditional gas processing plant, the olamine of choice for content for hydrogen sulfide removal is N-methyldiethanolamine (MDEA) (Mokhatab et al., 2006; Speight, 2008; 2014) but whether or not this olamine will suffice to remove the hydrogen sulfide without removal of excessive amounts of carbon dioxide is another issue.

Gas treatment may begin at the wellhead – condensates and free water usually are separated at the wellhead using mechanical separators, he observes. Gas, condensate and water are separated in the field separator and are directed to separate storage tanks and the gas flows to a gathering system. After the free water has been removed, the gas is still saturated with water vapor, and depending on the temperature and pressure of the gas stream, may need to be dehydrated or treated with methanol to prevent hydrates as the temperature drops. But this may not be always the case in actual practice.

2.2 Crude oil

Conventional crude oil exhibits a wide range of physical properties and several relationships can be made between various physical properties (Speight, 2014a). Whereas the properties such as viscosity, density, and boiling range may vary widely, the ultimate or elemental analysis varies over a narrow range for a large number of samples (Speight, 2014a, 2015). Thus, initial inspection of the tight oil (through an examination of the physical properties using standard test methods) is necessary from which it is possible to make deductions about the propensity for easy or difficult recovery. In fact, evaluation of reservoir fluids from physical property data as to which recovery sequences should be employed for any particular crude oil is a predominant part of the initial examination of reservoir fluids.

The chemical composition of crude oil is a much truer indicator of recovery behavior. Whether the composition is represented in terms of compound types or, more likely, in terms of generic compound classes, it can assist in determination of the nature and type of any potential interactions of the oil with the reservoir rock or the potential for changes in oil composition that can be affected by changes in pressure and temperature (Speight, 2014). Hence, chemical composition can play a large part in determining the nature of the products that arise from the recovery operations. It can also play a role in determining the means by which a particular feedstock should be processed (Speight, 2014) and this becomes particularly important when partial upgrading in the reservoir (in situ upgrading) is considered as an option during recovery.

2.3 Non-hydrocarbon fluids

The non-hydrocarbon fluids from hydraulic fracturing operations are made up of water, a variety of chemicals, and sand that is pumped into the underground shale rock formations under great pressure to recovery the natural gas and crude oil. There are two types of wastewater from hydraulic fracturing operations: (i) flowback water and (ii) produced water (Chapter 5). Flowback water refers to the fluid that returns to the surface upon completion of a hydraulic fracturing event prior to production. Produced water refers to the fluid that returns to the surface once the well starts producing natural gas and oil. Both types of water can contain liquid that was resident in the shale layer (formation brine). However, flowback water is primarily composed of fracking fluid and its associated chemicals.

After a well has been subjected to the fracture treatment, some of the fluid flows back to the surface, usually picking up by leaching additional chemicals that occur naturally in the formation. The composition of fracking fluids varies widely, depending primarily on the geology of the area being subjected to hydraulic fracturing. However, these fluids generally consist of a variety of chemicals and high levels of dissolved solids. The solutions are relatively clean prior to introduction into the drill holes, but the post-use solutions contain many more components, including high levels of dissolved organic constituents. As a result, analysis is challenging but, nevertheless, because of the complexity of the fluids, it is important to determine the metal content of both pre-use and post-use fracturing fluids. These analyses are used to evaluate how often the fluids can be reused and the measures that must be taken for safe disposal (Elliott et al., 2016).

The complexity of the water may be increased by re-use. For example, prior to reuse, the water is desalinated to remove salts, which can inhibit the effectiveness of additives and are known to cause scaling. For example, cations such as calcium, barium, and strontium may cause scale formation in water pumps and pipes thereby reducing extraction efficiency. To counter this, additional anti-scaling agents would need to be added to the fracking fluid prior to reuse. Occasionally organic acid derivatives (such as formate and acetate) are added to control the pH (acidity-basicity). These organic acids are sources of carbon for bacterial growth and bacterial growth in hydraulic fracturing wastewaters can result in the production of the toxic and corrosive hydrogen sulfide (H_2S) As a result of such possibilities, biocides are added to prevent bacterial growth. A variety of standard test methods are available for water testing (API, 2106; ASTM, 2019) which are instrumental in specifying and evaluating the methods and facilities used in examining the various characteristics of and contaminants in water for health, security, and environmental purposes. These water testing standards allow companies, concerned local government authorities, water distribution facilities, and environmental laboratories to test the quality of water and ensure safe consumption. However, rather than discuss the merits of each standard collection of test methods (Tables 6.3–6.5), only the necessary aspects of testing water will be presented here. The various test methods for evaluating reservoir fluids, such as crude oil are presented elsewhere (Chapter 4) (Speight, 2014a, 2015), it is pertinent at this point to present an overview of the evaluation of reservoir fluids.

TABLE 6.3 Selected EPA test methods for the detection of organic compounds in water.

EPA #	Method
600,777,113	Environmental pathways of selected chemicals in freshwater systems: Part I: Background and experimental procedures
600,479,019	Handbook for analytical quality control in water and wastewater laboratories
625,673,002	Handbook for monitoring industrial wastewater
815B97001	Manual for the certification of laboratories analyzing drinking water criteria and procedures quality assurance
815D03008	Membrane filtration guidance manual
821R96013	Method 1632: Determination of inorganic arsenic in water by hydride generation flame atomic absorption
821R95031	Method 1638: Determination of trace elements in ambient waters by inductively coupled Plasma-Mass spectrometry
821R96005	Method 1638: Determination of trace elements in ambient waters by inductively coupled plasma-mass spectrometry
821R96006	Method 1639: Determination of trace elements in ambient waters by stabilized temperature graphite furnace atomic absorption
821R96007	Method 1640: Determination of trace elements in ambient waters by on-line chelation preconcentration and inductively coupled Plasma-Mass spectrometry
600,479,020	Methods for chemical analysis of water and wastes
821B96005	Methods for organic chemical analysis of municipal and industrial wastewater
600,488,039	Methods for the determination of organic compounds in drinking water

TABLE 6.4 Selected EPA analytical methods for the analysis of contaminants in water.

Method	Technique	Title
150.1	pH, electrometric	Methods for chemical analysis of water and wastes (EPA/600/4–79/020)
200.7 Rev 4.4	Metals and trace elements by ICP/Atomic emission spectrometry	Methods for the determination of metals in environmental samples supplement 1 (EPA/600/r-94/111)
200.8 Rev 5.4	Trace elements by ICP/Mass spectrometry	Methods for the determination of metals in environmental samples supplement 1 (EPA/600/r-94/111)
200.9 Rev 2.2	Trace elements by stabilized temperature graphite furnace AA spectrometry	Methods for the determination of metals in environmental samples supplement 1 (EPA/600/r-94/111)
245.1 Rev 3.0	Mercury by cold vapor AA spectrometry - manual	Methods for the determination of metals in environmental samples supplement 1 (EPA/600/r-94/111)
245.2	Mercury by cold vapor AA spectrometry - automated	Methods for chemical analysis of water and wastes (EPA/600/4–79/020)
300.0 Rev 2.1	Inorganic anions by ion chromatography	Methods for the determination of inorganic substances in environmental samples (EPA/600/r-93/100)
300.1 Rev 1.0	Determination of inorganic anions in drinking water by ion chromatography	Methods for the determination of organic and inorganic compounds in drinking water, volume 1 (EPA 815-R-00-014)
375.2 Rev 2.0	Sulfate by automated colorimetry	Methods for the determination of inorganic substances in environmental samples (EPA/600/r-93/100)
525.2 Rev 2.0	Organic compounds by liquid- solid extraction and capillary column GC/Mass spectrometry	Methods for the determination of organic compounds in drinking water-supplement III (EPA/600/r-95-131)
550	Polycyclic aromatic hydrocarbon derivatives (PAHs) by liquid-liquid extraction and HPLC with coupled UV and fluorescence detection	Methods for the determination of organic compounds in drinking water supplement I (EPA/600/4–90/020)
550.1	Polycyclic aromatic hydrocarbon derivatives (PAHs) by liquid-solid extraction and HPLC with coupled UV and fluorescence detection	Methods for the determination of organic compounds in drinking water supplement I (EPA/600/4–90/020)

The water (brine) produced with oil has been trapped with the oil and is brought to the surface along with oil. Because the water has been in contact with the oil, it contains some of the chemical characteristics of the formation and the oil itself. Oil and gas wells produce more water than oil (as much as 7 barrels of water per barrel of oil in some fields). The composition (salt content) of co-produced water determines the need for anti-scaling

TABLE 6.5 Selected test methods for drinking water contaminants.

Contaminant	EPA	ASTM[a]	AWWA[b]
Aluminum	200.7, 200.8, 200.9		3120 B, 3113 B, 3111 D
Chloride	300.0	D4327, D512	4110 B, 4500-Cl– D, 4500-Cl–**B**
Color			2120 B
Copper	200.7, 200.8, 200.9	D1688, D1688	3120 B, 3111 B, 3113 B
Fluoride	300.0	D4327, D1179	4110 B, 4500-F– B, D, 4500-F– C, 4500-F-E
Foaming agents			5540C
Iron	200.7, 200.9		3120 B, 3111 B, 3113 B
Manganese	200.7, 200.8, 200.9		3120 B, 3111 B, 3113 B
Odor			2150 B
PH	150.1, 150.2	D1293	4500-H + B
Silver	200.7, 200.8, 200.9		3120 B, 3111 B, 3113 B
Sulfate	300.0, 375.2	D4327, D516	4110 B, 4500-SO4 F, 4500-SO4 C, D, 4500-SO4 E
Total dissolved solids			2540C
Zinc	200.7, 200.8		3120 B, 3111 B

[a] *ASTM International, Annual Book of ASTM Standards, 2019, West Conshohocken, Pennsylvania.*
[b] *AWWA, Standard Methods for the Examination of Water and Wastewater, American Water Works Association, Washington, DC.*

additives. There are strict regulations to limit disposal and beneficial use options as well as environmental impacts that pertain to oil field waters.

Reservoir temperatures may vary up to 90 °C (195 °F) or even higher, while surface conditions are typically on the order of 20–30 °C (68–86 °F). Pressure can vary from its atmospheric value (or lower in the case of vacuum distillation) to several thousand pounds per square inch (psi). Within such an ample range of conditions, reservoir fluids undergo severe transformations and exist as a single phase (gas, liquid, or solid) or co-exist in several forms (liquid plus gas, solid plus liquid, vapor plus solid or even in liquid-plus-liquid combinations).

Reservoir fluids are brought to the surface as a mixture of oil, gas and water, which is sent to a surface production facility before they can be disposed or sold to an industrial costumer (e.g. a refinery). A surface production facility is the system in charge of the separation of the well stream fluids into its three single phase components – oil, gas and water – and of their transport and processing into marketable products and/or their disposal in an environmentally acceptable manner. Once separated, the oil, natural gas and water follow different paths. Water is typically re-injected for reservoir pressure maintenance operations. The oil usually goes through a process of dehydration, which removes basic sediments and hydrocarbon fluids are assumed to comprise two components – stock tank oil and surface gas.

Furthermore, many types of crude oil and heavy oil are available throughout the world and the quality of crude oil is reflected in various properties such as sulfur content and

API gravity (Speight, 2014, 2015). Light crude oils (higher API gravity) and sweet crude oils (low sulfur content) are preferred to heavy crude oil (low API gravity), sour crude oils (high sulfur) − the light sweet crude oils can be recovered with far less sophisticated and energy-intensive processes.

Reservoir-fluid PVT properties are critical for efficient reservoir management throughout the life of the reservoir, from discovery to abandonment (Honarpour et al., 2006; Nagarajan et al., 2007). In fact, reliable data related to the properties of in-situ fluids are essential for the determination of in-place volumes and recovery-factor calculations as well as for technical evaluation of reservoir-development-depletion plans. Fluid characterization and distribution within the reservoir help in defining reservoir continuity and communication among various zones (Moffatt et al., 2013).

In the simplest sense, water testing includes the application of standards test methods for pH, chlorides, sulfates, nitrates, total dissolved solid, and a host of methods that can be used to analyze for the presence of various metals. But, since fluids from hydraulic fracturing operations contain a broad range of chemicals which can vary from low-to-high concentrations, efforts must be made to determine the chemical composed that are present in the fluid. Following from this, test methods should be applied to establish the lower limits of each constituent which can be measured and the method detection limits (MDLs) determined on the basis of the test method employed for the analysis. Moreover, the accuracy of each analytical method should be assessed by spiking the samples and measuring the recovery of the standard chemicals used for spiking. The accuracy of the method is demonstrated by all recoveries being within narrow limits which may be within 5% of the spiked value. Once the method detection limits and the accuracy of the method(s) have been established (which are subject to reproducibility and repeatability) (Speight, 2016b; ASTM, 2019), the fluid samples can be analyzed and the data reported with a high degree of confidence.

The issues of *quality assurance* and *quality control* must also be addressed during the analytical program. Within the environmental industry there seems to have been a great deal of confusion between the terms quality assurance and quality control. Quality assurance (QA) is an umbrella term that is correctly applied to everything that the laboratory does to assure product reliability. As the product of a laboratory is information, anything that is done to improve the reliability of the generated information falls under quality assurance. Quality controls (QC) are single procedures that are performed in conjunction with the analysis to help assess in a quantitative manner the success of the individual analysis. Examples of quality controls are blanks, calibration, calibration verification, surrogate additions, matrix spikes, laboratory control samples, performance evaluation samples, and determination of detection limits. The success of the quality control is evaluated against an acceptance limit. The actual generation of the acceptance limit is a function of quality assurance; it would not be termed a quality control (US EPA, 2015b).

Quality assurance includes all the quality controls, the generation of expectations (acceptance limits) from the quality controls, plus a great number of other activities. A few examples of these other activities include analyst training and certification, data review and evaluation, preparation of final reports of analysis, information given to clients related to what tests are needed to fulfill regulatory requirements, use of the appropriate tests in the laboratory, obtaining and maintaining laboratory certifications/accreditations, conducting internal and external audits, preparing responses to the audit results, the receipt, storage, and tracking of samples, and how - and from where - standards and reagents are purchased. The performance of QC is just one small aspect of the QA program.

The functions of quality assurance are embodied in the terms *analytically valid* and *legally defensible*. Analytically valid means that the target analyte has been: (i) correctly identified, (ii) quantified using fully calibrated tests, (iii) the sensitivity of the test (method detection limit) has been established, (iv) analysts have demonstrated that they are capable of performing the test, (v) the accuracy and precision of the test on the particular sample has been determined, and the possibility of false positive and false negative results has been evaluated through performance of blanks and other test-specific interference procedures.

3. Water requirements, use, and sources

A significant part of the development of natural gas and crude oil resources in tight formations is the hydraulic fracturing operation, a necessary part of which involves (i) securing access to reliable sources of water, (ii) the timing associated with this accessibility, and (iii) the requirements for obtaining permission to secure these supplies (API, 2009, 2010). However, being forewarned is to be forearmed when investigating potential options for securing water supplies to support hydraulic fracturing operations and an awareness of competing water needs, water management issues, and the full range of permitting and regulatory requirements in a region is critical, Thus, consultation with appropriate water management agencies who usually have top level responsibility for the management (including permitting) and protection of water resources is required.

It is necessary to initiate and pursue any form of transparent and proactive communication with local water planning agencies (and the public must also be informed) to ensure that natural gas and crude oil recovery operations do not disrupt the water needs of local communities. If the developer has an understanding of the water needs of local communities, this will help in the evolution of water acquisition and management plans so that the plans are acceptable to the community that is located close to the proposed natural gas and crude oil development area. The water needs for the project and the juxtaposition of the needs next to the needs of the community must be examined and such needs a major part of the development plan. In fact, although the water needed for horizontal drilling and hydraulic fracturing operations may represent a small volume relative to other water requirements, withdrawals associated with large-scale developments, conducted over multiple years, may have a cumulative impact to the groundwater and/or any watersheds. This potential cumulative impact can be minimized or avoided by working with local water resource managers to develop a plan of when and where withdrawals will occur.

Briefly, a *watershed* (the word is sometimes used interchangeably with *drainage basin* or *catchment*) is an area of land that drains all the streams and rainfall to a common outlet such as the outflow of a reservoir, mouth of a bay, or any point along a stream channel. The watershed consists of surface water (lakes, streams, reservoirs, and wetlands) and all of the underlying ground water and a large watershed may contain many smaller watersheds, depending on the outflow points. In addition, ridges and hills that separate two watersheds are often referred to as the *drainage divide*. All of the land that drains water to the outflow point is the watershed for that outflow location. Watersheds are important because the streamflow and the water quality of a river are affected by events (human-induced or not) that happen in the land area above the river-outflow point.

Thus, it is not surprising that hydraulic fracturing, the technology central to the success development of unconventional resources – the extraction of natural gas and crude oil from tight formations – has been the subject of intense scrutiny come under fire because of concerns related to the chemicals used and any other real or unproven effects. The industry is working to improve transparency and collaboration with landowners, mineral rights holders, regulators and communities.

Thus, when considering a project involving horizontal drilling and a hydraulic fracturing, the location of rivers and the amount of streamflow in rivers must be given serious consideration – the key concept is to determine the watershed of the river and identify the area of land where all of the water that falls in it and drains off of it goes to a common outlet, remembering that a watershed can be as small as a small pond or sufficiently large enough to encompass all the land that drains water into a major bay.

In order to commence a water requirements project, after pre-project communications have commenced, the operator(s) should conduct a detailed, documented review of the identified water sources available in an area that could be used to support hydraulic fracturing operations. Considerations factoring in this review should include: (i) evaluating source water requirements, (ii) fluid handling and storage, and (iii) transportation considerations.

3.1 Requirements

Although water is used in several stages of the natural gas and crude oil recovery from tight formations, the majority of water is typically consumed during the production stage. This is primarily due to the large volumes of water (2.3–5.5 million gallons) required to hydraulically fracture a tight formation (Clark et al., 2011). In addition, water in amounts on the order of 190,000 to 310,000 gallons is also used to drill and cement a natural gas and crude oil well during the drilling phase of the project (Clark et al., 2011). Once the natural gas or crude oil is produced, it is processed, transported and distributed to customers, and ultimately used. Water consumption occurs in each of these stages as well, with the most significant non-production consumption potentially occurring during end use.

A rate-limiting factor in further development of the oil tight formation resources, particularly in certain regions of the western United States is not only the effect of water quality but also the availability of water, which may not be a problem in other regions and countries. Water from a nearby river may be made available for the drilling process and for the hydraulic fracturing process but an important factor that must be taken into consideration in any water-use plan is the potential salt loading of the river water. With oil tight formation development near the river, the average annual salinity is anticipated to increase, unless some prevention or treatment is implemented. The economic damages associated with these higher salinity levels could be significant and have been the subject of extensive economic studies.

Water requirements for hydraulically fracturing projects may vary widely, but on average required several million gallons of water for deep unconventional tight reservoirs. While these water volumes may seem large, they generally represent a relatively small percentage of total water use in the areas where hydraulic fracturing are operative (Satterfield et al., 2008). Water used for hydraulic fracturing operations can come from a variety of sources, including (i) surface water bodies, (ii) municipal water supplies, (iii) groundwater, (iv) wastewater sources, or (v) water that has been recycled from other sources including previous hydraulic fracturing operations.

Nevertheless, in order to acquire the water necessary for use in hydraulic fracturing operations can give rise to a series of challenges, particularly when the water is used in in arid regions and has to be acquired from arid regions. Water is difficult to transport so most commercial activities extract the water they use locally. If large amounts are used for fracking, this will impact on the water table and ecology of the area, and it will also limit the amount of water for other activities taking place in the area. In fact, the volume of water required for a hydraulic fracturing operation is becoming more and more challenging and project operators have to seek new ways to secure reliable, affordable, supplies of water. In some areas, the operator may need to build large reservoirs to capture water during periods of high into local rivers when withdrawal is permitted and monitored by water resource authorities or for future use in storing the flowback water from a hydraulic fracturing project. Operators have also explored the option of using treated produced water from existing wells as a potential supply source of water for hydraulic fracturing operations. In all case of acquiring and using water, the implementation of these practices for fracturing operations (or, more generally, for water acquisition and use, must conform to local regulatory requirements where operations occur.

The management and disposal of water after it is used for hydraulic fracturing operations may present additional challenges for operators. After a hydraulic fracture stimulation is complete, the fluids returning to the surface within the first seven to fourteen days (often called flow back) will often require treatment for beneficial re-use and/or recycling or be disposed of by injection. This water may contain dissolved constituents from the formation itself along with some of the fracturing fluid constituents initially pumped into the well.

Typically, water for hydraulic fracturing is withdrawn from one location or watershed over a period of several days (Veil, 2010). Additionally, in some cases, the water may be acquired from remote, often environmentally sensitive headwater areas where even small withdrawals can have a significant impact on the flow regime. As a result, while hydraulic fracturing may account for a small fraction of the water supply, there can be more severe local impacts. In addition, much of the water injected underground is either not recovered or is unfit for further use once it is returned to the surface and often usually requires disposal in an underground injection well. This water use represents a consumptive use if it is not available for subsequent use within the basin from which it was extracted. Alternatively, the water may be treated and re-used for subsequent hydraulic fracturing projects (US GAO, 2012).

In terms of local impact, especially in areas of water-scarcity, the extraction of water for drilling and hydraulic fracturing (or even the production of water, as is the case in the production of coalbed methane) can have broad and serious environmental effects. The extraction of the water can (more likely, will) lower the water table thereby affecting biodiversity (i.e., the variety of the floral and faunal populations) and harm the local ecosystem as well as reducing the availability of water for use by local communities and in other productive activities, such as agriculture. Thus, the limited availability of water for hydraulic fracturing could become a significant constraint on the development of natural gas and crude oil in tight formations in water-stressed areas. In fact, water stress (water scarcity) is increasing around the world and all domestic and industrial users are becoming subject to intense scrutiny in terms of water consumption. Thus, water management and groundwater protection are vital issues for the natural gas and crude oil industries.

When the time comes (and this should be sooner rather than later) to evaluate the water requirements for a hydraulic fracturing project, it is necessary to conduct a pre-project comprehensive evaluation of the cumulative water demand on a stage-by-stage basis as well as the timing of these needs at an individual well site. This should include consideration of the water requirements for (i) drilling operations, (ii) dust suppression, (iii) emergency response, as well as (iv) the water requirements for hydraulic fracturing operations. A decision must be made as to whether or not the sources of water are adequate to support the total operation, with water of the desired quality, and can be accessed when needed for the planned development program.

3.2 Use

Hydraulic fracturing − the mainstay of oil and gas production from shale formations and from tight formations − uses between 1.2 and 3.5 million US gallons of water per well, with large projects using up to 5 million US gallons per well. Typically, a well requires 3 to 8 million US gallons of water over its lifetime. Water consumption for hydraulic fracturing occurs during: (i) drilling, (ii) extraction and processing of proppant sands, (iii) testing natural gas transportation pipelines, and (iv) gas processing plants. Typically, for most shale basins, water is acquired from local water supplies, including: (i) surface water bodies, such as rivers, lakes, and ponds, (ii) groundwater aquifers, (iii) municipal water supplies, (iv) treated wastewater from municipal and industrial treatment facilities, and (v) produced and/or flowback water that is recovered, treated, and re-used. In regions where hydraulic fracturing occurs, the sources of water should be well documented.

Thus, although water is used in several stages of the tight formation development, the majority of water is typically consumed during the production stage. This is primarily due to the large volumes of water (on the order of several million gallons depending upon the depth of the formation and the formation characteristics) required to hydraulically fracture a well (Clark et al., 2011). Water in amounts of several hundred thousand gallons is also used to drill and cement a shale gas well during construction (Clark et al., 2011). After fracturing a well, anywhere from 5% to 20% of the original volume of the fluid will return to the surface within the first two weeks as flowback water. An additional volume of water, equivalent to anywhere from 10% to almost 300% of the injected volume, will return to the surface as produced water over the life of the well. It should be noted that there is no clear distinction between so-called flowback water and produced water, with the terms typically being defined by operators based upon the timing, flow rate, or sometimes composition of the water produced.

Deep natural gas and crude oil projects use water primarily during drilling and stimulation, but produces a tremendous amount of energy over the approximate 20-year lifespan of the natural gas well (Mantell, 2009). Thus, water is an essential component of deep shale natural gas development. Operators use water for drilling, where a mixture of clay and water is used to carry rock cuttings to the surface as well as to cool and lubricate the drill bit. Drilling a typical deep shale well requires between 65,000 and one million gallons of water. Water is also used in hydraulic fracturing, where a mixture of water and sand is injected into the deep shale at high pressure to create small cracks in the rock and allows gas to freely flow to the surface. Hydraulically fracturing a typical deep shale well requires an average of 3.5 million gallons of water.

The water supply requirements of deep shale natural gas development are isolated in that the water needs for each well are limited to drilling and development, and the placement of shale gas wells are spread out over the entire shale gas play. In other words, these shale gas wells are not drawing water from one single source. Subsequent hydrofracturing treatments of wells to re-stimulate production may be applied, though their use is dependent upon the particular characteristics of the producing formation and the spacing of wells within the field. On the other hand, enhanced Oil Recovery (EOR) uses relatively large amounts of water due to the waterfloods used to force the oil out of the reservoir. Oil shale and tar sands (oil sands) also use significantly higher amounts of water due to the in-situ steam extraction process and the additional water used to process the liquid fuel (Mantell, 2009).

Geography plays an important role in determining fuel source water efficiency. For example, imported fuels such as foreign oil, Alaskan oil and gas, and even off-shore oil and gas, less water efficient depending on location of origin versus location of end use. As a general rule, unconventional oil and synthetic coal extraction and production processes are more water intensive than their conventional counterparts (Mantell, 2009). The most water inefficient fuel sources are irrigated biofuels including ethanol and biodiesel. Irrigation of the biofuel feedstock requires significant volumes of water input per unit of energy that can be derived from the crop. Biofuels also require a significant amount of water to process the raw fuel into a useable energy source. Water use efficiencies could be improved to a level similar to synthetic coal if only non-irrigated feedstock was used in energy development, although this would significantly decrease the amount of feedstock available due to the limited locations where non-irrigated growth is possible (Mantell, 2009).

The majority of water use occurs during the early exploration and drilling phase of gas and oil production from tight formations. Water is a necessary input and, although only a relatively small amounts of water is needed for drilling, more significant quantities of water are used during completions, or hydraulic fracturing operations (Chapter 5). Thus, in terms of water use, the issue is the application of hydraulic fracturing to release the gas form the shale formation − high-volume hydraulic fracturing to create fissures in the rock to release gas or oil trapped inside. Thus, water-related issues in shale drilling are leading to growing and complex policy and regulatory challenges and environmental compliance hurdles that could potentially challenge shale gas production expansion and increase operational costs.

Hydraulic fracturing (Chapter 5) is a technique used in oil and natural gas production to stimulate the production of hydrocarbon derivatives. After a well is drilled into reservoir rock that contains natural gas, crude oil, and water, every effort is made to maximize the production of the gas and oil (Speight, 2014a). In hydraulic fracturing, a fluid (usually water containing special high-viscosity fluid additives) is injected under high pressure. The pressure exceeds the rock strength and the fluid opens or enlarges fractures in the rock. These larger, man-made fractures start at the well and extend deep into the reservoir rock. After the formation is fractured, a *propping agent* (usually sand carried by the high-viscosity additives) is pumped into the fractures to keep them from closing when the pumping pressure is released. This allows the natural gas or the crude oil to move more freely from the rock pores to a production well and thence to the surface.

Even though it is often looked upon as a temporary process, hydraulic fracturing (and the accompanying horizontal drilling process) require considerable amount of water. For example, the drilling and completion (including hydraulic fracturing) phases of a well (leading to initiation of the production of natural gas or crude oil) is a short time period − typically on the order of two to eight weeks − compared to an expected production lifetime of a well on the order of 20−40 years. Estimates of water consumption during hydraulic fracturing vary from 0.2 barrels to 4 barrels of water for each barrel of oil recovered (with consumption at Bakken towards the low side of these estimates) (IEA, 2013). In terms of the total amount of water, op to 170,000 barrels of water per well may be used for drilling and fracturing and after the fracturing process has been completed, 30%−70% v/v of the injected water injected flows out of the well, but this amount is dependent upon the properties (such as size and mineralogy) of the reservoir and the returned water must be treated before disposal or before re-use. Such a level of water consumption can put a heavy strain on local water sources and, if projections of natural gas and light tight oil production are to be met, technology development to reduce consumption will be necessary. Another aspect of water use is that 3,000,000 to 5,00,000 gallons of water are typically necessary to hydraulically fracture a multi-stage well. The volume and quality of water used, is also characteristic of the reservoir properties (which vary by region and by play) and also by well design.

3.3 Sources

The types of water sources that are used by the oil and natural gas industry (for hydraulic fracturing) typically fall into three categories: (i) potable water (freshwater), (ii) oil and natural gas generated water (produced and flowback water), and (iii) the alternative water sources that are generally not useable by the public (brackish or non-potable water). The choice among sources depends on a variety of factors such as volume, availability, source-water quality, competing water uses, economics and regulatory requirements.

Potable water sources typically include freshwater from a groundwater source, surface water (from a lake or river) and municipal water supplies. Water is drawn from these sources over time in accordance with agreements and regulatory requirements and stored for use when a greater amount of water is necessary. A regular and slow withdrawal rate, can minimize impacts on water sources that are also used by communities.

Produced water (re-used and recycled water) used in oil and natural gas operations is typically flowback and produced water from the field operations. There are few instances of operators using other produced water sources, such as municipal and industrial. In an effort to reduce the use of freshwater sources, the industry is increasing the amount of flowback and produced and brackish water in hydraulic fracturing. There are several key factors that operators must consider concerning the re-use of produced water, including the: quantity of produced water; duration and consistency of produced water; produced water quality;

target formation characteristics; scale of the operation, and cost to re-use the water. Operational logistics such as fluid-handling capabilities, transportation considerations, storage capabilities and access to treatment locations or onsite treatment options, will influence the ability to re-use produced water. The availability of flowback and produced water is dependent on the amount of water that returns from the fracturing process and formation.

Currently, most of the flow-back fluid from fracking operations is either transported from well sites for disposal or is processed for re-use in further operations. Suspended solids must be removed from the water before re-use. Recycling this water can be costly and is a major focal point of many environmental groups and environmental regulators. New, more efficient, technologies have been developed which allow fracking fluid to be recycled on-site at reduced cost. However, hydraulic fracturing does not require water that is of potable (drinking water) quality. Recycling wastewater helps conserve water use and provide cost-saving opportunities. In gas recovery from the Marcellus tight formation, there are examples of companies reusing up to ninety-six percent of the produced water. Other examples of recycling and reuse include (KPMG, 2012):

(i) The use of portable distilling plants to recycle water in the Barnett Tight formation, particularly in regions such as the Granite Wash field in North Texas, where water resources are more critical than in other tight formation basins in the United States.

(ii) A water purification treatment center can recycle several thousand barrels of flowback and produced water per day generated from extracting oil and natural gas from a tight formation – this approach is being used in the Eagle Ford tight formation and in the Marcellus Tight formation.

(iii) The Marcellus tight formation also employs vapor recompression technology to reduce the cost of recycling fracturing water by using waste heat. The unit produces water vapor and solid residue that is disposed of in a waste facility. In addition, to reduce contamination risks during tight formation operations, many gas companies in the Marcellus tight formation are reducing the amount of chemical additives used in fracturing fluid while producing natural gas and crude oil.

(iv) A wastewater treatment company specializing in the oil and gas industry has designed a mobile integrated treatment system for hydraulic fracturing that allows the reuse of water for future drilling. Using dissolved air flotation technology, the system can treat up to 900 gallons per minute of fracking flowback water. The accelerated water treatment reduces the equipment burdens and logistics of traditional treatment methods and could significantly reduce operational costs.

(v) Produced water can have high total dissolved solids (TDS) concentrations that can be difficult to treat. Thermal distillation, reverse osmosis (RO), and other membrane-based desalination technologies can be deployed to desalinate produced water to a level fit for purpose.

Fluids other than water may be used in hydraulic fracturing process, including carbon dioxide, nitrogen, or propane, although their use is currently much less widespread than water. The use of flowback and produced water is also dependent on the type of fracturing fluids being used for that play. Hydraulic fracturing fluids (fracking fluids) (Chapter 5) are a complex mixture of many ingredients that are designed to perform a diverse set of functions and accommodate a variety of factors, including local geology, well depth, and length of the horizontal segment of the well. Although the precise recipe is unique to the formation, the fluid is typically composed of proppants (typically sand) to hold open the fractures and allow the natural gas to flow into the well, and chemicals that serve as friction reducers, gelling agents, breakers, biocides, corrosion inhibitors, and scale inhibitors. Industry representatives point out that chemicals represent a small percentage of the fracturing fluid; on average, fracking fluid for shale gas consists of more than 99% water and sand. Given the large volume of fluid that is injected underground, however, a small percentage can represent a large quantity of chemicals.

The sources for the supply of water for hydraulic fracturing project will depend on the cumulative amount of water that will be required for the long-term project that is planned. Water sources will need to be appropriate for the forecasted pace and level of development anticipated. Thus, the selection of a water source (or, more likely, because of the amount of water needed, water sources) ultimately depends upon the (i) the volume required, (ii) the water quality requirements, (iii) regulatory issues, (iv) physical availability, (v) competing uses for the water, and (6) the characteristics of the formation to be fractured, including water quality and compatibility considerations. If possible, wastewater from an industrial facility (or industrial facilities) should be considered as a water source, followed by groundwater sources and surface water sources (with the preference over non-potable sources over potable sources), with the least desirable (at least for long-term, large scale development) being any municipal water supplies.

However, in regard to the choice of the water source(s) will depend on local conditions and the availability of groundwater and surface water resources in proximity to planned operations. Most important, not all options may be available for all situations, and the order of preferences can vary from area to area. Furthermore, for water sources such as industrial wastewater, power plant cooling water, or recycled flow back water and/or produced water, additional treatment may be required prior to use for hydraulic fracturing. Contaminants in the water which are not removable to the desired levels for re-injection may render the water as unsatisfactory because it may deliver subterranean contamination in and around the drilling site and the reservoir and open up the real potential for groundwater contamination as well as contamination of aquifers that provide municipal water supplies and such results cannot assure project success.

Thus, water sources for hydraulic fracturing projects consists of: (i) surface water, (ii) groundwater, (iii) municipal water suppliers, (iv) wastewater and power plant cooling water, and (v) reservoir water and recycled flowback water.

3.3.1 Surface water

Many municipalities draw their principal water supplies from surface water sources, so the large-scale use of this source for hydraulic fracturing operations will undoubtedly impact not only municipal usage but also other competing uses and will, therefore, be of concern to local water management authorities and other public officials. In some circumstances there will be a need to identify water supply sources capable of meeting the needs of water requirements for vertical and horizontal drilling as well as for hydraulic fracturing and, in addition, it must be made clear to the relevant authorities that the water needs of the drilling/fracturing project will not compete or interfere with community needs as well as with currently existing uses.

Thus, necessary considerations in evaluating water supply requirements from surface water sources include not only the volume of water supplies required but also the sequence and scheduling of acquiring these supplies of water. Withdrawal from surface water bodies, such as rivers, streams, lakes, natural ponds, and private stock ponds will likely require permits from state agencies or from multi-state regulatory agencies, as well as permission from the relevant landowners − in some regions, water rights are also a key consideration. In addition, the water quality standards and regulations that have been established by the various regulatory authorities may prohibit any alteration in water flow (such as pertains, for example, to river flow and stream flow as well as flow into lakes) that would impair a high priority use of the fresh (surface) water, which is often defined by the local water management authorities. Also consideration should be given to ensure that water withdrawal from rivers and streams during periods of low river and/or stream flow do not affect fish and other aquatic life, fishing and other recreational activities, municipal water supplies, and the operational demands for water by other existing industrial facilities, such as power plants.

When the options for application of permits to use water are being considered, the applicant must know that water withdrawal permits can require compliance with specific metering, monitoring, reporting, record keeping, and other consumptive use requirements. In addition, compliance could also include specifications for the minimum measured quantity of water that must pass a specific point downstream of the water intake in order for a withdrawal to occur. Furthermore, in the case where stream flow is less than the prescribed minimum quantity, the withdrawal of water may be required to be reduced or even to cease. Thus it is necessary to consider the various issues that can arise with the timing and location of water withdrawals since impacted watersheds may be sensitive, especially in drought years, when the periods of flow are low or diminished during the years of the project or during periods of the year when activities such as agricultural irrigation place additional demands on the surface supply of water.

To be fully aware of the potential for water use, requests for (or proposals for the use of) surface water withdrawal should a consideration the following potential impacts that could control the timing and volume available: (i) ownership, allocation, or appropriation of existing water resources, (ii) water volume available for other needs, including public water supply, (iii) degradation of the designated best use of a stream or water course, (iv) impacts to downstream habitats and users, (v) impacts to fish and wildlife, (6) aquifer volume diminishment, (vii) and mitigation measures to prevent transfer of invasive species from one surface water body to another (as a result of water withdrawal and subsequent discharge into another surface water body).

In addition, state, regional, or local water management authorities may request that the applicant identify the source of water to be used for supplying hydraulic fracturing operations, and provide detailed information related to any newly proposed surface water source that has not been previously approved for use. Information that must be supplied could include the withdrawal location and the size of the upstream drainage area and available stream gauge data, along with demonstration of compliance relative to stream flow standards. In order to obtain approval for water use as well as maintaining a good relationship with the regulatory bodies, nearby local communities that use water from the area under consideration, and other interested parties it is obvious that requests for water withdrawals from sensitive watersheds should be carefully considered for their overall impact. Furthermore, in some jurisdictions, a variety of permits may be required for the transport of water via pipelines, canals, or streams, as well as transportation by tanker truck. Moreover, equipment or structures used for surface water withdrawal, such as standpipes, may also require permits.

With the continued development of resources in tight formations, additional regulatory requirements are likely to be associated with water use and requirements. For example, water could be sent to storage impoundments during periods of high flow to allow water withdrawal at a time of peak water availability. However, this approach would typically require the development of water storage capabilities to meet the overall demands of drilling and hydraulic fracturing projects over the course of the project which may even be a multi-year period to accommodate possible periods of drought.

Another alternative for ensuring adequate water supply is to use abandoned surface coal mining pits for the storage of water which provide more permanent facilities for the installation of a comprehensive water distribution system. However, the water quality in such storage areas must meet the operational requirements and with all regulatory requirements which would depend upon the nature of the exposed overburden that could allow subject leaching of undesirable chemical species during periods of heavy rain or winter run-off. In keeping with the concept of using surface coal-mining pits, another option is to excavate low lying areas to allow for collection of rain water. Again, such an option must meet with approval from state, regional, or local water management authorities to ensure compliance with storm water runoff program elements.

3.3.2 *Groundwater*

In order to use groundwater for drilling and hydraulic fracturing projects, many of the same types of considerations for groundwater as for surface water will need to be addressed. The primary concern regarding groundwater withdrawal is volume diminishment and, in some areas, the availability of fresh groundwater is limited, so withdrawal limitations could be imposed. To overcome such issues and where possible, consideration should be given to the use of non-potable water for drilling and hydraulic fracturing projects. Another that applies to the protection of groundwater sources is to locate water source wells for oil and gas operations at an appropriate distance from municipal wells, public wells, or private water supply wells. Furthermore, public wells or private water supply wells and fresh water springs within a defined distance of any proposed drilling/fracturing project for a water supply well should be identified and the characteristics of the wells evaluated for production capacity and water quality. As part of the well evaluation, there may also be the need to test the water currently available from these sources. This will require locating the public and private water wells and gathering obtaining information related to (i) well depth, (ii) completed interval and use, including whether the well is public or private, community or non-community, and (ii) the type of facility or establishment if it is not a private residence.

Guidance for groundwater protection related to well drilling and hydraulic fracturing operations is available (API, 2009, 2010) and maintaining well integrity is featured is a key design principle of all natural gas and crude oil wells, which is essential for two primary reasons: (i) to isolate the internal conduit of the well from the surface and subsurface environment, and (ii) to isolate and contain the produced fluid from a well to a production conduit within the well.

3.3.3 *Municipal water supplies*

Obtaining water supplies from municipal water suppliers can be considered, but again, the water needs for fracturing would need to be balanced with other uses and community needs. This option might be limited, since some areas may be suffering from current water supply constraints, especially during periods of drought, so the long term reliability of supplies from municipal water suppliers needs to be carefully evaluated.

3.3.4 *Wastewater and power plant cooling water*

Other possible options for source water to support hydraulic fracturing operations that could be considered are municipal wastewater, industrial wastewater, and/or power plant cooling water. However, the properties or specifications of this water source need to be compatible with the target formation and the plan for fracturing as well as whether treating is technically possible and whether treatment can deliver an overall successful project. In some cases, required water specification could be achieved with the proper mixing of supplies from these sources with supplies from surface water or groundwater sources.

3.3.5 *Reservoir water and recycled flow back water*

Produced reservoir water and recycled flow back water can be treated and re-used for fracturing, depending on the quality of the water. Natural formation water has been in contact with the reservoir formation for millions of years and thus contains minerals native to the reservoir rock. Some of this formation water is recovered with the flowback water after hydraulic fracturing, so that both contribute to the characteristics of the flow back water. However, the salinity, total dissolved solids (TDS, sometime referred to as *total dissolved salts*), and the overall quality of this formation/flow back water mixture can vary by geologic basin and specific rock strata. In addition, other water quality characteristics that may influence water management options for fracturing operations include concentrations of organic compounds, usually hydrocarbon derivatives, which are detected by analysis (using standard test methods) for oil and grease), suspended solids, soluble organics, iron, calcium, magnesium, and trace constituents such as benzene, boron, silicates, and possibly other constituents (ASTM, 2019).

Finally, whenever water is recycled and/or re-used, or additional sources of industrial wastewater are used to supply water for drilling and hydraulic fracturing operations, additional make up water may be required. In such cases, water management alternatives to be considered will depend on the volume and quality of both the recycled water and the make-up water, to ensure compatibility with each other and with the formation being fractured.

Much of the focus of recent policy decisions has been on the identification and the disclosure of the chemical constituents used in hydraulic fracturing fluid. In addition, if toxic chemical additives are used in the fracturing fluid, many regulatory authorities require open disclosure of the necessary information and in many cases disclosure of the chemicals employed in a fracturing project is mandated. However, some authorities do require the complete disclosure of the chemical constituents of fracturing fluid along with the concentration and volume of these chemicals. In addition, some regulations require disclosure to the state regulatory authorities rather than to the public, and most authorities allow companies to apply for trade secret exemptions. In regard to the concentration and volume of the chemicals used, it is worth noting at this point that many chemicals that have been classed as non-toxic below a specified dosage. For example, table salt (sodium chloride) is used by many persons at meal time but it is advisable not to try to consume a pound (454 g) at one sitting or it could be lethal. Thus, the laws of the use of toxic chemicals in hydraulic fracturing fluids need tweaking to specify the amount of chemicals used. This also applies to the use of chemicals that are indigenous to the environments since a concentration of a chemical that is above the indigenous amount may become toxic to the environment.

The primary hydraulic fracturing fluid systems are slickwater insofar as chemicals are added to the water to increase the fluid flow and increases the speed at which the pressurized fluid can be pumped into the wellbore. Such chemicals include crosslink or crosslinked gels. However, the procedure is not (and cannot be) standardized since the selection of the fracturing fluids is based on a variety of factors and the fluid systems are designed on the basis of several factors such as: (i) the characteristics of the target formation, (ii) the formation fluids, and (iii) the source of the make-up water source. In addition, the use of recycled flowback water and produced water will be more likely in a slickwater hydraulic fracture.

3.3.6 Other sources

Brackish or non-potable water is considered publicly unusable for hydraulic fracturing projects without significant treatment. Typically, brackish water is high in salinity, but has a lower salinity that than high-saline brine, and has total dissolved solids (TDS) levels are on the order of 1000 parts per million (ppm) or even higher. The type and dose of friction reducer can be adjusted to accommodate for higher total dissolved solids (TDS) water.

In the early exploration phase, water with a relatively low total dissolved solid content will be used for hydraulic fracturing. However, for tight formations (especially shale plays) that are beyond the phase of early exploration, the use of brackish water and recycled produced water is becoming an increasingly feasible option due to the advancements in the use of chemical additives and water-treatment technologies. Other wastewater sources are also given consideration for hydraulic fracturing projects. For example, acid mine drainage water is often given consideration for use in hydraulic fracturing projects. However, acid mine drainage is one of most serious threats to water since a mine draining acid can devastate rivers, streams, and aquatic life for prolonged periods measuring in decades and additional caution is advised when considering the use of such water. Pre-treated seawater is also being explored as an alternative water source for hydraulic fracturing. However, the viability of any alternative water source is dependent upon factors such as the fracturing fluid type considerations, water treatment and water transportation costs (e.g. proximity to an ocean).

3.4 Water contamination

Water contamination, especially groundwater contamination from the retrieval of natural gas and crude oil from tight formations can (and often does) occur through a variety of pathways. While the formations may be located at varying depths, often (but not always) far below underground, caution must be taken to assure that sources of drinking water are not contaminated and there must be, in the early stages of project planning, an accurate geological assessment of the formations – the project must be recognized as a multi-disciplinary project and not merely a recovery engineering project. However, if a well from the surface to the formation level must be drilled through any drinking water sources in order to access the natural gas or crude oil, assurance of well integrity has to be an essential part of the drilling operation. Vibrations and pressure pulses associated with drilling can cause (at least) short-term impacts to groundwater quality, including changes in color, turbidity, and odor. Chemicals (from the drilling fluid), natural gas, and crude oil can escape the well bore if it is not properly sealed and cased (Chapter 4, Chapter 18) and even though there are, in most cases, regulatory requirements for well casing and well integrity, accidents and failures can still occur. In addition, older and abandoned wells that have not been sealed correctly can also potentially serve as migration pathways for contaminants to enter groundwater systems. Natural fractures in subterranean formations as well as the fractures created during the fracturing process could also serve as pathways to contamination of groundwater. Finally, coalbed methane (Chapter 1) is generally found at shallower depths and in closer proximity to underground sources of drinking water and therefore accessing the natural gas from this source might pose a greater risk of contamination.

Bacteria in the fracturing fluid can cause formation biofouling, reducing permeability and gas production. The presence of sulfate-reducing bacteria can form hydrogen sulfide, making the well sour, creating safety issues and increasing costs. Permeability and gas production can be reduced by metals in water, specifically iron, which can oxidize and form deposits, and by suspended solids in the frac fluid such as sand, silt, clays and scale particles. Since some formations are a composite of shale carbonate shales, and salt crystals, the use of low a fracturing fluid low in total dissolved solids will increase dissolution of formation salts, potentially increasing reservoir permeability and gas production. Understanding the relationship between the fracturing fluid water quality and long-term well production is crucial when considering water treatment technologies for a good water management plan.

Another effect, the scaling tendency of source water, usually caused by poor compatibility of source water with formation water and poor compatibility of re-use water, is another consideration. Scaling can occur within the formation, potentially creating reduced permeability and ultimately reduced gas production. Scaling can also damage equipment casing, reducing functionality. Multivalent ions and chlorides in the water can limit friction reducer effectiveness and drive up horsepower costs for pumping in a hydraulic fracturing project. As brine, oil, and/or gas proceed from the formation to the surface, pressure and temperature change and certain dissolved salts can precipitate (referred to as *self-scaling*). If a brine is injected into the formation to maintain pressure and sweep the oil to the producing wells, there will eventually be a commingling with the formation water. Additional salts may precipitate in the formation or in the wellbore (scale from *incompatible waters*) and other factors (Table 6.6). Many of these scaling processes can and do occur simultaneously. Thus, wells producing water are likely to develop deposits of inorganic scales. Scales can and do coat perforations, casing, production tubulars, valves, pumps, and downhole completion equipment, such as safety equipment and gas lift mandrels. If allowed to proceed, this scaling will limit production, eventually requiring abandonment of the well. However, technology is available for removing scale from tubing, flowline, valves, and surface

TABLE 6.6 Factors involved in scale formation.

Suspended solid accumulation	Residual suspended solids not removed in the pre-treatment system can settle at low velocity points or deposit on surfaces; suspended material can also precipitate (coagulate, flocculate) with increases in temperature and concentration.
Organic fouling	Organic material in the feed water can precipitate with an increase in concentration and/or temperature; this material can deposit on surfaces and/or coagulate smaller suspended solid particles that wouldn't otherwise be a problem.
Calcium carbonate scale	Sufficient concentrations of calcium and carbonate can cause calcium carbonate ($CaCO_3$) scale; the potential for the formation of calcium carbonate scale increases as temperature and concentration increase; typically, carbonate scales are white, chalky and acid-soluble solids.
Sulfate scale	The presences of sulfate and barium, strontium, and/or calcium can cause formation of barium sulfate ($BaSO_4$), strontium sulfate ($SrSO_4$) and/or calcium sulfate ($CaSO_4$) scale; the potential for the formation sulfate-type scale material increases with concentration; sulfate scales are generally white, hard or glasslike, and acid-insoluble solids.
Silica scale	Silica can form solids in four ways: surface deposition (depositing directly to surfaces), bulk precipitation (particles collide to form larger particles), complexing (metal hydroxides bind with silica to form particles) and silica polymerization (silica molecules combine to form long strings); since silica fouling is impacted by metal hydroxide precipitation, the potential for silicate fouling increases with temperature, concentration, and is highly impacted by pH; silica deposits range from quartz-like hard scale to slimly deposits (generally white, gray, green or brown solids – the color can vary depending on the types of the metal hydroxides involved).

equipment, restoring at least some of the lost production level. Technology also exists for preventing the occurrence or reoccurrence of the scale, at least on a temporary basis.

Scale remediation techniques must be quick and non-damaging to the wellbore, tubing, and the reservoir. If the scale is in the wellbore, it can be removed mechanically or dissolved chemically. Selecting the best scale-removal technique for a particular well depends on knowing the type and quantity of scale, its physical composition, and its texture. As a simple example of scale reduction, seawater can reduce the likelihood of scaling caused by a formation brine that has a high calcium carbonate ($CaCO_3$) scaling potential. Seawater is often injected into reservoirs for pressure maintenance and enhancing oil recovery. When comingled with formation brine, the seawater can markedly decrease the calcium carbonate scaling potential of the mixture. As the percentage of seawater in the mixture increases, scaling potential decreases and may even become negative. Once the scaling potential becomes negative, the produced water can dissolve the calcium carbonate scale that may have formed in the flow lines.

Considerations related to water disposal should also be given suitable acknowledgment during the early stages of field development with the recognition that the need for water disposal will increases as activity increases through evolution of the project – moreover, demand for water disposal in terms of the volume of water can be surprising. Thus, as project evolves and water sources for long-term supply are considered, equal consideration should be given to disposal of the water respect to the collective volumes of all water use. In fact, water disposal issues are challenging in most project areas. Facilities accepting flowback water may be able to be designed to accept other water disposal streams thereby reducing overall treatment costs and creating more make-up water for re-use.

4. Effects on water sources

Unconventional natural gas and crude oil development (through hydraulic fracturing) has the potential to impact water quality at many stages of the process. Water from beneath the ground has been exploited for domestic use, livestock use, and irrigation since the earliest times. Although the precise nature of its occurrence was not necessarily understood successful methods of bringing the water to the surface have been developed. In fact, if water for domestic use is obtained from a private well, there should be an acute awareness of the vat ours issues related to water quality. Private well water quality is not regulated in the United States, and well owners are responsible for performing their own monitoring.

Drilling for natural gas and crude oil and natural gas, if properly conducted, does not necessarily contaminate groundwater. While properly drilled gas wells should keep contaminants from seeping into underground aquifers, some wells fail to do so, allowing methane and other chemicals to reach drinking water supplies. Unpredictable chemical releases from poorly managed drill sites, leaky wastewater pits, accidental spills, and truck accidents that occur above ground can also affect the quality of the well water.

After the fracturing process, a percentage of the water returns fairly quickly to the surface as wastewater (flowback). The briny water that has long been underground and comes up during continued operation of the well, called “produced water can contain naturally occurring contaminants like the radioactive element radium, along with other heavy metals and salts. All of this wastewater is toxic and must be collected and stored; it then must be treated or discharged – or reinjected into a deep disposal well.

The wastewater is often pumped into holding ponds where it can leak and settle into surrounding groundwater, and impact wildlife. The contamination of groundwater is of major concern for those who live near drilling operations and rely on drinking water wells. In addition, the contamination of watersheds that provide drinking water for millions of people in cities hundreds of miles away from any natural gas drilling sites poses a significant threat as well. Additionally, some of the fluids pumped into the ground during the gas extraction process flow back to the surface. This wastewater is called “flowback” and can be contaminated with industrial and naturally occurring toxic substances. Some of the contaminants can alter the taste, odor, or clarity of well water while others are difficult to detect. Municipal water supplies may also be at risk from hydraulic fracturing due to surface water discharges, insufficient treatment of contaminated wastewater, and byproducts formed at drinking water treatment facilities by the reaction between hydraulic fracturing contaminants and disinfectants.

Reservoir management is a multi-faceted operation (Fig. 6.1) and while on-site environmental management is a typical practice associated with hydraulic fracturing, it should be considered as being site-specific. In addition, hydraulic fracturing base fluids (themselves variable in composition), most commonly water, are typically stored in tanks at the well

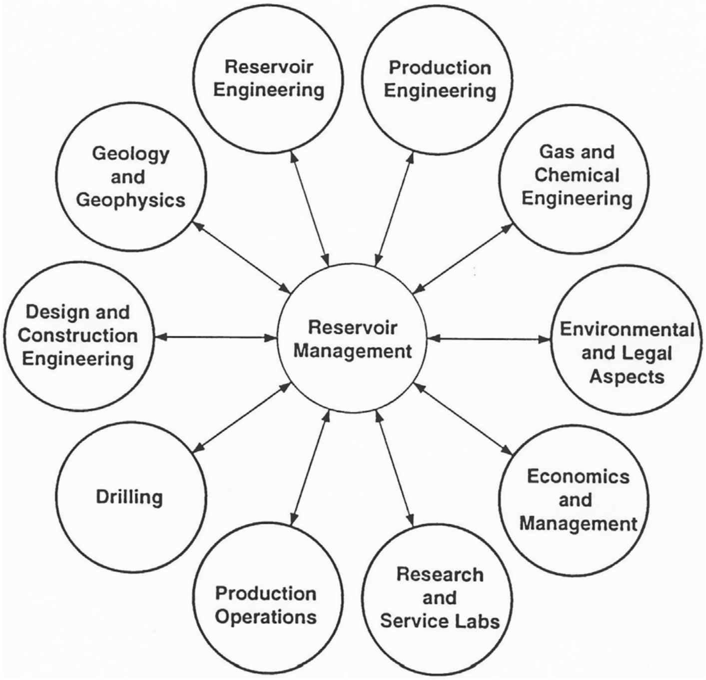

FIG. 6.1 Various aspects of reservoir management.

site while additives may be stored on a flatbed truck or van enclosure that holds a number of containers. At the commencement of operations, the fracturing fluid and any chemical additives are sent to a blender for mixing after which the fluid is transferred to the wellhead for injection. It is during the time that the fluids and additives are being are transferred and moved around the well site and through various pieces of equipment that faulty equipment or human error can cause spills of the various components of fracturing fluids.

The type and amount of fluids and chemicals stored on-site is largely determined by the geological characteristics of the formation to be fractured as well as by production goals and the chemical additives. Approximately 1%–2% v/v or less of the volume of water-based hydraulic fracturing fluid is composed of chemical additives which indicates that approximately 500 to 260,000 gallons or less of chemical additives may be brought on-site for hydraulic fracturing (US EPA, 2015a). Chemical additives can be composed of one or more chemicals and can be used in hydraulic fracturing fluids as acids, friction reducers, surfactants, scale inhibitors, iron control agents, corrosion inhibitors, and biocides (Table 6.7) (Arthur et al., 2009; Gregory et al., 2011; US EPA, 2015a). Moreover, for any analytical procedure or suite of analytical procedures, the following practices must be part of a strict testing protocol of sampling and identification of any chemicals by use of standards test methods that are not subject to intense criticism and can stand up to scrutiny in a court of law.

In order to withstand such scrutiny, the analytical records, as for any analytical process for materials such as natural gas, crude oil, crude oil products (Speight, 2015), must be complete

TABLE 6.7 Types of additives used in fracturing fluids.

Type	Compound	Comment
Acid	Hydrochloric acid (*muriatic acid*)	Used to clean cement from casing perforations and drilling mud clogging natural formation porosity, if any prior to fracturing fluid injection (dilute acids concentrations are typically on the order of 15% v/v acid)
Biocide	Glutaraldehyde	Fracture fluids typically contain gels which are organic and can therefore provide a medium for bacterial growth. Bacteria can break down the gelling agent reducing its viscosity and ability to carry proppant.
Breaker	Sodium chloride	Chemicals that are typically introduced toward the later sequences of a fracturing project to break down the viscosity of the gelling agent to better release the proppant from the fluid as well as enhance the recovery or flowback of the fracturing fluid,
Corrosion inhibitor	N,N-dimethyl formamide	Used in fracture fluids that contain acids; inhibits the corrosion of steel tubing, well casings, tools, and tanks.
Cross-linking agent	Borate salts	There are two basic types of gels that are used in fracturing fluids; linear and cross-linked gels. Cross-linked gels have the advantage of higher viscosity that do not break down quickly.
Friction reducer	Crude oil distillate (*mineral oil*)	Minimizes friction allowing fracture fluids to be injected at optimum rates and pressures
Gel	Guar gum	Gels are used in fracturing fluids to increase fluid viscosity allowing it to carry more proppant than a straight water solution. In general, gelling agents are biodegradable.

and should include but not necessarily restricted to the following information: (i) the precise (geographic or other) location from which the sample was obtained, (ii) the identification of the location by name, (iii) the character of the bulk material (solid, liquid, or gas) at the time of sampling, (iv) the means by which the sample was obtained, (v) the means and protocols that were used to obtain the sample, (vi) the date, the amount of sample that was originally placed into storage, (vii) any chemical analyses (elemental analyses, fractionation by adsorbents or by liquids, functional type analyses) that have been determined to date, (viii) any physical analyses that have been determined to date, (ix) the date of any such analyses, (x)the methods used for analyses that were employed, (xi) the analysts who carried out the work, and (xii) a log sheet showing the names of the persons (with the date and the reason for the removal of an aliquot) who removed the samples from storage and the amount of each sample (aliquot) that was removed for testing. In summary, there must be a means to accurately to track and identify the sample history so that each sample is tracked and defined in terms of source, activity, and the personnel involved in any of the above stages. Thus, the accuracy of the data from any subsequent procedures and tests for which the sample is used will be placed beyond a *reasonable doubt* and would stand the test of time in court should legal issues arise pertaining to the pollution of water-bearing formations.

Many shale formations contain quantities of potentially harmful chemical elements and compounds that could be dissolved into the hydraulic fracturing fluid and then return towards the surface during flowback. These include trace elements such as mercury, arsenic and lead; naturally occurring radioactive material (radium, thorium, uranium); and volatile organic compounds (VOCs). Thus, careful chemical monitoring of hydraulic fracturing fluids, including the flowback fluid and produced water, is required to mitigate the risks of contamination of the water sources.

Generally, the quality of produced water from hydraulic fracturing is somewhat less than pristine and cannot be readily used for another purpose without prior treatment. In fact, it is more correct to look upon the quality of produced water from any hydraulic fracturing project, although variable, as generally being poor and, in most situations, cannot be readily used for other purposes without prior treatment. Produced water may contain a wide range of contaminants in varying amounts, some of which occur naturally in the produced water but others are added through the process of hydraulic fracturing. The range of contaminants found in produced water can include: (i) salts, which include chlorides, bromides, and sulfides of calcium, magnesium, and sodium, (ii) metals, which include barium, manganese, iron, and strontium, among others, (iii) oil, grease, and dissolved organics, which include benzene and toluene, among others, and (iv) production chemicals, which may include friction reducers to help with water flow, biocides to prevent growth of microorganisms, and additives to prevent corrosion, as well as a variety of other chemicals (Tables 6.7 and 6.8).

TABLE 6.8 Examples of chemicals used in hydraulic fracturing fluids[a].

Chemical	Use
Acetic acid	pH buffer
Acrylic copolymer	Lubricant
Ammonium persulfate	Breaker used to reduce viscosity
Boric acid	Cross-linking agent to increase viscosity
Boric oxide	Cross-linking agent to increase viscosity
2-Butoxyethanol	Reduction of surface tension to aid gas flow
Carbonic acid	Cross-linking agent to increase viscosity
Carboxy-methyl hydroxy-propyl guar	Gelling agent (thickens fluid)
Crystalline silica (cristobalite)	Proppant (holds open fractures)
Crystalline silica (quartz)	Proppant (holds open fractures)
Citric acid	Iron control or for cleaning well bores
Diammonium peroxidisulfate	Breaker used to reduce viscosity
Disodium octaborate tetrahydrate	Gelling agent to increase viscosity
Gas oils (crude oil), hydrotreated	Guar liquefier
Fumaric acid	pH buffer
Gelatin	Corrosion inhibitor or gelling agent

TABLE 6.8 Examples of chemicals used in hydraulic fracturing fluids[a].—cont'd

Chemical	Use
Guar gum	Gelling agent
Hemicellulase enzyme	Breaker used to reduce viscosity
Hydrochloric acid	Cleaning of the wellbore prior to fracking
Hydroxy-ethyl cellulose	Gelling agent
Hydroxy-propyl guar	Gelling agent
Magnesium silicate hydrate	Gelling agent
Methanol	Gelling agent
Mono ethanol amine	Reduction of surface tension to aid gas flow
Ethylene glycol monobutyl ether	Gelling agent
Muriatic acid	Mutual solvent
Non-crystalline silica	Proppant
Poly (oxy-1,2-ethanediyl)	Proppant
Polydimethyldiallylammonium chloride	Clay control
Potassium carbonate	pH buffer
Potassium chloride	Clay inhibitor
1-Propanol	Complexing agent
Quaternary polyamines	Clay control
Sodium acetate	pH buffer
Sodium borate	pH buffer
Sodium bicarbonate	pH buffer
Sodium carbonate (soda ash)	pH buffer
Sodium chloride	Viscosity reducer
Sodium hypochlorite	Bactericide
Sodium persulfate	Viscosity reducer
Terpenes	Reduction of surface tension to aid gas flow
Tetramethyl ammonium chloride	Clay control
Zirconium complex	Cross-linking agent to increase viscosity

See: Veil (2010) and Waxman et al. (2011) for more comprehensive lists of chemicals used in hydraulic fracturing projects.

[a] *Listed alphabetically and not in order of preference. These additives are a relatively-common components of a water-based fracturing solution but are not necessarily used in* every *hydrofracturing operation. The exact blend and proportions of additives will vary based on the site-specific depth, thickness and other characteristics of the target formation.*

The specific quality of water produced by a given project, however, can vary widely and, after treatment, some of the produced water is disposed of or reused by producers in other ways, such as (i) discharging it to surface water, (ii) storing it in surface impoundments or ponds so that it can evaporate, (iii) irrigating crops, and (iv) reusing it for further hydraulic fracturing projects. Managing produced water in these ways can require more advanced treatment methods, such as distillation but the manner in which produced water is managed and treated is primarily a decision that must be made within the bounds of federal and state regulations.

In fact, the quality of water generated by a given well, however, can vary widely according to the same three factors that impact the volume of water produced from the well: the hydrocarbon being produced, the geographic location of the well, and method of production used. Typically, the type of hydrocarbon is a key driver of produced water quality, due to differences in geology across the formations in which the hydrocarbon derivatives are found. Specifically, the depth at which the hydrocarbon derivatives are found influences the salt and mineral content of produced water, and, in general, the deeper the formation is, the higher the salt and mineral content will be. Additionally, the amount of crude oil or natural gas that is mixed with the produced water brought to the surface can also vary considerably.

By far the most serious local environmental concern, and probably the most contentious, is that of groundwater contamination. The potential risk to groundwater comes from two sources: the injected fluid (water plus chemical additives) and the released natural gas. However, the major issue that is not often determined scientifically is the exact site of this contamination, either: (i) percolation or diffusion from the hydraulically fractured formation at depth, or (ii) leakage from a defective well bore that is closer to the land surface.

The nature of the hydraulic fracturing process dictates that a significant amount of water is produced as a byproduct from hydraulic fracturing. Furthermore, concern has been raised over the increasing quantities of water for hydraulic fracturing in areas that experience water stress. Use of water for hydraulic fracturing can divert water from stream flow, water supplies for municipalities and industries such as power generation industries as well as recreation and aquatic life. The large volumes of water required for most common hydraulic fracturing methods have also raised concerns for arid regions, which may require water overland piping from distant sources (Table 6.9) (Nicot and Scanlon, 2012).

The hydraulic fracturing fluids is not only water but also a mixture of water, proppant, and chemical additives – the precise mix of additives depends on the formation to be fractured which dictates the process operations and the composition of the fluids and the proppants (Speight, 2016c). Additives typically include gels to carry the proppant into the fractures, surfactants to reduce friction, hydrochloric acid to help dissolve minerals and initiate cracks, inhibitors against pipe corrosion and scale development, and biocides to limit bacterial growth (Tables 6.7 and 6.8). Chemical additives typically make up about 0.5% by volume of well fracturing fluids, but may be up to 2%. Some potential additives are harmful to human health, even at very low concentrations.

Production wells typically extend one mile or more below the ground surface, often passing through groundwater aquifers to reach crude oil-rich and natural gas-rich formations after which horizontal wells are drilled into the formation. Groundwater aquifers are typically separated from the shale formations by several thousand feet of rock, limiting the potential for any unreturned fracturing fluids to impact drinking water supplies. In addition,

TABLE 6.9 Considerations associated with water acquisition, use, and management in hydraulic fracturing operations.

Source water acquisition	Involves planning for the locale where the water supplies needed for hydraulic fracturing operations be acquired?
Transport	Involves planning for the transportation of the water from the source to the hydraulic fracturing site and, after recovery of the water as flowback water, from the hydraulic fracturing site to the point of water treatment and/or water disposal.
Storage	Involves planning for the water requirements and constraints that may exist for water storage on the hydraulic fracturing site; also involves site planning for source water considerations and fracture fluid requirements affect storage requirements.
Use	Involves planning for the methods of water use, the volume of water required, and the steps that must be taken (such as the addition of proppant and additives) to achieve the fracturing objectives.
Treatment and Re-use/Recycle	Involves planning for the treatment of the water produced from the fracturing operation and whether or not, after treatment, the water can be recycled for re-use.
Treatment and disposal	Involves planning for the treatment and disposal of that water if water is not to be recycled and or re-used; also needs decisions of what steps need to be taken either prior to disposal or with any treatment byproducts.

well casings and cement are designed to prevent contamination of any groundwater aquifers through which the well may be drilled.

There is the potential to over-pressure a well during the operation which may result in overlying formations becoming fractured, possibly serving as conduits for leakage of formation fluids and fracturing fluids into overlying formations, including aquifers. There is also the potential that over-pressured hydraulic fracturing operations could result in rapid upward leakage through the borehole into overlying formations, including aquifers and possibly even to the surface. The application of correct well design, completion, operations, and monitoring according to rules and regulations that already exist in most states and provinces will ensure that hydraulic fracturing operations do not negatively impact either the subsurface or surface environment. The result of mitigation efforts was that there was no quantifiable impact to local groundwater resources.

In addition, overweight drilling mud can cause a well bore to fail by fracture. The density (weight) of the drilling mud controls the fluid pressure exerted along the walls of the well bore. If the pressure of the mud exceeds the fracture pressure (the local minimum principal stress plus the fracture strength of the rock), a fracture can form and the drilling fluid can escape. However, pressures exceeding the rock fracture strength generated by overweight drilling muds are only likely at great depths (several thousand feet but within the depths of some shale formations), far beyond the extent of any groundwater aquifer and the risk of contamination from incorrect drilling mud composition may be limited.

To protect groundwater, proper well design, construction, and monitoring are essential. During well construction, multiple layers of telescoping pipe (or casing) are installed and cemented in place, with the intent to create impermeable barriers between the inside of the well and the surrounding rock. It is also common practice to pressure test the cement seal between the casing and rock or otherwise examine the integrity of wells. Wells that extend through a rock formation that contains high-pressure gas require special care in stabilizing the well bore and stabilizing the cement or its integrity can be damaged. Furthermore, differences in the type and sizes of well integrity datasets add to the challenge of generalizing well integrity failure rates (Davies et al., 2014, 2105).

However, the flow of hydraulic fracturing fluid into fractures can be significant and when flowback water is returned to the surface, fracturing fluids and naturally occurring substances (that have been extracted from the oil-containing or gas-containing formation) could potentially find a pathway into other geological features through natural faults or artificial penetrations (such as other non-related wells and underground mines). Groundwater resources can be protected through proper well design, construction, operation and maintenance – many states require periodic well integrity testing. However, in some geologic settings, methane can naturally originate from gas-producing rock layers below and close to the aquifer and be unrelated to the deeper fractured zone. Analysis of the crude oil and natural gas can be used to identify the origin of the crude oil and natural gas occurring in groundwater (Warner et al., 2012; Darrah et al., 2014).

Potential pathways for the fracturing fluids to contaminate water include events such as (i) surface spills prior to injection, (ii) migration of the injected fluid, (iii) surface spills of flowback water, and (iv) surface spills of produced water (US EPA, 2015c). Because the fracturing fluids are injected into the subsurface under high pressure, and because some of the fluids remain underground, there is concern that this mixture could move through the wellbore or fractures created in the reservoir rock by hydraulic pressure, and ultimately migrate up and enter shallow formations that are sources of freshwater (aquifers) (Cooley and Donnelly, 2012). There is also the possibility that geologic faults, previously existing fractures (which have not been identified due to an inadequate geological survey), and poorly plugged, abandoned wells could provide fluids with accessibility to aquifers (Osborn et al., 2011; Cooley and Donnelly, 2012; Molofsky et al., 2013; Vidic et al., 2013).

Thus, one challenge is to establish a baseline of the water quality before the fracturing operation commences. This will identify and distinguish the type and level of natural contaminants in the groundwater from those contaminants that are not indigenous to the groundwater as well as the amounts of indigenous contaminants that are in the groundwater. It is then possible, as an after the fact series of tests to determine any new contaminants or new levels of in-place contaminants that are the result of crude oil and natural gas development. Unfortunately and typically, there are no water quality analyses prior to hydraulic fracturing that can be used to provide a baseline comparison (Vidic et al., 2013).

Baseline water-quality testing, carried out prior to drilling for crude oil and natural gas, helps to document the quality of local natural groundwater and may identify natural or pre-existing contamination, or lack thereof, before drilling for crude oil and natural gas recovery begins. Without such baseline testing, it is difficult to know if contamination existed before drilling, occurred naturally, or was the result of crude oil and natural gas activity. Many natural constituents, including methane, elevated chlorides, and trace elements occur naturally in shallow groundwater in oil-producing and gas-producing areas and are unrelated to drilling activities. The quality of water in private wells is not regulated at the state or federal level, and many owners do not have their well water tested for contaminants. States handle contamination issues differently.

The current opinion is that all scientifically documented cases of groundwater contamination associated with hydraulic fracturing are related to poor well casings and their cements, or from leakages of fluid at the surface rather than from the hydraulic fracturing process itself. The absence of evidence implicating leakage from a fracture network could arise from the relatively short time span available for monitoring the signs of contamination, and potentially lower flow rates from a formation fracked at significant depth, although hydraulic fracturing has been performed in some areas for decades.

Surface spills related to the hydraulic fracturing – with the potential for seepage of the spilled chemical into a water system – occur mainly because of equipment failure or engineering or human misjudgments. Volatile chemicals held in waste water evaporation ponds can to evaporate into the atmosphere, or overflow. The runoff can also end up in groundwater systems. Groundwater may become contaminated by trucks carrying hydraulic fracturing chemicals and wastewater if they are involved in accidents on the way to hydraulic fracturing sites or disposal destinations. In addition, large quantities of chemicals must be stored at drilling sites and the volumes of liquid and solid waste that are produced and significant care must be taken that these materials do not contaminate surface water and soil during their transport, storage, and disposal.

Fluids used for slickwater hydraulic fracturing are typically more than 98% fresh water and sand by volume, with the remainder made up of chemicals that improve the effectiveness of the treatment, such as thickeners and friction reducers, and protect the production casing, such as corrosion inhibitors and biocides. These fluids are designed by service companies that tailor fracturing treatments to suit the needs of a particular project. Because the fluids in each fracturing treatment would contain a different subset of these chemicals, and because these chemicals could be hazardous in sufficient concentrations, baseline water testing is necessary to enable regulatory agencies to conduct and respond appropriately should contamination or exposure occur. The use of more environmentally benign fracturing fluids would also help limit the environmental and health risks posed by fracturing fluids in the case of contamination. Chemicals to be used in fracturing fluids are generally stored at drilling sites in tanks before they are mixed with water in preparation for a fracturing project.

In fact, the most important requirement for an assessment of the impact of hydraulic fractions projects on the flora and fauna is complete testing of air and water prior to drilling and at regular intervals after drilling has commenced. This includes chemicals used in the drilling muds, fracturing fluids and any process wastewater (the latter contains heavy metals and radioactive compounds normally found in shale formations. Currently, the extent of testing (particularly for organic compounds) is frequently inadequate and limited by lack of information on what substances were used during the drilling process due to inadequate testing (Bamberger and Oswald, 2012).

After each fracturing stage, the fracturing fluid, along with any water originally present in the shale formation, is flowed back through the wellbore to the surface. The flowback period typically lasts for periods of hours to weeks, although some injected water can continue to be produced along with gas several months after production has started. Recycling water minimizes both the overall amount of water used for fracturing and the amount that must be

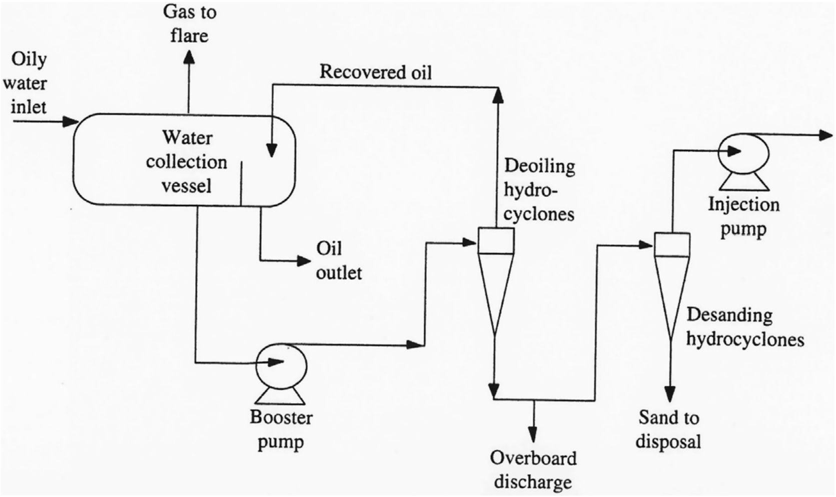

FIG. 6.2 Schematic of a water treatment process.

disposed of. Many water treatment processes are currently being investigated that could be potentially be used at large scale and have a significant impact on this problem (Fig. 6.2).

Flowback and water produced during the lifetime of a well can contain naturally occurring formation water that is millions of years old and therefore can display high concentrations of salts, naturally occurring radioactive material (NORM), and other contaminants including arsenic, benzene, and mercury. As a result, the water produced during hydraulic fracturing must be properly managed and disposed. Finally, one of the problematic aspects of handling flowback water is the temporary storage and transport of such fluids prior to treatment or disposal. In many cases, fluids may be stored in lined or even unlined open evaporation pits. Even if the produced water does not seep directly into the soil, a heavy rain can cause a pit to overflow and create contaminated runoff. Storing produced water in enclosed steel tanks, a practice already used in some wells, would reduce the risk of contamination while improving water retention for subsequent reuse. In addition, equipment used to move fluids between storage tanks or pits and the wellhead must be monitored and tested regularly to prevent spills, and precautions must be taken while transporting produced water to injection or treatment sites, whether via pipeline or truck.

Once production operations are in place and wells begin producing the fluids – produced water and oil – are often stored on site in large tanks while awaiting transport off-site. Safeguards put in place to protect the environment and public from tank releases include consistent measurements by pumpers, high level shut down sensors, continued equipment observations and maintenance, and secondary containments in place around the tanks to contain any fluids that may release from tank. Secondary containments may be constructed of properly packed and integrity tested earthen materials or up to specifically designed and manufactured metal containments with plastic liners. No matter the materials used in construction, secondary containments must be sufficiently large enough to contain all the fluids that could possibly escape the tanks.

Even with attempts to minimize the amount of on-site storage, some chemical and product storage is unavoidable and there are very valid concerns – including potential spills, leaks, tank or container overfill, and even the chance of traffic accidents on location or roadways leading to releases of chemicals and/or products. Release events could range from relatively small amounts from equipment leaks to possibly hundreds of barrels from tank release.

5. Water disposal

Water that originates from a hydraulic fracturing project often contains chemical additives to help carry the proppant and may become enriched in salts after being injected into tight formations. Therefore, the water that is recovered during natural gas and crude oil production from tight formations must be either treated or disposed of in a safe manner – a suggestion for disposal of such water is typically to inject the water into deep, highly saline formations through one or more wells drilled specifically for that purpose but the disposal method must follow clearly-defined regulations. Flowback water is infrequently re-used in hydraulic fracturing because of the potential for corrosion or scaling, where the dissolved salts may precipitate out of the water and block parts of the well or the formation thereby interfering with and influencing flow of the fluids.

In addition to chemicals that are added to the fracturing fluid, wastewater from natural gas and crude oil extraction may contain high levels of total dissolved solids (TDS), which can be a complex collection of inorganic compounds. Furthermore, the amount of saline water produced from tight formations can vary widely – from zero to (at least, depending upon the formation characteristics) several hundred barrels per day. The water may originate from the tight reservoir formation or from any adjacent formations that are connected to the reservoir formation through a natural fracture network or, more likely, through the process-induced fracture network. Typically, this water, like flowback water, is highly saline and must be treated or sent for disposal by injection into deep saline formations, which is also subject to clearly defined regulations. In fact, in some regulatory authorities that oversee the production of natural gas and crude oil have implemented regulations regarding the disclosure of chemicals used in the process of hydraulic fracturing to ensure that the subterranean environment is protected when re-injection of these chemicals is the method of disposal.

In terms of water use management, one alternative that states and natural gas and crude oil production projects are pursuing is to make use of seasonal changes in river flow to capture water when surface water flows are greatest. Utilizing seasonal flow differences allows planning of withdrawals to avoid potential impacts to municipal drinking water supplies or to aquatic or riparian communities. Also included is monitoring of stream water quality as well as game and nongame fish species in the reach of river surrounding the intake. In addition, new treatment technologies have made it possible to recycle the water recovered from hydraulic fracturing. The re-use of treated flowback fluids from hydraulic fracturing is being used (or at least, considered for use) for various projects.

Briefly, and by way of explanation, a riparian community is a community that exits in a riparian zone (riparian area), which is the interface between land and a river or between land and a stream. Plant habitats and communities along the river margins and banks, stream margins and banks (*riparian vegetation*) are characterized by collections of hydrophilic plants. Riparian zones are important in ecology and in environmental management because of their role in soil conservation, their habitat biodiversity, and the influence they have on fauna and aquatic ecosystems, including grasslands, woodlands, wetlands, or even non-vegetative growing areas. In some regions the terms riparian woodland, riparian forest, riparian buffer zone, and riparian strip are used to characterize a riparian zone.

The rate at which water returns to the surface is highly dependent upon the geology of the formation. In some formations, recycle of flowback water may be as high as 95% v/v of the flowback water whereas in other formations s the recycle operations may involve as little as 20% v/v of the flowback water. Thus, as might be anticipated in the light of similar statements elsewhere in this text, water management and water re-use are issues that are specific to the locality of the project as well as specific to the depth and characteristics of the gas-bearing or oil-bearing formation as well as the quality and quantity of water and the availability and affordability of management options (Veil, 2010). Over a 30-year life cycle, assuming a typical well is hydraulically fractured three times during that time period, construction and production of shale gas typically can consume between 7,000,000 and 17, 000, 000 gallons of water per well.

Once the natural gas or crude oil gas is produced, it is processed, and transported for further processing (cleaning, refining) (Chapters 7—10). Water consumption occurs in each of these stages as well, with the most significant non-production consumption potentially occurring during end use. Typically, crude oil from a hydraulic fracturing project is transported sent to a refinery for use as blending stock with other crude oil for the refinery feedstock, which may constitute a blend of three or more other crude oils (Chapter 10) and may give rise to issues arising from the incompatibility of the constituents of the blend (Chapter 17) (Speight, 2014a). The refinery requires additional water consumption but this additional consumption is not directly related to the water use during the hydraulic fracturing project. On the other hand, although natural gas can be combusted directly with no additional water consumption, if the end use of the gas is in the form of a transportation fuel, storage in a vehicle tank is required and the natural gas will most likely have to be compressed by means of an electric compressor (King and Webber, 2008; Wu et al., 2011). It then remains to select an option (or options) for treatment of the water either for re-use or for disposal.

Put simply, water treatment is any process which removes contaminants from the water or reduces the concentration of the contaminants so that the water is more acceptable for a specific end-use. In the present context, the end use may be industrial water supply, irrigation, river flow maintenance, water recreation or many other uses including being safely returned to the environment. In some cases, exceptional and assiduous treatment of the water can produce water suitable for use as drinking water. Thus, management of flowback water can generally by realized by any one (or more) of the management strategies: (i) disposal, (ii) re-use, and (iii) recycling (Halldorson and Horner, 2012).

In regard to the *disposal* option for the water, the flowback is transported to an injection well for disposal. This option for disposal is often chosen if there is a ready and relatively inexpensive, abundant supply of fresh water nearby and, most important, nearby injection wells can handle the flowback disposal volumes according to the relevant regulatory guidelines or laws. However, as fresh water availability decreases, costs increase and/or distance to injection wells for disposal increases, making the disposal scenario less appealing.

The *re-use* option (which may be the least expensive strategy) involves careful treatment of the flowback water to remove suspended solids and soluble organic constituents (such as naphthenic acids that are present in some crude oils) (Speight, 2014b) followed by blending the treated water with fresh water to generate a fluid that is suitable for use in a hydraulic fracturing project for a new well. This option, reduces the amount of fresh water required for the project and eliminates the need for the disposal option if all flowback water can be treated and re-used.

Finally, the *recycling* option treatment of the flowback water to produce a product that is typically of fresh-water quality. In this option, the recycled water is blended with makeup water from freshwater sources to generate a hydraulic fracturing fluid that is low in total dissolved solids. Recycling is used when (i) fresh water costs are high, a high quality, (ii) a fracturing fluid with a low total dissolved solids content is required, or (iii) other logistics such as hydraulic fracturing schedules do not permit re-use of the water. If the fracturing fluid is transferred by means of temporary above-ground pipelines (*fastlines*) may recycle the water to minimize potential environmental liability from spills or rupture of the pipeline.

The issue of the total dissolved solids in water is a continuous issue and during an active fracking project involving natural gas and crude oil production is continually being subject to inconsistent flowback water containing total dissolved solids (TDS) – ranging from 5000 to 200,000 ppm – and/or total suspended solids (TSS) ranging from 100 to 3000 ppm. In order to combat such impurities, a clarifier can pump can be used to pump flowback water from the source (such as a such as a *frac tank* or pit) into a unit which uses a solids settling system which enables suspended solids settle to the bottom of the unit where they are collected and dewatered. A major benefit of re-using water is that it reduces the financial, social and environmental costs associated with water transportation.

In addition, evaporation technology can be used to recycle contaminated water – the process involves boiling a solution so that contaminants remain in the liquid phase, while pure water vapor evaporates and can be condensed into distilled water. Also, mechanical vapor recompression (MVR) evaporation is a leading means of treating waste water – the process differs from conventional evaporation insofar as a compressor is used to generate steam rather than a heat source such as a boiler. High energy efficiency is achieved by utilizing the latent heat of the condensing steam as the primary energy source for boiling the wastewater.

6. Waste fluids

A variety of waste fluids are generated on site at natural gas and crude oil wells and one of the biggest challenges for protecting water resources from tight formation natural gas and crude oil activities is the wastewater generated during production. Wastes, such as drill cuttings, and wastewater generated during exploration, development, and production of crude oil and natural gas are categorized by the United States Environmental Protection Agency as *special wastes* that are exempted from federal hazardous waste regulations under Subtitle C of the Resource Conservation and Recovery Act.

Horizontal drilling development has the power to reduce the number of well sites and to group them so that management facilities such as storage ponds can be used for several wells. Make-up water is used throughout the development process to drill the well and to form the basis of the hydraulic fracturing fluid. Large volumes of water may be needed and are often stored at the well site in pits or tanks. For example, surface water can be piped into the pit during high-water runoff periods and used during the year for drilling and fracture treatments in nearby wells. Exhibit 14 shows one of these large storage ponds servicing the Marcellus development in Pennsylvania. Storage ponds are not suitable everywhere in the shale gas play; like steel tanks, they are appropriate in some locations and not in others.

After a hydraulic fracture treatment, when the pumping pressure has been relieved from the well, the water-based fracturing fluids begin to flow back through the well casing to the wellhead. This water is referred to as flowback water and consists of spent fracturing fluids and, in some cases, dissolved constituents from the formation itself (minerals present in the shales as well as brine waters that may be present within any natural pore space contained in the shale). The majority of flowback water is produced in a range of time from several hours to a couple of weeks. In various basins and shale gas plays, the extent of this volume of flowback water may account for less than 30% to more than 70% of the original volume of the fracture fluid.

In some cases, production of flowback water can continue for several months after gas production has begun. Natural formation waters that flow to the well are known as produced water. Regardless of the source of water, flowback or formation water, these waters that are produced back through the ellhead with the gas represent a production stream that must be managed and are collectively referred to as produced water. Gas shale operators manage produced water through a variety of mechanisms including underground injection, treatment and discharge, and recycling. Underground injection is not possible in every play area as suitable injection zones may not be available. Similar to a producing reservoir, there must be a porous and permeable formation capable of receiving injected fluids near the play area. If such is not locally available, it may be possible to transport the produced water to a more distant injection site. Treatment of produced waters may be feasible through either self-contained systems at well sites or fields or through municipal waste water treatment plants or commercial treatment facilities. The availability of municipal or commercial treatment plants may be limited to larger urban areas where treatment facilities with sufficient available capacity already exists; as in underground injection, transportation to treatment facilities may or may not be practical.

Fluids management involves the environmentally friendly disposal or re-use of excess fluids and is an integral and essential phase of project involved in the development of (and recovery of natural gas or crude oil from) tight formations because pollutants in the natural waterways (rivers, stream, and some case, he oceans) result in the reduction of the oxygen content of water leading to serious effects on (even elimination of) the aquatic life. This gives rise to the need, not only for water purification but also water conservation.

Furthermore, an important challenge is fluids management which involves: (i) treatment, (ii) recycling, (iii) reuse, and (iv) disposal of the flowback water and produced water. This water mix often contains residual fracturing fluid and may also contain substances found in the reservoir formations, such as trace elements of heavy metals and even naturally occurring radioactive materials (NORM). Also, the impact of the recovery operations on land and air must also be minimized. Production wells require roadways to connect drilling pads and there will be the need for either pipelines or trucks or both to transport natural gas, crude oil, or process waste as well as the need for storage units, and water treatment facilities. With the potential for several hundred truck trips per well site, pipeline use has the potential to minimize surface disturbance.

Wastewater from natural gas and crude oil exploration is generally classified into flowback and produced waters. Flowback water is the fluid that returns to the surface after the step of hydraulic fracturing and before natural gas and crude oil production begins, primarily during the days to weeks of well completion. This fluid can consist of 10%–40% v/v of the injected fracturing fluids and chemicals pumped underground that return to the surface mixed with an increasing proportion of natural brines from the tight formation formations through time.

Produced water is the fluid that flows to the surface during extended natural gas and crude oil production and primarily reflects the chemistry and composition of deep formation waters and capillary-bound fluids. These naturally occurring brines are often saline to hypersaline and contain potentially toxic levels of elements such as barium, arsenic, and radioactive radium. Wastewater from hydraulic fracturing operations is disposed of in several ways. Deep underground injection of wastewater comprises >95% of disposal in the United States. In contrast, deep injection of wastewater is not permitted in Europe unless the water is used to enhance natural gas and crude oil recovery. Wastewater in the United States is also sent to private treatment facilities or, increasingly, is recycled or reused (see above). More recently, wastewater is increasingly being sent to facilities with advanced treatment technologies such as desalination at rates approaching 90% reuse.

Currently, practices are in place for controlling water flow – ponds and pools are provided where drainage water accumulates and where suspended mineral matter (such as shale and clay particles) can ultimately be removed. Sedimentation, with or without the use of flocculants, can be applied to process the water in contained in lagoons. In other cases, water conservation programs are mainly aimed at restricting water flow seeping through the porous structure, boreholes and fractures in the water bearing strata. In addition, the protection of drinking water sources is also necessary.

One of the first steps in water management involves proper well construction to isolate the wellbore by use of cement and several different sets of steel casing (Chapter 4), is a critical step taken by the natural gas and crude oil industry to protect groundwater sources. The casings are individually cemented into the wellbore to provide barrier which isolate wellbore fluids from the rock formations. In the process, cement is pumped into the center of casing so that it circulates back to the surface in the space outside of the casing (the *annulus*), following the installation of each length (*string*) of casing in the well. After these steps are complete, the cement must be allowed to set prior to the continuation of drilling – a geophysical log is run to determine the integrity of the cement that surrounds the casing. This is an aid to ensure that the wellbore is adequately cemented and capable of withstanding the pressure associated with hydraulic fracturing. Prior to stimulation, the well is pressure tested to ensure the integrity of the casing system that has been installed underground.

Thus, under the various regulations, comprehensive rules are in place to ensure that wells are constructed in a manner (well integrity) (Chapter 4) that protects freshwater supplies. Specific guidelines vary between the various regulatory authorities but, in all cases, steel casing and cement are used to isolate and protect groundwater zones from deeper oil, natural gas and saline water zones.

6.1 Fracturing fluid requirements

The primary factor influencing water management associated with hydraulic fracturing is related to the fluid requirements for a successful hydraulic fracturing operation. All phases of water management ultimately depend on the requirements of the hydraulic fracturing properties needed for conducting a successful fracturing project. These requirements are the result of the geology of the reservoir formation and the formations above and below the reservoir, the operating environment, the design of the hydraulic fracturing process, the scale of the development process, and the results required for total project success.

The primary issue in understanding water management for a hydraulic fracturing project involves knowledge of the reservoir rock need and what will the rock will produce after completion of the fracturing process. The choice of the fracturing fluid dictates the fracturing design as well as the types of fracturing fluids and the additives that are required. Furthermore, the choice of the fracturing fluid dictates the transport and ultimate fate of the fracturing fluid used in the fracturing operations as well as the means by which the recovered fluids will need to be managed and disposed.

The typical hydraulic fracturing practice (if there is such a process that can be described as *typical*) is designed to create single fractures or multiple fractures in specific rock formations. These hydraulic fracture treatments are controlled and monitored processes designed for the site-specific conditions of the reservoir. Moreover, the process conditions are guided by (i) extraction of the target product i.e., natural gas or crude oil, (ii) the respective properties of the target product), (iii) the properties − including the mineralogy − of the target formation, (iv) the rock fracturing characteristics of the formation, (v) the properties of the formation water, (6) the anticipated water production, i.e. formation water versus fracturing flow back water, and (vii) the type of well drilled (horizontal or vertical) into the formation.

Thus, understanding the in-situ reservoir conditions is critical to successful stimulations, and in the design of the fracture treatment and fluid used as well as to water management. Hydraulic fracturing designs are continually evolving both during the fracture stimulation itself as well as over time as more related to fracturing the target formation is understood and this understanding evolves. Thus, while the concepts and general practices are similar, the details of a specific fracture operation can vary substantially from resource to resource, from area to area, and even from well to well.

6.2 Fracturing fluid composition

There is a wide variety of additives that could be included in the fracturing fluid mix to achieve successful fracturing (Chapter 5). These include proppants, gel and foaming agents, salts, acids, and other fluid additives and there is a movement (and a need) to maximize the utilization of environmentally benign additives and minimize the amount of additives required.

The characteristics of the resource target determine the required composition of the hydraulic fracturing fluid composition which, in turn can affect water management. For example, the tight formation may contain various naturally occurring trace metals and compounds that become available because of the induced fractures and are the leached from the reservoir rock by acidic water, by conversion to soluble species as a result of oxidation, and by the action of ionic species that occur in brines. Numerous inorganic and organic compounds have been formed naturally and occur in the tight formation and a stimulation fluid pumped into a well may require various chemicals to counteract any negative effects these compounds may have in the well or the reservoir. For example, iron compounds require an iron sequestering agent so that the compounds of iron will not precipitate out of the fracturing fluid and be deposited within the pore spaces of the reservoir, reducing the permeability of the reservoir and adding further complications to water management.

One of the major aspects of water management is, when developing plans for a hydraulic fracturing project in addition to considerations associated with successfully fracturing the target formations, the fluid management and disposal implications of the project and the fracture fluid formulations should receive major consideration. The best water management practice is to use additives that pose minimal risk of possible adverse environmental effects to the extent possible in delivering the needed effectiveness of the fracturing operation. While this is a highly desirable option, product substitution may not be possible in all situations because effective alternatives may not be available for all additives.

6.3 Fracturing fluid handling and storage

Fracturing fluid handling and storage is perhaps that major issue that arise when considering water management options. Fracturing fluid requirements and fracturing fluid composition are all aspects of fluid handling and storage that contribute to water management. Fluids handled at the well site both before and after hydraulic fracturing often must be stored on site, and must be transported from the source of supply to the point of ultimate treatment and/or disposal. Fluids used for hydraulic fracturing will generally be stored onsite in tanks or lined surface impoundments. Returned fluids, or flowback, may also be directed to tanks or lined pits. Furthermore, the volume of initial flowback water recovered during the first month or so following the completion of hydraulic fracturing operations may account for less than 10% v/v to more than 70% v/v of the original volume of the fracturing fluid. The vast majority of fracturing fluid injected is recovered in a very short period of time, usually to a maximum time period of several months.

Thus all of the components of the fracturing fluids, including and especially water, additives and proppants, should be managed properly on site before, during, and after the hydraulic fracturing process. If possible, to assist in water management, the components of the fracturing fluid should all be blended into the composite fracturing fluid on an as-needed basis. In addition, any unused products should be removed from the fracturing location as soon as is appropriate. Furthermore, the project planning process should take into consideration the possibility of unexpected delays in the fracturing operation and ensure that water and the additive materials are managed correctly.

If lined impoundments or pits are used for storage of fracturing fluids or flowback water, the pits must comply with applicable rules, regulations, good industry practice, and liner specifications. Thus, these impoundments must be designed and constructed in such a manner as to provide structural integrity for the life of their operation − correct design is imperative to the objective of preventing a failure or unintended discharge. If the fluids are to be stored in tanks, these tanks must meet appropriate state and federal standards, which may be specific to the use of the tank − for example, if the tank is used as a tank for flowback water or for more permanent production tank batteries.

6.4 Transportation

Before the onset of fracturing, water, sand and any other additives are generally delivered separately to the well site. Water is generally delivered in tanker trucks that may arrive over a period of days or weeks, or via pipelines from a supply source or treatment/recycling facility. Thus, water supply and management approaches should take into consideration the requirements and constraints associated with fluid transport.

Transportation of water to and from a well site can be a major expense and major activity. While trucking costs can be the biggest part of the water management expense, one option to consider as an alternative to trucking is the use of temporary or permanent surface pipelines but the transport of fluids associated with hydraulic fracturing by surface pipeline may not be practical, cost effective, or even feasible. Moreover, when fracture fluids are to be transported by truck, the project will need development of a basin-wide trucking plan that includes (i) the estimated amount of trucking required, (ii) the hours of operations, (iii) the appropriate off road parking/staging areas, and (iv) the trucking routes. Furthermore, considerations for the trucking plan for large volumes of fracture fluid include the following: (i) public input on route selection to maximize efficient driving and public safety, (ii) avoidance of peak traffic hours, school bus hours, community events, and overnight quiet periods, (iii) coordination with local emergency management agencies and highway departments, (iv) upgrades and improvements to roads that will be traveled frequently to and from many different well sites, (v) advance public notice of any necessary detours or road/lane closures, and (6) adequate off-road parking and delivery areas at the site.

The use of multi-well pads (Chapter 4) make the use of central water storage easier, reduces truck traffic, and allows for easier and centralized management of flow back water. In some cases, it can enhance the option of pipeline transport of water. Furthermore, in order to make truck transportation more efficient and have lees impact on the surrounding environment, it is worth considering the construction of storage ponds and drilling source wells in cooperation with any non-project (but interested) private property owners. The opportunity to construct or improve an existing pond, drilling a water well, and/or improving the roads on their property can be an extremely helpful (perhaps even a *win-win*) situation for the operator and the landowner by providing close access to a water source for the project as well as adding improvements to the nearby property that could benefit the property owner.

During drilling, used mud and saturated cuttings are produced and must be managed. The volume of mud approximately correlates with the size of the well drilled, so a horizontal well may generate twice as much drilling waste as a single vertical well however the horizontal well may replace as many as four vertical wells. Drilling wastes can be managed onsite either in pits or in steel tanks. Each pit is designed to keep liquids from infiltrating vulnerable water resources. On-site pits are a standard in the natural gas and crude oil industry but are not appropriate everywhere; they can be large and they disturb the land for an extended period of time. Steel tanks may be required to store drilling mud in some environments to minimize the size of the well site *footprint* or to provide extra protection for a sensitive environment. Steel tanks are not, of course, appropriate in every setting either but in rural areas or pits or ponds, where space is available at the well site, steel tanks are usually not needed (Arthur et al., 2008).

The drill cuttings are regarded as controlled or hazardous waste and can be disposed of in the following ways: (i) decontamination treatment, (ii) injection of the cuttings into the well, or (iii) transfer to a controlled hazardous-waste landfill. The lowest environmental effect for solids treatment, especially for offshore operation, is decontamination treatment followed by discharge. However, oil content in the treated cuttings of >1% still exists in the dried solids by conventional decontamination technology, which does not meet strict environmental regulations in some countries.

Horizontal drilling development has the power to reduce the number of well sites and to group them so that management facilities such as storage ponds can be used for several wells. Make-up water is used throughout the development process to drill the well and to form the basis of the hydraulic fracturing fluid. Large volumes of water may be needed and are often stored at the well site in pits or tanks. For example, surface water can be piped into the pit during high-water runoff periods and used during the year for drilling and fracture treatments in nearby wells. Storage ponds are not suitable everywhere in the area of a natural gas and crude oil resource – just as steel tanks are appropriate in some locations but not in others. Finally, it may be opportune for any hydraulic fracturing project to include consideration of utilizing agricultural techniques to transport the water used near the water sources. Large diameter, aluminum agricultural pipe is sometimes used to move the fresh water from the source to locations within a few miles where drilling and hydraulic fracturing activities are occurring. Water use by the natural gas and crude oil industry when working to recover these resources from tight formations has spurred the formation or expansion business involved in the supply the temporary pipe, pumps, installation, and after-project removal of these amenities.

7. Water management and disposal

When water returns to the surface from a tight formation drilling operation, it may be disposed of in a variety of ways, depending on the tight formation basin: (i) reused in a new well, with or without treatment, (ii) injected into on- or off-site disposal wells regulated by the United States Environmental Protection Agency, (iii) taken to a municipal wastewater treatment plant or a commercial industrial wastewater treatment facility – most wastewater treatment plants are not capable of treating the contaminants in natural gas and crude oil wastewater, (iv) or discharged to a nearby surface water body.

In the Marcellus Tight formation, one of the largest tight formation basins in the United States located in Pennsylvania and New York state, a large proportion of the hydraulic fracturing fluid is usually recovered after drilling and stored on-site in evaporation pits. Recovered fluid may be trucked off-site for use in another fracking operation or for treatment and disposal in surface waters, underground reservoirs, or at a wastewater treatment facility. The remainder of the fluid remains underground (Veil, 2010). However, in the water-deprived tight formation basins of Texas (such as Eagle Ford), more of the hydraulic fracturing fluid may remain underground. This water is much harder to track than surface water, which may lead to increased short and long-term risks for natural gas and crude oil companies.

While treatment of produced fluids (including water) from some hydraulic fracturing projects remains an option in some jurisdictions, requirements associated with the use of this option are likely to fall under stringent federal, states, or regional regulations. The project should be sufficiently well-planned to accommodate proper management and disposal of fluids associated with hydraulic fracturing operations (Table 6.7). Furthermore, considerations for fluid management should include provision for flowback water disposition, including the planned transport of the water from the well pad (truck or piping), and information related to any proposed piping as well as the planned for of disposal of the water (such as the treatment facility, the disposal well, water re-use, a centralized surface impoundment, or a centralized tank facility). There should also be clear identification and permit numbers for any proposed treatment facility or disposal well, and the location and construction and operational information for any proposed centralized flow back water surface impoundment.

Typically, a well permit will specify (often with the necessary details) that all fluids, including fracture fluids and flowback water, must be removed from the well site. In addition, any temporary storage pits used for fracturing fluids must be removed as part of reclamation. More specifically, water used in the hydraulic fracturing process is usually managed and disposed of in one of three ways: (i) injection into in permitted disposal wells under a regulatory program, (ii) delivery to a water treatment facility depending on permitting regulations which may, in some regions, allow treatment of the water to remove pollutants and to achieve all regulated specifications and then followed by regulated discharge of the water to the surface, and (iii) re-use if sufficiently pure for the purpose or prior passage through a recycling operation before re-use. . However, water disposal options are dependent on a variety of factors, including the availability of suitable injection zones and the possibility of obtaining permits for injection into these zones or the capacity of commercial and/or municipal water treatment facilities, and the ability of either operators or such plants to successfully obtain surface water discharge permits.

Part of the project plan should also ensure surface and groundwater quality is described in detail which may include any necessary sampling/analytical programs that will be sued to acquire samples for passage to an analytical facility. This information will provide unbiased analytical data for a better understanding of water quality before extensive drilling and hydraulic fracturing are initiated, and (more appropriately) will provide the baseline data that will assist in informing the local community related to existing groundwater quality. There should also be the move to collect any necessary additional site specific baseline water samples collected from public and private wells near the hydraulic fracturing operations, as well as from nearby surface water bodies (rivers, stream, lakes ponds) prior to drilling specific wells if existing information is not adequate. The actual parameters to be tested and for which analytical data will be required will depend to a great extent on site specific geology, hydrology, and water chemistry. Typically, the parameters for testing should include, but are not limited to total dissolved solids, total suspended solids, chloride ion concentrations, carbonate concentration, bicarbonate concentration, as well as the concentrations of sulfate, barium, strontium, arsenic, surfactant derivatives, methane, hydrogen sulfide, benzene, and naturally occurring radioactive material (NORM).

The primary potential destinations for flow back/production fluids generally include the following: (i) injection wells, which are regulated under either a state or federal program, (ii) municipal waste water treatment facilities, (iii) industrial waste treatment facilities, (iii) other industrial uses, and (iv) fracture flow-back water recycling/re-use.

7.1 Injection wells

The disposal of flowback fluids through injection, where an injection zone is available, is widely recognized as being a means of fluids disposal providing the procedure is environmentally benign, well regulated, and proven to have been effective (API, 2009, 2010). However, in order to manage the expected amount of water associated with large scale developments, additional injection wells in an area may need to be drilled and will have to be authorized through the relevant permitting procedures. Injection wells for the disposal of brine associated with natural gas and crude oil recovery operations will require state or federal permits. Therefore, whether the United States Environmental Protection Agency or the state regulatory agency has underground injection control program (UIC program) authority over the subsurface injection, new injection wells will require an injection well permit that meets the appropriate state and/or federal regulatory requirements.

7.2 Municipal waste water treatment facilities

Municipal wastewater treatment plants or commercial treatment facilities may be available as treatment centers and disposal options for the treatment of fracturing fluid flowback and/or other produced waters. However, sufficient available capacity already must exist for treatment of the flowback water and, thus, the availability of municipal treatment plants or commercial treatment plants may be limited to larger urban areas where large treatment facilities are already in operation. with. Moreover, the practicality of the transportation of the fluids from underground injection projects must be given serious consideration in any planning process.

If the size of the treatment plant means that treatment of the fluids is in order, the treating plant (especially it the plant is a publicly owned treatment works, POTW) must have a state-approved pretreatment program for accepting any industrial waste. In addition, the publicly owned treatment works must also notify appropriate regulatory authorities of any new industrial waste they plan to receive at their facility and certify that the facility is capable of treating the pollutants that are expected to be in that industrial waste. Furthermore, publicly owned treatment works are generally required to perform specific analyses to ensure the plant can handle the waste without disturbing (unbalancing) the system or causing a problem in the receiving water. Ultimately, approval is required of such analysis and modifications to the permits that are already in place at the publicly owned treatment works are necessary to ensure that water quality standards in receiving waters are maintained at all times. Thus, in an effort to assist in this review, the publicly owned treatment works may require that operators of a hydraulic fracturing project provide information pertaining to the chemical composition of the hydraulic fracturing additives, specifically to examine the potential environmental hazards in the mix as well as the possible toxicity of the mix.

7.3 Industrial waste treatment facilities

It is considered unlikely that future disposal needs will be met by publicly owned treatment works due to current regulatory restrictions and future regulatory restrictions. Thus, the construction of private or industry-owned treating facilities, perhaps built and operated by an industry cooperative or an environmental services company, is an alternative solution. In several regions, the current and evolving practice is to set up temporary treatment facilities located in active drilling development areas or to treat the waste stream onsite with mobile facilities. The temporary facilities can alleviate/reduce the trucking of waste streams by the use of transitory pipeline systems that serve local wells.

7.4 Other industrial uses

In terms of fluids disposal there may be other industrial uses for flowback water that are worthy of consideration but each proposed use will be highly dependent on site specific considerations, and some level of treatment to match the fluid properties with the site needs would (more than likely) be required. Two such examples are (i) the use of the flowback water to support drilling operations, or (ii) the use of this water as source water for water flooding operations, where water is injected into a partially depleted oil reservoir to displace additional oil and increase recovery (Speight, 2014a, 2016a).

Briefly, waterflood operations are regulated under state regulations and/or underground injection control program of the US Environmental Protection Agency which protects water sources such as drinking water sources (US EPA, 2015a). These authorities would review the proposed use of flowback fluids from hydraulic fracturing operations for suitability in a waterflood injection operation. Often, water injection operations and operations where a change in water or water source occurs are usually required to modify their permits to inject water from a new source. The water provider is required to submit an analysis of the water to be injected any time there is a change in the water or even the water source.

7.5 Flowback water recycling and Re-use

Effective management of flowback water requires knowledge of the characteristics of the water. Typically, flowback water contains salts, metals and organic compounds from the formation as well as many of the compounds that were introduced as additives to the influent stream. Thus, there is the need for an information base on the composition and properties of flowback water and on the influent water streams that are used to perform hydraulic fracturing.

There are instances where it may be more practical to treat the flowback water to a specified quality so that it could be re-used for a subsequent hydraulic fracturing project rather than treating the water to meet the necessary requirements that make the water suitable for surface discharge. Consequently, options for the recycling of fracture treatment flowback fluid should be an early consideration since water re-use and water recycling can be a key to enable large scale future natural gas and crude oil recovery operations that use hydraulic fracturing as the method of accessing and freeing the natural gas and crude oil. While this method is already underway in some areas and been successful, the ability to re-use hydraulic fracturing fluid does depend, to a large degree, on the type of treatment required and the volume of make-up water that is necessary for the operation.

The various options to be considered will depend on (i) the total water volume of water to be treated, (ii) the soluble constituents in the water that need to be treated, (iii) the concentrations of the soluble constituents, (iv) their treatability of the solubility of the constituents and whether or not the treatment will remove these constituents, and (v) the water re-use requirements, and (6) the water discharge requirements. If all of the above issues can be satisfied to allow re-use of the flow back water, such re-use can provide a practical solution that overcomes many of the constraints imposed by the limited source water supplies as well as by difficulty in disposal of the r-used water.

For example, the evolution of water treatment technologies is being adapted to work with the high saline water that results from hydraulic fracturing. Such technologies include innovations in reverse osmosis technology and innovations in membrane technology. In addition, distillation technology is in the process of refinement to improve the 75%–80% treating effectiveness of the current water re-use. However, distillation is also a very energy intensive process and it is possible that it may only become an option for all operations with technological improvements (as a piggy-back technology, i.e. as a secondary ancillary technology) to increase the treatment effectiveness and the overall efficiency of the process.

Pursuing any such alternate option for water treatment does require careful planning and knowledge of the composition of the flowback water and/or the produced reservoir water. Moreover, finding the correct option also requires careful selection of the chemical additives and design that do not bring about major water treatment issues. Success will be measured by the efficiency of the treatment technology and whether or not the technology makes it more economical to treat these hydraulic fracturing fluids and produce better results in terms of the quality of the treated water. The treatment of these hydraulic fracturing fluids may greatly enhance the quantity of acceptable, re-useable fluids, and provide more options for ultimate disposal of the re-used water. Such treatment facilities either could be run as integral part of the hydraulic fracturing project or the facility could even function as stand -alone, independent commercial enterprise.

In this context, a number of water treatment innovations do approaches exist and many other options continue to be developed and modified to address the specific treatment needs of flowback water from different sites and in different operating regions. Processes that can be utilized for water treatment (and this are adaptable to treatment of flowback water) include but are not limited to: (i) filtration, (ii) aeration and sedimentation, (iii) biological treatment, (iv) demineralization, (v) thermal distillation, (6) condensation, (vii) reverse osmosis, (viii) ionization, (ix) natural evaporation, (x) freeze/thaw procedures,

(xi) crystallization, and (xii) ozonization. This is by no means an exhaustive list, and new alternatives are continuously being considered and evaluated.

Because of the complexity of the hydraulic fracturing process and the varying quality of flowback water, it is likely that multiple processes will be required in many cases, if not in most cases. Some of the processes will serve as piggy-back processes (secondary processes) to the major process option ensure efficient treatment of the water that cannot be achieved by one process alone. Key considerations to the selection of the treatment process will be (i) the efficiency of the primary, (ii) the need for a piggy-back secondary process, (iii) the performance of the primary process with and without the secondary process, (iv) the volume of water processes in a specific time interval, (v) the environmental considerations associated with the resulting treated water, and (6) the cost-effectiveness of the water treatment process in terms of the primary with and without the secondary piggy-back option.

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C H A P T E R

7

Analysis of gas and condensate from tight formations

1. Introduction

Gas from tight formations (also referred to as tight gas and/or shale gas) is a category of natural gas that contains hydrocarbon derivatives that are predominantly the methane (C_1) to hexane (C_6) hydrocarbon derivatives. The tight gas may also contain inorganic compounds, such as nitrogen, hydrogen sulfide, carbon monoxide, and carbon dioxide. As such, tight gas (unless produced as a salable product that must meet specifications prior to sale) is often of uncertain and variable composition as well as being toxic to floral and faunal species (API, 2009). Thus, tight gas from different formations varies widely in composition and analyses, as does natural gas from conventional formations and the proportion of non-hydrocarbon constituents can vary over a very wide range (Speight, 2014a).

The non-hydrocarbon constituents of natural gas can be classified as two types of materials: (i) diluents, such as nitrogen, carbon dioxide, and water vapors, and (ii) contaminants, such as hydrogen sulfide and/or other sulfur compounds. Thus, a particular natural gas field could require production, processing, and handling protocols different from those used for gas from another field. In addtion, a tight gas stream is one of serval streams that are blended before processing within a refinery gas processing section or as a separate gas processing entity. For this reason, it is necessary to understand the composition and properties of other gas streams properties that enter the gas processing system.

The diluents of gas streams are typically the non-combustible gases that reduce the heating value of the gas and are on occasion used as *fillers* when it is necessary to reduce the heat content of the gas. On the other hand, the contaminants are detrimental to production and transportation equipment in addition to being obnoxious pollutants. Thus, the primary reason for gas refining is to remove the unwanted constituents of natural gas and to separate the gas into its various constituents. The processes are analogous to the distillation unit in a refinery where the feedstock is separated into its various constituent fractions before further processing to products. The major diluents or contaminants of natural gas are: (i) acid gas, which is predominantly hydrogen sulfide although carbon dioxide does occur to a lesser extent, (ii) water, which includes all entrained free water or water in condensed forms,

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(iii) liquids in the gas, such as higher boiling hydrocarbons as well as pump lubricating oil, scrubber oil, and, on occasion, methanol, and (iv) any solid matter that may be present, such as fine silica (sand) and scaling from the pipe. Thus, like any other refinery product, the tight gas must be processed to prepare it for final use and to ascertain the extent of contaminants that could cause environmental damage. Furthermore, gas processing is a complex industrial process designed to clean raw (dirty, contaminated) gas by separating impurities and various non-methane and fluids to produce what is known as *pipeline quality* dry natural gas.

Gas processing typically begins at the begins at the wellhead where the composition of the raw natural gas extracted from producing wells depends on the type, depth, as well as the geology and location of the underground reservoir (Speight, 2014a, 2017). Thus, gas processing plants purify raw gas to remove common contaminates such as water, carbon dioxide, and hydrogen. However, some of the substances which contaminate gas have economic value and are further processed for sale or for use in a refinery petrochemical plant. On the other hand, the gases produced within the refinery from the refinery processes are, in a sense, much more complex and often the composition cannot be predicted. Such gases contain a wider variety of useful hydrocarbons as well as higher amounts of hydrogen sulfide (from the hydrodesulfurization units). Gases such as ethane that are destined for use as petrochemical feedstocks must adhere to stringent composition controls that are dependent upon the process. For example, moisture content (ASTM D1142), oxygen content (ASTM D1945), carbon dioxide content (ASTM D1945), and sulfur content (ASTM D1072) must be monitored as they all interfere with catalyst performance in petrochemical processes.

There are many variables in treating natural gas and refinery gas. The precise area of application, of a given process is difficult to, define. Several factors must be considered: (i) the types of contaminants in the gas, (ii) the concentrations of contaminants in the gas, (iii) the degree of contaminant removal desired, (iv) the selectivity of acid gas removal required, (v) the temperature of the gas to be processed, (vi) the pressure of the gas to be processed, (vii) the volume of the gas to be processed, (viii) the composition of the gas to be processed, (ix) the carbon dioxide-hydrogen sulfide ratio in the gas, (x) the desirability of sulfur recovery due to process economics or environmental issues.

Thus, in many cases, the process complexities arise because of the need for recovery of the materials used to remove the contaminants or even recovery of the contaminants in the original, or altered, form. In any case, whatever the source of the gas, careful analysis before processing is necessary (Speight, 2013; Mokhatab et al., 2006; Speight, 2014a, 2019).

2. Types of gases

The gaseous products that occur in a refinery comprise mixtures that vary from natural gas to gases produced during refining (*refinery gas*, *process gas*) with which the tight gas might be blended prior to processing in the refinery. The constituents of each type of gas may be similar (except for the olefin-type gases produced during thermal processes) but the variations of the amounts of these constituents cover wide ranges. Thus, the gases products of a refinery are: (i) *liquefied petroleum gas*, (ii) *natural gas*, (iii) *shale gas*, and (iv) *refinery gas*, which also includes *still gas* and *process gas*. Each type of gas may be analyzed by similar methods although the presence of high boiling hydrocarbon derivatives and non-hydrocarbon derivatives such as carbon dioxide and hydrogen sulfide may require slight modifications to the various analytical test methods (Table 7.1).

However, at the onset, it is necessary that the analyst determine the type of gas to be analyzed. Mixtures of the various constituents named above are commonly encountered in material testing, and the composition varies depending upon the source and intended use of the material. Other non-hydrocarbon constituents of these mixtures are important analytes since they may be useful products or may be undesirable as a source of processing problems. Some of these components are helium, hydrogen, argon, oxygen, nitrogen, carbon monoxide, carbon dioxide, sulfur, and nitrogen containing compounds, as well as higher molecular weight hydrocarbon derivatives. In addition, raw tight gas (after it has been rendered suitable for transportation by preliminary treatment at the wellhead) may also be blended with conventional natural gas, with refinery gas, and (in some cases) with coal gas prior to processing.

Thus, it is even more important that the constituents of the gas streams are identified prior to entering the gas processing (gas refining) section of the refinery as well as after processing to remove impurities. It is at this stage that test methods are applied to ensure that the gas stream meets the specification pof the transport or the purchaser. For this reason, mention is made here of these potential gas streams. It is also essential that water be removed as soon as possible, even at the wellhead. While the presence of war itself is not such a disaster, the presence of water along with acid gases such as carbon dioxide and hydrogen sulfur can cause serious corrosion of the gas-handling equipment (Speight, 2014c).

The desired testing of these hydrocarbon mixtures (that often contain non-hydrocarbon constituents) involves (i) identification of the type of gas for component speciation and quantitation, and (ii) the influence of the composition not only on the bulk physical or chemical properties but, more important, the influence on the composition on the performance of the test method as well as the compatibility of the constituents of various gas streams when a gas stream consisting of several blended streams from different sources is sent to the gas processing section of the refinery.

TABLE 7.1 Standard test methods commonly applied to the determination of gas quality.

ASTM D1945, 2019. Standard Test Method for Analysis of Natural Gas by Gas Chromatography.
ASTM D3588, 2019. Standard Practice for Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels.
ASTM D1826, 2019. Standard Test Method for Calorific (Heating) Value of Gases in Natural Gas Range by Continuous Recording Calorimeter.
ASTM D1070, 2019. Standard Test Methods for Relative Density of Gaseous Fuels.
ASTM D4084, 2019. Standard Test Method for Analysis of Hydrogen Sulfide in Gaseous Fuels – Lead Acetate Reaction Rate Method.
ASTM 5199, 2019. Standard Test Methods for Measuring the Nominal Thickness of Geosynthetics.
ASTM D5454, 2019. Standard Test Method for Water Vapor Content in Gaseous Fuels Using Electronic Moisture Analyzer.

2.1 Shale gas

Shale gas (also called *tight gas*) is a description for a field in which natural gas accumulation is locked in tiny bubble-like pockets within layered low-permeability sedimentary rock such as shale. The terms *shale gas* and *tight gas* are often used interchangeably but there are differences — while shale gas is trapped in rock, tight gas describes natural gas that is dispersed within low-porosity silt or sand areas that create a tight-fitting environment for the gas. Typically, tight gas refers to natural gas that has migrated into a reservoir rock with high porosity but low permeability. These types of reservoirs are not usually associated with oil and commonly require horizontal drilling and hydraulic fracturing to increase well output to cost-effective levels. In general, the same drilling and completion technology that is effective with shale gas can also be used to access and extract tight gas. Shell uses proven technology in responsible ways to access this needed resource.

Shale gas is one of several types of unconventional gas resources that are currently produced (i) deep natural gas — natural gas that exists in deposits very far underground, beyond conventional drilling depths, typically 15,000 feet or more, (ii) shale gas — natural gas that occurs in low-permeability shale formations, (iii) tight natural gas — natural gas that occurs in low-permeability formations, (iv) geo-pressurized zones — natural underground formations that are under unusually high pressure for their depth, (v) coalbed methane — natural gas that occurs in conjunction with coal seams, and (vi) methane hydrates — natural gas that occurs at low temperature and high pressure regions such as the sea bed and is made up of a lattice of frozen water, which forms a *cage* around the methane.

Shale gas is natural gas produced from shale formations that typically function as both the reservoir and source rocks for the natural gas. In terms of chemical makeup, shale gas is typically a dry gas composed primarily of methane (60%—95% v/v), but some formations do produce wet gas. The Antrim and New Albany plays have typically produced water and gas. Gas shale formations are organic-rich shale formations that were previously regarded only as source rocks and seals for gas accumulating in the strata near sandstone and carbonate reservoirs of traditional onshore gas development.

Thus, by definition, *shale gas* in the hydrocarbon gas present in organic rich, fine grained, sedimentary rocks (shale and associated lithofacies). The gas is generated and stored in situ in gas shale as both adsorbed gas (on organic matter) and free gas (in fractures or pores). As such, shale containing gas is a self-sourced reservoir. Low-permeable shale requires extensive fractures (natural or induced) to produce commercial quantities of gas.

Shale is a very fine-grained sedimentary rock, which is easily breakable into thin, parallel layers. It is a very soft rock, but it does not disintegrate when it becomes wet. The shale formations can contain natural gas, usually when two thick, black shale deposits *sandwich* a thinner area of shale. Because of some of the properties of the shale deposits, the extraction of natural gas from shale formations is more difficult and perhaps more expensive than that of conventional natural gas. Shale basins are scattered across the United States.

Tight gas is a form of unconventional natural gas that is contained in a very low-permeability formation underground — usually hard rock or a sandstone or limestone formation that is unusually impermeable and non-porous (tight sand). In a conventional natural gas deposit, once drilled, the gas can usually be extracted quite readily and easily (Speight, 2019). Like shale gas reservoirs, tight gas reservoirs are generally defined as having low permeability (in many cases less than 0.1 milliDarcy (mD). Tight gas makes up a significant portion of the natural gas resource base − more than 21% v/v of the total recoverable natural gas in the United States is in tight formations and represents an extremely important portion of natural gas resources. In tight gas sands (low-porosity sandstones and carbonate reservoirs.), gas is produced through wells and the gas arose from a source outside the reservoir and migrates into the reservoir over geological time. Some *tight gas reservoirs* have also been found to be sourced by underlying coal and shale formation source rocks, as appears to be the case in the *basin-centered gas accumulations*.

Tight gas is the fastest growing natural gas resource in the United States and worldwide as a result of several recent developments. Advances in horizontal drilling technology allow a single well to pass through larger volumes of a shale gas reservoir and, thus, produce more gas. The development of hydraulic fracturing technology has also improved access to shale gas deposits. This process requires injecting large volumes of water mixed with sand and fluid chemicals into the well at high pressure to fracture the rock, increasing permeability and production rates.

To extract tight gas, a production well is drilled vertically until it reaches the shale formation, at which point the wellbore turns to follow the shale horizontally. As drilling proceeds, the portion of the well within the shale is lined with steel tubing (casing.). After drilling is completed, small explosive charges are detonated to create holes in the casing at intervals where hydraulic fracturing is to occur. In a hydraulic fracturing operation, the fracturing fluid is pumped in at a carefully controlled pressure to fracture the rock out to several hundred feet from the well. Sand mixed with the fracturing fluid acts to prop these cracks open when the fluids are subsequently pumped out. After fracturing, gas will flow into the well bore and up to the surface, where it is collected for processing and sales.

To prevent the fractures from closing when the pressure is reduced several tons of sand or other *proppant* is pumped down the well and into the pressurized portion of the hole. When the fracturing occurs millions of sand grains are forced into the fractures. If enough sand grains are trapped in the fracture, it will be propped partially open when the pressure is reduced. This provides an improved permeability for the flow of gas to the well (Chapter 5). However, extracting gas from a tight formation requires more severe extraction methods − several such methods do exist that allow natural gas to be extracted, including hydraulic fracturing and acidizing. It has been projected that shale formations and tight formations containing natural gas and crude oil with a permeability as low as one nanoDarcy may be economically productive with optimized spacing and completion of staged fractures to maximize yield with respect to cost. In any case, with all unconventional natural gas and crude oil reserves, the economic incentive must be there to encourage companies to extract this gas and oil instead of more easily obtainable, conventional natural gas and crude oil.

Chemically, shale gas is typically a dry gas composed primarily of methane (60%−95% v/v), but some formations do produce wet gas − in the United States the Antrim and New Albany plays have typically produced water and gas. Gas shale formations are organic-rich shale formations that were previously regarded only as source rocks and seals for gas accumulating in the strata near sandstone and carbonate reservoirs of traditional onshore gas development. The test methods applied to the analysis of shale gas are those same methods that are applied to the analysis on gas from typical crude oil-types reservoirs.

Similarly, but with the appropriate modifications due to the relative amounts of the hydrocarbon and non-hydrocarbon gases present, the same test methods can also be applied to coal gas, biogas, and landfill gas (Speight, 2011, 2013).

Gas production from unconventional shale gas reservoirs (such as tight shale formations) has become more common in the past decade. Produced shale gas observed to date has shown a broad variation in compositional makeup, with some having wider component ranges, a wider span of minimum and maximum heating values, and higher levels of water vapor and other substances than pipeline tariffs or purchase contracts may typically allow. Indeed, because of these variations in gas composition, each shale gas formation can have unique processing requirements for the produced shale gas to be marketable.

Ethane can be removed by cryogenic extraction while carbon dioxide can be removed through a scrubbing process. However, it is not always necessary (or practical) to process shale gas to make its composition identical to *conventional* transmission-quality gases. Instead, the gas should be interchangeable with other sources of natural gas now provided to end-users. The interchangeability of shale gas with conventional gases is crucial to its acceptability and eventual widespread use in the United States.

Although not highly sour in the usual sense of having high hydrogen sulfide content, and with considerable variation from play to resource to resource and even from well to well within the same resource (due to extremely low permeability of the shale even after fracturing), shale gas often contains varying amounts of hydrogen sulfide with wide variability in the carbon dioxide content. The gas is not ready for pipelining immediately after it has exited the shale formation.

The challenge in treating such gases is the low (or differing) hydrogen sulfide/carbon dioxide ratio and the need to meet pipeline specifications. In a traditional gas processing plant, the olamine of choice for content for hydrogen sulfide removal is N-methyldiethanolamine (MDEA) (Mokhatab et al., 2006; Speight, 2014a, 2019) but whether or not this olamine will suffice to remove the hydrogen sulfide without removal of excessive amounts of carbon dioxide is another issue.

Gas treatment may begin at the wellhead – condensates and free water usually are separated at the wellhead using mechanical separators. In this form of processing, the wellhead gas is usually separated at as high a pressure as possible, reducing compression costs when the gas is to be used for gas lift or delivered to a pipeline. After gas removal, lower molecular weight hydrocarbon derivatives and hydrogen sulfide are removed as necessary to obtain a product having a suitable vapor pressure for transport yet retaining most of the natural gasoline constituents. In addition to composition and thermal content (Btu/scf, Btu/ft^3), natural gas can also be characterized on the basis of the mode of the natural gas found in reservoirs where there is no or, at best only minimal amounts of, crude oil.

The gas, condensate and water are separated in the field separator and are directed to separate storage tanks and the gas flows to a gathering system. After the free water has been removed, the gas is still saturated with water vapor, and depending on the temperature and pressure of the gas stream, may need to be dehydrated or treated with methanol to prevent hydrates as the temperature drops. But this may not be always the case in actual practice.

2.2 Natural gas

Natural gas is the gaseous mixture associated with crude oil reservoirs and is predominantly methane, but does contain other combustible hydrocarbon compounds as well as non-hydrocarbon compounds (Mokhatab et al., 2006; Speight, 2014a, 2019). In fact, associated natural gas is believed to be the most economical form of ethane. The gas occurs in the porous rock of the crust of the Earth either alone or with accumulations of crude oil (Chapter 1). In the latter case, the gas forms the gas cap, which is the mass of gas trapped between the liquid crude oil and the impervious cap rock of the crude oil reservoir. When the pressure in the reservoir is sufficiently high, the natural gas may be dissolved in the crude oil and is released upon penetration of the reservoir as a result of drilling operations.

Natural gas (predominantly *methane*) denoted by the chemical structure CH_4 is the lowest boiling and least complex of all hydrocarbon derivatives. Natural gas from an underground reservoir, when brought to the surface, can contain other higher boiling hydrocarbon derivatives and is often referred to as *wet gas*. Wet gas is usually processed to remove the entrained hydrocarbon derivatives that are higher boiling than methane and, when isolated, the higher boiling hydrocarbon derivatives sometimes liquefy and are called *natural gas condensate*.

Natural gas is found in crude oil reservoirs as free gas (*associated gas*) or in solution with crude oil in the reservoir (*dissolved gas*) or in reservoirs that contain only gaseous constituents and no (or little) crude oil (*unassociated gas*) (Cranmore and Stanton, 2000; Speight, 2014a). The hydrocarbon content varies from mixtures of methane and ethane with very few other constituents (*dry* gas) to mixtures containing all of the hydrocarbon derivatives from methane to pentane and even hexane (C_6H_{14}) and heptane (C_7H_{16}) (*wet* gas). In both cases some carbon dioxide (CO_2) and inert gases, including helium (He), are present together with hydrogen sulfide (H_2S) and a small quantity of organic sulfur.

Other terminology that is of interest (even necessity) to understand are (i) dry gas and (ii) wet gas. There is *dry gas* or *lean gas*, which is mostly methane, and *wet gas*, which contains considerable amounts of higher molecular weight and higher-boiling hydrocarbon derivatives (Mokhatab et al., 2006; Speight, 2014a, 2019). *Sour gas* contains high proportions of much hydrogen sulfide whereas *sweet gas* contains little or no hydrogen sulfide. *Residue gas* is the gas remaining (mostly methane) after the higher molecular weight paraffins has been extracted). *Casinghead gas* is the gas derived from an oil well by extraction at the surface. Natural gas has no distinct odor and the main use is for fuel, but it can also be used to make chemicals and liquefied petroleum gas.

The term *petroleum gas(es)* in this context is also used to describe the gaseous phase and liquid phase mixtures comprised mainly of methane to butane (C_1 to C_4 hydrocarbon derivatives) that are dissolved in the crude oil and natural gas, as well gases produced during thermal processes in which the crude oil is converted to other products. It is necessary, however, to acknowledge that in addition to the hydrocarbon derivatives, gases such as carbon dioxide, hydrogen sulfide, and ammonia are also produced during crude oil refining and will be constituents of refinery gas that have to be removed. Olefins are also present in the gas streams of various processes and are not included in liquefied crude oil gas but are removed for use in petrochemical operations (Crawford et al., 1993).

Raw natural gas varies greatly in composition (Table 7.2) and the constituents can be several of a group of started hydrocarbon derivatives from methane to butane as is the case with gas from refinery processes and non-hydrocarbon derivatives (Table 7.3). The treatment required to prepare natural gas for distribution as an industrial or household fuel is specified in terms of the use and environmental regulations. Briefly, natural gas contains hydrocarbon derivatives and non-hydrocarbon gases. Hydrocarbon gases are methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butanes (C_4H_{10}), pentanes (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), and sometimes trace amounts of octane (C_8H_{18}), and higher molecular weight hydrocarbon derivatives. Some aromatics [BTX − benzene (C_6H_6), toluene ($C_6H_5CH_3$), and the xylenes ($CH_3C_6H_4CH_3$)] can also be present, raising safety issues due to their toxicity. The non-hydrocarbon gas portion of the natural gas contains nitrogen (N_2), carbon dioxide (CO_2), helium (He), hydrogen sulfide (H_2S), water vapor (H_2O), and other sulfur compounds (such as carbonyl sulfide (COS) and mercaptans (e.g., methyl mercaptan, CH_3SH) and trace amounts of other gases.

The trace gases are typically one or more of the following gases: argon, hydrogen, and helium may also be present. Generally, the hydrocarbon derivatives having a higher molecular weight than methane, carbon dioxide, and hydrogen sulfide are removed from natural gas prior to its use as a fuel. Gases produced in a refinery contain methane, ethane, ethylene,

TABLE 7.2 Composition of associated natural gas from a petroleum well.

Category	Component	Amount (%)
Paraffinic	Methane (CH_4)	70−98
	Ethane (C_2H_6)	1−10
	Propane (C_3H_8)	Trace-5
	Butane (C_4H_{10})	Trace-2
	Pentane (C_5H_{12})	Trace-1
	Hexane (C_6H_{14})	Trace-0.5
	Heptane and higher (C_7^+)	None-trace
Cyclic	Cyclopropane (C_3H_6)	Traces
	Cyclohexane (C_6H_{12})	Traces
Aromatic	Benzene (B_6H_6), others	Traces
Non-hydrocarbon	Nitrogen (N_2)	Trace-15
	Carbon dioxide (CO_2)	Trace-1
	Hydrogen sulfide (H_2S)	Trace occasionally
	Helium (He)	Trace-5
	Other sulfur and nitrogen compounds	Trace occasionally
	Water (H_2O)	Trace-5

TABLE 7.3 Possible constituents of natural gas and refinery gas.

			Density at 60 °F (15.6 °C), 1 atm	
Gas	**Molecular weight**	**Boiling point 1 atm °C (°F)**	**g/liter**	**Relative to air = 1**
Methane	16.043	-161.5 (-258.7)	0.6786	0.5547
Ethylene	28.054	-103.7 (-154.7)	1.1949	0.9768
Ethane	30.068	-88.6 (-127.5)	1.2795	1.0460
Propylene	42.081	-47.7 (-53.9)	1.8052	1.4757
Propane	44.097	-42.1 (-43.8)	1.8917	1.5464
1,2-Butadiene	54.088	10.9 (51.6)	2.3451	1.9172
1,3-Butadiene	54.088	-4.4 (24.1)	2.3491	1.9203
1-Butene	56.108	-6.3 (20.7)	2.4442	1.9981
cis-2-Butene	56.108	3.7 (38.7)	2.4543	2.0063
trans-2-Butene	56.108	0.9 (33.6)	2.4543	2.0063
iso-Butene	56.104	-6.9 (19.6)	2.4442	1.9981
n-Butane	58.124	-0.5 (31.1)	2.5320	2.0698
iso-Butane	58.124	-11.7 (10.9)	2.5268	2.0656

propylene, hydrogen, carbon monoxide, carbon dioxide, and nitrogen, with low concentrations of water vapor, oxygen, and other gases.

Carbon dioxide and hydrogen sulfide are commonly referred to as *acid gases* since they form corrosive compounds in the presence of water. Nitrogen, helium, and carbon dioxide are also referred to as *diluents* since none of these burn, and thus they have no heating value. Mercury can also be present either as a metal in vapor phase or as an organo-metallic compound in liquid fractions. Concentration levels are generally very small, but even at very small concentration levels, mercury can be detrimental due its toxicity and its corrosive properties (reaction with aluminum alloys).

A natural gas stream traditionally has high proportions of natural gas liquids (NGLs) and is referred to as rich gas. Natural gas liquids are constituents such as ethane, propane, butane, and pentanes and higher molecular weight hydrocarbon constituents. The higher molecular weight constituents (i.e., the C5+ product) are commonly referred to as natural gasoline. Rich gas will have a high heating value and a high hydrocarbon dew point (ASTM D1142, 2019). When referring to natural gas liquids in the gas stream, the term gallon per thousand cubic feet is used as a measure of high molecular weight hydrocarbon content. On the other hand, the composition of non-associated gas (sometimes called well gas) is deficient in natural gas liquids. The gas is produced from geological formations that typically do not contain much, if any, hydrocarbon liquids.

Carbon dioxide (ASTM D1945; ASTM D4984) in excess of 3% is normally removed for reasons of corrosion prevention (ASTM D1838). The first test method (ASTM D1945) is of significance for providing data for calculating physical properties of the sample, such as heating value and relative density, or for monitoring the concentrations of one or more of the components in a mixture. The method covers the determination of the chemical composition of natural gases and similar gaseous mixtures and may be abbreviated for the analysis of lean natural gases containing negligible amounts of hexane derivatives and higher hydrocarbon derivatives, or for the determination of one or more components, as required. The second test method (ASTM D4984) describes a rapid and simple field determination of carbon dioxide in natural gas pipelines. Available detector tubes provide a total measuring range of 100 ppm (parts per million) up to 60 % v/v, although the majority of applications will be on the lower end of this range (that is, under 5 % v/v). The third text method of this group (ASTM D1838) takes a different approach by the detecting the presence of components in liquefied petroleum gas which can be corrosive to copper. The copper corrosion limits provide assurance that difficulties will not be experienced in deterioration of the copper and copper-alloy fittings and connections that are commonly used in many types of utilization, storage, and transportation equipment.

Hydrogen sulfide (ASTM D2420; ASTM D4084; ASTM D4810) is also removed and the odor of the gas must not be objectionable (ASTM D6273) so mercaptan content (ASTM D1988) is important. A simple lead acetate test (ASTM D2420; ASTM D4084) is available for detecting the presence of hydrogen sulfide and is an additional safeguard that hydrogen sulfide is not present (ASTM D1835). This test method covers the specification for liquefied petroleum gas consisting of propane, propylene (propene), butane, and mixtures of these gases. The method is especially important when the products are intended for use as domestic, commercial and industrial heating, and engine fuels. However, care must be taken to in sampling of the liquefied gases for test results to be reliable and significant (Chapter 5). All four types of liquefied petroleum gas covered by this specification should conform to the specified requirements for vapor pressure, volatile residue, residue matter, relative density, and corrosion.

Many sources of natural and crude oil gases contain sulfur compounds that are odorous, corrosive, and poisonous to catalysts used in gaseous fuel processing. In fact, sulfur odorants are added (in the ppm range, i.e., 1–4 ppm v/v) to natural gas and liquefied petroleum gas for safety purposes. Some odorants are unstable and react to form compounds having lower odor thresholds. Quantitative analysis of these odorized gases ensures that odorant injection equipment is performing to specification. However, mercaptan derivatives, if present in a gas stream, may only produces a transitory yellow stain on the lead acetate paper that fades completely in less than 5 min (ASTM D2420; ASTM D4084). In the lead acetate test (ASTM D2420), the vaporized gas is passed over moist lead acetate paper under controlled conditions. Hydrogen sulfide reacts with lead acetate to form lead sulfide resulting in a stain on the paper varying in color from yellow to black, depending on the amount of hydrogen sulfide present. Other pollutants can be determined by gas chromatography (ASTM D5504; ASTM D6228).

The first test method (ASTM D5504), although not intended for application to gases other than natural gas and related fuels, this test method has been successfully applied to fuel type gases including refinery, landfill, cogeneration, and sewage digester gas. Refinery, landfill, sewage digester and other related fuel type gases inherently contain volatile sulfur compounds that are subject to federal, state, or local control. The methane fraction of these fuel type gases are occasionally sold to distributors of natural gas. For these reasons, both regulatory agencies and production and distribution facilities may require the accurate determination of sulfur to satisfy regulatory, production or distribution requirements. Fuel gases are also used in energy production or are converted to new products using catalysts that are poisoned by excessive sulfur in the feed gas. As a refresher note, gas chromatography is commonly used in the determination of fixed gas and organic composition of natural gas ASTM D1945). Other standard test methods for the analysis of sulfur in fuel gases include test methods for total sulfur content and standard test methods for hydrogen sulfide content ASTM D4468).

The second test method (ASTM D6228) describes a technique to determine individual sulfur species in gaseous fuel and the total sulfur content by calculation. Gas chromatography is used commonly and extensively to determine other components in gaseous fuels including fixed gas and organic components (ASTM D1945). This test method dictates the use of a specific GC technique with one of the more common detectors for measurement. The test method covers the determination of individual volatile sulfur-containing compounds in gaseous fuels by gas chromatography (GC) with a flame photometric detector (FPD) or a pulsed flame photometric detector (PFPD). The detection range for sulfur compounds is from 20 to 20 000 pg (pg) of sulfur (1 pg = 1×10^{-12} g = 0.001 ng).

This test method (ASTM D1142) covers the determination of the water vapor content of gaseous fuels by measurement of the dew-point temperature and the calculation therefrom of the water vapor content. The method is of considerable importance when it is necessary (on a contract basis) for application to the pipeline transmission of natural gas contain specifications limiting the maximum concentration of water vapor allowed. Excess water vapor can cause corrosive conditions, degrading pipelines and equipment and, in addition, the water can also condense and freeze or form methane hydrates causing blockages. Water-vapor content also affects the heating value of natural gas, thus influencing the quality of the gas. Since dew point can be calculated from composition, direct determination of dew point for a liquefied petroleum gas sample is a measure of composition. It is, of course, of more direct practical value and if there are small quantities of higher molecular weight material present, it is preferable to use a direct measurement.

The hydrocarbon dew point is reduced to such a level that retrograde condensation, *i.e.* condensation resulting from pressure drop, cannot occur under the worst conditions likely to be experienced in the gas transmission system. Similarly, the water dew point is reduced to a level sufficient to preclude formation of C_1 to C_4 hydrates in the system. The natural gas after appropriate treatment for acid gas reduction, odorization, and hydrocarbon and moisture dew point adjustment (ASTM D1142), would then be sold within prescribed limits of pressure, calorific value and possibly Wobbe Index (also called the Wobbe number, Wo) which is cv/√(sp. gr.). where cv is the calorific value and sp.gr. is the specific gravity.

2.3 Refinery gas

The terms *refinery gas* or *petroleum gas* are often used to identify liquefied petroleum gas or even gas that emanates as *light ends* (gases and volatile liquids) from the atmospheric distillation unit or from any one of several other refinery processes. For the purpose of this text, refinery gas not only describes liquefied petroleum gas but also natural gas and refinery gas (Parkash, 2003; Mokhatab et al., 2006; Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017). In this chapter, each gas is, in turn, and referenced by its name rather than the generic term *petroleum gas*. However, the composition of each gas varies and recognition of this is essential before the relevant testing protocols are selected and applied. Thus, refinery gas (fuel gas) is the non-condensable gas that is obtained during distillation of crude oil or treatment (cracking, thermal decomposition) of crude oil (Robinson and Faulkner, 2000; Parkash, 2003; Pandey et al., 2004; Gary et al., 2007; Speight, 2014a, 2017; Hsu and Robinson, 2017).

Refinery gas is produced in considerable quantities during the different refining processes and is used as fuel for the refinery itself and as an important feedstock for the production of petrochemicals. It consists mainly of hydrogen (H_2), methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), and olefins ($RCH = CHR^1$, where R and R^1 can be hydrogen or a methyl group) and may also include off-gases from petrochemical processes (Parkash, 2003; Pandey et al., 2004; Gary et al., 2007; Speight, 2014a, 2017; Hsu and Robinson, 2017). Olefins such as ethylene ($CH_2{=}CH_2$, boiling point: 104 °C, -155 °F), propene (propylene, $CH_3CH{=}CH_2$, boiling point: 47 °C, -53 °F), butene (butene-1, $CH_3CH_2CH = CH_2$, boiling point: 5 °C, 23 °F) *iso*-butylene ($(CH_3)_2C = CH_2$, -6 °C, 21 °F), *cis-* and *trans*-butene-2 ($CH_3CH{=}CHCH_3$, boiling point: ca. 1 °C, 30 °F) and butadiene ($CH_2{=}CHCH{=}CH_2$, boiling point: 4 °C, 24 °F) as well as higher boiling olefins are produced by various refining processes.

Still gas is broad terminology for low-boiling hydrocarbon mixtures and is the lowest boiling fraction isolated from a distillation (*still*) unit in the refinery (Speight, 2014a, 2017). If the distillation unit is separating low-boiling hydrocarbon fractions, the still gas will be almost entirely methane with only traces of ethane (CH_3CH_3) and ethylene ($CH_2{=}CH_2$). If the distillation unit is handling higher boiling fractions, the still gas might also contain propane ($CH_3CH_2CH_3$), butane ($CH_3CH_2CH_2CH_3$) and their respective isomers. *Fuel gas* and still gas are terms that are often used interchangeably but the term *fuel gas* is intended to denote the destination of the product which is to be used as a fuel for boilers, furnaces, or heaters.

A group of refining operations that contributes to gas production are the thermal cracking and catalytic cracking processes. The thermal cracking processes (such as the coking processes) produce a variety of gases, some of which may contain olefin derivatives ($>C{=}C<$). In the visbreaking process, fuel oil is passed through externally fired tubes and undergoes liquid phase cracking reactions, which result in the formation of lower-boiling fuel oil components. Substantial quantities of both gas and carbon are also formed in coking (both fluid coking and delayed coking) in addition to the middle distillate and naphtha. When coking a residual fuel oil or heavy gas oil, the feedstock is preheated and contacted with hot carbon (coke) which causes extensive cracking of the feedstock constituents of higher molecular weight to produce lower molecular weight products ranging from methane, via liquefied petroleum gas (es) and naphtha, to gas oil and heating oil. Products from coking processes tend to be unsaturated and olefin-type components predominate in the tail gases from coking processes.

The various catalytic cracking processes, in which higher boiling gas oil fractions are converted into gaseous products, various naphtha fractions, fuel oil, and coke by contacting the feedstock with the hot catalyst. Thus, both catalytic and thermal cracking processes, the latter being now largely used to produce chemical raw materials, result in the formation of unsaturated hydrocarbon derivatives, particularly ethylene ($CH_2{=}CH_2$), but also propylene (propene, $CH_3CH{=}CH_2$), isobutylene [isobutene, $(CH_3)_2C = CH_2$] and the n-butenes ($CH_3CH_2CH = CH_2$, and $CH_3CH{=}CHCH_3$) in addition to hydrogen (H_2), methane (CH_4) and smaller quantities of ethane (CH_3CH_3), propane ($CH_3CH_2CH_3$), and butane isomers [$CH_3CH_2CH_2CH_3$, $(CH_3)_3CH$]. Diolefins such as butadiene ($CH_2{=}CHCH{=}CH_2$) and are also present.

In a series of reforming processes, distillation fractions which include paraffin derivatives, and naphthene derivatives (cyclic non-aromatic) are treated in the presence of hydrogen and a catalyst to produce lower molecular weight products or are isomerized to more highly branched hydrocarbon derivatives. Also, the catalytic reforming process not only results in the formation of a liquid product of higher octane number but also produce substantial quantities of gaseous products. The composition of these gases varies in accordance with process severity and the properties of the feedstock. The gaseous products are not only rich in hydrogen but also contain hydrocarbon derivatives from methane to butane derivatives, with a preponderance of propane ($CH_3CH_2CH_3$), n-butane ($CH_3CH_2CH_2CH_3$) and isobutane [$(CH_3)_3CH$]. Since all catalytic reforming processes require substantial recycling of a hydrogen stream, it is normal to separate reformer gas into a propane ($CH_3CH_2CH_3$) and/or a butane [$CH_3CH_2CH_2CH_3/(CH_3)_3CH$] stream, which becomes part of the refinery liquefied petroleum gas production, and a lower-boiling gaseous fraction, part of which is recycled.

A further source of refinery gas is produced by the hydrocracking process which is a high-pressure pyrolysis process carried out in the presence of fresh and recycled hydrogen. The feedstock is again heavy gas oil or residual fuel oil, and the process is mainly directed at the production of additional middle distillates and gasoline. Since hydrogen is to be recycled, the gases produced in this process again must be separated into lower-boiling and higher-boiling streams. Any surplus recycle gas stream and the liquefied petroleum gas from the hydrocracking process are both saturated.

Both hydrocracker and catalytic reformer tail gases are commonly used in catalytic desulfurization processes (Speight, 2014a, 2017). In the latter, feedstocks ranging from low-boiling naphtha to vacuum gas oil are passed at pressures on the order of 500−1000 psi with hydrogen over a hydrofining catalyst. This results mainly in the conversion of organic sulfur compounds to hydrogen sulfide:

$$[S]_{\text{feedstock}} + H_2 \rightarrow H_2S + \text{hydrocarbon derivatives}$$

The process also has the potential to produce lower-boiling hydrocarbon derivatives by hydrocracking.

Refinery gas, usually in more than one stream, are typically treated for hydrogen sulfide removal and gas sales are usually on a thermal content (calorific value, heating value) basis with some adjustment for variation in the calorific value and hydrocarbon type (Canmore and Stanton, 2000; Speight, 2014a).

2.4 Coal gas

Gases of high calorific value are obtained by low-temperature or medium-temperature carbonization of coal. The composition of coal gas also changes during the course of carbonization at a given temperature and secondary reactions of the volatile products are important in determining gas composition (Speight, 2013).

The standard test methods for coal gas are instrumental in the testing and chemical analysis of natural gas, and other gaseous fuels (ASTM, 2019). These standards also include the thermophysical property tables for methane, ethane, propane, normal butane, and isobutane and the test methods also allow laboratories and other chemical facilities to examine and assess these fuels to ensure safe handling and use.

With the onset of renewable energy programs, it would be remiss not to mention prominent gases produced from biomass and waste materials, viz: biogas and landfill gas. Both types of gas contain methane and carbon dioxide as well as various other constituents and are often amenable to application of the testing method that are applied to natural gas.

3. Properties of gas streams

The characterization of natural gas depends on the characterization and properties of pure hydrocarbon derivatives. Calculation of the properties of a mixture depends on the properties of its constituents. However, calculation of the property of a mixture based on an average calculation neglects any interactions between the constituents.

In this chapter, first basic parameters and properties of pure compounds are defined. These properties are either temperature-independent or values of some basic properties at a fixed temperature.

However, the composition of natural gas is not universally constant, as it is normally drawn from several production fields. Variations in the composition of gas delivered by pipelines can be caused by: (i) variations in the proportion of the contribution from various sources at a given supply location, and (ii) time variations within a given supply source. These variations involve mainly the composition of the hydrocarbon mix and are not regulated by the general-purpose pipeline gas standards beyond keeping within the limits of the heating value and the Wobbe Index. For example, variations in composition across the United States could produce variations of 14% in heating value, 14% in density, 20% in Wobbe Index and 25% in stoichiometric air-fuel ratio. Thus, the composition of natural gas from a particular source or at a particular location can also vary over time which can cause difficulties in resolving the data from the application of standard test methods (Klimstra, 1978; Liss and Thrasher, 1992).

The actual composition of natural gas depends primarily on the production field from which it is extracted and limited variations in composition must therefore be accepted. Worldwide there are major differences in natural gas quality specifications. These specifications are mainly intended to meet pipeline requirements and the needs of industrial and domestic consumers. The gas quality specifications are based on gas composition and other properties that are determined by application of a series of standard test methods to the gas. Changes in gas quality can be used to ensure better gas industry operational efficiencies, but quality standards must take into account the impact on end-use gas-fired equipment performance. Some common gas quality parameters include (i) water content, (ii) hydrocarbon dewpoint, below which the gas will begin to condense, (iii) sulfur content, and (iv) the Wobbe Index, also called the Wobbe Number.

Natural gas is mainly used or burned in combustion processes but is also an important feedstock in chemicals production. Combustion is a complex chemical and physical phenomenon. The chemical energy contained within the fuel is released producing heat and light, and the fuel is converted to more stable products. To ensure that different natural gases behave similarly in combustion systems they must have similar combustion parameters (for example calorific value, Wobbe Index, and relative density). Gas quality is known to have an impact on combustion operation and efficiency, and systems are optimized to use one particular composition of the gas. If the gas quality changes, the system performance may deteriorate. Interchangeability of gases is achieved if combustion is not materially changed when one natural gas is substituted for another, particularly with regard to safety, efficiency and emissions).

There are two major technical aspects to which gas quality relates: (i) the pipeline specification in which stringent specifications for water content and hydrocarbon dewpoint are stated along with limits for contaminants such as sulfur − the objective is to ensure pipeline material integrity for reliable gas transportation purpose, and (ii) the interchangeability specification which may include analytical data such as calorific value and relative density which are specified to ensure satisfactory performance of end-use equipment.

Gas interchangeability is a subset of the gas quality specification ensuring that gas supplied to domestic users will combust safely and efficiently. The Wobbe number (Section 2.2.11) is a common, but not universal, measure of interchangeability and is used to compare the rate of combustion energy output of different composition fuel gases in combustion equipment. For two fuels with identical Wobbe Indices, the energy output will be the same for given pressure and valve settings.

Finally, in terms of properties (and any test methods that are applied to natural gas), it is necessary to recognize the other constituents of a natural gas stream that is produced from a reservoir. Thus, natural gas liquids are products other than methane from natural gas: ethane, butane, *iso*-butane, and propane. Natural gasoline may also be included in this group.

Natural gas liquids are, in fact, separate and distinct hydrocarbon derivatives contained within some streams of natural gas. Streams that contain commercial quantities of natural gas liquids are called *wet gas* and those with little or no liquids present are known as *dry gas* (see above). Chemical manufacturers use ethane in making *ethylene*, an important petrochemical. Butane and propane, and mixtures of the two, are classified as liquefied petroleum gas (LPG) that is used chiefly as a heating fuel in industry and homes. Pentane, hexane, and heptane are collectively referred to as *gas condensate* (*natural gasoline*, *casinghead gasoline*, *natural gas gasoline*). However, at high pressures, such as those existing in the deeper fields, the density of the gas increases and the density of the oil decreases until they form a single phase in the reservoir.

Wet natural gas contains natural gasoline in vapor form. The wet gas, also known as *casinghead gas*, is chiefly a mixture of methane, ethane, and the volatile hydrocarbon derivatives propane, butane, pentane (C_5H_{12}), hexane (C_6H_{14}), and heptane (C_7H_{16}). The latter three hydrocarbon derivatives form the main constituents of natural gasoline, which is re-covered in refineries in liquid form mainly by absorption or compression processes. Pentane, hexane, and heptane are liquids under normal atmospheric conditions and are the chief components of ordinary refinery gasoline. Natural gasoline is used as blending stock for refinery gasoline and may be *cracked* to produce lower boiling products, such as ethylene, propylene and butylene. Caution should be taken not to confuse *natural gasoline* with *straight-run gasoline* (often also incorrectly referred to as natural gasoline), which is the gasoline distilled unchanged from crude oil. The various tests that are applied to specifications for this group of low boiling liquids will be referenced in the chapters dealing with liquefied petroleum gas and gas condensate (Chapter ? Chapter ?).

It is therefore essential that the type of gas be identified and, it is even more essential that gas has received some form (at least a preliminary from) of separation (from gas liquids and gas condensate) so that the appropriate test can be applied to determination of the properties and behavior of the gas.

3.1 Chemical properties

Natural gas (predominantly *methane*) denoted by the chemical structure CH_4 is the lowest boiling and least complex of all hydrocarbon derivatives. Natural gas from an underground reservoir, when brought to the surface, can contain other higher boiling hydrocarbon derivatives and is often referred to as *wet gas*. Wet gas is usually processed to remove the entrained hydrocarbon derivatives that are higher boiling than methane and, when isolated, the higher boiling hydrocarbon derivatives sometimes liquefy and are called *natural gas condensate*.

Natural gas is found in crude oil reservoirs as free gas (*associated gas*) or in solution with crude oil in the reservoir (*dissolved gas*) or in reservoirs that contain only gaseous constituents and no (or little) crude oil (*unassociated gas*) (Cranmore and Stanton, 2000; Speight, 2014a). The hydrocarbon content varies from mixtures of methane and ethane with very few other constituents (*dry* gas) to mixtures containing all of the hydrocarbon derivatives from methane to pentane and even hexane (C_6H_{14}) and heptane (C_7H_{16}) (*wet* gas). In both cases some carbon dioxide (CO_2) and inert gases, including helium (He), are present together with hydrogen sulfide (H_2S) and a small quantity of organic sulfur.

The term *petroleum gas(es)* in this context is also used to describe the gaseous phase and liquid phase mixtures comprised mainly of methane to butane (C_1 to C_4 hydrocarbon derivatives) that are dissolved in the crude oil and natural gas, as well gases produced during thermal processes in which the crude oil is converted to other products. It is necessary, however, to acknowledge that in addition to the hydrocarbon derivatives, gases such as carbon dioxide, hydrogen sulfide, and ammonia are also produced during crude oil refining and will be constituents of refinery gas that must be removed. Olefins are also present in the gas streams of various processes and are not included in liquefied petroleum gas but are removed for use in petrochemical operations (Crawford et al., 1993).

Raw natural gas varies greatly in composition and the constituents can be several of a group of saturated hydrocarbon derivatives from methane to butane (Table 7.2) and non-hydrocarbon derivatives. The treatment required to prepare natural gas for distribution as an industrial or household fuel is specified in terms of the use and environmental regulations.

Briefly, natural gas contains hydrocarbon derivatives and non-hydrocarbon gases. Hydrocarbon gases are methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butanes (C_4H_{10}), pentanes (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), and sometimes trace amounts of octane (C_8H_{18}), and higher molecular weight hydrocarbon derivatives. Some aromatics [BTX − benzene (C_6H_6), toluene ($C_6H_5CH_3$), and the xylenes ($CH_3C_6H_4CH_3$)] can also be present, raising safety issues due to their toxicity. The non-hydrocarbon gas portion of the natural gas contains nitrogen (N_2), carbon dioxide (CO_2), helium (He), hydrogen sulfide (H_2S), water vapor (H_2O), and other sulfur compounds (such as carbonyl sulfide (COS) and mercaptans (e.g., methyl mercaptan, CH_3SH) and trace amounts of other gases. Carbon dioxide and hydrogen sulfide are commonly referred to as *acid gases* since they form corrosive compounds in the presence of water. Nitrogen, helium, and carbon dioxide are also referred to as *diluents* since none of these burn, and thus they have no heating value. Mercury can also be present either as a metal in vapor phase or as an organo-metallic compound in liquid fractions. Concentration levels are generally very small, but even at very small concentration levels, mercury can be detrimental due its toxicity and its corrosive properties (reaction with aluminum alloys).

A natural gas stream traditionally has high proportions of natural gas liquids (NGLs) and is referred to as rich gas. Natural gas liquids are constituents such as ethane, propane, butane, and pentanes and higher molecular weight hydrocarbon constituents. The higher molecular weight constituents (i.e., the C5+ product) are commonly referred to as natural gasoline. Rich gas will have a high heating value and a high hydrocarbon dew point. When referring to natural gas liquids in the gas stream, the term gallon per thousand cubic feet is used as a measure of high molecular weight hydrocarbon content. On the other hand, the composition of non-associated gas (sometimes called well gas) is deficient in natural gas liquids. The gas is produced from geological formations that typically do not contain much, if any, hydrocarbon liquids.

Non-associated natural gas, which is found in reservoirs in which there is no, or at best only minimal amounts of, crude oil (Chapter 1). Non-associated gas is usually richer in methane but is markedly leaner in terms of the higher molecular weight hydrocarbon derivatives and condensate. Conversely there is also *associated* natural gas (*dissolved* natural gas) that occurs either as free gas or as gas in solution in the crude oil. Gas that occurs as a solution with the crude oil is *dissolved gas*, whereas the gas that exists in contact with the crude oil (*gas cap*) is *associated gas* (Chapter 1) Associated gas is usually leaner in methane than the non-associated gas but is richer in the higher molecular weight constituents.

The most preferred type of natural gas is the non-associated gas. Such gas can be produced at high pressure, whereas associated, or dissolved, gas must be separated from crude oil at lower separator pressures, which usually involves increased expenditure for compression.

Thus, it is not surprising that such gas (under conditions that are not economically favorable) is often flared or vented.

Typically, natural gas samples are analyzed for molecular composition by gas chromatography and for stable isotopic composition by isotope ratio mass spectrometry. Carbon isotopic composition was determined for methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and butane, particularly iso-butane (C_4H_{10}) (ASTM D1945). Carbon dioxide (ASTM D1945; ASTM D4984) more than 3% is normally removed for reasons of corrosion prevention (ASTM D1838). Hydrogen sulfide (ASTM D2420; ASTM D4084; ASTM D4810) is also removed and the odor of the gas must not be objectionable (ASTM D6273) so mercaptan content (ASTM D1988) is important. A simple lead acetate test (ASTM D2420; ASTM D4084) is available for detecting the presence of hydrogen sulfide and is an additional safeguard that hydrogen sulfide is not present (ASTM D1835). The odor of the gases must not be objectionable. Methyl mercaptan, if present, produces a transitory yellow stain on the lead acetate paper that fades completely in less than 5 min. Other sulfur compounds (ASTM D5504; ASTM D6228) present in liquefied petroleum gas do not interfere.

In the lead acetate test (ASTM D2420), the vaporized gas is passed over moist lead acetate paper under controlled conditions. Hydrogen sulfide reacts with lead acetate to form lead sulfide resulting in a stain on the paper varying in color from yellow to black, depending on the amount of hydrogen sulfide present. Other pollutants can be determined by gas chromatography (ASTM D5504; ASTM D6228). The total sulfur content (ASTM D1072; ASTM D2784) is normally acceptably low, and frequently so low that it needs augmenting by means of alkyl sulfide derivatives, mercaptan derivatives or thiophene derivatives to maintain an acceptable safe level of odor. The relevant test method (ASTM D1072) is used for the determination of total sulfur in combustible fuel gases and is applicable to natural gases, manufactured gases, mixed gases, and other miscellaneous gaseous fuels. The method is particularly applicable for the determination of total sulfur in combustible fuel gases, when present in sulfur concentrations between approximately 25 and 700 mg/m^3.

Another important property of the gas streams discussed in this text is the hydrocarbon dew point. The hydrocarbon dew point is reduced to such a level that retrograde condensation, *i.e.* condensation resulting from pressure drop, cannot occur under the worst conditions likely to be experienced in the gas transmission system. Similarly, the water dew point is reduced to a level sufficient to preclude formation of C_1 to C_4 hydrates in the system. Generally, pipeline owners prefer that the specifications for the transmission of natural gas limit the maximum concentration of water vapor allowed. Excess water vapor can cause corrosive conditions, degrading pipelines and equipment. The water can also condense and freeze or form methane hydrates (Chapter 8) causing blockages. Water—vapor content also affects the heating value of natural gas, thus influencing the quality of the gas.

One relevant text method (ASTM D1142) This test method permits the determination of water content of natural gas. The method covers the determination of the water vapor content of gaseous fuels by measurement of the dew-point temperature and the calculation therefrom of the water vapor content. However, if the dew point of the condensable hydrocarbon derivatives is higher than the water vapor dew point, when such hydrocarbon derivatives are present in large amounts, they may interfere with the performance of the test method.

Liquefied petroleum gas, natural gas, and refinery gas are mixtures of products or naturally occurring materials and, fortunately are relatively simple mixtures and do not suffer

TABLE 7.4 Number of isomers for the selected hydrocarbons.

Carbon atoms	Number of isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
15	4347
20	366,319
25	36,797,588
30	4,111,846,763
40	62,491,178,805,831

the complexities of the isomeric variations of the higher molecular weight hydrocarbon derivatives (Table 7.4) (Drews, 1998; Speight, 2014a). Thus, because of the lower molecular weight constituents of these gases and their volatility, gas chromatography has been the technique of choice for fixed gas and hydrocarbon speciation and mass spectrometry is also a method of choice for compositional analysis of low molecular weight hydrocarbon derivatives (ASTM D2421; ASTM D2650).

Test method ASTM D2421 describes the procedure for the interconversion of the analysis of C_5 and lower molecular weight hydrocarbon mixtures to gas-volume (mole), liquid-volume, or mass basis. For custody transfer and other purposes, it is frequently necessary to convert a component analysis of a low-boiling hydrocarbon mixture from one basis (either gas volume, liquid volume, or mass) to another. The component distribution data of low-boiling hydrocarbon mixtures can be used to calculate physical properties such as relative density, vapor-pressure, and calorific value. More recently, piggy-back methods (such as gas chromatography/mass spectrometry and other double technique methods) have been developed for the identification of gaseous and low boiling liquid constituents of mixtures. The hydrocarbon composition is limited to set to the total amount of ethane, butane, or pentane as well as ethylene and total dienes.

By limiting the number of hydrocarbon derivatives that are lower boiling than the main component, the vapor pressure control is reinforced. The limitation on the amount of higher boiling hydrocarbon derivatives supports the volatility clause. The vapor pressure and volatility specifications will often be met automatically if the hydrocarbon composition is correct. Information on the vapor pressures of liquefied petroleum gas products is pertinent to selection of properly designed storage vessels, shipping containers, and customer utilization equipment to ensure safe handling of these products.

The determination of the vapor pressure of liquefied petroleum gas is important for safety reasons to ensure that the maximum operating design pressures of storage, handling, and fuel systems will not be exceeded under normal operating temperature conditions. For liquefied petroleum gas, vapor pressure is an indirect measure of the most extreme low temperature conditions under which initial vaporization can be expected to occur. It can be considered a semi-quantitative measure of the amount of the most volatile material present in the product. On test method (ASTM D1267) 113 °F) covers the determination of the gauge vapor pressures of liquefied petroleum gas products at temperatures of 37.8 °C (100 °F) up to and including a test temperature of 70 °C (158 °F).

The amount of ethylene in a gas stream is limited because it is necessary to restrict the number of unsaturated components to avoid the formation of deposits caused by the polymerization of the olefin constituents. In addition, ethylene (boiling point: 104 °C, -155 °F) is more volatile than ethane (boiling point: 88 °C, -127 °F) and therefore a product with a substantial proportion of ethylene will have a higher vapor pressure and volatility than one that is predominantly ethane. Butadiene is also undesirable because it may also produce polymeric products that form deposits and cause blockage of lines.

Currently the preferred method for the analysis of liquefied petroleum gas, and indeed for most crude oil-related gases, is gas chromatography (ASTM D2163). This test method covers the quantitative determination of individual hydrocarbon derivatives in liquefied petroleum gas and mixtures of propane and propene, excluding high-purity propene in the range of C_1 to C_5. Component concentrations are determined in the range of 0.01−100 vol percent. This method can be used for the identification and measurement of both main constituents and trace constituents. However, the method does not fully determine hydrocarbon derivatives higher molecular weight than C_5 and non-hydrocarbon constituents, and additional tests may be necessary to fully characterize a liquefied petroleum gas sample Thus, there may be some accuracy issues that arise in the measurement of the higher boiling constituents due to relative volatility under the conditions in which the sample is held.

Capillary column gas chromatography is an even quicker and equally accurate alternative. Mass spectrometry is also suitable for analysis of crude oil gases. Of the other spectroscopic techniques, infrared and ultra-violet absorption may be applied to crude oil gas analysis for some specialized applications. Gas chromatography has also largely supplanted chemical absorption methods of analysis but again these may have some limited specialized application. Once the composition of a mixture has been determined it is possible to calculate various properties such as specific gravity, vapor pressure, calorific value and dew point.

Simple evaporation tests in conjunction with vapor pressure measurement give a further guide to composition. In these tests, a liquefied petroleum gas sample is allowed to evaporate naturally from an open graduated vessel. Results are recorded based on volume/temperature changes, such as the temperature recorded when 95% v/v has evaporated, or volume left at a particular temperature (ASTM D1837). This test method is a measure of the relative purity of the various types of liquefied petroleum gas and is a benefit in the assurance of volatility performance. The test results, when properly related to vapor pressure and density of the product, can be used to indicate the presence of butane and higher molecular weight constituents in propane-type liquefied petroleum gas, and pentane and higher molecular weight constituents in propane/butane-type fuel gases as well as in butane-type fuel gases. The presence of hydrocarbon compounds less volatile than those of which the liquefied petroleum gas is primarily composed is indicated by an increase in the 95% v/v evaporated temperature. When the type and concentration of higher boiling components is required, chromatographic analysis should be used.

Specific gravity again can be calculated, but if it is necessary to measure it several pieces of apparatus are available. For determining the density or specific gravity of liquefied petroleum gas in its liquid state there are two methods, using a metal pressure pycnometer. A pressure hydrometer may be used (ASTM D1267) for the relative density that may also be calculated from compositional analysis (ASTM D2598). Various procedures, manual and recording, for specific gravity or density in the gaseous state are given in two methods (ASTM D1070). Calculation of the density is also possible using any one of four models, depending upon the composition of the gas (ASTM D4784).

The hydrocarbon composition of natural gasoline (although not specifically a gas) for petrochemical use must undergo a compositional analysis (ASTM D2427) and a test for total sulfur (ASTM D1266). An issue that arises during the characterization of liquefied petroleum gas relates to the accurate determination of heavy residues (i.e., higher molecular weight hydrocarbon derivatives and even oils) in the gas. Test methods using procedures similar to those employed in gas chromatographic simulated distillation are becoming available. In fact, the presence of any component substantially less volatile than the main constituents of the liquefied petroleum gas will give rise to unsatisfactory performance. It is difficult to set limits to the amount and nature of the *residue* which will make a product unsatisfactory. Obviously small amounts of oil-like material can block regulators and valves. In liquid vaporizer feed systems, even gasoline type material can cause difficulty. The residue as determined by the *end point index* (EPI) (ASTM D2158) is a measure of the concentration of contaminants boiling above 37.8 °C (100 °F) that may be present in the gas. Other methods are available which measure residue more directly and for particular applications it may be possible to relate the values obtained to the performance required and so set satisfactory limits.

Analytical methods are available in standard form for determining volatile sulfur content and certain specific corrosive sulfur compounds that are likely to be present. Volatile sulfur determination is made by a combustion procedure (ASTM D1266) that uses a modification of the standard wick-fed lamp. Many laboratories use rapid combustion techniques with an oxy-hydrogen flame in a Wickbold or Martin-Floret burner (ASTM D2784).

The first test method (ASTM D1266), provides a method for monitoring the sulfur level of various crude oil products and additives. The test method covers the determination of total sulfur in liquid crude oil products in concentrations from 0.01% to 0.4% w/w. The direct burning procedure described in the test method is applicable to the analysis of such materials as naphtha, gasoline, kerosene, and other liquids that can be burned completely in a wick lamp. The blending procedure is applicable to the analysis of gas oils and distillate fuel oils, high-sulfur content crude oil products, and many other materials that cannot be burned satisfactorily by the direct burning procedure. Phosphorus compounds normally present in commercial gasoline do not interfere. A correction is given for the small amount of acid resulting from the combustion of the lead anti-knock fluids in gasolines. Appreciable concentrations of acid-forming or base-forming elements from other sources interfere when the titration procedure is employed since no correction is provided in these cases.

A special sulfate analysis procedure is also described in the test that permits the determination of sulfur in concentrations as low as 5 mg/kg. The data can be used to predict performance, handling, or processing properties. In some cases, the presence of sulfur components is beneficial to the product and monitoring the depletion of sulfur compounds provides useful information. In other cases, the presence of sulfur compounds is detrimental to the processing or use of the product.

The comparable lamp method for the determination of sulfur in liquefied petroleum gas (ASTM D2784) is also suitable for the determination of sulfur. For the determination of sulfur in higher-boiling crude oil products that cannot be burned in a lamp, alternate standard test methods are available. This test method (ASTM D2784) is valid for sulfur levels on the order of >1 μg/g of sulfur in liquefied petroleum gas but the samples should not contain more than 100 μg/g of chlorine. In the test, the sample is bummed in an oxy-hydrogen bummer or in a lamp in a closed system in a carbon dioxide-oxygen atmosphere. The latter is not recommended for trace quantities of sulfur due to inordinately long combustion times needed. The sulfur oxides produced are absorbed and oxidized to sulfuric acid in a hydrogen peroxide solution. The sulfate ions are then determined by either titrating with barium perchlorate solution using a Thorin methylene blue mixed indicator, or by precipitating as barium sulfate and measuring the turbidity of the precipitate with a photometer.

Trace hydrocarbon derivatives that may be regarded as contaminants may be determined by the gas chromatographic methods already discussed. Higher molecular weight hydrocarbon derivatives in small amounts may not be completely removed from the column. If accurate information is required related to the nature and amount of higher-boiling constitunets, the temperature programming or a concentration procedure may be used.

Analytical methods for determining traces of various other impurities, such as chlorides (ASTM D2384) are known to be in use. Such information is valuable in cases where chloride is deleterious in the use of this product; also, chloride contributes to corrosion problems in processing units in instances where further processing of this material is involved. The presence of acetylene derivatives in refinery gases, although unlikely, must still be considered. Acetylene derivatives can be determined using a chemical test method while carbonyls are determined by the classical hydroxylamine hydrochloride reaction.

The determination of traces of higher boiling hydrocarbon derivatives and oily matter involves use of a method for residue that involves a preliminary weathering. The residue after weathering is dissolved in a solvent and the solution applied to a filter paper. The presence of residue is indicated by the formation of an oil stain. The procedure is taken further by combining the oil stain observation with other observed values to calculate an End Point Index (ASTM D2158). The method is not very precise, and work is proceeding in several laboratories to develop a better method for the determination of residue in the form of oily matter.

The odor of liquefied petroleum gas has to be detectable to avoid the risk of explosion. Odor is a very subjective matter and no standard method is available. It is desirable to set up some system in which the concentration of gas can be measured in relation to its explosive limits and in which some variables can be standardized, e.g. flow-rate and orifice size. This will ensure that in any one location the liquefied petroleum gas is always being assessed under similar conditions from day to day.

Propane, iso-butane (boiling point: 12 °C, 11 °F), and butane generally constitute this sample type and are used for heating, motor fuels, and as chemical feedstocks (ASTM D2504; ASTM D2505; ASTM D2597). Test method ASTM D2597 covers the analysis of demethanized liquid hydrocarbon streams containing nitrogen/air and carbon dioxide, and purity products such as an ethane/propane mix. This test method is limited to mixtures containing less than 5 mol % of heptanes and higher molecular weight fractions. The heptane derivaitves and higher-boiling fraction, when present in the sample, is analyzed by either (i) reverse flow of carrier gas after -hexane and peak grouping or (ii) precut column to elute heptane derivatives and higher-boiling higher molecular weight hydrocarbon derivatives first as a single peak. For purity mixes without heptane derivatives and higher molecular weight hydrocarbon derivatives, no reverse of carrier flow is required. In the case of unknown samples with a relatively large fraction of the higher-boiling constituents and where precise results are important, it is desirable to determine the molecular weight (or other pertinent physical properties) of these fractions. Since this test method makes no provision for determining physical properties, the physical properties needed can be determined by an extended analysis or agreed to by the contracting parties.

Procedures for the determination of hydrogen, helium, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, propane, butanes, pentanes, and hexanes as well as higher molecular weight hydrocarbon derivatives in natural and reformed gases by packed column gas chromatography are available (ASTM D1945; ASTM D1946). These compositional analyses from these two test methods can be used to calculate many other properties of gases, such as density, heating value, and compressibility. The first five components listed are determined using a molecular sieve column (argon carrier gas), while the remaining components are determined using polydimethylsiloxane partition or porous polymer columns. The hexanes-plus analysis is accomplished by back-flushing the column after the elution of pentane or by the use of a back-flushed pre-column.

Important constituents of natural gas not accounted for in these analyses are moisture (water) and hydrogen sulfide, as well as other sulfur compounds (ASTM D1142; ASTM D1988; ASTM D4888; ASTM D5504; ASTM D5454; ASTM D6228). Olefins (ethylene, propylene, butylene derivatives, and pentylene derivatives) that occur in refinery (process) gas have specific characteristics and require specific testing protocols (ASTM D5234; ASTM D5273; ASTM D5274).

Thus, hydrocarbon analysis of ethylene is accomplished by two methods (ASTM D2505; ASTM D6159) one of which (ASTM D6159) uses wide-bore (0.53-mm) capillary columns, including an alumina-potassium chloride (Al_2O_3/KCl) PLOT column. Another method (ASTM D2504) is recommended for determination of non-condensable gases and yet another (ASTM D2505) is used for the determination of carbon dioxide.

Hydrocarbon impurities in propylene can be determined by gas chromatographic methods (ASTM D2712; ASTM D2163) and another test is available for determination of traces of methanol in propylene (ASTM D4864). A gas chromatographic method (ASTM D5303) is available for the determination of trace amounts of carbonyl sulfide in propylene using a flame photometric detector. Also, sulfur in crude oil gas can be determined by oxidative microcoulometry (ASTM D3246).

Commercial butylenes, high-purity butylenes, and butane-butylene mixtures are analyzed for hydrocarbon constituents (ASTM D4424) and hydrocarbon impurities in 1,3-butadiene can also be determined by gas chromatography (ASTM D2593). The presence of butadiene dimer and styrene are determined in butadiene by gas chromatography (ASTM D2426).

In general, gas chromatography will undoubtedly continue to be the method of choice for characterization of low-boiling hydrocarbon materials. New and improved detection devices and techniques, such as chemiluminescence, atomic emission, and mass spectroscopy, will enhance selectivity, detection limits, and analytical productivity. Laboratory automation through auto-sampling, computer control, and data handling will provide improved precision and productivity, as well as simplified method operation.

Compositional analysis can be used to calculate calorific value, specific gravity, and compressibility factor (ASTM D3588).

Mercury in natural gas is also measured by atomic fluorescence spectroscopy (ASTM D6350) and by atomic absorption spectroscopy (ASTM D5954).

3.2 Physical properties

Test methods for gaseous fuels have been developed over many years, extending back into the 1930s. Bulk physical property tests, such as density and heating value, as well as some compositional tests, such as the Orsat analysis and the mercuric nitrate method for the determination of unsaturation, were widely used. More recently, mass spectrometry has become a popular method of choice for compositional analysis of low molecular weight and has replaced several older methods (ASTM D2421; ASTM D2650). Gas chromatography (ASTM D1945) is another method of choice for hydrocarbon identification in gases.

In fact, gas chromatography in one form or another will continue to be the method of choice for characterization of low molecular weight hydrocarbon derivatives. Developments in high-speed test methods using gas chromatographic instrumentation and data processing are already leading to new and revised test methods. Other detection techniques such as chemiluminescence, atomic emission, and mass spectrometry will undoubtedly enhance selectivity, detection limits, and analytical productivity. Furthermore, laboratory automation using auto-sampling and data handling will provide improved precision and productivity accompanied by simplified method operation.

Specifications for crude oil gases typically focus on liquefied petroleum gas, propane, and butane and the specifications generally define physical properties and characteristics of liquefied petroleum gas which make them suitable for private, commercial, or industrial applications. The specifications do not purport to specifically define all possible requirements to meet all possible applications and the user is cautioned to exercise judgment in formulating final specifications for specific applications.

The Gas Processors Association, its management, and supporting companies claim no specific knowledge of how manufacturers and users will produce, handle, store, transfer or consume the products defined herein and therefore, are not responsible for any claims, causes of action, liabilities, losses or expenses resulting from injury or death of persons and/or damage to property arising directly or indirectly from the use of liquefied petroleum gas or these specifications relating to liquefied petroleum gas (GPA, 1997).

Liquefied petroleum gas is composed of hydrocarbon compounds, predominately propane and butane, produced during the processing of natural gas and also in the conventional processing of crude oil (Mokhatab et al., 2006; Speight, 2014a, 2019). The composition of liquefied petroleum gas may vary depending on the source and the relative content of propane and butane content. These hydrocarbon derivatives exist as gases at atmospheric pressure and ambient temperatures, but are readily liquefied under moderate pressures for transportation and utilization. There are many uses for liquefied petroleum gas, the major ones being as (i) petrochemical, synthetic rubber, and motor gasoline feedstocks, and as (ii) commercial, domestic and industrial fuel.

The following may be accepted as a general guide for the common uses for the four fuel types covered by these specifications: (i) commercial Propane is the preferred fuel type for domestic, commercial and industrial fuels; it is also a suitable fuel for low severity internal combustion engines, (ii) commercial butane is used principally as feedstock for petrochemicals, synthetic rubber, and as blending stocks or feedstocks in the manufacture of motor gasoline; use as a fuel is generally limited to industrial applications where vaporization problems are not encountered; however, small quantifies are used as domestic fuel, (iii) commercial butane-propane mixtures cover a broad range of mixtures, which permits the tailoring of fuels or feedstocks to specific needs; (iv) propane is less variable in composition and combustion characteristics than other products covered by these specifications; it is also suitable as a fuel for internal combustion engines operating at moderate to high engine severity.

Hydrocarbon gases are amenable to analytical techniques and there has been the tendency, and it remains, for the determination of both major constituents and trace constituents than is the case with the higher molecular weight hydrocarbon derivatives. The complexity of the mixtures that are evident as the boiling point of crude oil fractions and crude oil products increases make identification of many of the individual constituents difficult, if not impossible. In addition, methods have been developed for the determination of physical characteristics such as calorific value, specific gravity, and enthalpy from the analyses of mixed hydrocarbon gases, but the accuracy does suffer when compared to the data produced by methods for the direct determination of these properties.

Bulk physical property tests, such as density and heating value, as well as some compositional tests, such as the Orsat analysis (the measurement of the quantitative amounts by selective absorption of carbon dioxide, oxygen, and carbon monoxide) and the mercuric nitrate method for the determination of unsaturation, are still used.

However, the choice of a particular test rests upon the decision of the analyst that, then, depends upon the nature of the gas under study. For example, judgment by the analyst is necessary whether or not a test that is applied to liquefied petroleum gas is suitable for natural gas insofar as inference from the non-hydrocarbon constituents will be minimal.

3.2.1 Calorific value

The calorific value (heat of combustion) gives an indication of the satisfactory combustion of hydrocarbon gases, which depends upon the matching of burner and appliance design with certain gas characteristics. It is the amount of energy generated by the complete combustion of a unit mass of the gas. The US system of measurement uses British Thermal Units (Btu) per pound or Btu per standard cubic foot when expressed on a volume basis. This property is an indicator of the performance and torque potential of the gas for a defined engine configuration. Various types of test methods are available for the direct determination of calorific value (ASTM D1826; ASTM D3588). The calorific value is an important property insofar as it is used to calculate the Wobbe Index (Wobbe index) (Section 4.2.11).

The heating value of natural gas (or any fuel gas) may be determined experimentally using a calorimeter in which fuel is burned in the presence of air at constant pressure. The products are allowed to cool to the initial temperature and a measurement is made of the energy released during complete combustion. All fuels that contain hydrogen release water vapor as a product of combustion, which is subsequently condensed in the calorimeter. The resulting measurement of the heat released is the higher heating value (HHV), also known as the gross heating value, and includes the heat of vaporization of water. The lower heating value (LHV), also known as the net heating value, is calculated by subtracting the heat of vaporization of water from the measured HHV and assumes that all products of combustion including water remain in the gaseous phase. Both the HHV and LHV may also be calculated from the gas compositional analysis (ASTM D3588).

There are two types of calorific value: the superior calorific value, which includes condensation heat of the water content in the exhaust gases and is used for gas billing, and the inferior calorific value, which does not include this condensation heat and tends to be the preferred variable for engine applications. The lower calorific value is also often referred as the lower heating value (LHV), and the higher calorific value named the higher heating value (HHV).

3.2.2 *Composition*

Tight gas is a mixtures of naturally occurring materials and, fortunately, are relatively simple mixtures and do not suffer the complexities of the isomeric variations of the higher molecular weight hydrocarbons (Table 4.4) (Drews, 1998; Speight, 2014).

Thus, because of the lower molecular weight constituents of these gases and their volatility, gas chromatography has been the technique of choice for fixed gas and hydrocarbon speciation and mass spectrometry is also a method of choice for compositional analysis of low molecular weight hydrocarbon derivatives (ASTM D2421; ASTM D2650). More recently, piggy-back methods (such as gas chromatography/mass spectrometry and other double technique methods) have been developed for the identification of gaseous and low boiling liquid constituents of mixtures. The hydrocarbon composition is limited to set to the total amount of ethane, butane, or pentane as well as ethylene and total dienes.

By limiting the amount of the different hydrocarbon derivatives that are lower boiling than the main component, the vapor pressure control is reinforced. Tests are available for vapor pressure 38 °C (100 °F) and at 45 °C (113 °F) (ASTM D1267). Information on the vapor pressures of liquefied petroleum gas products under temperature conditions from 37.8 to 70 °C (100−158 °F) is pertinent to selection of properly designed storage vessels, shipping containers, and customer utilization equipment to ensure safe handling of these products. Thus, determination of the vapor pressure of liquefied petroleum gas is important for safety reasons to ensure that the maximum operating design pressures of storage, handling, and fuel systems will not be exceeded under normal operating temperature conditions. For liquefied petroleum gas, vapor pressure is an indirect measure of the most extreme low temperature conditions under which initial vaporization can be expected to occur. The vapor pressure, as determined by this test method, can be considered to be a semi-quantitative measure (an estimate or indication) of the amount of the most volatile material present in the product. Boiling hydrocarbon derivatives supports the volatility clause. The vapor pressure and volatility specifications will often be met automatically if the hydrocarbon composition is in order with the specification. As stated above, the amount of ethylene is limited because not only because it is necessary to restrict the amount of the unsaturated components (olefins) so as to avoid the formation of deposits caused by the polymerization of the olefin(s) but also to control the volatility of the sample. Ethylene (boiling point: 104 °C, -155 °F) is more volatile than ethane (boiling point: 88 °C, -127 °F) and therefore a product with a substantial proportion of ethylene will have a higher vapor pressure and volatility than one that is predominantly ethane. Butadiene is also undesirable because it may also produce polymeric products that form deposits and cause blockage of lines.

Currently the preferred method for the analysis of tight gas, and indeed for most crude oil-related gases, is gas chromatography (ASTM D2163). This technique can be used for the identification and measurement of both main constituents and trace constituents. However, there may be some accuracy issues that arise in the measurement of the higher boiling constituents due to relative volatility under the conditions in which the sample is held.

However, assuming the reliability of the data from this test method, the hydrocarbon component distribution of liquefied petroleum gas and propylene mixtures is often required for end-use sale of this material. Applications such as chemical feed stocks or fuel require precise compositional data to ensure uniform quality. Trace amounts of some hydrocarbon impurities in these materials can have adverse effects on their use and processing. In addition, the distribution of the constituents of liquefied petroleum gas and propylene mixtures can be used to calculate physical properties such as relative density, vapor pressure, and motor octane (ASTM D2598). This test method covers, through compositional analysis, the approximate determination of the following physical characteristics of commercial propane, special-duty propane, commercial propane/butane mixtures, and commercial butane (ASTM D1835): vapor pressure, relative density, and motor octane number (MON).

Vapor pressure is an important specification property of commercial propane, special duty propane, propane/butane mixtures, and commercial butane that assures adequate vaporization, safety, and compatibility with commercial appliances. Relative density, while not a typical criterion contained in specifications, is necessary for determination of filling densities and custody transfer. The motor octane number (MON) is useful in determining the suitability of a product as a fuel for internal combustion engines. Precision and accuracy of compositional data are extremely important when these data are used to calculate various properties of these crude oil products.

Capillary column gas chromatography is an even quicker and equally accurate alternative. Mass spectrometry is also suitable for analysis of crude oil gases. Of the other spectroscopic techniques, infrared and ultra-violet absorption may be applied to crude oil gas analysis for some specialized applications. Gas chromatography has also largely supplanted chemical absorption methods of analysis but again these may have some limited specialized application. Once the composition of a mixture has been determined it is possible to calculate various properties such as specific gravity, vapor pressure, calorific value and dew point. In liquefied petroleum gas where the composition is such that the hydrocarbon dew point is known to be low, a dew point method will detect the presence of traces of water (ASTM D1142).

The hydrocarbon dew point is often considered to be the most important factor when performing any type of gas sampling. In the simplest terms, hydrocarbon dew point is the point at which the gas components begin to change phase from gaseous to liquid. When phase change occurs, certain components of the gas stream drop out and form liquids thereby making an accurate gas sample impossible to obtain. The hydrocarbon dew point is a function of gas composition and pressure. A hydrocarbon dew point curve is a reference chart that determines the specific pressure and temperature at which condensation occurs. No two hydrocarbon dew point curves are alike due to differing gas compositions. However, since dew point can be calculated from composition, direct determination of dew point for a particular liquefied petroleum gas sample is a measure of composition. It is, of course, of more direct practical value and if there are small quantities of higher molecular weight material present, it is preferable to use a direct measurement.

Simple evaporation tests in conjunction with vapor pressure measurement give a further guide to composition. In these tests a liquefied petroleum gas sample is allowed to evaporate naturally from an open graduated vessel. Results are recorded on the basis of volume/temperature changes, such as the temperature recorded when 95% v/v has evaporated, or volume left at a particular temperature (ASTM D1837). As stated above, this test method is a measure of the relative purity of the various types of liquefied petroleum gas and is a benefit in the assurance of volatility performance. The test results, when properly related to vapor pressure and density of the product, can be used to indicate the presence of butane and higher molecular weight constituents in propane-type liquefied petroleum gas, and pentane and higher molecular weight constituents in propane/butane-type fuel gases as well as in butane-type fuel gases. The presence of hydrocarbon compounds less volatile than those of which the liquefied petroleum gas is primarily composed is indicated by an increase in the 95% v/v evaporated temperature. When the type and concentration of higher boiling components is required, chromatographic analysis should be used.

Specific gravity again can be calculated, but if it is necessary to measure it several pieces of apparatus are available. For determining the density or specific gravity of liquefied petroleum gas in its liquid state there are two methods, using a metal pressure pycnometer. A pressure hydrometer may be used (ASTM D1267) for the relative density that may also be calculated from composition al analysis (ASTM D2598). Various procedures, manual and recording, for specific gravity or density in the gaseous state are given in two methods (ASTM D1070). In this test method (ASTM D1070), accurate and reliable test protocols are provided to measure the relative density of gaseous fuels on an intermittent or continuous basis. The test protocols cover the determination of relative density of gaseous fuels, including liquefied petroleum gas, in the gaseous state at normal temperatures and pressures. The methods specified are sufficiently varied in nature so that one or more may be used for laboratory, control, reference, gas measurement, or in fact, for any purpose in which it is desired to know the relative density of gas or gases as compared to the density of dry air at the same temperature and pressure. These measurements are frequently used for regulatory or contract compliance custody transfer and process control.

The hydrocarbon composition of tight gas condensate (although not specifically a gas) for petrochemical use must undergo a compositional analysis (ASTM D2427) and a test for total sulfur (ASTM D1266). In the method for compositional analysis of the fraction (ASTM

D2427), the hydrocarbon-type analyses of naphtha and gasoline fractions (low-boiling and highly-volatile fuels) is accomplished after stabilization by depentanization prior to analysis.

A knowledge of the composition of lower-boiling hydrocarbon derivatives in the overhead from the depentanization process is useful in converting analyses of the depentanized fraction to a total sample basis. Thus, the presence of pentane and lower-molecular weight hydrocarbon derivatives in gasoline, naphtha, and similar crude oil distillates can have an adverse effect of the result of a test method. Pentane and lower-boiling hydrocarbon derivatives are separated by this test method so that the depentanized residue can be analyzed and so the pentane and lower molecular weight hydrocarbon derivatives can be analyzed by other methods, if desired.

An issue that arises during the characterization of tight gas relates to the accurate determination of the relatively high-boiling residue (i.e., higher molecular weight hydrocarbon derivatives and even oils) in the gas. Test methods using procedures similar to those employed in gas chromatographic simulated distillation are becoming available. In fact, the presence of any component substantially less volatile than the main constituents of the liquefied petroleum gas will give rise to unsatisfactory performance. It is difficult to set limits to the amount and nature of the *residue* which will make a product unsatisfactory. For example, liquefied petroleum gas that contain certain anti-icing additives can give erroneous results by this test method.

Control over the residue content (ASTM D1835) is of considerable importance in end-use applications of liquefied petroleum gas. In liquid feed systems, residues can lead to troublesome deposits and, in vapor withdrawal systems, residues that are carried over can foul regulating equipment. Any residue that remains in the vapor-withdrawal systems will accumulate, can be corrosive, and will contaminate subsequent product. Water, particularly if alkaline, can cause failure of regulating equipment and corrosion of metals. Obviously small amounts of oil-like material can block regulators and valves. In liquid vaporizer feed systems, the gasoline type material could cause difficulty.

The residue as determined by the *end point index* (EPI) (ASTM D2158) is a measure of the concentration of contaminants boiling above 37.8 °C (100 °F) that may be present in the gas. Other methods are available which measure residue more directly and for particular applications it may be possible to relate the values obtained to the performance required and so set satisfactory limits.

Analytical methods are available in standard form for determining volatile sulfur content and certain specific corrosive sulfur compounds that are likely to be present. Many laboratories use rapid combustion techniques with an oxy-hydrogen flame in a Wickbold or Martin-Floret burner (ASTM D2784). This test method (ASTM D2784) is valid for sulfur levels of >1 μg/g of sulfur in liquefied petroleum gas but the samples should not contain more than 100 μg/g of chlorine. In the test, the sample is bummed in an oxy-hydrogen bummer or in a lamp in a closed system in a carbon dioxide-oxygen atmosphere. The latter is not recommended for trace quantities of sulfur due to inordinately long combustion times needed. The sulfur oxides produced are absorbed and oxidized to sulfuric acid in a hydrogen peroxide solution. The sulfate ions are then determined by either titrating with barium perchlorate solution using a thorinmethylene blue mixed indicator, or by precipitating as barium sulfate and measuring the turbidity of the precipitate with a photometer.

Trace hydrocarbon derivatives that may be regarded as contaminants may be determined by the gas chromatographic methods already discussed. Higher molecular weight hydrocarbon derivatives in small amounts may not be completely removed from the column. If accurate information is required related to the nature and amount of the higher boiling constituents, then a temperature programming procedure or a procedure involving the concentration of the constituents may be used.

Analytical methods for determining traces of various other impurities, such as chlorides (ASTM D2384) are known to be in use. The presence of acetylenes in refinery gases, although unlikely, must still be considered. Acetylenes can be determined using a chemical test method while carbonyls are determined by the classical hydroxylamine hydrochloride reaction.

The determination of traces of higher boiling hydrocarbon derivatives and oily matter involves use of a method for residue that involves a preliminary weathering. The residue after weathering is dissolved in a solvent and the solution applied to a filter paper. The presence of residue is indicated by the formation of an oil stain. The procedure is taken further by combining the oil stain observation with other observed values to calculate an End Point Index (ASTM D2158). The method is not very precise, and work is proceeding in several laboratories to develop a better method for the determination of residue in the form of oily matter.

In tight gas sample where the composition is such that the hydrocarbon dew point is known to be low, a dew point method will detect the presence of traces of water (ASTM D1142).

The odor of liquefied petroleum gas has to be detectable to avoid the risk of explosion. Odor is a very subjective matter and no standard method is available. It is desirable to set up some system in which the concentration of gas can be measured in relation to its explosive limits and in which some variables can be standardized, e.g. flow-rate and orifice size. This will ensure that in any one location the liquefied petroleum gas is always being assessed under similar conditions from day to day.

Propane, iso-butane (boiling point: 12 °C, 11 °F), and butane generally constitute this sample type and are used for heating, motor fuels, and as chemical feedstocks (ASTM D2597; ASTM D2504; ASTM D2505).

Procedures for the determination of hydrogen, helium, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, propane, butanes, pentanes, and hexanes as well as higher molecular weight hydrocarbon derivatives in natural and reformed gases by packed column gas chromatography are available (ASTM D1945; ASTM D1946). These compositional analyses are used to calculate many other properties of gases, such as density, heating value, and compressibility. The first five components listed are determined using a molecular sieve column (argon carrier gas), while the remaining components are determined using polydimethylsiloxane partition or porous polymer columns. The hexanes-plus analysis is accomplished by back-flushing the column after the elution of pentane or by the use of a back-flushed pre-column.

Important constituents of natural gas not accounted for in these analyses are moisture (water) and hydrogen sulfide, as well as other sulfur compounds (ASTM D1142; ASTM D1988; ASTM D4888; ASTM D5504; ASTM D5454; ASTM D6228).

Olefins (ethylene, propylene, butylene derivatives, and pentylene derivatives) that occur in refinery (process) gas have specific characteristics and require specific testing protocols

(ASTM D5234; ASTM D5273; ASTM D5274). Ethylene is one of the highest volume chemicals produced in the world, with global production exceeding 100 million metric tons annually. Ethylene is primarily used in the manufacture of polyethylene, ethylene oxide, and ethylene dichloride, as well as many other lower volume products. Most of these production processes use various catalysts to improve product quality and process yield. Impurities in ethylene can damage the catalysts, resulting in significant replacement costs, reduced product quality, process downtime, and decreased yield.

Ethylene is typically manufactured through the use of steam cracking. In this process, gaseous or low-boiling liquid hydrocarbon derivatives are combined with steam and heated to 750−950 °C (1380−1740 °F in a pyrolysis furnace. Numerous free radical reactions are initiated, and larger hydrocarbon derivatives are converted (cracked) into lower molecular weight hydrocarbon derivatives. In addition, the high temperatures used in steam cracking promote the formation of unsaturated or olefin compounds, such as ethylene. Ethylene feedstocks must be tested to ensure that only high purity ethylene is delivered for subsequent chemical processing.

Samples of high purity ethylene typically contain only two minor impurities, methane and ethane, which can be detected in low ppm v/v concentrations. However, steam cracking can also produce higher molecular weight hydrocarbon derivatives, especially when propane, butane, or low-boiling liquid hydrocarbon derivatives are used as starting materials. Although fractionation is used in the final production stages to produce a high purity ethylene product, it is still important to be able to identify and quantify any other hydrocarbon derivatives present in an ethylene sample. Achieving sufficient resolution of all of these compounds can be challenging due to their similarities in boiling point and chemical structure.

The analysis of ethylene is accomplished by two methods (ASTM D2505; ASTM D6159) one of which (ASTM D6159) uses wide-bore (0.53-mm) capillary columns, including an alumina-potassium chloride (Al_2O_3/KCl) PLOT column. Another method (ASTM D2504) is recommended for determination of non-condensable gases and yet another (ASTM D2505) is used for the determination of carbon dioxide.

Hydrocarbon impurities in propylene can be determined by gas chromatographic methods (ASTM D2712; ASTM D2163) and another test is available for determination of traces of methanol in propylene (ASTM D4864). A gas chromatographic method (ASTM D5303) is available for the determination of trace amounts of carbonyl sulfide in propylene using a flame photometric detector. Also, sulfur in crude oil gas can be determined by oxidative microcoulometry (ASTM D3246).

Commercial butylenes, high-purity butylenes, and butane-butylene mixtures are analyzed for hydrocarbon constituents (ASTM D4424) and hydrocarbon impurities in 1,3-butadiene can also be determined by gas chromatography (ASTM D2593). The presence of butadiene dimer and styrene are determined in butadiene by gas chromatography (ASTM D2426). Carbonyl derivatives in C4 hydrocarbon derivatives can be determined by use a peroxide method (ASTM D5799).

In general, gas chromatography will undoubtedly continue to be the method of choice for characterization of low-boiling hydrocarbon materials. New and improved detection devices and techniques, such as chemiluminescence, atomic emission, and mass spectroscopy, will enhance selectivity, detection limits, and analytical productivity. Laboratory automation through auto-sampling, computer control, and data handling will provide improved precision and productivity, as well as simplified method operation.

Compositional analysis can be used to calculate calorific value, specific gravity, and compressibility factor (ASTM D3588).

Mercury in tight gas is also measured by atomic fluorescence spectroscopy (ASTM D6350) and by atomic absorption spectroscopy (ASTM D5954).

3.2.3 *Density and relative density*

The density of low-boiling hydrocarbon derivatives can be determined by several methods (ASTM D1070) including a hydrometer method (ASTM D1298) or by a pressure hydrometer method (ASTM D1657). The specific gravity (relative density) (ASTM D1070; ASTM D1657) by itself has little significance compared to its use for higher molecular weight liquid crude oil products) and can only give an indication of quality characteristics when combined with values for volatility and vapor pressure. It is important for stock quantity calculations and is used in connection with transport and storage.

The relative density typically relates to the density of natural as relative to the density of air (Table 7.5) although, in some cases, the density of hydrogen may be used for comparison to the density of natural gas. The relative density, as a measure of gas density relative to air at reference conditions this is used for interchangeability specifications to limit the higher hydrocarbon content of the gas. An increased higher hydrocarbon content could lead to combustion problems such as increased carbon monoxide emissions, soot formation, engine knock or spontaneous ignition on gas turbines even at the same Wobbe index value.

The statement is often made that natural gas is lighter (less dense) than air. This statement often arises because of the continued insistence by engineers and scientists that the properties of a mixture are determined by the mathematical average of the properties of the individual constituents of the mixture. Such mathematical bravado and inconsistency of thought is detrimental to safety and needs to be qualified.

The *relative density* (*specific gravity*) is the ratio of the density (mass of a unit volume) of a substance to the density of a given reference material. Specific gravity usually means relative density (of a liquid) with respect to water.

TABLE 7.5 Relative density (specific gravity) of natural gas hydrocarbons relative to air.

Gas	Specific gravity
Air	1.000
Methane, CH_4	0.5537
Ethane, C_2H_6	1.0378
Propane, C_3H_8	1.5219
Butane, C_4H_{10}	2.0061
Pentane, C_5H_{12}	2.487
Hexane, C_6H_{14}	2.973

$$\text{Relative density} = [\rho(\text{substance})]/[\rho(\text{reference})]$$

As it pertains to gases, particularly in relation to safety considerations at commercial and industrial facilities in the United States, the relative density of a gas is usually defined with respect to air, in which air is assigned a *vapor density* of one (unity). With this definition, the vapor density indicates whether a gas is denser (greater than one) or less dense (less than one) than air. The vapor density has implications for container storage and personnel safety − if a container can release a dense gas, its vapor could sink and, if flammable, collect until it is at a concentration sufficient for ignition. Even if not flammable, it could collect in the lower floor or level of a confined space and displace air, possibly presenting a smothering hazard to individuals entering the lower part of that space.

Gases can be divided into two groups based upon their vapor density: (i) gases which are more dense than air, and (ii) gases which are as light as air or less dense than air. Gases that have a vapor density greater than one will be found in the bottom of storage containers and will tend to migrate downhill and accumulate in low lying areas. Gases that have a vapor density which is the same or less than the vapor density of air will disperse readily into the surrounding environment. Additionally, chemicals that have the same vapor density as air (1.0) tend to disperse uniformly into the surrounding air when contained and, when released into the open air, chemicals that are less dense than air will travel up and away from the ground.

Methane is the only hydrocarbon constituent of natural gas that is less dense than air (Table 7.5). The higher molecular weight hydrocarbon derivatives have a higher vapor density than air and are likely, after a release, to accumulate in low-lying areas and represent a danger to investigator (of the release). However, the other hydrocarbon constituents of unrefined natural gas (i.e., ethane, propane, butane, etc.) are denser than air. Therefore, should a natural gas leak occur in field operations, especially where the natural gas contains constituents other than methane, only methane dissipates readily into the air whereas the other hydrocarbon constituents that are more dense than air do not readily dissipate into the atmosphere. This poses considerable risk if these constituents of natural gas accumulate or pool at ground level when it has been erroneously assumed that natural gas is less dense than air.

3.2.4 Dew point

The dew point or dew point temperature of a gas is the temperature at which the water vapor (ASTM D2029) or low-boiling hydrocarbon derivatives contained in the gas is transformed into the liquid state. The formed liquid is (condensate) exists as a liquid below the dew point temperature but above the dew point the liquid is a gaseous component of the gas.

3.2.5 Flammability

The flammability range: the range of temperature over which natural gas is flammable. The flammability limits of natural gas in air is an expression of the percent concentration in air (by volume) is given for the lower and upper limit. These values give an indication of relative flammability. The limits are sometimes referred to as *lower explosive limit* (LEL) and *upper explosive limit* (UEL).

By way of explanation, before a fire or explosion can occur, three conditions must be met simultaneously. A fuel (ie. combustible gas) and oxygen (air) must exist in certain proportions, along with an ignition source, such as a spark or flame. The ratio of fuel and oxygen that is required varies with each combustible gas or vapor. The minimum concentration of a particular combustible gas or vapor necessary to support its combustion in air is defined as the lower explosive limit (LEL) for that gas. Below this level, the mixture is too lean to burn. The maximum concentration of a gas or vapor that will burn in air is defined as the upper explosive limit (UEL). Above this level, the mixture is too rich to burn. The range between the LEL and UEL is known as the flammable range for that gas or vapor. Typically, the values given for the upper explosive limit and the lower explosive limit (Table 7.6) are valid only for the conditions under which they were determined (usually room temperature and atmospheric pressure using a 2 inch tube with spark ignition). The flammability range of most materials expands as temperature, pressure and container diameter increase.

The vapor density has implications for flammability during storage. If a container can release a dense gas, its vapor could sink and, if flammable, collect until it is at a concentration sufficient for ignition. Even if not flammable, it could collect in the lower floor or level of a confined space and displace air, possibly presenting a smothering hazard to individuals entering the lower part of that space.

3.2.6 High molecular weight hydrocarbons derivatives

Tight gas and indeed any of natural gas stream which consists primarily of methane can commonly contain varying amounts of other higher molecular weight hydrocarbon derivatives from ethane to octane. It is, therefore, necessary to present the effects of the higher hydrocarbon derivaitves in this sub-section.

Because natural gas is not a pure product, as the reservoir pressure drops when non-associated gas is extracted from a field under supercritical (pressure/temperature) conditions, the higher molecular weight components may partially condense upon isothermal depressurizing (retrograde condensation). The liquid thus formed may get trapped as the pores of the gas reservoir get depleted or eve in a pipeline during transportation. One method to circumvent this problem is to re-inject dried gas free of condensate to maintain the gas pressure in the reservoir, transportation, or storage system and to allow re-evaporation and extraction of condensates. More frequently, the liquid condenses at the surface, and one of the tasks of the gas processing operations is to collect this condensate which is often referred to as natural gas natural gas liquids (NGLs).

Some gas utilities may add propane/air mixtures to natural gas during peak demand periods. Propane has a low vapor pressure and if present in significant quantities it will form a liquid phase at elevated pressures and low temperatures. Fuel variability due to vaporization of this liquid condensate at reduced storage cylinder pressure can lead to difficulty in controlling the air-fuel ratio. In addition, the significant presence of the higher molecular weight hydrocarbon derivatives in the gas mixture lowers its knock rating and can lead to potential engine damage.

There may also be substantial amounts of oil can be added to the gas during compression, which can subsequently condense and interfere with the operation of compressed natural gas engine components such as gas pressure regulators. On the other hand, a minimum level of

TABLE 7.6 Lower explosive limits (LET) and upper explosive limits (UEL) for various constituents of gases, gas condensate, and natural gasoline.

Constituent	LEL	UEL
Benzene	1.3	7.9
1,3-Butadiene	2	12
Butane	1.8	8.4
n-Butanol	1.7	12
I-Butene	1.6	10
cis-2-Butene	1.7	9.7
trans-2-Butene	1.7	9.7
Carbon monoxide	12.5	74
Carbonyl sulfide	12	29
Cyclohexane	1.3	7.8
Cyclopropane	2.4	10.4
Diethylbenzene	0.8	
2,2-Dimethylpropane	1.4	7.5
Ethane	3	12.4
Ethyl benzene	1	6.7
Ethylene	2.7	36
Gasoline	1.2	7.1
Heptane	1.1	6.7
Hexane	1.2	7.4
Hydrogen	4	75
Hydrogen sulfide	4	44
Isobutane	1.8	8.4
Isobutylene	1.8	9.6
Methane	5	15
3-Methyl-1-butene	1.5	9.1
Methyl mercaptan	3.9	21.8
Pentane	1.4	7.8
Propane	2.1	9.5
Propylene	2.4	11
Toluene	1.2	7.1
Xylene	1.1	6.6

carryover oil is required for durable gas injector operation. Various injector manufacturers recommend different minimum oil levels.

Oil in the gas at the compressor outlet is commonly removed by coalescing filters, however, they are insufficient in many cases, as up to 50% of the carryover oil exists in vapor form in the warm (or hot) compressor outlet gas. Additional measures will need to be considered, for example, by additional cooling of the discharge gas or by using synthetic oil or mineral oil or a combination of mineral oil and a suitable adsorption filter downstream of the coalescing filter (Czachorski et al., 1995).

3.2.7 Methane number

The main parameter for rating the knock resistance of gaseous fuels is the Methane Number (MN), which is analogous to the Octane Number for gasoline and suitable test methods for determine the methane number of a gaseous fuel are being developed. (Malenshek and Olsen, 2009).

Different scales have been used to rate the knock resistance of compressed natural gas (CNG) including the Motor Octane Number (MON) and the Methane Number. The differences in these ratings are the reference fuel blends used for comparison to the natural gas. Methane number uses a reference fuel blend of methane, with a Methane Number of 100, and hydrogen, with a Methane Number of 0. Correlations have been generated between the reactive hydrogen/carbon ratio (H/C) and the Motor Octane Number and between Motor Octane Number and Methane Number.

$$\begin{gathered}\mathrm{MON} = -406.14 + 508.04 \times (\mathrm{H/C}) - 173.55 \ast (\mathrm{H/C})2 + 20.17 \ast (\mathrm{H/C})3\ \mathrm{MN} \\ = 1.624 \ast \mathrm{MON} - 119.1\end{gathered}$$

Thus, if a gas mixture has a Methane Number of 70, its knock resistance is equivalent to that of a gas mixture of 70% methane and 30% hydrogen.

To ensure safe engine operation the methane number must always be at least equal to the methane number requirement (MNR) of the gas engine. The methane number required by the engine is affected by design and operating parameters, with the adjustment of the methane number requirement being achieved by changing engine operation. Changes in ignition timing, air/fuel ratio and output are effective measures to reduce the methane number requirement.

3.2.8 Sulfur content

Sulfur compounds in natural gas are in the form of mercaptans, hydrogen sulfide, and odorants. The first two are naturally occurring at source (gas fields) and have already been reduced by treatment at the gas processing plant.

The manufacturing processes for liquefied petroleum gas are designed so that the majority, if not all, of the sulfur compounds are removed. The total sulfur level is therefore considerably lower than for other crude oil fuels and a maximum limit for sulfur content helps to define the product more completely. The sulfur compounds that are mainly responsible for corrosion are hydrogen sulfide, carbonyl sulfide and, sometimes, elemental sulfur. Hydrogen sulfide and mercaptans have distinctive unpleasant odors. Control of the total sulfur content, hydrogen sulfide and mercaptans ensures that the product is not corrosive or nauseating. Stipulating a satisfactory copper strip test further ensures the control of the corrosion.

Total sulfur in gas can be determined by combustion (ASTM D1072), by the lamp method (ASTM D1266), or by hydrogenation (ASTM D4468). Trace total organic and bound nitrogen is determined (ASTM D4629). The current test method for heavy residues in liquefied petroleum gas (ASTM D2158) involves evaporation of a liquefied petroleum gas sample, measuring the volume of residue and observing the residue for oil stain on a piece of filter paper.

Corrosive sulfur compounds can be detected by their effect on copper and the form in which the general copper strip corrosion test (ASTM D1838) for crude oil products is applied to liquefied petroleum gas. Hydrogen sulfide can be detected by its action on moist lead acetate paper and a procedure is also used as a measure of sulfur compounds. The method follows the principle of the standard Doctor test (ASTM D4952).

3.2.9 Volatility and vapor pressure

The vaporization and combustion characteristics of liquefied petroleum gas are defined for normal applications by volatility, vapor pressure, and to a lesser extent, specific gravity.

Volatility is expressed in terms of the temperature at which 95% of the sample is evaporated and presents a measure of the least volatile component present (ASTM D1837). Vapor pressure is, therefore, a measure of the most extreme low temperature conditions under which initial vaporization can take place. By setting limits to vapor pressure and volatility jointly the specification serves to ensure essentially single component products for the butane and propane grades (ASTM D1267; ASTM D2598). By combining vapor pressure/volatility limits with specific gravity for propane-butane mixtures, essentially two-component systems are ensured. The residue (ASTM D1025; ASTM D2158), i.e. non-volatile matter, is a measure of the concentration of contaminants boiling above 37.8 °C (100 °F) that may be present in the gas.

In a closed container, the vapor pressure of a pure compound is the force exerted per unit area of walls by the vaporized portion of the liquid. Vapor pressure can also be defined as a pressure at which the vapor phase and the liquid phase of a pure substance are in equilibrium with each other. The vapor pressure is also called saturation pressure and the corresponding temperature is called saturation temperature. In an open air under atmospheric pressure, a liquid at any temperature below its boiling point has its own vapor pressure that is less than 1 atm. When vapor pressure reaches 1 atm (14.7 psi) the saturation temperature becomes the normal boiling point. Vapor pressure increases with temperature and the highest value of vapor pressure for a substance is its critical pressure in which the corresponding temperature is the critical temperature.

Vapor pressure is a very important thermodynamic property of any substance and it is a measure of the volatility of a fluid. Compounds with a higher tendency to vaporize have higher vapor pressures. More volatile compounds are those that have lower boiling points and are called *light compounds*. For example, propane (C_3) has boiling point less than that of n-butane (nC_4) and as a result it is more volatile. At a fixed temperature, vapor pressure of propane is higher than that of butane. In this case, propane is called the light compound (more volatile compound) and butane the heavy compound (less volatile compound). Generally, more volatile compounds have higher critical pressure and lower critical temperature, and lower density and lower boiling point than those of less volatile (higher molecular weight) compounds, although this is not true for the case of some isomeric compounds.

Vapor pressure is a useful parameter in calculations related to hydrocarbon losses and flammability of hydrocarbon vapor in the air. More volatile compounds are more ignitable than higher molecular weight compounds. For example, n-butane is added to gasoline to improve its ignition characteristics. Low-vapor-pressure compounds reduce evaporation losses and chance of vapor lock. Therefore, for a fuel there should be a compromise between low and high vapor pressure. However, one of the major applications of vapor pressure is in calculation of equilibrium ratios for phase equilibrium calculations. For pure hydrocarbon derivatives, values of vapor pressure at the reference temperature of 100 °F (38 °C) are provided by the API [2]. For natural gas, the method of Reid is used to measure vapor pressure at 100 °F. *Reid vapor pressure* (RVP) is measured by the ASTM D 323 and it is approximately equivalent to vapor pressure at 100 °F (38 °C).

For natural gasoline, the primary criteria are volatility (vapor pressure and knock performance. Determination of the vapor pressure (ASTM D323; ASTM D4953; ASTM D5191) and distillation profile (ASTM D216) are essential. Knock performance is determined is determined by rating in knock test engines by both the motor method (ASTM D2700) and the research method (ASTM D2699). The knock characteristics of liquefied petroleum gas can also be determined. Other considerations for natural gasoline are copper corrosion (ASTM D130) and specific gravity (ASTM D1298), the latter determination being necessary for measurement and transportation.

3.2.10 Water content

The use of natural gas with high water content can result in the formation of liquid water, ice particles or hydrates at low operating temperatures and high pressure which will interfere with consistently smooth flow of fuel into the engine and cause problems such as. poor drivability or even engine stoppage. Thus, it is a fundamental requirement that liquefied petroleum gas should not contain free water (ASTM D2713). Dissolved water may give trouble by forming hydrates and giving moisture vapor in the gas phase. Both of these will lead to blockages. Therefore, test methods are available to determine the presence of water using electronic moisture analyzers (ASTM D5454), dew-point temperature (ASTM D1142), and length-of-stain detector tubes (ASTM D4888).

3.2.11 Wobbe Index

The Wobbe Index (also called the Wobbe number) gives a measure of the heat input to an appliance through a given aperture at a given gas pressure. Using this as a vertical co-ordinate and the flame speed factor as the horizontal co-ordinate a combustion diagram can be constructed for an appliance, or a whole range of appliances, with the aid of appropriate test gases. The concept behind defining the Wobbe Index is to have a measure for the interchangeability of gases, i.e. gases with the same Wobbe Index (under defined pressure conditions) generate the same output during combustion. However, a distinction is made between what is referred to as the higher Wobbe Index and the lower Wobbe Index, depending on whether the superior or the inferior calorific value are used in the formula.

The natural gas after appropriate treatment for acid gas reduction, odorization, and hydrocarbon and moisture dew point adjustment (ASTM D1142), would then be sold within prescribed limits of pressure, calorific value and possibly Wobbe Index (also called the Wobbe index) which equals the calorific value divided by the specific gravity), and the flame speed. The Wobbe Index is typically expressed as a factor or an arbitrary scale on which that of hydrogen is 100. This factor can be calculated from the gas analysis. In fact, calorific value and specific gravity can be calculated from compositional analysis (ASTM D3588). Thus:

$$\mathrm{WI} = \mathrm{cv}/\sqrt{\mathrm{sg}}$$

WI is the Wobbe index or Wobbe Index that is typically expressed in Btu/scf, CV is the calorific value (higher heating value, HHV), and SG is the specific gravity.

Combustion equipment may be sensitive to changes in gas composition, due to several factors such as the introduction of new natural gas supplies can impact the performance of certain combustion equipment. A gas with a higher Wobbe number gas may have the following impacts: (i) energy input (firing rate) may increase (ii) excess air level may decrease, (iii) carbon monoxide emissions may increase, (iv) soot generation may increase, and (v) NOx emissions may change. On the other hand a lower number gas generally has the opposite effect. In this respect, the elevated levels of ethane, propane, carbon dioxide, or nitrogen in certain shale gases are of concern regarding their interchangeability with traditional natural gas supplies and the composition of the gas supplied to the consumer may have to be adjusted accordingly.

For example, the Wobbe Index of a gas with a specific gravity is 0.6 and a BTU/cubic foot heating value of 1000 is as follows: Wobbe Index $= 1000/\sqrt{0.6} = 1291$ A gas with a specific gravity of 0.6 and a BTU/cubic foot of 1050 is well within the typical range mentioned in the AGA bulletin: Wobbe Index $= 1050/\sqrt{0.6} = 1356$ In fact, for pure methane and the next two, higher molecular weight hydrocarbon derivatives – ethane and propane – have the following properties:

	Btu/ft^3	**sp.gr.**	**Wobbe number**
Methane	1012	0.55	1365
Ethane	1773	1.04	1739
Propane	2522	1.52	2046

The ethane content of gas is important because liquefied natural gas tends to contain much more ethane than domestic natural gas sources. Wobbe numbers for mixtures containing ethane can be well above 1400, which could be beyond the ratings of some gas-operated equipment. Gas companies must make sure the liquefied natural gas that is mixed with other sources in order to reduce the Wobbe number. Otherwise, expensive processing may need to be introduced to make an adjustment. Thus, tight gas with higher proportions of ethane and propane may require more assiduous treatment (Chapter 8) before use in combustion equipment designed for use with processed conventional natural gas that is predominantly methane.

Gas turbines can operate with a large range of fuels, but the fuel variation that a particular installation can cope with is limited. The Modified Wobbe index (MWI) is used particularly by gas turbine manufacturers because it takes into account the temperature of the fuel. The Modified Wobbe Index is the ratio of the lower heating value to the square root of the product of the specific gravity and the absolute gas temperature:

$$\mathrm{MWI} = \mathrm{LHV}/\sqrt{\mathrm{SG}_{\mathrm{gas}} \times \mathrm{T}_{\mathrm{gas}}}$$

This is equivalent to:

$$\mathrm{MWI} = \mathrm{LHV}/\sqrt{(\mathrm{MW}_{\mathrm{gas}}/28.96) \times \mathrm{T}_{\mathrm{gas}}}$$

LHV is the lower heating value of the fuel gas (Btu/scf), $\mathrm{SG}_{\mathrm{gas}}$ is the specific gravity of the fuel gas relative to air, $\mathrm{MW}_{\mathrm{gas}}$ is the molecular weight of the fuel gas, $\mathrm{T}_{\mathrm{gas}}$ is the absolute temperature of the fuel gas (in degrees Rankine), and 28.96 is the molecular weight of dry air.

Any change in the heating value of the gas will require a corresponding change in the flow rate of the fuel to the machine, incorporation of temperature effects is important in calculating energy flows in turbines where a large input temperature variation is possible. The allowable MWI range is established to ensure that required fuel nozzle pressure ratios are maintained during all combustion/turbine modes of operation. For older, diffusion-type combustors, the gas turbine control system can typically accommodate variations in the Modified Wobbe Index as large as ±15%. But for newer, dry low NOx (DLN) combustors, variations in the MWI of only ±3% could cause problems. Fuel instability can be caused by velocity changes through a precisely sized fuel-nozzle orifice which can cause flame instability, resulting in pressure pulsations and/or combustion dynamics which can, in the worst case, destroy the combustion system.

Also, since the Wobbe Index is an indicator of the interchangeability of fuel gases; it (alone or with other analyses) can be used to control blending of fuel gases. Since the Wobbe Index and the Btu value of fuel gases make similar curves, either could be used to control blending of fuel gases; thereby, controlling the amount of nitrogen in the blended fuel (Segers et al., 2011). Another important combustion criterion is the gas modulus, $M = P/W$ where P is the gas pressure and W the Wobbe Index of the gas. This must remain constant if a given degree of aeration is to be maintained in a pre-aerated burner using air at atmospheric pressure.

Finally, despite the common acceptance of Wobbe Index as the main interchangeability parameter, a variety of units and reference temperatures are used across the world.

4. Analytical methods

Because of the wide range of chemical and physical properties, a wide range of tests have been (and continue to be) developed to provide an indication of the means by which a particular gas should be processed (Table 7.7) although certain of these test methods are in more

TABLE 7.7 Test methods for gaseous fules and low-boiling hydrocarbons.

ASTM D130	Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test
ASTM D216	Distillation of Natural Gasoline
ASTM D323	Vapor Pressure of Petroleum Products (Reid Method)
ASTM D1025	Nonvolatile Residue of Polymerization Grade Butadiene
ASTM D1070	Relative Density (Specific Gravity) of Gaseous Fuels
ASTM D1072	Total Sulfur in Fuel Gases
ASTM D1142	Water Vapor Content of Gaseous Fuels by Measurement of Dew-Point Temperature
ASTM D1265	Sampling Liquefied Petroleum (LP) Gases
ASTM D1266	Sulfur in Petroleum Products (Lamp Method)
ASTM D1298	Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
ASTM D1826	Calorific Value of Gases in Natural Gas Range by Continuous Recording Colorimeter
ASTM D1945	Analysis of Natural Gas by Gas Chromatography
ASTM D1265	Sampling Liquefied Petroleum (LP) Gases
ASTM D1267	Vapor Pressure of Liquefied Petroleum (LP) Gases (LP-Gas Method)
ASTM D1657	Density or Relative Density of Light Hydrocarbons by Pressure Hydrometer
ASTM D1837	Volatility of Liquefied Petroleum (LP) Gases
ASTM D1838	Copper Strip Corrosion by Liquefied Petroleum (LP) Gases
ASTM D2158	Residues in Liquefied Petroleum (LP) Gases
ASTM D2163	Analysis of Liquefied Petroleum (LP) Gases and Propane Concentrates by Gas Chromatography
ASTM D2384	Traces of Volatile Chlorides in Butane- Butene Mixtures

(*Continued*)

ASTM D2421	Practice for Interconversion of Analysis of C5 & Lighter Hydrocarbons to Gas-Volume, Liquid Volume or Mass Basis
ASTM D2426	Butadiene Dimer and Styrene in Butadiene Concentrates by Gas Chromatography
ASTM D2427	Determination of C, through C, Hydrocarbons in Gasolines by Gas Chromatography
ASTM D2504	Noncondensable Gases in C3 and Lighter Hydrocarbon Products by Gas Chromatography
ASTM D2505	Ethylene, Other Hydrocarbons, and Carbon Dioxide in High-Purity Ethylene by Gas Chromatography
ASTM D2593	Butadiene Purity and Hydrocarbon Impurities by Gas Chromatography
ASTM D2597	Test Method for Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography
ASTM D2598	Calculation of Certain Physical Properties of Liquefied Petroleum (LP) Gases from Compositional Analysis
ASTM D2699	Knock Characteristics of Motor Fuels by the Research Method
ASTM D2700	Knock Characteristics of Motor and Aviation Type Fuels by the Motor Method
ASTM D2712	Hydrocarbon Traces in Propylene Concentrates by Gas Chromatography
ASTM D2713	Dryness of Propane (Valve Freeze Method)
ASTM D2784	Sulfur in Liquefied Petroleum Gases (Oxy-Hydrogen Burner or Lamp)
ASTM D3246	Sulfur in Petroleum Gases by Oxidative Microcoulometry
ASTM D3700	Practice for Containing Hydrocarbon Fluid Samples Using a Floating Piston Cylinder
ASTM D4953	Test Method for Vapor Pressure of Gasoline-Oxygenate Blends (Dry Method)
ASTM D5191	Test Method for Vapor Pressure of Petroleum Products (Mini Method)

common use than others (Table 7.1). Initial inspection of the nature of the crude oil will provide deductions related to the most logical means of refining or correlation of various properties to structural types present and hence attempted classification of the crude oil. Proper interpretation of the data resulting from the inspection of crude oil requires an understanding of their significance. Having decided what characteristics are necessary, it then remains to describe the product in terms of a specification. This entails selecting suitable test methods and setting appropriate limits. Many specifications in widespread use have evolved usually by the addition of extra clauses (rarely is a clause deleted). This has resulted in unnecessary restrictions that, in turn, result in increased cost of the products specified.

Test methods for gaseous fuels have been developed over many years, extending back into the 1930s. Bulk physical property tests, such as density and heating value, as well as some compositional tests, such as the Orsat analysis and the mercuric nitrate method for the determination of unsaturation, were widely used. More recently, mass spectrometry has become a popular method of choice for compositional analysis of low molecular weight and has replaced several older methods (ASTM D2421; ASTM D2650). Gas chromatography (ASTM D1945) is another method of choice for hydrocarbon identification in gases.

In fact, gas chromatography in one form or another will continue to be the method of choice for characterization of low molecular weight hydrocarbon derivatives. Developments in high-speed test methods using gas chromatographic instrumentation and data processing are already leading to new and revised test methods. Other detection techniques such as chemiluminescence, atomic emission, and mass spectrometry will undoubtedly enhance selectivity, detection limits, and analytical productivity. Furthermore, laboratory automation using auto-sampling and data handling will provide improved precision and productivity accompanied by simplified method operation.

Specifications for crude oil gases typically focus on liquefied petroleum gas, propane, and butane and the specifications generally define physical properties and characteristics of liquefied petroleum gas which make them suitable for private, commercial, or industrial applications. The specifications do not purport to specifically define all possible requirements to meet all possible applications and the user is cautioned to exercise judgment in formulating final specifications for specific applications.

The Gas Processors Association, its management, and supporting companies claim no specific knowledge of how manufacturers and users will produce, handle, store, transfer or consume the products defined herein and therefore, are not responsible for any claims, causes of action, liabilities, losses or expenses resulting from injury or death of persons and/or damage to property arising directly or indirectly from the use of liquefied petroleum gas or these specifications relating to liquefied petroleum gas (GPA, 1997).

Liquefied petroleum gas is composed of hydrocarbon compounds, predominately propane and butane, produced during the processing of natural gas and also in the conventional processing of crude oil (Mokhatab et al., 2006; Speight, 2014a, 2019). The composition of liquefied petroleum gas may vary depending on the source and the relative content of propane and butane content. These hydrocarbon derivatives exist as gases at atmospheric pressure and ambient temperatures, but are readily liquefied under moderate pressures for transportation and utilization.

There are many uses for liquefied petroleum gas, the major ones being as (i) petrochemical, synthetic rubber, and motor gasoline feedstocks, and as (ii) commercial, domestic and industrial fuel. The following may be accepted as a general guide for the common uses for the four fuel types covered by these specifications: (i) commercial Propane is the preferred fuel type for domestic, commercial and industrial fuels; it is also a suitable fuel for low severity internal combustion engines, (ii) commercial Butane is used principally as feedstock for petrochemicals, synthetic rubber, and as blending stocks or feedstocks in the manufacture of motor gasoline; use as a fuel is generally limited to industrial applications where vaporization problems are not encountered; however, small quantifies are used as domestic fuel, (iii) commercial butane-propane mixtures cover a broad range of mixtures, which permits the tailoring of fuels or feedstocks to specific needs; (iv) propane is less variable in composition and combustion characteristics than other products covered by these specifications; it is also suitable as a fuel for internal combustion engines operating at moderate to high engine severity.

Hydrocarbon gases are amenable to analytical techniques and there has been the tendency, and it remains, for the determination of both major constituents and trace constituents than is the case with the higher molecular weight hydrocarbon derivatives. The complexity of the mixtures that are evident as the boiling point of crude oil fractions and crude oil products increases make identification of many of the individual constituents difficult, if not impossible. In addition, methods have been developed for the determination of physical characteristics such as calorific value, specific gravity, and enthalpy from the analyses of mixed hydrocarbon gases, but the accuracy does suffer when compared to the data produced by methods for the direct determination of these properties. However, the choice of a particular test rests upon the decision of the analyst that, then, depends upon the nature of the gas under study.

Specifications are normally prescriptive on concentrations for impurities, such as maximum values for oxygen, total sulfur and hydrogen sulfide and maximum values for dew points of water and hydrocarbon derivatives. A limited number of countries have introduced specifications for maximum hydrogen content. These impurity specifications are necessary for protection of pipeline systems and/or customer facilities from corrosion and mechanical or other damage. Often, gas quality specifications also include a general "impurity clause" aimed at proscribing (trace) components which are not monitored but could, if present in the gas, cause operational and/or other problems to the end-user.

Substances may be added to the gas to protect the pipe work or instrumentation on the network. Cast iron pipes are jointed with lead and yarn that is kept swollen to maintain the seal by adding ethylene glycol. Mechanical or rubber joints are kept swollen by injecting distillate into the gas flow. With the emergence of poly-ethylene pipe the need for such additives is steadily reducing. Other additives include valve-flush agents that are used during maintenance procedures.

4.1 Sampling

One of the more critical aspects for the analysis of low boiling hydrocarbons is the question of volumetric measurement (ASTM D1071) and sampling (ASTM D1265). However, sampling liquefied petroleum gas from a liquid storage system is complicated by existence of two phases (gas and liquid) and the composition of the supernatant vapor phase will, most probably, differ from the composition of the liquid phase. Furthermore, the compositions of both phases will vary as a sample (or sample) is removed from one or both phases. An accurate check of composition can only be made if samples are taken during filling of the tank or from a fully charged tank.

For reservoirs that consists of tight formations and shale formations and where the gas likely contains gas condensate constituents that are at pressures above the dew point in the reservoir, it is important (in fact, necessary) to acquire and maintain the sample as a single-phase fluid. If the fluid pressure drops below the dew point, it may take a considerable period to recombine the sample. Moreover, changes that occur in a sample in the wellbore to the surface may be irreversible. Thus, a sample that is single-phase when collected should he kept in a single phase when brought to surface. Sample bottle designed for this purpose are available. A single-phase sample bottle uses a nitrogen cushion to increase the pressure in the sample and although the sample cools as it is brought to surface the nitrogen cushion on the sample maintains the pressure above the dew point pressure, which is the pressure at which the first drop of liquid is formed when the sample passes from the vapor phase to a two-phase system.

In addition, natural gas, under certain conditions may undergo the phenomenon known as retrograde condensation. This phenomenon is associated with the behavior of the gas mixture in the critical region wherein, at constant temperature, the vapor phase in contact with the liquid phase may be condensed by a decrease in pressure or at constant pressure where the vapor is condensed by an increase in temperature. Caution is advised when dealing with gas from tight formations and tight shale formations where condensation of the liquid from the gaseous phase can cause blockages in the flow channels thereby negating the benefit (increased flow of the gas) of the hydraulic fracturing process.

In general, the sampling of gaseous constituents and of liquefied gases is the subject of a variety of sampling methods (ASTM D5503), such as the manual method (ASTM D1265; ASTM D4057), the floating piston cylinder method (ASTM D3700), and the automatic sampling method (ASTM D4177; ASTM D5287). Methods for the preparation of gaseous and liquid blends are also available (ASTM D4051; ASTM D4307) including the sampling and handling of fuels for volatility measurements (ASTM D5842).

Sampling methane (CH_4) and ethane (C_2H_6) hydrocarbons is usually achieved using stainless steel cylinders, either lined or unlined. However, other containers may also be employed dependent upon particular situations. For example, glass cylinder containers or polyvinyl fluoride (PVT) sampling bags may also be used but, obviously, cannot be subjected to pressures that are far in excess of ambient pressure. The preferred method for sampling propane (C_3H_8) and butane (C_4H_{10}) hydrocarbons is by the use of piston cylinders (ASTM D3700) although sampling these materials as gases is also acceptable in many cases. The sampling of propane and higher boiling hydrocarbons is dependent upon the vapor pressure of the sample (IP 410). Piston cylinders or pressurized steel cylinders are recommended for high-vapor pressure sampling where significant amounts of low boiling gases are present while atmospheric sampling may be used for samples having a low-vapor pressure.

4.2 Gas chromatography

Gas chromatography is used to give detailed information on the composition of natural gas from which physical properties (such as the gas interchangeability parameters Wobbe Index and Calorific Value) of the gas are calculated. The ASTM defines methods that should be used to evaluate the performance of a gas chromatograph. Presenting the instrument with a number of gases of known composition that are traceable to national or international standards and that cover the composition range of each component provides information on the linearity of the detector and any bias that will result from using a single-point calibration.

4.3 Infrared absorption

Infrared radiation (IR, wavelength range is some _m) is absorbed by gases such as carbon monoxide (CO), carbon dioxide (CO_2), sulfur dioxide (SO_2), or nitric oxide (NO) at a wavelength that is specific for the gas. As IR radiation passes through a measuring cell filled with the gas to be analyzed an increase in the gas concentration causes a corresponding increase in IR absorption and thus a decrease in the radiation intensity received by the IR detector. To ensure selectivity for just one gas component two different principles are used: The **dispersive** principle uses radiation, which has been dispersed by a prism or grating before entering the measuring cell. Only two wavelengths (or narrow wavelength ranges) of the entire spectrum are used, one that the component in question absorbs and one that not, as a reference. The ratio of absorption at these two wavelengths is a measure for the gas concentration.

The non-dispersive (NDIR) principle uses a broad band of radiation from a lamp or glower without dispersion before entering the measuring cell. When a component that does absorb infrared radiation is present in the sample gas the radiation intensity reaching the detector will be reduced at the specific part of the spectrum. Two methods are in use for detecting the level of absorption:

- A *gas detector* filled specifically with the gas of interest will, from the broadband radiation leaving the measuring cell, detect only the component of interest resp. its variations caused by the varying concentration of the component in the sample gas passing through the measuring cell. Radiation absorption affects the gas pressure in the detector cell; these pressure variations are used to generate a detector signal as measure of the concentration of the gas of interest.
- A *solid state IR detector* is used together with a narrow-band interference filter that allows from the broadband spectrum of IR radiation only the radiation range of the component of interest (e.g. CO2) to pass through. As the IR radiation passes through the measuring cell a variation in CO2 concentration will cause a proportional variation in the IR absorption and thus in the detector.

4.4 Ultraviolet absorption

Certain gas components, such as sulfur dioxide or nitric oxide, absorb also ultraviolet (UV) radiation. For these components the UV method competes with the IR method offering the major advantage, that water does not cause any interference effect in the UV absorption range. In contrast to infrared (IR) light sources, however, ultraviolet (UV) light sources are more expensive and therefore the ultraviolet method is used preferably for particular applications.

4.5 Chemiluminescence detector

The method using a chemiluminescence detector (CLD) is mainly used for the determination of low concentrations of NO and NO2. It is based on the feature of NO to react with ozone (O_3) resulting in the emission of characteristic light radiation (chemiluminescence). The intensity of the emitted radiation is proportional to the NO concentration. Such analyzers (CLD, chemiluminescence detectors) are very common for analysis of NO and NO2 in car exhaust gases. They comprise essentially an ozone generator, an enrichment and reaction chamber, and a photomultiplier detector.

4.6 Thermal conductivity

This principle (mostly applied for the analysis of hydrogen) uses the different values of thermal conductivity of two gases (sample and reference gas). In the analyzer a Wheatstone bridge circuit is built in the filaments of which act at the same time as source of heat and as detector of temperature changes. The bridge is positioned with one part in the sample gas and with the other part in the reference gas. The different cooling of the filaments due to the different gas compositions result in an electrical signal that is used for further processing.

4.7 Flame ionization detection

The sample gas together with the hydrocarbon derivatives is introduced into a flame (usually hydrogen/air) where the hydrocarbon derivatives are ionized. The positively charged ions are collected by a negatively charged collecting electrode generating a current proportional to the hydrocarbon concentration. The different sensitivity of this principle to different hydrocarbon compounds is taken into account by applying specific response factors during data evaluation.

5. Gas condensate

The fluids present in a reservoir are the result of a series of thermodynamic changes of pressure and temperature suffered by the original mixture of hydrocarbon derivatives over time and during its migration from the container rock to the trap (Chapter 2). In addition, just as crude oil, can vary in composition over the life of a production well (Whiston and Belery, 1994; Speight, 2014a), gas-condensate wells can also experience a significant decrease in condensate productivity and condensate composition once the flowing bottom-hole pressure drops below the dew-point pressure (Wheaton and Zhang, 2000; Fahimpour and Jamiolahmady, 2014). Also, reservoir pressure and temperature increase with depth and their relative relationship will influence the behavior of the low-boiling and high-boiling components that the fluid could contain (Wheaton, 1991). Typically, the content of low-boiling constituents in a mixture of hydrocarbon derivatives increases with temperature and depth, which may result in reservoirs near the critical point; gas condensate reservoirs are included in this kind of fluids.

Natural gas reservoirs have also been divided into three groups: (i) a dry gas reservoir, (ii) a wet gas, and (iii) a retrograde-condensate gas (Chapter 1). A dry-gas reservoir is a reservoir that produces a single composition of gas that is constant in the reservoir, wellbore, and lease-separation equipment throughout the life of a field. Some liquids may be recovered by processing in a gas plant. A wet-gas reservoir is a reservoir that produces a single gas composition to the producing well perforations throughout its life. Gas condensate will form either while flowing to the surface or in lease-separation equipment (Thornton, 1946).

The term *gas condensate* (or *condensate*) is often applied to any liquid composed of low-boiling hydrocarbon derivatives produced from a gas well (Table 7.8). However, the term *condensate reservoir* should be applied only to those reservoirs situations in which condensate is formed in the reservoir because of retrograde behavior. Wet-gas reservoirs can always be treated as containing single-phase gas in the reservoir, while retrograde-condensate reservoirs may not. Wet-gas reservoirs generally produce low-boiling liquids with gravities similar to those for retrograde condensates, but with yields less than approximately 20 standard stock barrels per million cubic feet (STB/MMscf). More pertinent to the present text, like the condensate from conventional natural gas wells, condensate is an important component of what comes out of wells drilled into tight formations.

Generally, gas condensate fields are typically a single subsurface accumulation of gaseous hydrocarbon derivatives including low-boiling hydrocarbon derivatives (C_5 to C_8 hydrocarbon derivatives) and, less frequently, constituents with a higher molecular weight (typically C_9 to C_{12} hydrocarbon derivatives) (Owens, 2019). In case of the isothermal reduction of the formation pressure, part of the condensate constituents will condense in the form of gas condensate. Reservoirs with the relative amount of at least 5−10 g of condensate per cubic meter are usually referred to as gas condensate reservoirs. Gas condensate reservoirs can

TABLE 7.8 Typical chemical and physical properties of condensate.

Property	Comment/Value
Appearance	Amber to dark brown
Physical Form	Liquid
Odor	Due to presence of hydrogen sulfide
Vapor Pressure	5 to 15 psia (Reid VP) @ 37.8 °C (100 °F)
Initial Boiling Point/Range	-29 to 427 °C (-20 to 800 °F)
Solubility in Water	Negligible
Specific Gravity (water = 1)	0.78 to 0.825 @ 15.6 °C (60 °F)
API gravity	50 to 40
Flash Point	-46 °C (-51 °F)
Lower Explosive Limits (% v/v in air)	1.1
Upper Explosive Limits (% v/v in air)	6.0
Auto-ignition Temperature	310 °C (590 °F)

be confined in any formations that from suitable traps and arbitrarily defined in two ways: (i) primary gas condensate reservoirs formed at the depths in excess of 10,000 feet below the surface that are separate from crude oil accumulations, and (ii) secondary gas condensate reservoirs formed through partial vaporization of the constituents of the crude oil. There are saturated gas condensate fields (the formation pressure is equal to the pressure of initial condensation) and non-saturated gas condensate fields (the initial condensation pressure is lower than the formation pressure) according to the thermo-baric conditions.

Gas condensate (sometimes referred to as *naphtha*, *low-boiling naphtha*, or *ligroin*) contains significant amounts of C_{5+} components (usually to C_8 or C_{10} components depending upon the source), and they exhibit the phenomenon of *retrograde condensation* at reservoir conditions, in other words, as pressure decreases, increasing amounts of liquid condenses in the reservoir (down to approximately 2000 psia). This results in a significant loss of in situ condensate reserves that may only be partially recovered by revalorization at lower pressures.

There is also a refinery-produced hydrocarbon product that is also somewhat interchangeable with natural gasoline and lease condensates, and that is naphtha, specifically low-boiling naphtha (also called light naphtha). Most of the naphtha is produced from crude oil in the first step of the refining process − distillation (Parkash, 2003; Pandey et al., 2004; Gary et al., 2007; Speight, 2014a, 2017; Hsu and Robinson, 2017). Low-boiling naphtha is composed primarily of pentane hydrocarbon derivatives and hexane hydrocarbon derivatives with minor amounts of higher molecular weight hydrocarbon derivatives. Condensate can be processed through a splitter (effectively a stand-alone, small crude oil distillation tower) that separates the condensate boiling range materials from the lower-boiling natural gas liquids and higher-boiling hydrocarbon derivatives to yield a clean condensate product that can be used as both a feedstock for refinery upgrading processes and for the production of petrochemicals. Thus, the low-boiling naphtha fraction is similar in properties to the typical lease condensate and natural gasoline and is included in this chapter as a means of comparison.

A retrograde-condensate gas reservoir initially contains a single-phase fluid, which changes to two phases (condensate and gas) in the reservoir when the reservoir pressure decreases. Additional condensate forms with changes in pressure and temperature in the tubing and during lease separation. From a reservoir standpoint, dry and wet gas can be treated similarly in terms of producing characteristics, pressure behavior, and recovery potential. Studies of retrograde-condensate gas reservoirs must consider changes in condensate yield as reservoir pressure declines, the potential for decreased well deliverability as liquid saturations increase near the wellbore, and the effects of two-phase flow on wellbore hydraulics.

However, the terms used in discussing gas condensate have not been formally accepted as a standard nomenclature and tend to be general descriptions of the condensate rather than chemical descriptions. For example, both distillate and condensate are used synonymously to describe the low-boiling liquid produced during the recovery of natural gas and it has become the standard procedure to adopt somewhat arbitrarily a set of terms, and to explain the meaning of each term as introduced to avoid confusion. Generally, some wells produce, together with large volumes of gas, a water-white or light straw-colored liquid which resembles gasoline or kerosene in appearance. This liquid has been called distillate because of the resemblance to products obtained in the refinery by distilling the volatile components from crude oil. Also, the liquid has been called condensate because it is condensed out of the gas produced by the well. The latter term shall be used throughout this paper.

Condensate differs substantially from conventional crude oil insofar as (i) the color of crude oil typically varies from dark green to black − typically, condensate is almost colorless, (ii) crude oil typically contains some naphtha which is often incorrectly referred to as gasoline − condensate is almost equivalent in boiling range to the low-boiling naphtha fraction of crude oil, (iii) crude oil usually contains dark-colored, high molecular weight non-volatile components − condensate does not contain any dark-colored, high molecular weight non-volatile components, and (iv) the API gravity of crude oil, which is measure of the weight per unit volume or density, is commonly less than 45° − condensate typically has an API gravity on the order of 50° and higher (Speight, 2014a, 2015). Furthermore, although the difference between retrograde-condensate and wet gas is notable, there is much less distinction between wet gas and dry gas. For both wet gas and dry gas, reservoir engineering calculations are based on a single-phase reservoir gas. The only issue is whether there is a sufficient volume of produced liquid to be considered in such calculations as material balance or wellbore hydraulics. Retrograde systems require more-complex calculations using equation of state that depend upon data produced in an analytical or research laboratory.

When production of a hydrocarbon reservoir commence, analysis plays a major role in determining the types of fluids that are present, along with their main physicochemical characteristics (Speight, 2014a, 2015). Generally, that information is obtained by performing a pressure-volume-temperature (PVT) analysis on a fluid sample of the reservoir as well as other physical analyses which relate to phase behavior and other phenomena, especially the viscosity-temperature relationship (Whitson et al., 1999; Loskutova et al., 2014). Conventional production measurements, such as a drill stem test (DST) are the only parameters that can be measured almost immediately after a well is completed (Breiman and Friedman, 1985; Kleyweg, 1989; Dandekar and Stenby, 1997).

From a reservoir engineering perspective, the issues which must be addressed (by analysis) in a gas condensate reservoir are: (i) the variation of the condensate yield will vary during the life of a reservoir, and (ii) the manner in which the two-phase gas/oil flow near to the wellbore affects *gas* productivity (Whitson et al., 1999). Both of these issues are strongly related to the pressure-volume-temperature properties of the fluid system (though productivity is more affected by relative permeability effects).

It is in the development of gas condensate reservoirs that analytical data reach a high level of importance. Compositional grading in gas condensate reservoirs is important to (i) the design of the pattern of placement of the production wells, (ii) estimation of in-place surface volumes, reserves, and (iii) prediction of fluid communication vertically (between geologic layers) and horizontally (between fault blocks) (Organick and Golding, 1952; Niemstschik et al., 1993). Prediction of a potential underlying crude oil reserve is often required in discovery wells which are drilled up-structure and encounter only gas which is near-saturated. In such cases, accurate sampling, accurate analysis (though the use of standard test methods) (Speight, 2015, 2018;; ASTM, 2019), and pressure-volume-temperature modeling are of paramount importance (Pedersen and Fredenslund, 1987; McCain, 1990; Marruffo et al., 2001). A pressure-volume-temperature model should describe accurately the key phase, volumetric, and viscosity behavior dictating the key processes affecting rate-time performance and ultimate recovery of gas and oil at the wellhead.

However, a pressure-volume-temperature model may not be capable of accurately describing *all* pressure-volume-temperature properties with equal accuracy. Models based on equations of state often have difficulty matching retrograde phenomena (compositional variation of gas, and liquid dropout), particularly when the system is near-critical, or only small amounts of condensation occur just below the dewpoint (tail-like retrograde behavior). Also, the viscosity is physical property that is often difficult to predict for reservoir condensates, and a measure of the viscosity is not usually available for completion (sometimes referred to as *tuning*) the viscosity model. Consequently, it is important to determine which pressure-volume-temperature properties are most important for the accurate engineering of reservoir and well performance for a given field development. Different fields require different degrees of accuracy for different pressure-volume-temperature properties, dependent on field development strategy (depletion vs. gas cycling), low or high permeability, saturated or highly undersaturated, geography (offshore or onshore), and the number of wells available for delineation and development.

The pressure-volume-temperature properties that are important to the engineering of all gas condensate reservoirs include: (i) the Z-factor, (ii) the gas viscosity, (iii) the variation of the condensate composition (C_{7+}) with pressure, and (iv) the viscosity of the oil as well as any liquid dropout (Lee et al., 1966; Hall and Yarborough, 1973). These properties are particularly important to reservoirs produced by pressure depletion. For gas condensate reservoirs undergoing gas cycling it may also be important to quantify phase behavior (vaporization, condensation, and near-critical miscibility) which develops in gas cycling *below the dewpoint*.

Thus, an important aspect of any estimation of a reservoir fluid(s) is a matter obtaining preliminary values of properties such as: (i) the amount of heptane and higher-boiling constituents (C_{7+}), (ii) the molecular weight of the original fluid, (iii) the maximum retrograde condensation, and (iv) the dew point pressure, P_d (Nemeth and Kennedy, 1967; Breiman and Friedman, 1985; Potsch and Bräuer, 1996; Dandekar, and Stenby, 1997; Elsharkawy, 2001; Marruffo et al., 2001.). Most of these properties are an extremely important aspect of the development of a gas condensate reservoir and the early availability of such data will allow the production engineers to carry out reservoir studies that will ensure an efficient exploitation and maximize the final recovery of the liquids present in the reservoir. The only parameter needed to use these correlations is the value of the gas condensate ratio (GCR) of the fluid during the early stage of production (Paredes et al., 2014). Providing the input data are satisfactory, the empirical equations should be valid for *any* gas condensate reservoir, although a range of usability is proposed for a better performance of the correlations.

5.1 Types of condensate

The hydrocarbon products described in the following paragraphs have been used for years as feedstocks (i) for refinery upgrading processes, (ii) for gasoline blending, and (iii) as feedstocks for petrochemical processes, among other uses. All of these product categories in the condensate family — lease condensates, plant condensates (natural gasoline), and low-boiling naphtha — are, in general terms, composed of the same hydrocarbon constituents (Sujan et al., 2015; Speight, 2018, 2019). However, it is only the lease condensates that are produced directly from the wellhead without further processing. This distinction turns out to be important when the specifications derived by means of the application of standard analytical test methods are applied to these products.

5.1.1 Gas condensate

By way of recall, natural-gas condensate is a low-density mixture of hydrocarbon liquids (as opposed to natural gas liquids that are typically the low-boiling hydrocarbon derivatives (such as ethane, propane, and the butane isomers that are gases at ambient temperature and pressure) that are present as gaseous components in the unprocessed natural gas produced. Some low-molecular weight hydrocarbon derivatives within the unprocessed natural gas will condense to a liquid state if the temperature is reduced to a temperature that is below the hydrocarbon dew point temperature at a set pressure.

Typically, gas condensate can be produced along with significant volumes of natural gas and is recovered at atmospheric temperatures and pressures from the wellhead gas production. The raw (unrefined) gas condensate is produced from a reservoir come out of the ground as mixtures of various hydrocarbon compounds including natural gas liquids, pentane derivatives (C_{5s}), hexane derivatives (C_{6s}), and depending on the condensate, a mixture of higher molecular weight hydrocarbon derivatives in the heptane (C_7) to decane (C_{10}) or even dodecane (C_{12}) carbon-number range.

5.1.2 Lease condensate

Lease condensate is produced at the wellhead as an unprocessed (unrefined) liquid except for stabilization at or near the wellhead. Lease condensates have wide range of API gravity from 45 to 75°. Lease condensates are produced at many sites in the United States, particularly near to the Gulf Coast of the United States from fields such as Eagle Ford and other shale basins.

Lease condensate can be produced along with significant volumes of natural gas and is typically recovered at atmospheric temperatures and pressures from the wellhead gas production. These raw condensates come out of the ground as mixtures of various hydrocarbon compounds including natural gas liquids (NGLs), pentane derivatives (C5+), hexane derivatives (C6+), and depending on the condensate, varying amounts of higher molecular weight hydrocarbon derivatives in the C7, C8 and even higher molecular weight range.

A lease condensate has an API gravity ranging between 45 and 75°. Those with a high API (which is typically clear or translucent in color) contain substantial amounts of natural gas liquids (including ethane, propane and butane) and not many of the higher molecular weight hydrocarbon derivatives. The lower-API gravity condensates with a lower API gravity (on the order of 45°) level look more like crude oil and have much higher concentrations of the higher-boiling higher molecular weight hydrocarbon derivatives (C7, C8+). In between, a wide range of condensates vary in color.

The higher API gravity condensate can be difficult to handle due to their high vapor pressure and are usually stabilized at the wellhead. In this wellhead process (as compared to the more detailed processes, the condensate is passed through a stabilizer which may be nothing more than a large tank (Fig. 7.1) or a series of tanks (Fig. 7.2) that allows the high vapor pressure components (the NGLs) to vaporize and to be collected for processing as natural gas liquids. That leaves a stabilized condensate that has a lower vapor pressure which is easier to handle, particularly when it must be shipped by truck or rail.

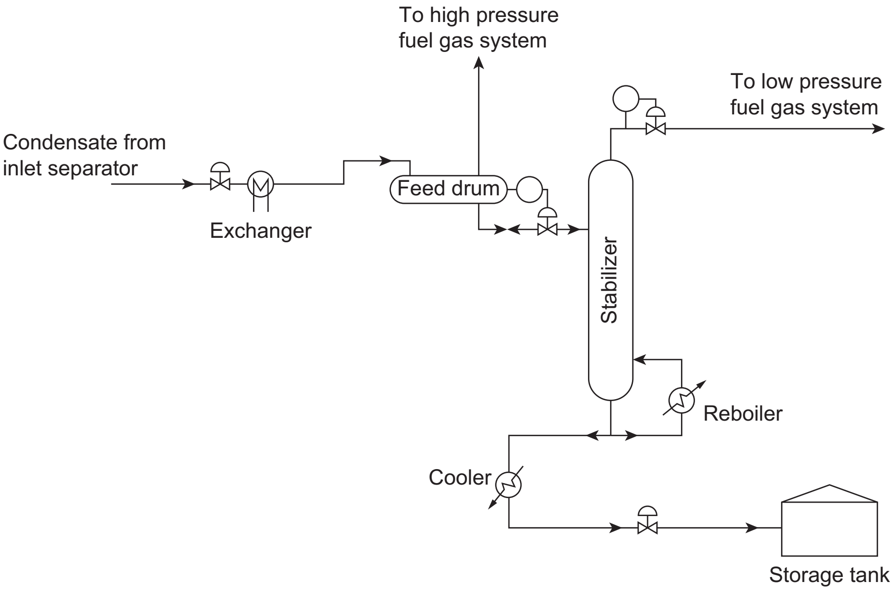

FIG. 7.1 The single-tower process for condensate stabilization by fractionation (Mokhatab et al., 2006).

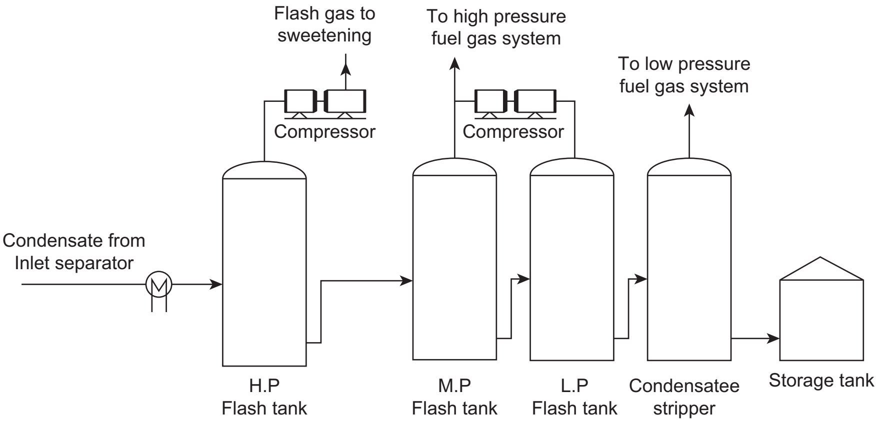

FIG. 7.2 Schematic of the condensate stabilization by flash vaporization (Mokhatab et al., 2006).

5.1.3 *Plant condensate*

Plant condensate is a product of plants that process natural gas liquids and is almost equivalent to natural gasoline. Plant condensate is an alternate term that may be applied to natural gasoline which is composed of hydrocarbon components that are similar to the hydrocarbon constituents in lease condensate, i.e. pentane derivatives (C_{5s}), some hexane derivatives (C_{6s}) and small quantities of higher molecular weight hydrocarbon derivatives. Since it comes from a processing plant, plant condensate is considered to be processed product rather than a naturally-occurring product.

Furthermore, since plant condensate (or natural gasoline) is the product of a processing plant, the quality of the natural gasoline (defined by the specifications) are in closer ranges than lease condensates. However, both products can be used interchangeably in some markets, such as crude blending and as a diluent for tar sand bitumen (Speight, 2014a, 2017).

5.2 Production

The operating method for each reservoir should be based upon the characteristics of the gas condensate at reservoir conditions. Other factors such as richness of the gas, size of the reserve, capacities of wells, nature of the reservoir, and mode of occurrence of the gas condensate must be considered. Marketing conditions and other economic factors also are important. Due to the increasing volume of the gas market, and prospects for chemical conversion of gas to liquid fuel by the Fischer-Tropsch process, many operators will be required to make a choice or compromise between complete pressure maintenance and gas sales. This can be done intelligently with known methods of evaluation.

Gas-condensate fields (also called gas-distillate) are today quite commonplace on the Louisiana and Texas Gulf Coast of the United States but are not necessarily confined to that area. The frequency with which they are being discovered and their economic importance in the crude oil industry have increased tremendously with the trend toward deeper drilling. A common understanding of best operating practices by oil operators, land or royalty owners, regulatory bodies, and legislators is necessary if all parties of Interest are to cooperate in realizing the maximum potentialities from these fields. During the past decade in particular, much has been learned and written regarding each of the many phases of gas-condensate operations.

There are many different equipment configurations for the processing required to separate natural gas condensate from a raw natural gas. In the example used here (Fig. 7.3), the raw natural gas feedstock from a gas well or a group of wells is cooled to lower the gas

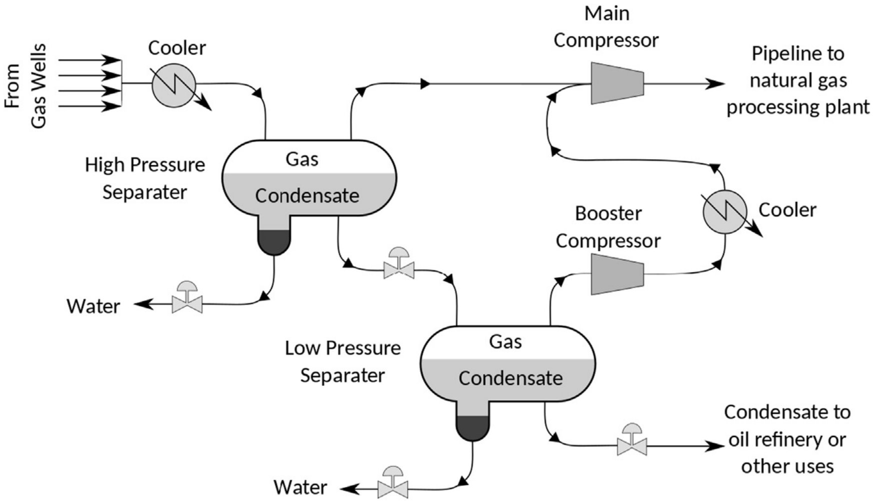

FIG. 7.3 Example of a gas condensate separation process.

temperature to below the hydrocarbon dew point at the feedstock pressure which condenses a large part of the gas condensate hydrocarbon derivatives. The feedstock mixture of gas, liquid condensate, and water is then routed to a high-pressure separator vessel where the water and the raw natural gas are separated and removed. The raw natural gas from the high-pressure separator is sent to the main gas compressor. Then, the, he gas condensate from the high-pressure separator flows through a throttling control valve to a low-pressure separator. The reduction in pressure across the control valve causes the condensate to undergo a partial vaporization (flash vaporization). The raw natural gas from the low-pressure separator is sent to a booster compressor which raises the gas pressure and sends it through a cooler, and then to the main gas compressor. The main gas compressor raises the pressure of the gases from the high-pressure and low-pressure separators to the pressure that is required for the transportation of the gas by pipeline to the natural gas processing plant.

At the processing plant, the raw natural gas will be dehydrated and acid gases as well as other impurities will be removed from the gas stream after which the ethane, propane, butane isomers, pentane derivative, plus any other high molecular weight hydrocarbon derivatives will also be removed and recovered as valuable byproducts (Chapter 7). The water removed from both the high and low-pressure separators may need to be processed to remove hydrogen sulfide (H_2S) before the water can be disposed of underground or reused in some fashion. Some of the raw natural gas may be re-injected into the producing formation to help maintain the reservoir pressure, or for storage pending later installation of a pipeline.

At the raw natural gas processing plant, the gas is dehydrated, and acid gases and other impurities are removed from the gas (Chapter 6, Chapter 7). Then the ethane, propane butane isomers and the pentanes and higher molecular weight hydrocarbon derivatives (the C_5+ fraction) are also be removed and recovered as byproducts. The water removed from both the high and low-pressure separators will probably need to be processed to remove hydrogen sulfide before the water can be disposed of or reused in some fashion.

However, the production of condensate can be complicated because of the pressure sensitivity of some condensates. During production, there is a risk of the condensate changing from gas to liquid if the reservoir pressure drops below the dew point pressure. The reservoir pressure can be maintained by fluid injection if gas production is preferable to liquid production.

5.3 Condensate stabilization

Gas condensate is lower molecular weight than crude oil, higher molecular weight than natural gas liquids, and, in its natural form, can be dangerous to store and transport. Therefore, stabilizing is often required to ensure the condensate meets safety specifications, usually measured by vapor pressure. In addition. condensate is often considered to be an extremely high-quality light (low-density, high volatility) crude oil. In comparison to typical crude oil, condensate needs to undergo fewer refining processes and is therefore very economical from the start. Because of the less complex refining process condensate and the potential used of condensate as a blend-stock for various products, it is a resource that is very much in demand.

Whenever gas condensate is produced from a well, a major issue that arises because of the separation of gas condensate and further use of the condensate, is the presence of more volatile constituents such as the hydrocarbon gases: methane, ethane, propane and butane isomers that are dissolved in the condensate liquids. In some cases, the gas condensate recovered from natural gas may be shipped without further processing but is stabilized often for blending into the crude oil stream and thereby sold as crude oil. In the case of raw gas condensate, there are no specifications for the product other than the process requirements.

Condensate stabilization is the process of increasing the amounts of the intermediate constituents (C_3 to C_5 hydrocarbon derivatives) and higher molecular weight constituents (C_6 and C_{6+} hydrocarbon derivatives) in the condensate. This process is performed primarily to reduce the vapor pressure of the condensate liquids so that a vapor phase is not produced upon flashing the liquid to atmospheric storage tanks. In other word, the scope of this process is to separate the very low-boiling hydrocarbon gases – methane and ethane in particular – from the higher molecular weight hydrocarbon components (C_3+).

Thus, an example of condensate stabilization is the use of a flash procedure to remove the lower boiling hydrocarbon derivatives. For example, after degassing and dewatering in the production separation process, pressurized liquid condensate enters the condensate stabilizer and flows through an exchanger in which hot, stabilized condensate is used to preheat the unstabilized condensate. After preheating, the unstabilized condensate flows to the line heater, where it is heated to stabilization temperature on the order of 95–120 °C (205–250 °F). The heated, unstabilized condensate is sent to a flash-distilled in the condensate separator at approximately 35–45 psig to remove low-density hydrocarbon vapors and any remaining water. The stabilized condensate flows through the plate exchanger for cooling and then off-skid to atmospheric storage. Vapors from the condensate separator are routed through an air-cooled condenser to the natural gas liquids separator, where condensed propane and butane are recovered.

The stabilized liquid condensate typically has a vapor pressure specification, as the product will be injected into a pipeline or transport pressure vessel, which has definite pressure limitations. Condensates may contain a relatively high percentage of intermediate components and can be separated easily from entrained water due to its lower viscosity and greater density difference with water. Thus, condensate stabilization should be considered for each gas well production facility and stabilization. Stabilization of condensate streams can be accomplished through either (i) flash vaporization or fractionation.

5.3.1 Flash vaporization

Stabilization by flash vaporization is a simple operation employing only two or three flash tanks. This process is similar to stage separation utilizing the equilibrium principles between vapor and condensate phases. Equilibrium vaporization occurs when the vapor and condensate phases are in equilibrium at the temperature and pressure of separation.

In the process (Figs. 7.1 and 7.2), condensate from the inlet separator after passing through the exchanger enters to the high-pressure flash tank, where the pressure is maintained at 600 psia. A decrease in pressure, on the order of 300 psia is obtained, which assists flashing of large amounts of lower molecular weight ends, which join the sour vapor stream after recompression. The vapor can either be processed further and put into the sales gas or be recycled into the reservoir and used as gas lift to produce more crude oils. The bottom liquid from the high-pressure tank flows to the middle pressure flash tank operated at 300 psia. Additional methane and ethane are released in this tank. The bottom product is withdrawn again to the low-pressure tank operated at 65 psia. To ensure efficient separation, condensate is degassed in the stripper vessel at the lowest possible pressure prior to storage. This reduces excess flashing of condensate in the storage tank and reduces the inert gas blanket pressure required in it.

5.3.2 Stabilization by fractionation

In this single-tower process (Fig. 7.1), low-boiling constitunets such as methane, ethane, propane, and butane isomers are removed and recovered and the residue (that is nonvolatile under the process conditions) remains at the bottom of the column is composed mainly of pentanes and higher molecular weight hydrocarbon derivatives. The bottom product is thus a liquid free of all gaseous components able to be stored safely at atmospheric pressure.

The process, in its simplicity, is a derivation of the atmospheric tower for the distillation of crude oil in the refinery and uses the principle of reflux distillation. Thus, as the liquid descends in the column, it becomes leaner in lower-boiling constituents and richer in higher-boiling constituents. At the bottom of the tower some of the liquid is circulated through a reboiler to add heat to the tower. As the gas goes up from tray to tray, more and more of the heavy ends get stripped out of the gas at each tray and the gas becomes richer in the light ends and leaner in the heavy ends.

Overhead gas from the stabilizer, which would seldom meet market specifications for the natural gas market, is then sent to the low-pressure fuel gas system through a back-pressure control valve that maintains the tower pressure to set point. Liquids leaving the bottom of the tower have undergone a series of stage flashes at ever-increasing temperatures, driving off the low-boiling components, which exit the top of the tower. These liquids must be cooled to a sufficiently low temperature to keep vapors from flashing to atmosphere in the condensate storage tank.

In some cases, the tower process may operate as a non-reflux tower which is a simpler but less-efficient operation than the reflux tower operation since a condensate stabilization column with reflux will recover more intermediate components from the gas stream.

5.3.3 Condensate storage

Once the condensate has been stabilized, the stabilized product may require storage prior to sales. Condensate is stored between production and shipping operations in condensate storage tanks, which are usually of floating roof type (external and internal). If the condensate does not meet the specifications, the off-specification condensate may be routed to an off-specification condensate storage fixed roof tank (vertical and horizontal) until it is recycled to the condensate stabilization unit by the relevant recycle pump if the latter is available at the plant.

5.4 Properties

Briefly and by way of an explanation that relates to the properties of the liquid, *gas condensate* is a mixture of low-boiling hydrocarbon liquids obtained by condensation of hydrocarbon vapors: predominately butane, propane, and pentane with some higher molecular weight hydrocarbon derivatives and relatively little methane or ethane. *Natural gas liquids* (NGL) are the hydrocarbon liquids that condense during the processing of hydrocarbon gases that are produced from oil or gas reservoir and *natural gasoline* is a mixture of liquid hydrocarbon derivatives extracted from natural gas that is suitable for blending with the various refinery streams that are used to blend to produce the final sales gasoline (Speight, 2014a, 2017).

Gas condensate is generally recognized as a collection group of hydrocarbon derivatives that do not fit easily into mainstream product categories. Other definitions place condensates as liquid hydrocarbon derivatives somewhere between crude oil and natural gas liquids (NGLs). Technically, all condensates are similar to natural gasoline, the highest-boiling of the natural gas liquids. However, the term *condensate* can refer to several products made up of similar hydrocarbon compounds. Along with naphtha, the main uses of condensate fall into the general areas of (i) a blend-stock for gasoline and other liquid fuels, and (ii) a blend-stock for solvents.

On the other hand, naphtha is produced in the refinery by any one of several methods that include (i) fractionation of straight-run, cracked, and reforming distillates, or even fractionation of crude oil, (ii) solvent extraction, (iii) hydrogenation of cracked distillates, (iv) polymerization of unsaturated compounds, i.e. olefin derivatives, and (v) alkylation processes. In fact, the naphtha that has a low-to-high boiling range (0–200 °C, 32 to 390 °F) if often a combination of product streams from more than one of these processes and may contain constituents (such as olefins and even di-olefins) that are not typically found in the natural (non-thermal) gas condensate. On occasion, depending upon availability, gas condensate, natural gas liquids, and natural gasoline are combined with the naphtha streams to complement the composition and volatility requirements of a liquid stream for gasoline manufacture. In addition, the types of uses found for naphtha demands compatibility with the many other materials employed in the formulation of the naphtha, including gas condensate and natural gasoline. Thus, the solvent properties of a given fraction must be carefully measured and controlled. For most purposes volatility is important, and, because of the wide use of naphtha in industrial and recovery plants, information on some other fundamental characteristics is required for plant design.

When a condensed liquid (such as gas condensate) is present in gas streams, the analysis is more complicated. In the case of gas condensate, besides bulk analysis, there may be interest on surface-composition (often quite distinct to that of the bulk phase). Compositional analysis in which the components of the mixture are identified, may be achieved by (i) physical means, which is measurement of physical properties, (ii) pure chemical means, which is measurement of chemical properties, or more commonly (iii) by physico-chemical means. Gas analysis is even more may be dangerous and difficult if the composition is a complete unknown. However, when some main constituents are known to occur, the analysis gains accuracy (and may be easier) if the known component is removed; this is particularly important in the case of water vapor, which may condense on the instruments, or constituents when the molecular behavior may complicate spectral analyses. A more comprehensive list and description of the properties is available elsewhere (Speight, 2018).

Finally, the term *petroleum solvent* is often used synonymously with *naphtha*. However, naphtha may also be produced from tar sand bitumen, coal tar, and oil shale kerogen by thermal processes as well as by the destructive distillation of wood and from synthesis gas (mixtures of carbon monoxide and hydrogen produced by the gasification of coal and/or biomass or other feedstocks) which is then converted to liquid products by the Fischer Tropsch process (Davis and Occelli, 2010; Chadeesingh, 2011; Speight, 2011, 2013, 2014a, 2014b). For that reason and to remain within the context of this book, this chapter deals only with the low-boiling naphtha fraction that is produced by the processing of crude oil in refineries (Speight, 2014a, 2017, 2015; Hsu and Robinson, 2017, 2018).

5.4.1 Chemical composition

In terms of composition, natural-gas condensate is a low-density mixture of hydrocarbon liquids that are present as gaseous components in the raw natural gas produced from many natural gas fields. Natural gas condensate is also called condensate, or gas condensate, or sometimes natural gasoline because it contains hydrocarbon derivatives (n-hydrocarbon and other hydrocarbon isomers) within the naphtha boiling range (Table 7.4). Some gas species within the raw natural gas will condense to a liquid state if the temperature is reduced to below the hydrocarbon dew point temperature at a set pressure (Elsharkawy, 2001. Thus, condensates are a group of hydrocarbon derivatives that do not match the typical refinery product categories and have been defined as liquid hydrocarbon derivatives that lie between crude oil and natural gas liquids (NGLs). However, the reality is that most condensates differ significantly from crude oils and condensates are not like natural gas liquids but are similar only to natural gasoline, the highest boiling of the natural gas liquids. One the other hand, gas condensate and natural gasoline are often comparable to the lower boiling faction of naphtha.

More generally, naphtha is an intermediate hydrocarbon liquid stream derived from the crude oil and is usually desulfurized and then catalytically reformed to produce high-octane naphtha before blending into the streams that make up gasoline. Because of the variations in crude oil composition and quality as well as differences in refinery operations, it is difficult (if not impossible) to provide a definitive, single definition of the word naphtha since each refinery produces a site-specific naphtha − often with a unique boiling range (unique initial point and final boiling point) as well as other physical and compositional characteristics. On a chemical basis, crude oil naphtha is difficult to define precisely because it can contain varying amounts of the constituents (paraffin derivatives, naphthene derivatives, aromatic derivatives, and olefin derivatives) in different proportions depending on the source, in addition to the potential isomers of the paraffin derivatives that exist in the naphtha boiling range (the C_5 to C_8 or the C_5 to C_{10} boiling range) (Table 7.4).

In the refinery, naphtha is an unrefined or refined low-boiling distillate fraction, which usually boiling below 250 °C (480 °F), but often with a fairly wide boiling range depending upon the crude oil from which the naphtha is produced as well as the process which generates the naphtha. More specifically, there is a range of special-purpose hydrocarbon fractions that can be described as *naphtha*. For example, the 0−100 °C (32−212 °F) fraction from the distillation of crude oil is referred to as *light virgin naphtha* and the 100−200 °C

(212−390 °F) fraction is referred to as *heavy virgin naphtha*. The product stream from the fluid catalytic cracker is often split into three fractions: (i) boiling <105 °C/<220 °F is *light FCC naphtha*, (ii) the fraction boiling from 105 to 160 °C (220−320 °F) is *intermediate FCC naphtha* and (iii) the fraction boiling from 160 to 200 °C (320−390 °F) is referred to as *heavy FCC naphtha* (Occelli, 2010) These boiling ranges can vary from refinery to refinery and even within a refinery when the crude oil feedstock changes or blends of crude oil are used as refinery feedstock.

The so-called *petroleum ether* solvents are specific boiling range naphtha solvents, as is *ligroin*. Thus, the term *petroleum solvent* describes a special liquid hydrocarbon fractions obtained from naphtha and used in industrial processes and formulations. These fractions are also referred to as *industrial naphtha*. Other solvents include *white spirit* that is subdivided into *industrial spirit* (distilling between 30 °C and 200 °C, 86 °F to 390 °F) and *white spirit* (light oil with a distillation range of 135 °C−200 °C (275 °F to 390 °F). The special value of naphtha as a solvent lies in its stability and purity.

Regulatory requirements have enhanced the need for better test methods to control manufacturing and the distribution of gasolines. The addition of alcohol and ether as important blending components to gasoline to meet air quality standards has necessitated modifying some existing test methods and the development of new procedures. The desire to reduce manufacturing costs, coupled with the regulatory requirements, have enhanced the application of more cost-effective test methods including rapid screening procedures and wider use of online analyzers. During the early 1950s, instrumental analytical techniques, such as mass spectrometry, infrared, and ultraviolet spectroscopy, were being explored and used for hydrocarbon composition and structural analysis. Beginning with the mid 1950s, publications on gas chromatography began to appear in the literature, and this new technique was soon being used for analyzing a wide variety of hydrocarbon streams. As commercial instrumentation was developed, the application of gas chromatography grew rapidly, with volumes of information being published from its beginning up to the present time. Recently, more rapid spectrometry methods such as infrared and near-infrared and the use of hyphenated analytical techniques, for example GC−MS, have been applied with success to the characterization of low-boiling distillates.

The proportion of aromatic constituents in hydrocarbon liquids is a key characteristic of that will affect a variety of properties of the oil including its boiling range, viscosity, stability, and compatibility of the oil with polymers. In the current context, this is particularly the case for gas condensate and, especially, for natural gasoline where the context of aromatic constituents may influence the compatibility of the gas condensate or the natural gasoline as a blend stock with other refinery liquids. The aromatic hydrogen and aromatic carbon contents determined by a standard test method can be used to evaluate changes in aromatic contents of hydrocarbon oils due to changes in processing conditions and to develop processing models in which the aromatic content of the hydrocarbon oil is a key processing indicator. Existing methods for estimating the content of the aromatic constituents use physical measurements, such as refractive index, density, and number average molecular weight or infrared absorbance and often depend on the availability of suitable standards. These procedures do not require standards of known aromatic hydrogen or aromatic carbon contents and are applicable to a wide range of hydrocarbon liquids with the caveat that the hydrocarbon liquids must be soluble in chloroform at ambient temperature.

However, it must be recognized that composition varies with depth in crude oil reservoirs (Speight, 2014a) and component segregation due to gravitational forces is usually given as the physical explanation for the variation in composition. The result of gravitational segregation is that a gas condensate gets richer at greater depths, with increasing C_{7+} mole fraction (and dewpoint pressure) (Whitson and Belery, 1994). However, not all fields show compositional gradients with depth as predicted by the isothermal model. Some fields show practically no gradient over large depths while other oil fields have gradients larger than predicted by the isothermal model (Høier and Whitson., 1998). Variation in C_{7+} composition with depth will obviously affect the calculation of initial surface condensate in place, compared with a calculation based on a constant composition.

Sulfur compounds are most commonly removed or converted to a harmless form by chemical treatment with lye, doctor solution, copper chloride, or similar treating agents (Mokhatab et al., 2006; Speight, 2014a, 2017, 2019). Hydrorefining processes (Speight, 2014a, 2017) are also often used in place of chemical treatment. When used as a solvent, gas condensate and natural gasoline can be blended with naphtha (subject to incompatibility restrictions (Chapter 6) (Speight, 2014a) and are selected because of the low content of sulfur-containing constituents. Such blends, also with a low content of aromatic derivatives may have a slight odor, but the aromatic derivatives increase the solvent power of the blend and there is not always the need to remove the aromatic derivatives from the blend (or prior to the blending operation) unless an odor-free product is specified.

5.4.2 Physical properties

The physical properties of gas condensate depend, as should be expected, on the types of hydrocarbon derivatives present in these liquids. In general, the aromatic hydrocarbon derivatives having the highest solvent power and the straight-chain aliphatic compounds the lowest. The solvent properties can be assessed by estimating of the amount of the various hydrocarbon types present be made. This method provides an indication of the solvent power of the condensate on the basis that aromatic constituents and naphthene-type constituents provide dissolving ability that paraffinic constituents do not.

When a hydrocarbon reservoir is discovered it is important to know the type of fluids that are present as well as their main physicochemical characteristics, this is normally obtained by performing a pressure-volume-temperature analysis to a representative fluid sample of the reservoir. In most cases, having a pressure-volume-temperature analysis can take several months, which limits the number and type of reservoir studies that can be carried out during this period (Paredes et al., 2014). The only parameter that can be measured almost immediately after a well is completed, are conventional production measurements. In some cases, this production measurement can be obtained before completing the well by using special testing or measuring equipment such as a drill stem test (DST).

It is important to obtain preliminary values of properties such as: molar percentage of heptane and higher molecular weight components (% mole of C_{7+}), molecular weight of the original fluid (MW), maximum retrograde condensation (MRC) and dew point pressure (P_d). Most of these properties are very important for exploitation of gas condensate reservoir and their early availability will allow engineers to carry out reservoir studies that will ensure an efficient exploitation and maximize the final recovery of the liquids present in the reservoir.

Fluids present in an oil reservoir are the result of a series of thermodynamic changes of pressure and temperature suffered by the original mixture of hydrocarbon derivatives over time and during its migration from the container rock to the trap. Reservoir pressure and temperature increase with depth and their relative relationship will influence the behavior of the lower-boiling and higher-boiling components that the fluid stream could contain. In general, the content of low-boiling constituents in a mixture of hydrocarbon derivatives increases with temperature and depth, which may result in reservoirs near the critical point; gas condensate reservoirs are included in this kind of fluids (Ovalle et al., 2007).

Certain fluid properties are required for studies related to management of gas/condensate reservoirs or prediction of condensate reserves. Often these studies must begin before laboratory data become available, or possibly when laboratory data are not available. Correlations to estimate values of these properties have been developed that are based solely on commonly available field data. These properties are the dewpoint pressure of the reservoir fluid, changes in the surface yield of condensate as reservoir pressure declines, and changes in the specific gravity of the reservoir gas as reservoir pressure declines (Gold et al., 1989). No correlations based solely on field data have been published for any of these properties.

Reservoir fluid properties are used to characterize the condition of a fluid at a given state. A reliable estimation and description of the properties of hydrocarbon mixtures is fundamental in crude oil and natural engineering analysis and design. Fluid properties are not independent, just as pressure, temperature, and volume are not independent of each other. Equations of State provide the means for the estimation of the pressure-volume-temperature relationship, and from them many other thermodynamic properties can be derived. Compositions are usually required for the calculation of the properties of each phase.

The field data required are initial producing gas/condensate ratio from the first-stage separator, initial stock-tank liquid gravity in degrees API, specific gravity of the initial reservoir gas, reservoir temperature, and selected values of reservoir pressure. The dewpoint pressure correlation is based on data of 615 samples of gas condensates with worldwide origins. The other two correlations are based on 851 lines of constant-volume-depletion data from 190 gas-condensate samples, also with worldwide origins.

There are many condensate sources, and each has its own unique gas condensate composition. In general, gas condensate has a specific gravity ranging from 0.5 to 0.8, and is composed of hydrocarbon derivatives such as propane, butane, pentane, hexane, and often higher molecular weight hydrocarbon derivatives up to decane. Natural gas compounds with more carbon atoms (e.g. pentane, or blends of butane, pentane and other hydrocarbon derivatives with additional carbon atoms) exist as liquids at ambient temperatures. Additionally, condensate may contain other impurities such as: (i) hydrogen sulfide, H_2S, (ii) thiols, traditionally also called mercaptans and denoted as RSH, where R is an organic group such as methyl, ethyl, propyl, and the like, (iii) carbon dioxide, CO_2, (iv) straight-chain alkane derivatives having from 2 to 10 carbon atoms, denoted as C_2 to C_{12}, (v) cyclohexane and perhaps other naphthene derivatives, and (vi) aromatic derivatives such as benzene, toluene, xylene isomers, and ethylbenzene (Pedersen et al., 1989).

The primary difficulties in producing condensate reservoirs are as follows: (i) liquid deposition near the wellbore causes a decrease in gas deliverability that can approach 100% in a reservoir with less than 50-md permeability, and (ii) a large amount of the most valuable hydrocarbon components is left in the reservoir rather than produced. Thus, the compositional analyses of gas condensate are used to describe the fluid makeup on a component basis, including calculation of British thermal unit (BTU) (energy content) of gases and optimization of separator conditions for liquid yield. In addition, the suitability of the condensate as a blending component in a gasoline plant (Speight, 2014a, 2015, 2017) is an important aspect of determining the compatibility of the condensate with the other components of the blend.

Correlation equations for gas condensates based on readily available field data have been developed. The correlations can be used to predict dewpoint pressures, decreases in surface condensate yields after reservoir pressure has decreased below dewpoint pressure, and decreases in reservoir-gas specific gravity at reservoir pressures below dewpoint pressure. A value of dewpoint pressure is essential data for any reservoir study. A reasonably accurate estimate of dewpoint pressure for a specific reservoir fluid is necessary in situations in which laboratory data are not available or before laboratory data are obtained. Laboratory measurements of dewpoint pressure and other gas properties of 615 gas condensates with worldwide origins were used to develop a dewpoint-pressure correlation based on initial producing gas/condensate ratio, initial stock-tank oil gravity, and specific gravity of the original reservoir gas. This is the first proposed dewpoint-pressure correlation that does not require some laboratory-measured quantity.

Estimation of decreases in producing yields after the reservoir pressure drops below the dewpoint pressure is necessary for accurate prediction of condensate reserves. The reduction in surface yields can be as much as 75% during the primary production of a gas condensate. This reduction must be considered in the prediction of ultimate recovery of a condensate. A surface-yield correlation has been developed that is a function of a selected reservoir pressure, initial stock-tank oil gravity, specific gravity of the original reservoir gas, and reservoir temperature. The data set included laboratory studies of 190 gas-condensate samples. This is the first proposal offered in crude oil literature of a correlation to estimate the decreases in surface yield.

The defining property that distinguishes crude oil and gas condensate black and volatile oils is the content of the equilibrium gases. The volatilized-oil (also called lease condensate or distillate) content of a gas represents its condensable liquid portion. Condensable refers to the portion that condenses or drops out during pressure reduction and ultimately results as stock-tank liquid. Condensation may take place within the reservoir as the gas passes through the lease separators. Physically, intermediate-hydrocarbon components, typically the C_2 to C_7, dominate this fraction. Gas condensates and wet gases also contain volatilized oil. Volatilized oil is reported conventionally as part of the crude-oil reserves and production and should not be confused with and is distinctly different from natural-gas liquids. Natural-gas liquids are derived from the gas-processing plant and are, therefore, products of a gas processing plant. The volatilized-oil content of gases is quantified in terms of their volatilized-oil/gas ratio, typically expressed in units of STB/MMscf or stock-tank m^3 per standard m^3 of separator gas.

Finally, a comment on the sampling and analysis of gas condensate which invokes similar principles to this used in the sampling of gas (Speight, 2018; ASTM, 2019). Before a field development starts, the primary goal of sampling is to obtain representative samples (Chapter 5) of any of the fluids (including gas and gas condensate) found in the reservoir at initial conditions. It may be difficult to obtain a representative sample because of two-phase flow effects near the wellbore. This occurs when a well is produced with a flowing bottomhole pressures below the saturation pressure of the reservoir fluids. It is also commonly thought that non-representative samples of reservoir are the result if gas coning (or liquid coning) occurs during sampling.

Briefly, coning is a production problem in which gas cap gas or bottom water infiltrates the perforation zone in the near-wellbore area and reduces oil production. Gas coning is distinctly different from, and should not be confused with, free-gas production caused by a naturally expanding gas cap. Likewise, water coning should not be confused with water production caused by a rising water/oil contact from water influx. Coning is a rate-sensitive phenomenon generally associated with high producing rates. Coning is typically a near-wellbore phenomenon and only develops once the pressure forces drawing fluids toward the wellbore overcome the natural buoyancy forces that segregate gas and water from oil.

The most representative in-situ samples are usually obtained when the reservoir fluid is single phase at the point of sampling, be it bottomhole or at the surface. Even this condition, however, may not ensure representative sampling. And, samples obtained during gas coning in an oil well can provide accurate in-situ representative samples if a proper laboratory procedure is followed (Fevang and Whitson, 1994).

Because reservoir fluid composition can vary horizontally, between fault blocks, and as a function of depth, it is essential that a sample of reservoir fluid is obtained that is representative of the volume being drained by the well during the test. Unfortunately, the concept of a representative sample is typically *a sample that correctly reflects the composition of reservoir fluid at the depth or depths being tested*. If there is any doubt that a sample is not representative (according to the above definition), then it is often the best course of action to not use the sample. If such a sample is used for analysis, the validity of the pressure-volume-temperature analysis done on the non-representative sample, and consequently the measured data should not be used when developing the pressure-volume-temperature model.

5.4.3 Color

Condensate liquids are generally colorless (*water white*) or near-colorless or may even be light in color (brown, orange, or green) and have an API gravity that is typically on the order of 40 and 60° API (Table 7.9). The yields of these liquids can be as high as 300 stock tank barrels per million cubic feet (STB/MMscf). It has been suggested (McCain, 1990) that when yields are below approximately 20 stock tank barrels per million cubic feet, even though phase-behavior considerations may show retrograde behavior, the amount of liquid dropout in the reservoir can be insignificant.

5.4.4 Density

Density (the mass of liquid per unit volume at 15 °C or the amount of mass contained in a unit volume of fluid) and the related terms *specific gravity* (the ratio of the mass of a given volume of liquid at 15 °C to the mass of an equal volume of pure water at the same temperature), and *relative density* (same as *specific gravity*) are important properties of crude oil products as it is a part of product sales specifications, although it only plays a minor role in studies

TABLE 7.9 Examples of the approximate composition of dry gas, wet gas, and gas condensate.

Component or Property	Dry Gas	Wet Gas	Condensate
Carbon dioxide, CO_2	0.10	1.41	2.37
Nitrogen, N_2	2.07	0.25	0.31
Methane, CH_4	86.12	92.46	73.19
Ethane, C_2H6	5.91	3.18	7.80
Propane, C_3H8	3.58	1.01	3.55
iso-Butane, i-C_4H_{10}	1.72	0.28	0.71
n-Butane, n-C_4H_{10}	–	0.24	1.45
iso-Pentane, i-C_5H_{12}	–	0.13	0.64
n-Pentane, n-C_5H_{12}	–	0.08	0.68
Hexane derivatives, C_6H_{14}	–	0.14	1.09
Heptanes plus, $\geq C_7H_{16}$	–	0.82	8.21

TABLE 7.10 Density of various hydrocarbon liquids – possible constituents of gas condensate and natural gasoline.

Hydrocarbon (phase)	Formula	Molecular weight	Density
Benzene	C6H6	78.114	0.877
Decane	C10H18	142.285	0.73
Heptane	C7H16	100.204	0.684
Hexane	C6H14	86.177	0.66
Hexene	C6H12	84.161	0.673
Iso-pentane	C5H12	72.15	0.626
Octane	C8H18	114.231	0.703
Toluene	C7H8	92.141	0.867

of product composition. Usually a hydrometer, pycnometer, or digital density meter is used for the determination in all these standards.

Density is the single-most important property of a fluid (Table 7.10) and the density of gas condensate is dependent upon the density and relative amounts of the hydrocarbon constituents. For liquids, density is high, which translates to a very high molecular concentration and short intermolecular distances. For gases, density is low, which translates to low molecular concentrations large intermolecular distances (Rayes et al., 1992; Piper et al., 1999).

Density is an important parameter for condensate and related liquids and the determination of density (specific gravity) provides a check on the uniformity of the condensate and it permits calculation of the weight per gallon. The temperature at which the determination is carried out and for which the calculations are to be made should also be known and be in accordance with the volatility of the sample. Any such method must be subject to vapor pressure constraints and are used with appropriate precautions to prevent vapor loss during sample handling and density measurement. In addition, some test methods should not be applied if the samples are sufficiently colored and that the absence of air bubbles in the sample cell cannot be established with certainty. The presence of such bubbles can have serious consequences for the reliability of the test data.

The all-important parameter to calculate density is the Z-factor, both for the liquid and vapor phases. Empirical correlations for Z-factor for natural gases were developed before the advent of digital computers. Although their use is in decline, they can still be used for fast estimates of the Z-factor. These methods are invariably based on some type of corresponding states development. According to the theory of corresponding states, substances at corresponding states will exhibit the same behavior (and hence the same Z-factor) (Standing and Katz, 1942; Hall and Yarborough, 1973).

The specific gravity is the ratio of fluid density to the density of a reference substance, both defined at the same pressure and temperature. These densities are usually defined at standard conditions (14.7 psia and 60 °F). For a condensate, oil or a liquid, the reference substance is water. By definition, the specific gravity of water is unity and, using the API scale, water has an API gravity of 10. Light crude oils have an API greater than or equal to 45° while the API gravities of gas condensates range between 50° and 70° API.

5.4.5 Dew point pressure

The dewpoint pressure is the pressure where an incipient liquid phase condenses from a gas phase. Practically, the dewpoint marks the pressure where (i) reservoir gas phase composition changes and becomes leaner, and (ii) condensate accumulation starts in the reservoir. These two changes can have a profound effect on reservoir and well performance – or, they may have little impact.

The importance of the *actual dewpoint pressure* will vary from reservoir to reservoir, but in most situations accurate dewpoint determination is *not important*. First, in the context of compositional variation with pressure (and associated variation of condensate yield with pressure) accurate determination of the thermodynamic dewpoint pressure is *not* of particular importance. In fact, knowledge of the specific dewpoint at all as long as the variation of composition (C7+ content) with pressure is well defined "near" the thermodynamic dewpoint. Second, when the bottomhole flowing pressure (BHFP) drops below the dewpoint and two phases start flowing near the wellbore, gas relative permeability drops and well *productivity* drops.

Another (less common) need for dewpoint pressure is when an underlying saturated oil zone *may* exist, and a pressure-volume-temperature model is used to predict the existence and location of the gas-oil contact (GOC). In this case, the pressure-volume-temperature model dewpoint should be tuned precisely to an accurately measured dewpoint pressure. It is not uncommon that a predicted gas-oil contact may vary considerably because of uncertainty in the (PVT-model) dewpoint pressure. Thus, an accurate description of the dewpoint pressure will have an impact on the prediction of initial crude oil and gas in place, placement of delineation wells, and potential field development strategy. In this situation, accurate dewpoint measurement and equally-accurate modeling of the measured dewpoint should be given due attention.

5.4.6 Flammability

Gas condensate and natural gasoline are, like naphtha, (i) readily flammable, (ii) will evaporate quickly from most surfaces, and (iii) must be very carefully contained at all times. Condensate can be ignited by heat, sparks, flames, or other sources of ignition (such as static electricity, pilot lights, mechanical/electrical equipment, and electronic devices such as cell phones) The vapors may travel considerable distances to a source of ignition where they can ignite, flash back, or explode. The condensate vapors are more dense than air and can accumulate in low areas. If container is not properly cooled, it can rupture in the heat of a fire. Hazardous combustion/decomposition products, including hydrogen sulfide, may be released by this material when exposed to heat or fire. If the condensate contains a high percentage of aromatic constituents, it can also be smoky, toxic and carcinogenic. Some condensate-based fuels have a reduced aromatic content, but many are naturally high or augmented in aromatic derivatives that arise from blends with aromatic naphtha.

The flash point is the lowest temperature at atmospheric pressure (760 mm Hg, 101.3 kPa) at which application of a test flame will cause the vapor of a sample to ignite under specified test conditions. The sample is deemed to have reached the flash point when a large flame appears and instantaneously propagates itself over the surface of the sample. The flash point data is used in shipping and safety regulations to define *flammable* and *combustible* materials. Flash point data can also indicate the possible presence of highly volatile and flammable constituents in a relatively non-volatile or non-flammable material. Sine the flash point of gas condensate and the flash point of natural gasoline are low, such as test method can also indicate the possible presence of even more highly volatile and flammable constituents in these two liquids.

Flash point for a hydrocarbon or a fuel is the minimum temperature at which vapor pressure of the hydrocarbon is sufficient to produce the vapor needed for spontaneous ignition of the hydrocarbon with the air with the presence of an external source, i.e., spark or flame. From this definition, it is clear that hydrocarbon derivatives with higher vapor pressures (lower molecular weight compounds) have lower flash points. Generally, flash point increases with an increase in boiling point. Flash point is an important parameter for safety considerations, especially during storage and transportation of volatile crude oil products (i.e., liquefied petroleum gas, light naphtha, gasoline) in a high-temperature environment.

The prevalent temperature within and around a storage tank should always be less than the flash point of the fuel to avoid possibility of ignition. Flash point is used as an indication of the fire and explosion potential of a crude oil product. Flash point should not be mistaken with *fire point*, which is defined as the minimum temperature at which the hydrocarbon will continue to burn for at least 5 s after being ignited by a flame. For such materials, ignition is dependent upon the thermal and kinetic properties of the decomposition, the mass of the sample, and the heat transfer characteristics of the system. Also, the method can be used, with appropriate modifications, for chemicals that are gaseous at atmospheric temperature and pressure of which gas condensate and natural gasoline are example.

5.4.7 *Solubility*

Other methods that are applicable to hydrocarbon liquids typically involve determination of the surface tension from which the solubility parameter is calculated and then provides an indication of dissolving power and compatibility. A similar principal is applied to determine the amount of insoluble material in lubricating oil using *n*-pentane and can be applied to liquid fuels. The insoluble constituents measured can also assist in evaluating the performance characteristics of a liquid fuel in determining the cause of equipment failure and line blockage (Speight, 2014a; Speight and Exall, 2014).

Water solubility ranges from very low for the longest-chain alkanes to high solubility for the simplest mono-aromatic constituents. Generally, the aromatic compounds are more soluble than the same-sized alkanes, iso-alkanes and cycloalkanes. This indicates that the components likely to remain in water are the one- and two-ring aromatic derivatives (C_6 to C_{12}). The C_9 to C_{16} alkanes, iso-alkanes and one- and two-ring cycloalkanes are likely to be attracted to sediments based on their low water solubility and moderate to high octanol-water partition coefficient (log K_{ow}) and organic carbon-water partition coefficient (log K_{oc}) values.

5.4.8 *Solvent power*

For hydrocarbon liquids, solvent tests are generally performed to ensure the quality of a given product as supplied by the producer to the consumer. In this case the purpose would be to provide data related to the properties of gas condensate and natural gasoline to the refiner and the potential benefits or adverse effect of using gas condensate or natural gasoline as blending stock in the refinery. Many solvent tests are of a somewhat empirical nature such as aniline point and mixed aniline point. The data from these test methods and the need for the test methods are frequently cited in specifications and serve a useful function as control tests. Solvent purity, however, is typically monitored mainly by gas chromatography, with individual non-standardized tests routinely being used by the associated industry.

5.4.9 *Sulfur content*

Sulfur-containing components exist in some gas condensate and natural gasoline samples. Individual sulfur components can be speciated (ASTM, 2019) and the method uses a gas chromatographic capillary column coupled with either a sulfur chemiluminescence detector or atomic emission detector (AED). The total sulfur content (especially the content of hydrogen sulfide) is an important test parameter in hydrocarbon liquid that are designated as liquid fuels or are used as blending stock for sales (Kazerooni et al., 2016).

5.4.10 *Surface tension*

Surface tension and interfacial tension exist when two phases are present, and the phases can be gas/oil, oil/water, or gas/water. The surface tension between gas and crude oil ranges from near zero to approximately 34 dyn/cm and is a function of pressure, temperature, and the composition of each phase. Interfacial tension is the force that holds the surface of a particular phase together and is normally measured in dynes/cm.

More specifically, the surface tension is a measure of the surface free energy of liquids, i.e., the extent of energy stored at the surface of liquids. Although it is also known as interfacial force or interfacial tension, the name *surface tension* is usually used in systems where the liquid is in contact with gas. Qualitatively, it is described as the force acting on the surface of a liquid that tends to minimize the area of its surface, resulting in liquids forming droplets with spherical shape, for instance. Quantitatively, since its dimension is of force over length (lbf/ft in English units), it is expressed as the force (in lbf) required to break a film of 1 ft of length. Equivalently, it may be restated as being the amount of surface energy (in lbf-ft) per square feet.

The interfacial tension is similar to surface tension in that cohesive forces are also involved. However, the main forces involved in interfacial tension are adhesive forces (tension) between the liquid phase of one substance and either a solid, liquid or gas phase of another substance. The interaction occurs at the surfaces of the substances involved, that is at their interfaces.

The gas-liquid interfacial tension at high pressures is commonly measured by a pendant-drop apparatus (ASTM, 2019). In this technique, a liquid droplet is allowed to hang from the tip of a capillary tube in a high pressure visual cell filled with its equilibrated vapor. The shape of liquid droplet at static conditions, controlled by the balance of gravity and surface forces, is determined and related to the gas-liquid interfacial tension. The pendant-drop method can also be applied to measure the interfacial tension of hydrocarbon-water systems.

The productivity of gas condensate wells can significantly be declined as the condensate bank evolves around the wellbore. Wettability alteration of formation minerals from strongly liquid-wet to intermediate gas-wet conditions using liquid-repellent fluorinated chemicals has shown promising results to mitigate such liquid-blockage issues (Fahimpour and Jamiolahmady, 2014).

5.4.11 *Volatility*

Distillation, as a means of determining the boiling range (hence the *volatility*) of crude oil and crude oil products has been in use since the beginning of the crude oil industry and is an important aspect of product specifications. Depending on the design of the distillation unit, either one or two naphtha steams may be produced: (i) a single naphtha with an end point of approximately 205 °C (400 °F) and similar to straight-run gasoline, or (ii) this same fraction divided into low-boiling naphtha (light naphtha) and high-boiling naphtha (heavy naphtha). The end point of the light naphtha is varied to suit the subsequent subdivision of the naphtha into narrower boiling fractions and may be of the order of 120 °C (250 °F). On the other hand, condensate is almost always equivalent to the low-boiling naphtha fraction.

Naphtha (*petroleum naphtha*), which distills below 240 °C (465 °F), is a generic term applied to refined, partly refined or unrefined crude oil products and the liquid products isolated from natural gas streams and is the volatile fraction of the crude oil, which is used as a solvent or as a precursor to gasoline. In fact, not less than 10% v/v of material should distil below 75 °C (167 °F); not less than 95% v/v of the material should distil below 240 °C (465 °F) under standard distillation conditions, although there are different grades of naphtha within this extensive boiling range that have different boiling ranges (Hori, 2000; Parkash, 2003; Pandey et al., 2004; Gary et al., 2007; Speight, 2014a, 2017; Hsu and Robinson, 2017) and the focus of this chapter is on the low-boiling liquid fraction of gas streams (gas condensate, natural gasoline) which are typically equivalent to the low-boiling fraction of naphtha (boiling range 0–200 °C, 32 to 390 °F).

Gas condensate, natural gasoline and naphtha are often referenced by a boiling range, which is the defined temperature range in which the fraction distils. The ranges are determined by standard methods (ASTM, 2019), it being especially necessary to use a recognized method since the initial and final boiling points which ensure conformity with volatility requirements and absence of *heavy ends* are affected by the testing procedure. Thus, one of the most important physical parameters of gas condensate and natural gasoline is the boiling range distribution. The significance of the boiling range distribution is the indication of volatility that dictates the evaporation rate that is an important property for gas condensate and natural gasoline used in coatings and similar application where the premise is that the gas condensate and natural gasoline evaporates over time.

Since the end use dictates the required composition of condensate blends with natural gasoline, and crude oil-derived naphtha, most blends are available in both high and low solvency categories and the various text methods can have major significance in some applications and lesser significance in others. Hence the application and significance of tests must be considered as those that produce data that aids in the determination of the proposed end use of the product. To emphasize this point, naphtha contains varying amounts of its constituents viz., paraffin derivatives, naphthene derivatives, aromatic derivatives and olefins in different proportions in addition to potential isomers of paraffin that exist in naphtha boiling range. Naphtha resembles gasoline in terms of boiling range and carbon number, being a precursor to gasoline. Naphtha is used as automotive fuel, engine fuel, and jet-B (naphtha type).

Volatility, solvent properties (dissolving power), purity and odor determine the suitability of condensate for a particular use. The use of condensate (but specifically naphtha) as an incendiary device in warfare, and as an illuminant dates back to AD 1200. Condensate, like naphtha, may be is characterized as lean (high paraffin content) or rich (low paraffin content). The rich naphtha with higher proportion of naphthene content is easier to process in the Platforming unit (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017; Hsu and Robinson, 2017).

If spilled or discharged in the environment, condensate represents a threat of the toxicity of the constituents to land and/or to aquatic organisms. A significant spill may cause long-term adverse effects in the aquatic environment. The constituents of naphtha predominantly fall in the C_5 to C_{12} carbon range: alkanes, some cycloalkanes, perhaps aromatic derivatives. On the other hand, naphtha may also contain a preponderance of aromatic constituents (up to 65%), others contain up to 40% alkenes, while all of the others are aliphatic in composition, up to 100%.

The determination of the boiling range distribution of distillates such as gas condensate and natural gasoline by gas chromatography (ASTM, 2019) not only helps identify the constituents but also facilitates on-line controls at the refinery. This test method is designed to measure the entire boiling range of gas condensate and natural gasoline with either high or low Reid vapor pressure (ASTM, 2019). In the method, the sample is injected into a gas chromatographic column that separates hydrocarbon derivatives in boiling point order.

While pure hydrocarbon derivatives such as pentane, hexane, heptane, benzene, toluene, xylene, and ethyl benzene which may be characterized by a fixed boiling point, but the constituents of gas condensate and natural gasoline (being mixtures of many hydrocarbon derivatives) are typically is less easy to identify. The distillation test does however give a useful indication of their volatility. The data obtained should include the initial and final temperatures of distillation together with sufficient temperature and volume observations to permit a characteristic distillation curve to be drawn.

This information is especially important when a formulation includes other volatile liquids since the performance of the product will be affected by the relative volatility of the constituents. An illustration of the importance of this aspect is found in the use of specifically defined boiling point naphtha in cellulose lacquers, where a mixture with ester, alcohols, and other solvents may be employed. The naphtha does not act as a solvent for the cellulose ester but is incorporated as a diluent to control the viscosity and flow properties of the mixture. If the solvent evaporates too rapidly blistering of the surface coating may result, while if the solvent evaporates unevenly, leaving behind a higher proportion of the naphtha, precipitation of the cellulose may occur leading to a milky opaqueness known as blushing. Because of the composition, such used are often prohibited for condensate unless that condensate can be used satisfactorily as a blend without having an adverse influence on the specification of the product.

Although much dependence is placed on the assessment of volatility by distillation methods, some specifications include measurement of drying time by evaporation from a filter paper or dish. Laboratory measurements are expressed as *evaporation rate* either by reference to a pure compound evaporated under similar conditions as the sample under test or by constructing a time weight loss curve under standard conditions. Although the results obtained on the condensate can provide a useful guide, it is preferable, wherever possible, to carry out a performance test on the final product when assessing formulations.

In choosing gas condensate and/or natural gasoline for a particular purpose it is necessary to relate volatility to the fire hazard associated with its use, storage and transport, and also with the handling of the products arising from the process. This is normally based on the characterization of the gas condensate or the natural gasoline solvent by flash point limits.

The *vapor pressure* or *equilibrium vapor pressure* is the pressure exerted by a vapor that is in thermodynamic equilibrium with the condensed phase (solid or liquid) at a given temperature in a closed system. The equilibrium vapor pressure is an indication of the evaporation rate of a liquid. A substance with a high vapor pressure at normal temperatures is often referred to as volatile.

The vapor pressure of any substance increases non-linearly with temperature and the atmospheric boiling point of a liquid (also known as the normal boiling point) is the temperature at which the vapor pressure equals the ambient atmospheric pressure. With any incremental increase in that temperature, the vapor pressure becomes sufficient to overcome atmospheric pressure and lift the liquid to form vapor bubbles inside the bulk of the substance. Bubble formation deeper in the liquid requires a higher pressure, and therefore higher temperature, because the fluid pressure increases above the atmospheric pressure as the depth increases. More pertinent to low-boiling hydrocarbon mixtures such as condensate, the vapor pressure that a single component in the mixture contributes to the total pressure in the system is called the partial pressure.

The vapor pressure of liquids such as gas condensate, natural gasoline, and gasoline is a critical physical test parameter for hydrocarbon liquids. By way of definition, the vapor pressure of a substance is the pressure of a vapor in thermodynamic equilibrium with its condensed phase in a closed system. The Reid vapor pressure (RVP) is the measure of the absolute pressure exerted by a liquid at 37.8 °C (100 °F), at a vapor to liquid ratio of 4:1 The true vapor pressure (TVP) is the equilibrium vapor pressure of a mixture when the vapor to liquid ratio = 0, e.g., floating roof tanks.

Typically, the lower molecular weight condensates (higher API gravity) can be difficult to handle due to their high vapor pressure and are usually stabilized at the wellhead (often referred to as stabilization in the field) insofar as the condensate is run through a stabilizer which may be nothing more than a big tank that allows the high vapor pressure components (the NGLs) to vaporize and to be collected for processing as natural gas liquids. That leaves a stabilized condensate that has a lower vapor pressure which is easier to handle, particularly when it must be shipped by truck or rail.

The primary quality criterion for the vapor pressure of gas condensate is the Reid vapor pressure (RVP), which is a is a common measure of the volatility of condensate, natural gasoline, naphtha, and gasoline and is the absolute vapor pressure exerted by a liquid at 37.8 °C (100 °F) (Speight, 2015; Speight, 2018; ASTM, 2019). The Reid vapor pressure is affected by atmospheric pressure (plant elevation) and maximum ambient temperature. Thus, to store the condensate in floating roof storage tanks, it is very crucial to control the Reid vapor pressure at the desired level (especially in warm seasons). The emissions of gas condensate from a storage tank are normally categorized as occurring from standing storage losses or working losses (sometime referred to as breathing losses, which can be confusing). The term breathing loss refers to those emissions that result without any corresponding change in the liquid level within the storage tank.

The Reid vapor pressure differs slightly from the true vapor pressure (TVP) of a liquid due to small sample vaporization and the presence of water vapor and air in the confined space of the test equipment. More specifically, the Reid vapor pressure is the absolute vapor pressure and the true vapor pressure is the partial vapor pressure.

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CHAPTER

8

Processing gas from tight formations

1. Introduction

Natural gas production from shale reservoirs and other tight reservoirs has been proven to be feasible from the numerous operations in various tight reservoirs in North America, but many challenges still remain for the full exploitation of these unconventional reservoirs. The production process requires stimulation by horizontal drilling coupled with hydraulic fracturing because of the extremely low permeability of the reservoir rocks which prohibits natural movement of the gas to a well. Moreover, maximization or optimization of reservoir producibility can only be achieved by a thorough understanding of the occurrence and properties of the shale gas resources (Chapter 1, Chapter 2) as well as the producibility of the gas from the reservoir (Chapter 3) (Kundert and Mullen, 2009). These needs demonstrate the importance of a thorough characterization of shale gas reservoir (Table 8.1) as well as an understanding of the means by which subterranean formations deform during geologic time as well as the effects of such deformation on the stresses within the formations (Scouten, 1990; Speight, 2012, 2013a; Sone, 2012, 2014a, 2019b).

As a refresher on the issue of nomenclature (Chapter 1), there are several general definitions that have been applied to natural gas from conventional formations that can also be applied to gas from tight formations (Table 8.2). Thus, *lean* gas is gas in which methane is the major constituent. W*et* gas contains considerable amounts of the higher molecular weight hydrocarbon derivatives. S*our* gas contains hydrogen sulfide whereas *sweet* gas contains very little, if any, hydrogen sulfide. *Residue gas* is natural gas from which the higher molecular weight hydrocarbon derivatives have been extracted and *casinghead gas* is derived from crude oil but is separated at the separation facility at the wellhead. Gas condensate (sometimes referred to as condensate) is a mixture of low-boiling hydrocarbon liquids obtained by condensation of hydrocarbon vapors. The condensate is predominately propane (C_3H_8) butane (C_4H_{10}), and pentane (C_5H_{12}) with minor amounts of higher-boiling hydrocarbon derivatives (up to C_8H_{18}) but relatively little methane or ethane. Depending upon the source of the condensate, benzene (C_6H_6), toluene ($C_6H_5CH_3$), xylene isomers ($CH_3C_6H_4CH_3$), and ethyl benzene ($C_6H_5C_2H_5$) may also be present (Speight, 2014a, 2019a).

The shale gas resources (Chapter 2) represent a major contribution to the resource base of the United States (Nehring, 2008). However, it is important to note that there is considerable variability in the quality of the resources, both within and between gas shale resources.

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TABLE 8.1 Variation in shale properties for different shale gas reservoirs.

	Density	Carbonate	Clay	Porosity	Kerogen[a]
Sample source	g/cc	% w/w	% w/w	% v/v	% w/w
Barnett	2.37–2.67	0–60	3–39	1–9	2–11
Haynesville	2.49–2.62	20–53	20–39	4–8	3–6
Eagle ford	2.43–2.54	46–78	6–21	0–5	4–11

[a] *Kerogen refers to unidentified organic material, typically insoluble in organic solvents.*

TABLE 8.2 Typical Composition (% v/v) of Fluids Produced from Gas Reservoirs.

Component	Dry gas	Wet gas	Condensate
CO_2	0.1	1.4	2.4
N_2	2.1	0.3	0.3
C1	86.1	92.5	73.2
C2	5.9	3.2	7.8
C3	3.6	1.1	3.6
C4	1.7	0.3	0.7
C5	0.5	0.1	0.6
C6	–	0.1	1.1
C7+	–	0.8	8.2

Elevated levels of ethane, propane, carbon dioxide, or nitrogen in certain gases from shale formations are of concern regarding their interchangeability with traditional natural gas supplies. This high level of variability in individual well productivity clearly has consequences with respect to the variability of individual well economic performance. Not all shale gas plays are the same and, as a result, shale gas from one play can be considerably different (in terms of the necessary gas processing requirements) and the processing requirements for shale gas can vary from area to area. The more popular areas are the Barnett, Haynesville, and Fayetteville shales in the South and the Marcellus, New Albany, and Antrim shales in the East and Midwest (Fig. 8.1). These plays represent a large portion of current and future gas production.

However, because shale is composed primarily of tiny grains of clay minerals and quartz, the mineral components of mud, the composition of the shale reservoir can vary – specifically the rock properties such as porosity, permeability, capillary entry pressure, pore volume compressibility, pore size distribution and flow path (collectively known as *petrophysics*) can vary considerably (Sone, 2012). These materials were deposited as sediment in water, which was then buried, compacted by the weight of overlying sediment, and cemented together to form a rock (*lithification*). Clay minerals are a type of sheet silicate related to mica that usually

FIG. 8.1 Shale gas resources (shale gas plays) in the contiguous United States, Canada, and Mexico. *Adapted from US EIA, 2012. Energy Information Administration, United States Department of Energy, Washington, DC.*

occurs in the form of thin plates or flakes. As the sediment was deposited, the flakes of clay tended to stack together flat, one on top of another like a deck of cards, and as a result, lithified shale often has the property of splitting into paper-thin sheets. This is a convenient way to identify shale from other fine-grained rocks like limestone or siltstone.

This process, while appearing to be ordered in such a description, is in fact subject to geological disorder and thence subject to differing methods of entrapment of the organic material, and different methods or rates of decompositon, different rates of formation of the gas, and hence different composition of the shale gas. The primary point of this subsection is that the geochemical and geological characteristics of each reservoir are relatively unique and must be carefully examined to determine resources. Furthermore, general rules are difficult to apply − innovation in unconventional drilling and completion techniques has added substantial reserves to otherwise uneconomic areas and has also been a key part of safe and efficient development (Cramer, 2008; Grieser et al., 2007). This can affect the economics of shale gas production and gas cleaning (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a).

A major driver of shale economics is the amount of hydrocarbon liquid produced along with gas. Some areas contain wet gas with appreciable amounts of liquid, which can have a considerable effect on the breakeven economics, particularly if the price of oil is high compared to the price of gas. The liquid content of a gas is often measured in terms of the *condensate ratio*, which is expressed in terms of barrels of liquid per million cubic feet of gas (bbls/MMcf). In some operations, for example in the case of a condensate ratio in excess of fifty barrels per million cubic feet (50 bbls/MMcf), the liquid production alone can provide an adequate return on the investment, even if the gas cannot realize a fair market value.

It is the purpose of this chapter to present a review of the various gas processing technologies are appropriate for the variety of gas qualities being produced and planned to be produced. In particular, the focus of this chapter is a brief description of the processes that are an integral part within the concept of production of a pipeline-able product (methane) for sale to the consumer (Table 8.3).

There is one additional issue that must be resolved if shale gas is to be a major contributor to the US energy resources (or to the energy resource plans of any country). The issue is the amenability of the gas to be included in current gas processing scenarios (Mokhatab et al., 2006; Speight, 2019a). On the understanding that shale gas reservoirs will vary in properties such as origin, permeability, and porosity, differences in properties of the shale gas must be anticipated (Bustin et al., 2008) (Chapter 1, Chapter 2). While shale gas resources represent a significant portion of current and future production, all shale gas is not constant in composition and gas processing requirements for shale gas can vary from area to area (Bullin and Krouskop, 2008; Weiland and Hatcher, 2012).

TABLE 8.3 Examples of pipeline specifications for natural gas.

Components mol%	Minimum	Maximum
Methane	75	
Ethane		10
Propane		5
Butanes		2
Pentanes plus		0.5
Nitrogen and other inerts		3–4
Carbon dioxide		3–4
Hydrogen sulfide		0.25–1.0 gr/100 ft^3
Mercaptan sulfur		0.25–1.0 gr/100 ft^3
Total sulfur		5-20 gr/100 ft^3
Water vapor		7.0 lbs/mm ft^3
Oxygen		0.2–1.0 ppm v/v
Heating value	950	1150 Btu/ft^3

In addition, analysis of the gas composition of Devonian shale wells indicates that the composition of produced gas shifts during the production history of the well (Schettler et al., 1989). Gas composition changes during production indicate that different components of natural gas produced have different decline curves. Thus, the total decline curve is the sum of the decline curves of the individual gas components. The classic mechanisms of viscous flow and ideal-gas void-volume storage and, as such, do not explain gas fractionation in gas wells. In fact, the only way to explain observed fractionation with such classic mechanisms is to assume that total flow has several sources within the wellbore, each with different characteristic compositions and decline curves.

2. Tight gas composition and properties

Briefly, and by way of re-introduction, a gas shale reservoir has an extremely low permeability compared to most conventional reservoirs (typically a *sandstone reservoir*) (Chapter 2). In fact, the effective bulk permeability in a tight shale reservoir is typically much less than 0.1 milliDarcy − on the order of I milliDarcy down to 1 microDarcy (Fig. 8.1), although exceptions exist where the rock is naturally fractured as has been observed in the well-fractured Antrim shale in the Michigan Basin of the United States. However, the role of natural microfractures in producing natural gas or crude oil from a tight reservoir or in assisting artificial fracturing is not fully understood (Chapter 4, Chapter 5). In most cases, it is usual for the reservoir to require artificial stimulation, such as horizontal drilling leading to hydraulic fracturing (Fig. 8.1), to increase permeability to the well in order to produce gas in economical quantities. However, producing the gas from the reservoir is not the end of the story. Other issues (such as variations in gas composition) arise with the ensuing effects of changing composition on gas processing operations.

Shale gas is a valuable natural resource that is being eagerly sought out and drilled for using fracturing techniques. The gas is mainly composed of methane, although it does contain constituents that to be separated from the methane to make the gas useable commercially. The other compounds found in shale gas include natural gas liquids, which are hydrocarbon derivatives of a heavier nature that will be separated in processing plants as liquids. These liquids include ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), and octane (C_8H_{18}) as well as a higher-boiling hydrocarbon mixture (gas condensate, which may include the aforementioned C_{6+} hydrocarbon derivatives) and water. The gaseous components of raw shale gas include sulfur dioxide, hydrogen sulfide, helium, nitrogen and carbon dioxide. Mercury may also be found in smaller concentrations in most reservoirs where natural gas is obtained. The mercury found will be lowered in concentration until it is below the detectable threshold of one part per trillion. Gas in shale deposits varies in composition insofar as it, but in different areas, it may contain different amounts of the same basic compounds. The variability in the composition of natural gas composition depends not only on the region in which the gas originated but also on the properties of the reservoir.

Shale gas is natural gas produced from shale formations that typically function as both the reservoir and source rocks for the natural gas (Speight, 2013b). In terms of chemical makeup, shale gas is typically a dry gas composed primarily of methane (60%−95% v/v), but some formations do produce wet gas. The Antrim and New Albany plays have typically produced water and gas. Gas shale formations are organic-rich shale formations that were previously regarded only as source rocks and seals for gas accumulating in the strata near sandstone and carbonate reservoirs of traditional onshore gas.

Contaminants such as carbon dioxide and hydrogen sulfide are removed at a treatment facility near the field or at a gas processing plant. This typically is achieved using a physical solvent called an amine solution. Carbon dioxide and hydrgoen sulfide are both highly corrosive especially when water is present in the gas stream — this creates an acidic environment that increases the risk of corrosion of the equipment or the pipeline (Speight, 2014b). If the gas is treated using an amine solution, it later must be dehydrated to pipeline quality. Dehydration can be accomplished through absorption or adsorption methods — these separation and dehydration steps are similar for all gases (Mokhatab et al., 2006; Speight, 2014a, 2019a). f nitrogen is present in significant amounts, it must be removed at a cryogenic plant with supercooling equipment so that the gas meets the minimum heating value required by the pipeline.

Gas production from unconventional shale gas reservoirs (such as tight shale formations) has become more common in the past decade. Produced shale gas observed to date has shown a broad variation in compositional makeup, with some having wider component ranges, a wider span of minimum and maximum heating values, and higher levels of water vapor and other substances than pipeline tariffs or purchase contracts may typically allow. Indeed, because of these variations in gas composition, each shale gas formation can have unique processing requirements for the produced shale gas to be marketable.

Ethane can be removed by cryogenic extraction while carbon dioxide can be removed through a scrubbing process. However, it is not always necessary (or practical) to process shale gas to make its composition identical to *conventional* transmission-quality gases. Instead, the gas should be interchangeable with other sources of natural gas now provided to end-users. The interchangeability of shale gas with conventional gases is crucial to its acceptability and eventual widespread use in the United States.

Although not highly sour in the usual sense of having high hydrogen sulfide content, and with considerable variation from play to resource to resource and even from well to well within the same resource (due to extremely low permeability of the shale even after fracturing) (Speight, 2013b), shale gas often contains varying amounts of hydrogen sulfide with wide variability in the carbon dioxide content. The gas is not ready for pipelining immediately after it has exited the shale formation.

The challenge in treating such gases is the low (or differing) hydrogen sulfide/carbon dioxide ratio and the need to meet pipeline specifications. In a traditional gas processing plant, the olamine of choice for content for hydrogen sulfide removal is N-methyldiethanolamine (MDEA) (Mokhatab et al., 2006; Speight, 2014a, 2019a) but whether or not this olamine will suffice to remove the hydrogen sulfide without removal of excessive amounts of carbon dioxide is another issue.

Gas treatment may begin at the wellhead — condensates and free water usually are separated at the wellhead using mechanical separators, he observes. Gas, condensate and water are separated in the field separator and are directed to separate storage tanks and the gas flows to a gathering system. After the free water has been removed, the gas is still saturated with water vapor, and depending on the temperature and pressure of the gas stream, may need to be dehydrated or treated with methanol to prevent hydrates as the temperature drops. But this may not be always the case in actual practice.

TABLE 8.4 Variation in Composition of Shale gas from Different Formations (Martini et al., 2003; Hill et al., 2007; Bullin and Krouskop, 2008)[a].

	Methane	Ethane	Propane	Carbon dioxide	Nitrogen
Source of gas	**% v/v**	**% v/v**	**% v/v**	**% v/v**	**% v/v**
Antrim shale	27–86	3–5	0.4–1	0–9	1–65
Barnett shale	80–94	2–12	0.3–3	0.3–3	1–8
Fayetteville shale	97	1	0	1	1
Haynesville shale	95	<1	0	5	0.1
Marcellus shale	79–96	3–16	1–4	0.1–1	0.2–0.4
New albany shale	97–93	1–2	0.6–3	5–11	0[b]

[a] *Samples were taken from different wells within each formation and a range of composition indicates variations in composition from different wells within a shale formation.*

[b] *The yields of hydrocarbon constituents having a higher molecular weight than propane was not recorded.*

Tight gas as it is bought to the surface (*wellhead gas*) is different from the gas that the consumers receive, and is much less pure. In fact, differences in natural gas composition occur between different reservoirs, and two wells in the same field may also yield gaseous products that are different in composition (Table 8.4) (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a). Indeed, there is no single composition of components which might be termed *typical* natural gas no matter the source of the gas. As with gas from conventional reservoirs (Table 8.5), methane (with varying amounts of and ethane) constitute the bulk of the combustible components; carbon dioxide (CO_2) and nitrogen (N_2) are the major non-combustible (inert) components of shale gas (Table 8.4). Other constituents such as hydrogen sulfide (H_2S), mercaptans (thiols; RSH), as well as trace amounts of other sulfur-containing constituents may also be present.

TABLE 8.5 Range of composition of natural gas from conventional reservoirs.

Methane	CH_4	70%–90%
Ethane	C_2H_6	0%–20%
Propane	C_3H_8	
Butane	C_4H_{10}	
Pentane and higher hydrocarbons	C_5H_{12}	0%–10%
Carbon dioxide	CO_2	0%–8%
Oxygen	O_2	0%–0.2%
Nitrogen	N_2	0%–5%
Hydrogen sulfide, carbonyl sulfide	H_2S, COS	0%–5%
Rare gases: Argon, Helium, Neon, Xenon	A, He, ne, Xe	Trace

Tight gas refers to natural gas (mainly methane) found in fine-grained, organic-rich rocks (shale, sandstone, and carbonate rocks) (Chapter 1, Chapter 2) (Holditch, 2006). In addition, the descriptor word *shale* does not refer to a specific type of rock but, in addition to shale (mudstone), has also been may also be used to describes rocks with more fine-grained particles (smaller than sand) than coarse-grained particles, such as (i) siltstone, (ii) fine-grained sandstone interlaminated with shale, as well as (iii) carbonate rocks. Thus, shale (including the additional rock types above (tight sand formations and tight carbonate formations), is a source rock that has not released all of the generated hydrocarbon derivatives. In fact, source rocks that are *tight* or *inefficient* at expelling hydrocarbon gases (and liquids) may be the best prospects for shale gas (or liquid) potential. Thus, in gas shale, shale is a reservoir rock, source rock, and also a trap for natural gas. The natural gas found in these rocks is considered unconventional, similar to coalbed methane.

Shale gas is generated by any combination of (i) primary thermogenic degradation of organic matter, (ii) secondary thermogenic decomposition of crude oil, and (iii) biogenic degradation of organic matter. Gas generated by thermogenic and biogenic pathways may both exist in the same shale reservoir. After generation, the gas is stored in the shale (tight) formation in three different ways: (i) by adsorption, which refers to *adsorbed gas* that is physically attached (adsorption) or chemically attached (chemisorption) to organic matter or to clay minerals, (ii) non-adsorbed gas, which refers to *free gas* (also referred to as *non-associated gas*) that occurs within the pore spaces in the reservoir rock or in spaces created by the rock cracking (fractures or microfractures), and (ii) by solution, which refers to gas (also referred to as *associated gas*) that exists in solution in liquids such as crude oil, heavy crude oil, and (in the current context) in gas condensate that occurs in some tight reservoirs with the gas (Speight, 2014a). The amount of adsorbed gas component (typically, methane) usually increases with an increase in organic matter or surface area of organic matter and/or clay. On the beneficial side, a higher free-gas (non-associated) content in unconventional tight reservoirs generally results in higher initial rates of production because the free gas resides in fractures and pores and, when production is commenced) moves easier through the fractures (induced channels) relative to any adsorbed gas. However, the high, initial flow rate will decline rapidly to a low, steady rate as the non-associated gas is produced leaving the adsorbed gas to move to the well as it is slowly released from the shale. The flow rate of an individual component of a gas mixture can be obtained by multiplying the total flow rate by the mole fraction of the individual component. Even though the composition of gas from each source is assumed not to change, the composition of gas at the wellbore can change with time if the relative flows change with time (Schettler et al., 1989).

2.1 Composition

Tight gas is certainly not the same everywhere. The gas from the Antrim Shale, for example, has high nitrogen concentration, as does at least one well tested in the Barnett Shale. New Albany wells show high carbon dioxide concentrations while several wells in the Marcellus Shale contain up to 16% v/v ethane. Economically treating and processing these gases requires all the same techniques as conventional gas plus the ability to handle a great deal of variability in the same field.

A gas can be characterized by consideration of the pure components that are contained in the gas and there needs to be statements for each substance, such as the proportion of the substance in the gas mixture on a molecule-count basis. To do this, analytical methods are necessary that can be used for the task. Most gases contain, hydrocarbon derivatives, water, carbon dioxide, hydrogen sulfide, nitrogen, oxygen, and other impurities. The need for the application of analytical techniques to the determination of the properties of natural gas and other gases such as biogas and landfill gas has increased over the past five decades because of the increase in the use of natural gas. In addition, the need for the analysis of any gas is an essential part of gas use and safety.

Gas composition is a critical issue when choosing the most appropriate methods for gas processing (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a). Indeed, this is an issue that must be resolved if shale gas is to be a major contributor to the US energy resources (or to the energy resource plans of any country). The issue is the amenability of the gas to be included in current gas processing scenarios (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a). On the understanding that shale gas reservoirs – because of the variation in mineral composition (Table 8.1) – will vary in properties such as origin, permeability, and porosity, there will also be differences in properties of the shale gas, not only from different formations but also even depending upon placement of the well within a formation must be anticipated (Chapter 1, Chapter 2) (Bustin et al., 2008).

The composition of natural gas from tight formations is influenced by several variables: (i) the composition of the organic matter in the formation from which the gas is sourced, (ii) the thermal maturity at which the gas is generated from the source rock, (iii) the gas generation process, specifically whether gas is generated through primary cracking of kerogen, from secondary cracking of oil to gas, or from secondary cracking of wet gas to dry gas, (iv) fractionation during gas migration from source to reservoir, (v) leakage from the reservoir; (vi) bacterial alteration by oxidation of gases. In addition, the influence of the minerals in the tight formation on gas composition by hastening, delaying, or changing any of the maturation reactions cannot be discounted and in fact should be given consideration. The outcome of gas formation is that the multi-component gases can vary in composition to such an extent that, while some of these processes may be difficult to identify and describe, the end result is the effect that gas composition can have on the options for gas processing.

In addition, gas from tight formation can, by virtue of the immobility of the gas in the low-permeability formation, can exhibit distinct vertical and horizontal variation in composition (Harris et al., 2013). Tight gas has also been claimed to contain less water with depth (i.e., the deeper gas is dryer that the shallower gas) but the composition of the gas may still have a wide range of bulk gas compositions at a given depth. In some cases, there is a distinct shift to a lower gas density at greater depths indicating a preponderance of the lower molecular weight hydrocarbon constituents to the point where some tight gases may be almost pure methane (Harris et al., 2013).

Furthermore in addition to processes that influence the formation of tight gas there are also maturation processes (i.e., distinct chemical processes) that can, and have, have influenced the composition of the tight natural gas, which includes: (i) mixing of gases produced by primary cracking with gases from the secondary cracking of oil; however there is no evidence of gases produced by secondary cracking of wet gas to dry gas, (ii) gases produced by primary cracking from similar source rocks at varying thermal maturity, (iii) gas composition that is altered by bacterial oxidation of hydrocarbon gases, yielding gases that are dry. Furthermore, the obvious stratigraphic variability of the gas composition in some formations and the variation in gas compositions at particular depths suggest complex migration pathways, probably through fracture systems and localized channeling of migrating gases through relatively permeable beds (Cumella and Scheevel, 2008). However, the variation in gas composition cannot be attributed to the ubiquitous vertical diffusion of gases or to the rapid migration of the gas through fractures that have been induced by high pressure effects (Harris et al., 2013).

Thus, while natural gas resources for tight shale formations and from other tight formations does, indeed, represent a significant portion of current and future production, it is essential to recognize that all shale gas is not constant in composition and gas processing requirements for shale gas will vary depending upon the area from which the gas was produced (Bullin and Krouskop, 2008; Weiland and Hatcher, 2012). In addition, analysis of the composition of the gas from of Devonian shale wells indicates that the composition of produced gas shifts during the production history of the well (Schettler et al., 1989). This may serve to indicate that the composition of the gas changes during production because the different components of natural gas produced have different decline curves and that the total decline curve is the sum of the decline curves of the individual components of the gas. This also suggests that there is fractionation of the gas within the reservoir due to adsorption or absorption phenomena and that the classic mechanisms of viscous flow and ideal-gas void-volume storage do not explain fractionation of the gas within the reservoir and even in the production wells. In fact, in order to explain this apparent fractionation is to assume that total gas from the reservoir to the surface facility arises from several sources within the reservoir and the gas from each source produced gas has a different compositions and, hence, a decline curve. Moreover, the flow rate of an individual component of a gas mixture can be obtained by multiplying the total flow rate by the mole fraction of the individual component and even if the composition of gas from each source is assumed to remain constant, the composition of the natural gas at the wellbore will change with time if the relative flow rate changes with time (Schettler et al., 1989).

Another alternative that can be used to describe the changing composition of the gas is to assume that the gas composition changes observed at the wellbore reflect changing composition of gas from at least some of the sources themselves. Candidates for such differences in gas composition include (i) adsorption of the gas components on the reservoir rock, (ii) adsorption of the gas components on any non-gaseous organic material in the reservoir, (iii) solution of the gas components in any organic or inorganic liquids in the reservoir, (iv) absorption and diffusion of the gas components within the pore system of the reservoir rock.

The tendency of the components of the gas for adsorption is associated with the presence of certain types of minerals in the reservoir – clay minerals are especially adept at providing surface (sites) for adsorption to occur. Likewise, the presence of organic material can also provide sites for adsorption to occur. Dissolution of the gas components in any organic or inorganic liquids in the reservoir is associated with the presence of conventional crude oil or heavy crude oil or even gas condensate while the absorption/diffusion phenomenon is associated with diffusion of the gas components through small pores such as those present in microporous reservoirs and which give passage to gas components having a specific molecular size. Because these factors are commonly present, any factor or a combination of factors may he involved in explaining fractionation in many reservoirs (Schettler et al., 1989; Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a). Thus, as reservoir depletion occurs, the composition of the gas produced may approach the composition of the gas originally in the reservoir. Thus, composition shifts during production will be expected but may not be observed because of the site specify of the phenomenon. The site specificity arises because of differences such as, but not limited to: (i) gas composition, (ii) reservoir mineralogy, (iii) reservoir temperature, (iv) reservoir pressure.

Thus, it must be assumed (until proven otherwise) that the gas composition changes observed at the wellbore reflect changing composition of gas from at least some of the sources themselves. Candidates for such differences in gas composition include the presence of adsorption, solution, and/or diffusion. The occurrence of adsorption is associated with the presence of certain minerals in the reservoir, such as clay. Likewise, solution is associated with the presence of conventional crude oil or heavy crude oil or even gas condensate. The diffusion phenomenon is associated with diffusion through small pores such as those present in microporous reservoirs. Because these factors are commonly present, this second alternative may he involved in explaining fractionation in many reservoirs (Schettler et al., 1989). Thus, as reservoir depletion occurs, the composition of the gas produced may approach the composition of the gas originally in the reservoir. Thus, composition shifts during production will be expected but may not be expected, however, when the storage mechanism is associated solely with matrix porosity.

As a result of these various phenomena that can cause changes in gas composition, shale gas processors must be concerned about the elevated ethane and nitrogen levels across a field. Other concerns are the increased requirements of urban gas processing. In addition, the rapid production growth in emerging shale areas can be difficult to handle.

2.2 Properties

Shale gas refers to natural gas (mainly methane) found in fine-grained, organic-rich rocks (gas shale) (Chapter 1, Chapter 2). In addition, the descriptor word *shale* does not refer to a specific type of rock but, in addition to shale (mudstone), has also been may also be used to describes rocks with more fine-grained particles (smaller than sand) than coarse-grained particles, such as (i) siltstone, (ii) fine-grained sandstone interlaminated with shale, as well as (iii) carbonate rocks. Thus, shale (including the additional rock types above, is a source rocks that has not released all of the generated hydrocarbon derivatives. In fact, source rocks that are *tight* or *inefficient* at expelling hydrocarbon derivatives may be the best prospects for shale gas potential. Thus, in gas shale, shale is a reservoir rock, source rock, and also a trap for natural gas. The natural gas found in these rocks is considered unconventional, similar to coalbed methane.

Shale gas is generated by any combination of (i) primary thermogenic degradation of organic matter, (ii) secondary thermogenic decomposition of crude oil, and (iii) biogenic degradation of organic matter. Gas generated by thermogenic and biogenic pathways may both exist in the same shale reservoir.

Gas is stored in shale in three different ways: (i) *adsorbed gas*, which physically attached (adsorption) or chemically attached (chemisorption) to organic matter or to clay, (ii) *free gas*, which is also referred to as *non-associated gas*, (Speight, 2014a), which occurs within the pore spaces in the rock or in spaces created by the rock cracking (fractures or microfractures), and (ii) solution gas, which is also referred to as *associated gas*, (Speight, 2014a), which exists in solution in liquids such as crude oil and heavy crude oil. The amount of adsorbed methane usually increases with an increase in organic matter or surface area of organic matter and/or clay.

Higher free-gas content in unconventional shale gas reservoirs generally results in higher initial rates of production because the free gas resides in fractures and pores and is easier to get out relative to adsorbed gas. The high, initial flow rates decline rapidly to a low, steady rate within approximately one year as adsorbed gas is slowly released from the shale.

Compared to most conventional reservoirs (typically a *sandstone reservoir*), the gas shale reservoir has an extremely low permeability. In fact, the effective bulk permeability in gas shale is typically much less than 0.1 millidarcies (md), although exceptions exist where the rock is naturally fractured; for example, the well-fractured Antrim shale in the Michigan Basin in the United States. In most cases, it is normal for the well to need artificial stimulation, such as fracturing, to increase permeability to the well. This helps the well to produce gas in economical quantities. The role of natural microfractures in reservoir production or in assisting artificial fracturing is not well understood.

Shale gas projects have recently contributed significantly to increased production in the US There is an expectation that rapid exploitation of shale gas development is also likely to occur in other regions of the world. The shale formations in the United States that presently produce gas commercially exhibit an unexpectedly wide variation in the values of five key parameters: (i) thermal maturity, expressed as vitrinite reflectance, (ii) adsorbed-gas fraction, (iii) reservoir thickness, (iv) total organic carbon content, and (v) volume of gas in place (Chapter 2). In addition, the degree of natural fracture development in an otherwise low-matrix-permeability shale reservoir is a controlling factor in gas producibility and, possibly in gas properties.

A wide range of reservoir properties (Chapter 2) controls both the rate and volume of shale-gas production from the gas shale formations, notable: (i) thermal maturity, (ii) gas in place, total organic carbon content, (iii) reservoir thickness, and (iv) proportion of adsorbed gas. Natural fracture networks are required to augment the extremely low shale-matrix permeability. Therefore, geology and geochemistry must be considered together when evaluating a given shale system both before and after drilling as well as gas processing options. In addition, it is very likely that not only the amount and distribution of gas within the shale but also the composition of the shale gas is determined by, among other things: (i) the initial reservoir pressure, (ii) the petrophysical properties of the rock, and (iii) the adsorption characteristics of the rock − thus during production there are three main processes that can be operative.

Initial gas production is dominated by depletion of gas from the fracture network. This form of production declines rapidly due to limited storage capacity. After the initial decline rate stabilizes, the depletion of gas stored in the matrix becomes the primary process involved in production. The amount of gas held in the matrix is dependent on the particular properties of the shale reservoir which can be hard to estimate. Secondary to this depletion process is desorption whereby adsorbed gas is released from the rock as pressure in the reservoir declines. The rate of gas production via the desorption process depends on there being a significant drop in reservoir pressure. At the same time, the composition of the gas can, and undoubtedly does, change due to the action of any one of these parameters or due to the interaction of any two of the above parameters or the interaction of all three of the above parameters.

Furthermore, in the Western Canadian Sedimentary Basin (WCSB), Devonian–Mississippian (D–M) and Jurassic shale formations have complex, heterogeneous pore volume distributions as identified by low pressure carbon dioxide and nitrogen sorption Ross and Bullin (2009). In fact, high pressure methane isotherms on dried and moisture equilibrated shale samples show a general increase of gas sorption with total organic carbon (TOC) content. Methane sorption in Devonian-Mississippian formations increases with increasing total organic carbon content and micropore volume, indicating that microporosity associated with the organic fraction is a primary control not only on methane sorption but also on shale gas composition.

The sorption capacity for a Jurassic shale formations may be unrelated to micropore volume and the large adsorbed gas capacities of organic-rich Jurassic shale formations, independent of surface area, imply a portion of that a portion of the methane is stored by solution in matrix bituminite (Ross and Bullin, 2009). Solute methane does not appear to be an important contributor to gas storage in Devonian-Mississippian shale formations (Ross and Bullin, 2009). In fact, it is likely that structural transformation of Devonian-Mississippian organic matter has occurred during thermal diagenesis creating and/or opening up microporosity onto which gas can sorb thereby also influencing the composition of the shale gas. Furthermore, inorganic constituents also influence modal pore size, total porosity and sorption characteristics of shale formation thereby adding a further parameter to those parameters (above) that influence changes in the shale gas composition. Clay are known to provide excellent adsorption surfaced for crude oil constituents (Speight, 2014a) and are also capable of adsorbing gas into the internal structure, the amount of which is dependent on clay-type.

The uncertainties of reservoir properties and fracture parameters (Chapter 2, Chapter 3) have significant effect on shale gas properties and production, making the process of optimization of hydraulic fracturing treatment design for economic gas production much more complex. It is extremely important to identify reasonable ranges for these uncertainty parameters and evaluate their effects on well performance, because the detailed reservoir properties for each wellbore are difficult to obtain.

Gas production from unconventional shale gas reservoirs has become more common in the past decade, and there are increasing demands to understand the petrophysical and mechanical properties of these rocks. Characterizing these organic-rich shale formations can be challenging as these rocks vary quite significantly (Passey et al., 2010). For instance, formations in the Barnett shale are known to be more silica-rich, whereas Eagle Ford shale rocks are generally carbonate-rich containing relatively smaller amounts of silica and clays. Formations in these shale gas reservoirs also exhibit a wide range of composition within a single reservoir. There are also indications that it is not only the amount of clay or organics, but also the maturity of the shale formations that control the anisotropy of these organic rich shale formations (Vanorio et al., 2008; Ahmadov et al., 2009).

Not surprisingly, gas-bearing shale formations are complex reservoirs (with a porosity on the order of porosity of 4–6 porosity units and a total organic carbon content of ≥4% w/w), which represent significant variety in reservoir characteristics (i.e., mineralogy, porosity, permeability, gas content, and pressure). In addition, the porosity shale porosity changes at very different rates in different regions and formations. Moreover, the gas in these shale formations occurs both as a free phase within pores and fractures and as gas adsorbed onto organic matter. Not surprisingly, and in accordance with the varying shale reservoir properties, it must be anticipated that there will be differences in shale gas composition and properties.

Thus, although shale gas represents a large, new source of natural gas and natural gas liquids (NGLs), shale gas is certainly not the same everywhere. Produced shale gas observed to date has shown a broad variation in compositional makeup, with some having wider component ranges, a wider span of minimum and maximum heating values, and higher levels of water vapor and other substances than pipeline tariffs or purchase contracts may typically allow. Indeed, because of these variations in gas composition, each shale gas formation can have unique processing requirements for the produced shale gas to be marketable. Ethane can be removed by cryogenic extraction while carbon dioxide can be removed through a scrubbing process. However, it is not always necessary (or practical) to process shale gas to make its composition identical to *conventional* transmission-quality gases. Instead, the gas should be interchangeable with other sources of natural gas now provided to end-users. The interchangeability of shale gas with conventional gases is crucial to its acceptability and eventual widespread use in the United States.

Although not highly sour in the usual sense of having high hydrogen sulfide content, and with considerable variation from play to resource to resource and even from well to well within the same resource (due to extremely low permeability of the shale even after fracturing) (Chapter 1, Chapter 3), shale gas often contains varying amounts of hydrogen sulfide with wide variability in the carbon dioxide content. The gas is not ready for pipelining immediately after it has exited the shale formation.

The challenge in treating such gases is the low (or differing) hydrogen sulfide/carbon dioxide ratio and the need to meet pipeline specifications. In a traditional gas processing plant, the olamine of choice for content for hydrogen sulfide removal is N-methyldiethanolamine (MDEA) (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a) but whether or not this olamine will suffice to remove the hydrogen sulfide without removal of excessive amounts of carbon dioxide is another issue.

Gas treatment may begin at the wellhead — condensates and free water usually are separated at the wellhead using mechanical separators, he observes. Gas, condensate and water are separated in the field separator. Extracted condensate and free water are directed to separate storage tanks and the gas flows to a gathering system. After the free water has been removed, the gas is still saturated with water vapor, and depending on the temperature and pressure of the gas stream, may need to be dehydrated or treated with methanol to prevent hydrates as the temperature drops. But this may not be always the case in actual practice.

Thus, there is the real need to evaluate gas processing operations and the ability of a processing plant to treat a variety of shale gases to pipeline specifications. Solvent selection, strength, temperature and circulation rate, as well as the type and quantity of internals used in the contactor, are some of the process parameters and design variables that must be considered (Weiland and Hatcher, 2012).

2.2.1 Antrim shale formation

The Antrim shale is a shallow shale gas resource in Michigan. The Antrim shale is unique because the gas is predominately biogenic: methane is created as a by-product of bacterial consumption of organic material in the shale. Significant associated water is produced requiring central production facilities for dehydration, compression and disposal. The carbon dioxide level in these samples varies from 0% to 11% v/v (Table 8.4). Carbon dioxide is a naturally occurring byproduct of shale gas produced by desorption and, as a result, the carbon dioxide levels in this gas increase during the productive life of a well. Individual well production varies from fifty to sixty thousand cubic feet per day. Significant associated water is produced, requiring central production facilities for dehydration, compression and disposal (Bullin and Krouskop, 2008).

The Antrim shale gas, for example, has high nitrogen concentration, as does at least one well tested in the Barnett shale formation. New Albany shale gas show high carbon dioxide concentrations while several wells in the Marcellus gas shale have tested up to 16% v/v. Economically treating and processing these gases requires all the same techniques as conventional gas − plus the ability to handle a great deal of variability in the same field. These differences in quality of shale gas introduces a note of caution into gas processing because of the variability of the composition and properties of the gas (Bullin and Krouskop, 2008; Weiland and Hatcher, 2012).

2.2.2 Barnett shale formation

The Barnett shale formation of north Texas is the more familiar of shale gas resources and grandfather of shale gas plays. Much of the technology used in drilling and production of shale gas has been developed for this resource. The Barnett shale formation lies around the Dallas-Ft. Worth area of Texas and produces gas at depths of 6500 to 9500 feet. The initial discovery region was in a core area on the eastern side of the play. As drilling has moved westward, the form of the hydrocarbon derivatives in the Barnett shale has varied from dry gas prone in the east to oil prone in the west. As a result of such variations in composition, blending may be the most appropriate methods for equalizing the variations. With the richness of the gas, the Barnett plants remove substantial amounts of natural gas liquids each day.

The Barnett shale formation is the most well-known of shale gas formations (Chapter 2). Much of the technology used in drilling and production of shale gas has been developed on this resource (Bullin and Krouskop, 2008; Weiland and Hatcher, 2012). The Barnett shale formation and produces at depths of 6500−9500 feet with a production rate on the order of 0.5−4 million cubic feet per day (ft^3/d) with estimates of three hundred to five hundred and fifty cubic feet of gas per ton of shale. The initial discovery region was in a core area on the eastern side of the resource and as the drilling and gas recovery has moved westward, the composition of the shale gas has changed from *dry gas* production in the east to *wet gas* and *oil* production in the west.

The Barnett shale resource play, for example, contains several hundred parts per million (ppm v/v) of hydrogen sulfide and much higher amounts of carbon dioxide (in the (percent v/v range) of carbon dioxide. In other shale resources, such as Haynesville and the Eagleville field (Eagle Ford resource), the hydrogen sulfide content is known to be present. In other gas shale resources, such as the Antrim resource and the New Albany resource, underlying Devonian formations may communicate with and contaminate the shale formations. In addition, some of the shale gas resources have low carbon dioxide content but have a sufficiently high content of hydrogen sulfide to require treating. Thus, even after removing the natural gas liquids, there are reasons for the shale gas needs further treatment to remove hydrogen sulfide and carbon dioxide to meet pipeline specifications.

2.2.3 *Fayetteville shale formation*

The Fayetteville shale is an unconventional gas reservoir located on the Arkansas side of the Arkoma Basin and ranges in thickness from 50 to 550 feet at a depth of 1500 to 6500 feet. The gas (Table 8.4) primarily requires only dehydration to meet pipeline specifications. The formation is estimated to hold between fifty-eight to sixty-five billion cubic feet ($58-65 \times 10^6$ ft^3) per square and initial production rates were on the order of 0.2–0.6 million cubic feet per day for vertical wells and one to three and one-half million cubic feet per day for horizontal wells. In 2003, production in one area had exceeded five hundred million cubic feet per day (Bullin and Krouskop, 2008).

2.2.4 *Haynesville shale formation*

The Haynesville shale gas resource is the newest shale area to be developed. It lies in northern Louisiana and East Texas. The formation is deep (>10,000 feet), high bottomhole temperature (175 °C, 350 °F), and high pressure (3000 to 4000 psi). The wells showed initial production rates up to twenty or more million cubic feet of gas per day with estimates of one hundred to three hundred and thirty cubic feet of gas per ton of shale (Bullin and Krouskop, 2008).

The gas requires treating for carbon dioxide removal (Table 8.4). Operators in this field are using amine treating to remove the carbon dioxide with a scavenger treatment on the tail gas to remove hydrogen sulfide.

2.2.5 *Marcellus shale formation*

The Marcellus shale lies in western Pennsylvania, Ohio, and West Virginia. The formation is shallow at depths of 2000 to 8000 feet and 300 to 1000 feet thick. The gas composition varies across the field, much as it does in the Barnett – the gas becomes richer from east to west (Table 8.4). Initial production rates have been reported to be on the order of 0.5–4 million cubic feet per day (ft^3/d), with estimates of 60–100 cubic feet of gas per ton of shale (Bullin and Krouskop, 2008).

The Marcellus shale gas has relatively little carbon dioxide and nitrogen. In addition, the gas is *dry* and does not require removal of natural gas liquids for pipeline transportation. Early indications are that the Marcellus gas has sufficient liquids to require processing.

2.2.6 *New Albany shale formation*

The New Albany shale is black shale in Southern Illinois extending through Indiana and Kentucky. The formation is 500 to 4900 feet deep and 100–400 feet thick. The gas composition (Table 8.4) is variable and low flow rates of wells in the New Albany shale require that production from many wells must be combined to warrant processing the gas. Vertical wells typically produce twenty-five to seventy-five thousand cubic feet per day while horizontal wells can have initial production rates up to two million cubic feet per day (Bullin and Krouskop, 2008).

3. Gas treating processes

Gas processing cleaning (also called *gas cleaning* and *gas refining*) is a necessary procedure to produce the product that meet the various specifications. Gas processing is a necessary part of the natural gas value chain. Gas processing is, in fact, an integrated system of unit processes that are used to remove objectionable products such as acid gases (e.g., carbon dioxide and hydrogen sulfide) and to separate natural gas into other useful gas streams. Thus, gas processing is instrumental in ensuring that the natural gas intended for use is as clean and pure as possible, making it the clean burning and also an environmentally-sound energy choice.

Treatment often begins at the wellhead at which point condensate and free water usually are separated at the wellhead using mechanical separators. Gas, condensate and water are separated in the field separator, he details. Extracted condensate and free water are directed to separate storage tanks and the gas flows to a gathering system. After the free water has been removed, the gas is still saturated with water vapor, and depending on the temperature and pressure of the gas stream, may need to be dehydrated or treated with methanol to prevent hydrates as the temperature drops.

Contaminants such as carbon dioxide and hydrogen sulfide are removed at a treatment facility near the field or at a gas processing plant. Removing the carbon dioxide near the field is often done for pipeline protection. This is achieved using a physical solvent (usually referred to as an olamine or amine solution. Carbon dioxide and hydrogen sulfide are both highly corrosive (even more so in the presence of water in the gas stream). If the gas is treated using an olamine solution, it later must be dehydrated to pipeline quality. Dehydration can be accomplished through absorption or adsorption methods. These separation and dehydration steps are similar for all gases. If nitrogen is present in significant amounts, it must be removed at a cryogenic plant with supercooling equipment so that the gas meets the minimum heating value required by the pipeline.

Process selectivity indicates the preference with which the process removes one acid gas component relative to (or in preference to) another. For example, some processes remove both hydrogen sulfide and carbon dioxide; other processes are designed to remove hydrogen sulfide only. It is important to consider the process selectivity for, say, hydrogen sulfide removal compared to carbon dioxide removal that ensures minimal concentrations of these components in the product, thus the need for consideration of the carbon dioxide to hydrogen sulfide in the gas stream.

Natural gas, as it is used by consumers, is composed almost entirely of methane and is much different from the natural gas that exists in the reservoir and that is brought up to the wellhead. Although the processing of natural gas is in many respects less complicated than the processing and refining of crude oil, it is equally as necessary before its use by end users. The natural gas used by consumers is composed almost entirely of methane, but the natural gas produced at the wellhead, although still composed primarily of methane, is by no means as pure. Raw (untreated) natural gas is produced from three types of wells: (i) wells that produce crude oil and natural gas, (ii) wells that produce natural gas only, and (iii) wells that produce gas condensate and natural gas.

Gas processing (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a) consists of separating all of the various hydrocarbon derivatives and fluids from the pure natural gas (Fig. 8.2). Major transportation pipelines usually impose restrictions on the make-up of the natural gas that is allowed into the pipeline and, as a result, the natural gas must be purified before it can be transported. Thus, gas processing is necessary to ensure that the natural gas intended for use is as clean and pure as possible.

Pipeline quality standards limit the amount of carbon dioxide, nitrogen, oxygen and water vapor that can be in the gas stream and also set a heating value limit on the order of 1035 ± 50

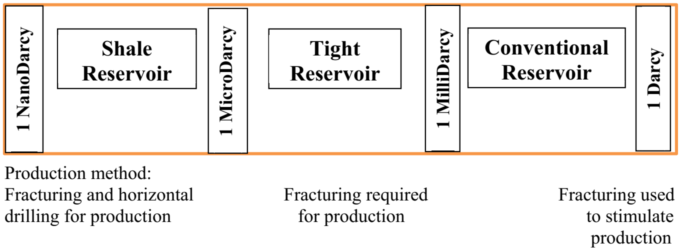

FIG. 8.2 Illustration of reservoir types based on permeability and production methods.

Btu per cubic foot. In some cases, when plants are not yet available, waivers are granted for a limited time which enables producers to begin marketing gas from new fields as the processing plant is built. If the gas is not pipeline quality, it typically is processed at a refrigeration or cryogenic plant. In refrigeration units, the gas is cooled to separate the natural gas liquids which removes more than 90% of the propane and approximately 40% of the ethane. Other higher-boiling constituents are removed almost entirely. In cryogenic units, gas temperature is reduced to −85 to −100 °C (−120 to −150 °F). The temperature drop causes the ethane and other heavier hydrocarbon derivatives to condense, removing more of the natural gas liquids and 90–95% v/v of the ethane.

The actual practice of processing gas streams to pipeline dry gas quality levels can be quite complex, but usually involves four main processes to remove the various impurities. Gas streams produced during crude oil and natural gas refining, while ostensibly being hydrocarbon in nature, may contain large amounts of acid gases such as hydrogen sulfide and carbon dioxide. Most commercial plants employ hydrogenation to convert organic sulfur compounds into hydrogen sulfide. Hydrogenation is effected by means of recycled hydrogen-containing gases or external hydrogen over a nickel molybdate or cobalt molybdate catalyst (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a).

Gas processing is an instrumental part of the natural gas value chain insofar as it is instrumental in ensuring that the natural gas is as clean and pure as possible (the gas meets the specifications that render the gas suitable for use) by making the gas the clean burning and an environmentally sound energy choice. Once the natural gas has been fully processed, and is ready to be consumed, it must be transported from those areas that produce natural gas, to those areas that require it.

It is also at the gas plant that process selectivity plays a major role in gas processing. Process selectivity indicates the preference with which the process removes one acid gas component relative to (or in preference to) another. For example, some processes remove both hydrogen sulfide and carbon dioxide; other processes are designed to remove hydrogen sulfide only. It is important to consider the process selectivity for, say, hydrogen sulfide removal compared to carbon dioxide removal that ensures minimal concentrations of these components in the product, thus the need for consideration of the carbon dioxide to hydrogen sulfide in the gas stream.

Although the processing of natural gas is in many respects less complicated than the processing and refining of crude oil, it is equally as necessary before its use by end users. The natural gas used by consumers is composed almost entirely of methane. However, natural gas found at the wellhead, although still composed primarily of methane, is by no means as pure. Typically, the operations at the gas processing plant involve (i) water removal, (ii) separation of natural gas liquids, and (iii) sulfur and carbon dioxide removal.

In summary, refinery process gas, in addition to hydrocarbon derivatives, may contain other contaminants, such as carbon oxides (CO_x, where x = 1 and/or 2), sulfur oxides (So_x, where x = 2 and/or 3), as well as ammonia (NH_3), mercaptans (R—SH), and carbonyl sulfide (COS). The presence of these impurities may eliminate some of the sweetening processes, since some processes remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes not designed to remove (or incapable of removing) large amounts of acid gases whereas they are capable of removing the acid gas impurities to very low levels when the acid gases are present only in low-to-medium concentration in the gas (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a).

3.1 Water removal

In addition to separating crude oil and condensate from the gas stream, the water associated with the gas stream must also be removed. Most of the liquid, free water associated with extracted natural gas can be removed by simple separation methods at or near the wellhead but the removal of any water that still remains in the natural gas requires a more complex treatment. This treatment consists of a dehydration step at the gas processing plant and can involve one of two processes, either (i) absorption, or (ii) adsorption. Again, for clarification, *absorption* occurs when the water vapor is removed for the gas stream by a dehydrating agent whereas *adsorption* occurs when the water vapor is condensed and collected on the surface of a dehydrating agent. Natural gas from tight formation does not usually contain as much water as natural gas from conventional reservoirs but the occasion for water removal at the gas processing plant my still be necessary.

3.1.1 Absorption

Throughout this chapter, two terms are used frequently: (i) absorption and (ii) adsorption. *Absorption* is achieved by dissolution (a physical phenomenon) or by reaction (a chemical phenomenon) and is an approach in which the absorbed gas is ultimately distributed throughout the absorbent (liquid). The process depends only on physical solubility and may include chemical reactions in the liquid phase (*chemisorption*). Common absorbing media used are water, aqueous amine solutions, caustic, sodium carbonate, and nonvolatile hydrocarbon oils, depending on the type of gas to be absorbed. Usually, the gas-liquid contactor designs which are employed are plate columns or packed beds. Absorption is achieved by dissolution (a physical phenomenon) or by reaction (a chemical phenomenon). Chemical adsorption processes adsorb sulfur dioxide onto a carbon surface where it is oxidized (by oxygen in the flue gas) and absorbs moisture to give sulfuric acid impregnated into and on the adsorbent.

Absorption differs from *adsorption*, in that it is not a physical-chemical surface phenomenon, but an approach in which the absorbed gas is ultimately distributed throughout the absorbent (liquid). The process depends only on physical solubility and may include chemical reactions in the liquid phase (*chemisorption*). Common absorbing media used are water, aqueous amine solutions, caustic, sodium carbonate, and nonvolatile hydrocarbon oils, depending on the type of gas to be absorbed. Usually, the gas-liquid contactor designs which are employed are plate columns or packed beds (Mokhatab et al., 2006; Speight, 2014a, 2019a). Thus, absorption is achieved by dissolution (a physical phenomenon) or by reaction (a chemical phenomenon) (Barbouteau and Galaud, 1972; Ward, 1972; Mokhatab et al., 2006; Speight, 2014a, 2019a). Chemical adsorption processes adsorb sulfur dioxide onto a carbon surface where it is oxidized (by oxygen in the flue gas) and absorbs moisture to give sulfuric acid impregnated into and on the adsorbent.

The number of steps and the type of process used to produce pipeline-quality natural gas most often depends upon the source and makeup of the wellhead production stream. In some cases, several of the steps (Fig. 8.2) may be integrated into one unit or operation, performed in a different order, or performed at alternative locations, or not required at all (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a).

Liquid absorption processes (which usually employ temperatures below 50 °C (120 °F) are classified either as *physical solvent processes* or *chemical solvent processes*. The former processes employ an organic solvent, and absorption is enhanced by low temperatures, or high pressure, or both. Regeneration of the solvent is often accomplished readily (Staton et al., 1985; Mokhatab et al., 2006; Speight, 2014a, 2019a). In chemical solvent processes, absorption of the acid gases is achieved mainly by use of alkaline solutions such as amines or carbonates (Kohl and Riesenfeld, 1985). Regeneration (desorption) can be brought related to by use of reduced pressures and/or high temperatures, whereby the acid gases are stripped from the solvent.

Solvents used for emission control processes should have: (i) a high capacity for acid gas, (ii) a low tendency to dissolve hydrogen, (iii) a low tendency to dissolve low-molecular weight hydrocarbon derivatives, (iv) low vapor pressure at operating temperatures to minimize solvent losses, (v) low viscosity, (vi) low thermal stability, (vii) absence of reactivity toward gas components, (viii) a low tendency for fouling, (ix) a low tendency for corrosion, and (xi) be economically acceptable (Speight, Mokhatab et al., 2006; Speight, 2014a, 2014b, 2019a).

Amine washing of gas emissions involves chemical reaction of the amine with any acid gases with the liberation of an appreciable amount of heat and it is necessary to compensate for the absorption of heat. Amine derivatives such as ethanolamine (monoethanolamine, MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), and diglycolamine (DGA) have been used in commercial applications (Katz, 1959; Kohl and Riesenfeld, 1985; Maddox et al., 1985; Polasek and Bullin, 1985; Jou et al., 1985; Pitsinigos and Lygeros, 1989; Mokhatab et al., 2006; Speight, 2014a, 2019a).

The chemistry can be represented by simple equations for low partial pressures of the acid gases:

$$2RNH_2 + H_2S \rightarrow (RNH_3)_2S$$
$$2RHN_2 + CO_2 + H_2O \rightarrow (RNH_3)_2CO_3$$

At high acid gas partial pressure, the reactions will lead to the formation of other products:

$$(RNH_3)_2S + H_2S \rightarrow 2RNH_3HS$$
$$(RNH_3)_2CO_3 + H_2O \rightarrow 2RNH_3HCO_3$$

The reaction is extremely fast, the absorption of hydrogen sulfide being limited only by mass transfer; this is not so for carbon dioxide. Regeneration of the solution leads to near complete desorption of carbon dioxide and hydrogen sulfide. A comparison between monoethanolamine, diethanolamine, and diisopropanolamine shows that monoethanolamine is the cheapest of the three but shows the highest heat of reaction and corrosion; the reverse is true for diisopropanolamine.

An example of absorption dehydration is known as *glycol dehydration* and diethylene glycol (DEG, $HOCH_2CH_2CH_2CH_2OH$), the principal agent in this process, has a chemical affinity for water and removes water from the gas stream. The *glycol dehydration* process is an example of a process that provides *absorption dehydration* and in the process, a liquid desiccant provides the means to absorb water from the gas stream. Ethylene glycol ($HOCH_{2-}CH_2OH$), was, initially, the principal chemical agent in this process, has a very strong affinity for water and when the glycol is in contact with a stream of water-wet natural gas, the ethylene glycol absorbs the water from the gas stream. Initially, the process used ethylene glycol as the absorbent but, with the advancement of the technology, glycol dehydration now involves the use of an aqueous solution of a glycol derivative in which the glycol is either diethylene glycol (DEG) or triethylene glycol (TEG) (Table 8.6), which is brought into contact with the water-wet gas stream in a contactor. The glycol solution will absorb water from the wet gas and, one absorbed, the glycol sinks to the bottom of the contactor while the natural gas, stripped of most of the water content, is then transported out of the dehydrator. The glycol solution, bearing all of the water stripped from the natural gas, is put through a specialized boiler designed to vaporize only the water out of the solution where the boiling point differential facilitates removal of the water for the makes it relatively easy to remove water from the glycol solution after which the glycol is recycled to the contactor.

In this process, a liquid desiccant dehydrator serves to absorb water vapor from the gas stream. In the process, glycol dehydration involves using a glycol solution, usually either diethylene glycol or triethylene glycol (TEG, $HOCH2CH2CH2CH_2CH_2CH_2OH$), which is brought into contact with the wet gas stream in a *contactor*. The glycol solution absorbs the water from the wet gas and, once absorbed, the glycol-wager mix increases in density (becomes heavier) and sinks to the bottom of the contactor where it (the mixture) is removed.

TABLE 8.6 Olamines used for gas processing.

Olamine	Formula	Acronym	Molecular weight	Specific gravity	Melting point, °C	Boiling point, °C	Flash point, °C
Ethanolamine (monoethanolamine)	$HOC_2H_4NH_2$	MEA	61.08	1.01	10	170	85
Diethanolamine	$(HOC_2H_4)_2NH$	DEA	105.14	1.097	27	217	169
Triethanolamine	$(HOC_2H_4)_3NH$	TEA	148.19	1.124	18	335[d]	185
Diglycolamine (hydroxyethanolamine)	$H(OC_2H_4)_2NH_2$	DGA	105.14	1.057	−11	223	127
Diisopropanolamne	$(HOC_3H_6)_2NH$	DIPA	133.19	0.99	42	248	127
Methyldiethanolamine	$(HOC_2H_4)_2NCH_3$	MDEA	119.17	1.03	−21	247	127

d: With decompositon

The natural gas, having been stripped of most of its water content, is then transported out of the dehydrator. The glycol solution, bearing all of the water stripped from the natural gas, is put through a specialized boiler designed to vaporize only the water out of the solution. The boiling point differential between water (100 °C, 212 °F) and glycol (204 °C, 400 °F) makes it relatively easy to remove water from the glycol solution, allowing it to be reused in the dehydration process.

As well as absorbing water from the wet gas stream, the glycol solution occasionally carries with it small amounts of methane and other compounds found in the wet gas. In the past, this methane was simply vented out of the boiler. In addition to losing a portion of the natural gas that was extracted, this venting contributes to air pollution and the greenhouse effect. In order to decrease the amount of methane and other compounds that are lost, flash tank separator-condensers work to remove these compounds before the glycol solution reaches the boiler. Essentially, a flash tank separator consists of a device that reduces the pressure of the glycol solution stream, allowing the methane and other hydrocarbon derivatives to vaporize (*flash*).

In some cases, a flash tank separator-condensers has been added to the unit which, in addition to absorbing water from the gas stream, will also regenerate small amounts of methane and other compounds that the glycol solution occasionally carries with it from the contactor stage having also absorbed these constituents from the gas stream. In the past, this methane was may have been vented and lost to the product streams as well as making a contribution to atmospheric pollution (Chapter 9). In order to decrease the amount of methane and other compounds that are lost, the flash tank separator-condensers enables removal of the absorbed hydrocarbon constituents before the glycol solution reaches the boiler. In the flash tank separator, the pressure is reduced which allows the lower boiling hydrocarbon constituents (i.e., lower boiling than the glycol solvent) thereby allowing the methane and other hydrocarbon derivatives to vaporize (*flash*) from the solution. The glycol solution is then sent to the boiler, which may also be fitted with air or water cooled condensers, at which point any remaining hydrocarbon derivatives are captured, combined with other hydrocarbon streams, fractionated, and sent to the various product streams. The insertion of a flash-separator-condenser system into the process is valuable adaption for the treatment of natural gas streams from tight formation because of the content of hydrocarbon constituents that are higher molecular weight than methane (Table 8.4).

After dehydration, the glycol solution then travels to the boiler, which may also be fitted with air or water-cooled condensers, which serve to capture any remaining organic compounds that may remain in the glycol solution. The regeneration (stripping) of the glycol is limited by temperature: diethylene glycol and triethylene glycol decompose at or before their respective boiling points. Such techniques as stripping of hot triethylene glycol with dry gas or vacuum distillation are recommended. In practice, absorption systems recover 90–99% v/v of methane that would otherwise be flared into the atmosphere.

3.1.2 Adsorption

Adsorption is a physical-chemical phenomenon in which the gas is concentrated on the surface of a solid or liquid to remove impurities. Removal of water by adsorption of the water on to a solid adsorbent (often referred to as solid desiccant dehydration) is another process option for the dehydration of gas streams.

In the process, it is typically carbon that is the adsorbing medium-the carbon can be regenerated by *desorption* of the adsorbed material (Fulker, 1972; Mokhatab et a., 2006; Speight, 2014a, 2019a). The quantity of material adsorbed is proportional to the surface area of the solid and, consequently, adsorbents are usually granular solids with a large surface area per unit mass. Subsequently, the captured gas can be desorbed with hot air or steam either for recovery or for thermal destruction.

Adsorber units are widely used to increase a low gas concentration prior to incineration unless the gas concentration is very high in the inlet air stream. Adsorption also is employed to reduce problem odors from gases. There are several limitations to the use of adsorption systems, but it is generally felt that the major one is the requirement for minimization of particulate matter and/or condensation of liquids (e.g., water vapor) that could mask the adsorption surface and drastically reduce its efficiency. Thus, in any gas processing plant, it is necessary to know not only the composition of the gas entering the plan but also the composition of the gas entering (and exiting) each of the unit processes that constitute the gas processing plant and methods involving gas chromatographic analysis are particularly useful (ASTM D1945; ASTM D1946; ASTM D2597). This type of analytical data can prevent overloading the unit process and (through the removal of corrosive constituents) mitigate the potential for equipment corrosion.

Solid adsorbent or solid-desiccant dehydration is the primary form of dehydrating natural gas using adsorption, and usually consists of two or more adsorption towers, which are filled with a solid desiccant. Typical desiccants include activated alumina or a granular silica gel material. Wet natural gas is passed through these towers, from top to bottom. As the wet gas passes around the particles of desiccant material, water is retained on the surface of these desiccant particles. Passing through the entire desiccant bed, almost all of the water is adsorbed onto the desiccant material, leaving the dry gas to exit the bottom of the tower.

The *solid-desiccant dehydration* process is also a well-used process for dehydrating natural gas using adsorption and the unit usually consists of two or more adsorption towers, each of which is filled with a solid desiccant and the typical desiccants are: (i) activated alumina or (ii) a granular silica gel material. In the process, water-wet natural gas is passed through the towers, in a top-to-bottom direction and, as the gas stream passes through the desiccant and around the desiccant particles, water is adsorbed on to the surface of the desiccant particles. By this means (i.e. passing the gas stream through the entire desiccant bed) almost all of the water is adsorbed onto the desiccant material, leaving the dry gas stream to exit the bottom of the tower.

The solid-desiccant dehydrator process is typically more effective than the glycol dehydrator process, and solid desiccant units are often installed in a straddle mode along natural gas pipelines and are ideally suited for large volumes of natural gas that is under very high pressure (as is often the case in pipelines) and are, as a result, usually located on a pipeline downstream of a compressor station. The process requires two or more towers due to the fact that after a certain period of use, the desiccant in a particular tower becomes saturated with water and needs to be regenerated. The regeneration stage involves taking the tower off-stream at which time a pre-heated high-temperature gas is passed through the desiccant to vaporizes any residual water in the desiccant after which the dry desiccant is brought back on stream for further use in the process.

Typical desiccants include activated alumina or a granular silica gel material. Wet natural gas is passed through these towers, from top to bottom. As the wet gas passes around the particles of desiccant material, water is retained on the surface of these desiccant particles. Passing through the entire desiccant bed, almost all of the water is adsorbed onto the desiccant material, leaving the dry gas to exit the bottom of the tower.

Solid-desiccant dehydrators are typically more effective than glycol dehydrators, and are usually installed as a type of straddle system along natural gas pipelines. These types of dehydration systems are best suited for large volumes of gas under very high pressure, and are thus usually located on a pipeline downstream of a compressor station. Two or more towers are required due to the fact that after a certain period of use, the desiccant in a particular tower becomes saturated with water. To 'regenerate' the desiccant, a high-temperature heater is used to heat gas to a very high temperature. Passing this heated gas through a saturated desiccant bed vaporizes the water in the desiccant tower, leaving it dry and allowing for further natural gas dehydration.

Molecular sieves − a class of aluminosilicates which produce the lowest water dew point, and which can be used to simultaneously sweeten, dry gases and liquids (Maple and Williams, 2008) − are commonly used in dehydrators ahead of plants designed to recover ethane and other natural gas liquids. These plants operate at very cold temperatures and require very dry feed gas to prevent formation of hydrates. Dehydration to −100 °C (−148 °F) dew point is possible with molecular sieves. Water dew points less than −100 °C (−148 °F) can be accomplished with special design and definitive operating parameters (Mokhatab et al., 2006; Speight, 2014a, 2019a).

Solid-adsorbent dehydrators are typically more effective than glycol dehydrators, and are usually installed as a type of straddle system along natural gas pipelines. These types of dehydration systems are best suited for large volumes of gas under very high pressure, and are thus usually located on a pipeline downstream of a compressor station. Two or more towers are required due to the fact that after a certain period of use, the desiccant in a particular tower becomes saturated with water. To 'regenerate' the desiccant, a high-temperature heater is used to heat gas to a very high temperature. Passing this heated gas through a saturated desiccant bed vaporizes the water in the desiccant tower, leaving it dry and allowing for further natural gas dehydration.

Although two-bed adsorbent treaters have become more common (while one bed is removing water from the gas, the other undergoes alternate heating and cooling), on occasion, a three-bed system is used: one bed adsorbs, one is being heated, and one is being cooled. An additional advantage of the three-bed system is the facile conversion of a two-bed system so that the third bed can be maintained or replaced, thereby ensuring continuity of the operations and reducing the risk of a costly plant shutdown.

Silica gel (SiO_2) and alumina (Al_2O_3) have good capacities for water adsorption (up to 8% by weight). Bauxite (crude alumina, Al_2O_3) adsorbs up to 6% by weight water, and molecular sieves adsorb up to 15% by weight water. Silica is usually selected for dehydration of sour gas because of its high tolerance to hydrogen sulfide and to protect molecular sieve beds from plugging by sulfur. Alumina *guard beds* (which serve as protectors by the act of attrition and may be referred to as an *attrition catalyst*) (Speight, 2000) may be placed ahead of the molecular sieves to remove the sulfur compounds. Downflow reactors are commonly used for adsorption processes, with an upward flow regeneration of the adsorbent and cooling in the same direction as adsorption.

Solid desiccant units generally cost more to buy and operate than glycol units. Therefore, their use is typically limited to applications such as gases having a high hydrogen sulfide content, very low water dew point requirements, simultaneous control of water, and hydrocarbon dew points. In processes where cryogenic temperatures are encountered, solid desiccant dehydration is usually preferred over conventional methanol injection to prevent hydrate and ice formation (Kindlay and Parrish, 2006).

3.1.3 Chemical treatment

In *chemical conversion processes*, contaminants in gas emissions are converted to compounds that are not objectionable or that can be removed from the stream with greater ease than the original constituents. For example, a number of processes have been developed that remove hydrogen sulfide and sulfur dioxide from gas streams by absorption in an alkaline solution.

Carbonate washing is a mild alkali process for emission control by the removal of acid gases (such as carbon dioxide and hydrogen sulfide) from gas streams (Mokhatab et al., 2006; Speight, 2014a, 2019a) and uses the principle that the rate of absorption of carbon dioxide by potassium carbonate increases with temperature. It has been demonstrated that the process works best near the temperature of reversibility of the reactions:

$$K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3$$
$$K_2CO_3 + H_2S \rightarrow KHS + KHCO_3$$

Water washing, in terms of the outcome, is analogous to washing with potassium carbonate (Kohl and Riesenfeld, 1985; Mokhatab et al., 2006; Speight, 2014a, 2019a), and it is also possible to carry out the desorption step by pressure reduction. The absorption is purely physical and there is also a relatively high absorption of hydrocarbon derivatives, which are liberated at the same time as the acid gases.

Catalytic oxidation is a chemical conversion process that is used predominantly for destruction of volatile organic compounds and carbon monoxide. These systems operate in a temperature regime of 205–595 °C (400–1100 °F) in the presence of a catalyst. Without the catalyst, the system would require higher temperatures. Typically, the catalysts used are a combination of noble metals deposited on a ceramic base in a variety of configurations (e.g., honeycomb-shaped) to enhance good surface contact.

Catalytic systems are usually classified on the basis of bed types such as *fixed bed* (or *packed bed*) and *fluid bed* (*fluidized bed*). These systems generally have very high destruction efficiencies for most volatile organic compounds, resulting in the formation of carbon dioxide, water, and varying amounts of hydrogen chloride (from halogenated hydrocarbon derivatives). The presence in emissions of chemicals such as heavy metals, phosphorus, sulfur, chlorine, and most halogens in the incoming air stream act as poison to the system and can foul up the catalyst.

Thermal oxidation systems, without the use of catalysts, also involve chemical conversion (more correctly, chemical destruction) and operate at temperatures in excess of 815 °C (1500 °F), or 220–610 °C (395–1100 °F) higher than catalytic systems.

3.1.4 Filters and scrubbers

Historically, *particulate matter control* (*dust control*) (Mody and Jakhete, 1988) has been one of the primary concerns of industries, since the emission of particulate matter is readily observed through the deposition of fly ash and soot as well as in impairment of visibility. Differing ranges of control can be achieved by use of various types of equipment. Upon proper characterization of the particulate matter emitted by a specific process, the appropriate piece of equipment can be selected, sized, installed, and performance tested. The general classes of control devices for particulate matter are as follows:

Cyclone collectors are the most common of the inertial collector class. Cyclones are effective in removing coarser fractions of particulate matter. The particle-laden gas stream enters an upper cylindrical section tangentially and proceeds downward through a conical section. Particles migrate by centrifugal force generated by providing a path for the carrier gas to be subjected to a vortex-like spin. The particles are forced to the wall and are removed through a seal at the apex of the inverted cone. A reverse-direction vortex moves upward through the cyclone and discharges through a top center opening. Cyclones are often used as primary collectors because of their relatively low efficiency (50–90% is usual). Some small-diameter high-efficiency cyclones are utilized. The equipment can be arranged either in parallel or in series to both increase efficiency and decrease pressure drop. These units for particulate matter operate by contacting the particles in the gas stream with a liquid. In principle the particles are incorporated in a liquid bath or in liquid particles which are much larger and therefore more easily collected.

Fabric filters are typically designed with non-disposable filter bags. As the dusty emissions flow through the filter media (typically cotton, polypropylene, Teflon, or fiberglass), particulate matter is collected on the bag surface as a dust cake. Fabric filters are generally classified on the basis of the filter bag processing mechanism employed. Fabric filters operate with collection efficiencies up to 99.9% although other advantages are evident.

Wet scrubbers are devices in which a counter-current spray liquid is used to remove particles from an air stream. Device configurations include plate scrubbers, packed beds, orifice scrubbers, venturi scrubbers, and spray towers, individually or in different combinations. Other methods include use of high-energy input *venturi scrubbers* or electrostatic scrubbers where particles or water droplets are charged, and flux force/condensation scrubbers where a hot humid gas is contacted with cooled liquid or where steam is injected into saturated gas. In the latter scrubber the movement of water vapor toward the cold-water surface carries the particles with it (*diffusiophoresis*), while the condensation of water vapor on the particles causes the particle size to increase, thus facilitating collection of fine particles. The *foam scrubber* is a modification of a wet scrubber in which the particle-laden gas is passed through a foam generator, where the gas and particles are enclosed by small bubbles of foam.

Electrostatic precipitators operate on the principle of imparting an electric charge to particles in the incoming air stream, which are then collected on an oppositely charged plate across a high-voltage field. Particles of high resistivity create the most difficulty in collection. Conditioning agents such as sulfur trioxide (SO_3) have been used to lower resistivity. Important parameters include design of electrodes, spacing of collection plates, minimization of air channeling, and collection-electrode rapping techniques (used to dislodge particles). Techniques under study include the use of high-voltage pulse energy to enhance particle charging, electron-beam ionization, and wide plate spacing. Electrical precipitators are capable of efficiencies >99% under optimum conditions, but performance is still difficult to predict in new situations.

3.1.5 Membrane processes

Membrane separation process are very versatile and are designed to process a wide range of feedstocks and offer a simple solution for removal and recovery of higher boiling hydrocarbon derivatives (natural gas liquids) from natural gas (Foglietta, 2004) as well as cleaning other gases such as biogas (Schweigkofler and Niessner, 2001; Popat and Deshusses, 2008; Deng and Hagg, 2010; Matsui and Imamura, 2010.). Synthetic membranes are made from a variety of polymers including polyethylene, cellulose acetate, polysulfone, and polydimethylsiloxane (Isalski, 1989; Robeson, 1991). The material from which the membrane is manufactured plays an important role in the ability of the membrane to provide the desired performance characteristics. For process optimization, the membrane should have a high permeability as well as sufficient selectivity. It is also important to match the membrane properties to that of the system operating conditions (for example pressures and gas composition).

The separation process is based on high-flux membranes that selectively permeates higher boiling hydrocarbon derivatives (compared to methane) and are recovered as a liquid after recompression and condensation. The residue stream from the membrane is partially depleted of higher boiling hydrocarbon derivatives, and is then sent to sales gas stream. Gas permeation membranes are usually made with vitreous polymers that exhibit good selectivity but, to be effective, the membrane must be very permeable with respect to the separation process.

Polymeric membranes are a common option for the separation of carbon dioxide from flue gas because of the maturity of the technology in a variety of industries, namely the petrochemical industry. The ideal polymer membrane has both a high selectivity and permeability. Polymer membranes are examples of systems that are dominated by the solution-diffusion mechanism. The membrane is considered to have holes which the gas can dissolve (solubility) and the molecules can move from one cavity to the other (diffusion).

Silica membranes can be produced with high uniformity (the same structure throughout the membrane) and the high porosity of these membranes is accompanied by high permeability. Synthesized membranes have smooth surfaces and can be modified on the surface to drastically improve selectivity. For example, silica membrane surfaces that have been functionalized by inclusion of an amine (on the surface) allows the membranes to separate carbon dioxide from flue gas streams more effectively (Jang et al., 2011).

Zeolites (crystalline aluminosilicate minerals) with a regular repeating structure of molecular-sized pores also can be used to produce workable membranes. These membranes selectively separate molecules based on pore size and polarity and are thus highly tunable to specific gas separation processes. In general, smaller molecules and those with stronger zeolite-adsorption properties are adsorbed onto zeolite membranes with larger selectivity. The capacity to discriminate based on both molecular size and adsorption affinity makes zeolite membranes an attractive candidate for carbon dioxide separation from natural gas.

3.2 Liquids removal

Natural gas coming directly from a well (including wells producing gas from tight formations) contains many hydrocarbon constituents (Tables 8.4 and 8.5) that are classed as *natural gas liquids* (NGLs) (being liquid under conditions where methane remains a gas) that are commonly removed. In most instances, natural gas liquids have a higher value as separate product streams (i.e., as separated ethane, methane, propane, butanes and pentanes plus) and, as a result, it is economical to remove these constituents from the natural gas stream. The removal of natural gas liquids usually takes place in a relatively centralized processing plant, and uses techniques similar to those used to dehydrate natural gas. Wellhead processing of tight gas for removal of the higher molecular weight hydrocarbon constituents is also a possibility but, as might be excepted, is dictated by the economics of the separation and the transportation of the individual hydrocarbon streams. In summary, the extraction of natural gas liquids from the natural gas stream produces both cleaner, purer natural gas, as well as the valuable hydrocarbon derivatives that are the constituents of the natural gas liquids.

There are two steps to the separation of the natural gas liquids from a natural gas stream (i) the natural gas liquids, i.e. the hydrocarbon constituents, must be extracted from the natural gas and (ii) the natural gas liquids must be individually separated to yield the individual constituents.

In order to process and transport associated dissolved natural gas, the first step must be the separation of the gas from the crude oil in which the gas dissolved. This separation of natural gas from oil is most often done using equipment installed at or near the wellhead. The actual process used to separate oil from natural gas, as well as the equipment that is used, can vary widely. Although dry pipeline quality natural gas is may be identical (or almost identical) across different geographic areas, raw natural gas from different regions may have different compositions and separation requirements (Chapter 1). The most basic type of separator is known as a conventional separator which consists of a closed tank, where the force of gravity serves to separate the heavier liquids like oil, and the lower-boiling gases, such as natural gas.

An example of the type of separator is the *low-temperature separator* which is often used for wells producing high pressure gas along with light crude oil or with gas condensate. These separators use pressure differentials to cool the wet natural gas and separate the oil and condensate.

In the process, wet gas enters the separator, being cooled slightly by a heat exchanger. The gas then travels through a high-pressure liquid *knockout pot*, which serves to remove any liquids into a low-temperature separator. The gas then flows into this low-temperature separator through a choke mechanism, which expands the gas as it enters the separator. This rapid expansion of the gas allows for the lowering of the temperature in the separator. After liquid removal, the dry gas then travels back through the heat exchanger and is warmed by the incoming wet gas. By varying the pressure of the gas in various sections of the separator, it is possible to vary the temperature, which causes the oil and some water to be condensed out of the wet gas stream.

There are two basic steps to the treatment of natural gas liquids in the natural gas stream (i) the liquids must be extracted from the natural gas, and (ii) the natural gas liquids must be separated themselves, down to their base components. These two processes account for approximately 90% v/v of the total production of natural gas liquids.

There are two principle techniques for removing natural gas liquids from the natural gas stream: (i) the absorption method and (ii) the cryogenic expander process.

3.2.1 Absorption process

The *absorption* process for the extraction of natural gas liquids from gas streams is similar in principle to the absorption dehydration process with the exception that in order to absorb natural gas liquids an absorption oil is used instead of ethylene glycol or a derivative (diethylene glycol or triethylene glycol). In the process, the natural gas stream is passed through an absorption tower where it is brought into contact with the absorption oil (*lean absorption oil*) which dissolves a high proportion (if not all) of the natural gas liquids. The absorption oil containing the hydrocarbon constituents (rich absorption oil, fat absorption oil) exits the absorption tower through the base bottom. The absorption oil-hydrocarbon mixture (absorption oil plus ethane, propane, butanes, pentanes, and other higher molecular weight hydrocarbon derivatives is fed into *lean oil stills* where the mixture is heated to a temperature above the boiling point of the highest boiling constituents of the natural gas liquids but below the boiling point of the oil for recovery of the hydrocarbon derivatives as a mixture. This process allows for the recovery of approximately 75% v/v of the lower boiling hydrocarbon derivatives and up to 90% v/v of the hydrocarbon derivatives having a higher molecular weight (and higher boiling point than pentane originally in the natural gas stream.

The basic absorption process as described above can be modified to improve process effectiveness efficiency or to facilitate the extraction of specific hydrocarbon derivatives. For example, the *refrigerated oil absorption* process in which the lean oil is cooled through refrigeration prior to the introduction of the gas stream into the contactor, propane recovery can be upwards of 90% v/v and approximately 40% v/v of the ethane can be extracted from the natural gas stream. Furthermore, the extraction of the other, higher molecular weight hydrocarbon derivatives can near quantitative (approximately 100% v/v) using this refrigeration option.

The absorption method of extraction is very similar to using absorption for dehydration. The main difference is that, in the absorption of natural gas liquids, absorbing oil is used as opposed to glycol. This absorbing oil has an affinity for natural gas liquids in much the same manner as glycol has an affinity for water. Before the oil has picked up any natural gas liquids, it is termed *lean* absorption oil. As the natural gas is passed through an absorption tower, it is brought into contact with the absorption oil which soaks up a high proportion of the natural gas liquids. The rich absorption oil, now containing natural gas liquids, exits the absorption tower through the bottom. It is now a mixture of absorption oil, propane, butanes, pentanes, and other heavier hydrocarbon derivatives. The rich oil is fed into lean oil stills, where the mixture is heated to a temperature above the boiling point of the natural gas liquids, but below that of the oil. This process allows for the recovery of around 75% v/v butane derivatives, and 85%–90% v/v pentane derivaitves as well as higher molecular weight hydrocarbon derivatives from the natural gas stream.

3.2.2 Cryogenic process

The cryogenic process is a process designed to extract natural gas liquids from natural gas streams. Absorption processes can extract almost all of the higher molecular weight constituents of natural gas liquids but the lower molecular weight hydrocarbon derivatives, such as ethane, are more difficult to recover from the natural gas stream. However, if it is economically favorable to extract ethane and other lower molecular weight hydrocarbon derivatives from the gas stream, a cryogenic process typically offers a higher recovery rate.

A cryogenic process involves decreasing the temperature of the gas stream to a temperature on the order of -85 °C (-120 °F). The reduction in enrapture of the gas stream can be achieved by different methods but one of the most effective is known as the turbo expander process in which external refrigerants are used to cool the natural gas stream. Then, an expansion turbine is used to rapidly expand the chilled gases which causes the temperature to drop significantly and causes ethane and other hydrocarbon derivatives to condense out of the gas stream while maintaining methane in gaseous form. This process allows for the recovery of approximately 90%–95% v/v of the ethane originally in the gas stream and, in addition, the expansion turbine is used to convert of a part of the energy released (when the natural gas stream is expanded) for recompression of the gaseous methane effluent, thus saving energy costs associated with extracting ethane.

The process allows for the recovery of approximately 90%–95% v/v of the ethane originally in the gas stream. The extraction of natural gas liquids from the natural gas stream produces both cleaner, purer natural gas, as well as the valuable hydrocarbon derivatives that are the natural gas liquids themselves.

3.3 Fractionation of natural gas liquids

Natural gas liquids have taken on a new prominence as shale gas production has increased and prices have fallen. As natural gas prices have stayed low, company interests have shifted away from dry natural gas production to more liquids-based production. NGL is a general term for all liquid products separated from natural gas at a gas processing plant and includes ethane, propane, butane, and pentane isomers. When natural gas liquids are present with methane, which is the primary component of natural gas, the natural gas is referred to *wet gas* (sometime the unusual term *hot gas* is used in place of *wet gas*). Once the natural gas liquids are removed from the methane, the natural gas is referred to as *dry gas*, which is the gas that is sent to consumers. Also of importance in the commercial world, each of the constituents natural; has liquids (i.e. ethane, propane, butane, and pentane isomers) has its own market and its own value.

Once natural gas liquids have been extracted from the natural gas stream, they must be separated into the individual components of the bulk fraction as the next step. The fractionation process that is used to accomplish the separation is based on the different boiling points of the different individual hydrocarbon derivatives in the natural gas liquids stream and the fractionation occurs in stages which consist of boiling off of the different hydrocarbon derivatives one by one.

Thus, after separation of the natural gas liquids have been removed from the natural gas stream, they must be broken down into their base components to be useful. That is, the mixed stream of different natural gas liquids must be separated. The process used to accomplish this task is called fractionation which is based on the different boiling points of the different hydrocarbon derivatives in the natural gas liquids stream. Essentially, fractionation occurs in stages consisting of the boiling off of hydrocarbon derivatives one by one.

The fractionation process occurs in stages consisting of the boiling off of hydrocarbon derivatives one by one. The name of a particular fractionator gives an idea as to its purpose, as it is conventionally named for the hydrocarbon that is boiled off. The entire fractionation process is broken down into steps, starting with the removal of the lower-boiling natural gas liquids from the gas stream. The fractionators are used in the following order: (i) the deethanizer, which separates the ethane from the natural gas liquids stream, (ii) the depropanizer, which separates propane from the deethanized stream, (iii) the debutanizer, which removes the butane isomers from the deethanized-depropanized stream and leaves the pentane derivaitves and higher molecular weight hydrocarbon derivatives in what reasons of the natural gas liquids stream. After the debutanization step, the butanes stream is sent to a butane splitter (also referred to as a deisobutanizer) which is used to separate the iso-butane from the n-butane.

The separation process produced a series of stream that are suitable as petrochemical feedstocks (or alternatively or in addition, depending upon the yield of iso-butane) the iso-butane can also be sent to an alkylation unit to produce an alkylated product that can be used as blend stock for gasoline manufacture (Speight, 2014a).

3.4 Nitrogen removal

Nitrogen may often occur in sufficient quantities in natural gas and, consequently, lower the heating value of the gas. Thus, several plants for *nitrogen removal* from natural gas have been built, but it must be recognized that nitrogen removal requires liquefaction and fractionation of the entire gas stream, which may affect process economics. In many cases the nitrogen-containing natural gas is blended with a gas having a higher heating value and sold at a reduced price depending upon the thermal value (Btu/ft^3).

3.5 Acid gas removal

In addition to water and natural gas liquids removal, one of the most important parts of gas processing involves the removal of hydrogen sulfide and carbon dioxide. Natural gas from some wells contains significant amounts of hydrogen sulfide and carbon dioxide and is usually referred to as *sour gas*. Sour gas is undesirable because the sulfur compounds it contains can be extremely harmful, even lethal, to breathe and the gas can also be extremely corrosive. The process for removing hydrogen sulfide from sour gas is commonly referred to as *sweetening* the gas.

3.5.1 Hydrogen sulfide and carbon dioxide removal

The primary process for sweetening sour natural gas is quite similar to the processes of glycol dehydration and removal of natural gas liquids by absorption. In this case, however, amine (*olamine*) solutions are used to remove the hydrogen sulfide (the *amine process*). The sour gas is run through a tower, which contains the olamine solution. There are two principle amine solutions used, monoethanolamine (MEA) and diethanolamine (DEA). Either of these compounds, in liquid form, will absorb sulfur compounds from natural gas as it passes through. The effluent gas is virtually free of sulfur compounds, and thus loses its sour gas status. Like the process for the extraction of natural gas liquids and glycol dehydration, the amine solution used can be regenerated for reuse. Although most sour gas sweetening involves the amine absorption process, it is also possible to use solid desiccants like iron sponge (*q.v.*) to remove hydrogen sulfide and carbon dioxide.

Treatment of gas to remove the acid gas constituents (hydrogen sulfide and carbon dioxide) is most often accomplished by contact of the natural gas with an alkaline solution. The most commonly used treating solutions are aqueous solutions of the ethanolamine or alkali carbonates, although a considerable number of other treating agents have been developed in recent years (Mokhatab et al., 2006; Speight, 2014a, 2019a). Most of these newer treating agents rely upon physical absorption and chemical reaction. When only carbon dioxide is to be removed in large quantities or when only partial removal is necessary, a hot carbonate solution or one of the physical solvents is the most economical selection.

The most well-known hydrogen sulfide removal process is based on the reaction of hydrogen sulfide with iron oxide (often also called the iron sponge process or the dry box method) in which the gas is passed through a bed of wood chips impregnated with iron oxide. The iron oxide process is the oldest and still the most widely used batch process for sweetening natural gas and natural gas liquids (Duckworth and Geddes, 1965; Anerousis and Whitman, 1984; and Zapffe, 1963). The process was implemented during the 19th century. In the process the sour gas is passed down through the bed. In the case where continuous regeneration is to be utilized a small concentration of air is added to the sour gas before it is processed. This air serves to continuously regenerate the iron oxide, which has reacted with hydrogen sulfide, which serves to extend the on-stream life of a given tower but probably serves to decrease the total amount of sulfur that a given weight of bed will remove.

The process is usually best applied to gases containing low to medium concentrations (300 ppm) of hydrogen sulfide or mercaptans. This process tends to be highly selective and does not normally remove significant quantities of carbon dioxide. As a result, the hydrogen sulfide stream from the process is usually high purity. The use of iron sponge process for sweetening sour gas is based on adsorption of the acid gases on the surface of the solid sweetening agent followed by chemical reaction of ferric oxide (Fe_2O_3) with hydrogen sulfide:

$$2Fe_2O_3 + 6H_2S \rightarrow 2Fe_2S_3 + 6H_2O$$

The reaction requires the presence of slightly alkaline water and a temperature below 43 °C (110 °F) and bed alkalinity (pH + 8 to 10) should be checked regularly, usually on a daily basis. The pH level should be maintained through the injection of caustic soda with the water. If the gas does not contain sufficient water vapor, water may need to be injected into the inlet gas stream.

The ferric sulfide produced by the reaction of hydrogen sulfide with ferric oxide can be oxidized with air to produce sulfur and regenerate the ferric oxide:

$$2Fe_2S_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6S$$

$$S_2 + 2O_2 \rightarrow 2SO_2$$

The regeneration step is exothermic and, as a result, air must be introduced slowly so the heat of reaction can be dissipated. If air is introduced quickly the heat of reaction may ignite the bed. Some of the elemental sulfur produced in the regeneration step remains in the bed. After several cycles this sulfur will form a cake on the surface of the ferric oxide, decreasing the reactivity of the bed. Typically, after 10 cycles the bed must be removed, and a new bed introduced into the vessel.

The iron oxide process is one of several metal oxide-based processes that scavenge hydrogen sulfide and organic sulfur compounds (mercaptans) from gas streams through reactions with the solid based chemical adsorbent (Kohl and Riesenfeld, 1985; Mokhatab et al., 2006; Speight, 2014a, 2019a). They are typically non-regenerable, although some are partially regenerable, losing activity upon each regeneration cycle. Most of the processes are governed by the reaction of a metal oxide with hydrogen sulfide to form the metal sulfide. For regeneration, the metal oxide is reacted with oxygen to produce elemental sulfur and the regenerated metal oxide. In addition, to iron oxide, the primary metal oxide used for dry sorption processes is zinc oxide.

Slurry Processes were developed as alternatives to the iron oxide (iron sponge process). Slurries of iron oxide have been used to selectively absorb hydrgoen sulfide and these are (i) the Chemsweet process and (ii) the Sulfa-Check process (Mokhatab et al., 2006).

The Chemsweet process is a batch process for the removal of hydrgoen sulfide from natural gas streams. The chemicals involved are a mixture of zinc oxide (ZnO), zinc acetate [Zn(OCOCH$_3$, or ZnAc$_2$], water, and a dispersant to keep the zinc oxide particles in suspension. When one part is mixed with five parts of water the acetate dissolves and provides a controlled source of zinc ions that react instantaneously with the bisulfide ions (HS^-) and sulfide ions (S^{2-}) that are formed when hydrgoen sulfide dissolves in water. The zinc oxide replenishes the zinc acetate from the acetic acid (CH_3COOH or HAc)that is formed during the reaction. The chemical reactions are:

Sweetening:

$$ZnAc_2 + H_2S \rightarrow ZnS + 2HAc$$

Regeneration:

$$ZnO + 2HAc \rightarrow ZnAc_2 + H_2O$$

Overall:

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

The presence of carbon dioxide is of little consequence to the process since the pH of the Chemsweet slurry is low enough to prevent significant absorption of carbon dioxide, even when the ratio of carbon dioxide to hydrgoen sulfide is very high (Manning and Thompson, 1991).

The Sulfa-Check® is a process that can be employed for the selective removal of hydrogen sulfide and mercaptan derivatives (RSH) from natural gas (Mokhatab et al., 2006). This process is accomplished in a one-step single vessel design using an aqueous solution of sodium nitrite ($NaNO_2$) buffered to stabilize the pH above 8. Also, there is enough strong base to raise the pH of the fresh material to 12.5. The process reaction involves conversion of hydrogen sulfide to elemental sulfur:

$$NaNO_2 + 3H_2S \rightarrow NaOH + NH_3 + 3S + H_2O$$

The carbon dioxide in the gas stream reacts with the sodium hydroxide to form the carbonate and bicarbonate that can be represented simply as:

$$CO_2 + NaOH \rightarrow NaHCO_3$$
$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$$

The spent solution is slurry of fine sulfur particles in a solution of sodium and ammonium salts (Manning and Thompson, 1991).

Chemical absorption processes with aqueous alkanolamine solutions (sometimes referred to as olamine processes or amine processes) (Fig. 8.3) are used for treating gas streams containing hydrgoen sulfide and carbon dioxide. However, depending on the composition and operating conditions of the feed gas, different amines can be selected to meet the product

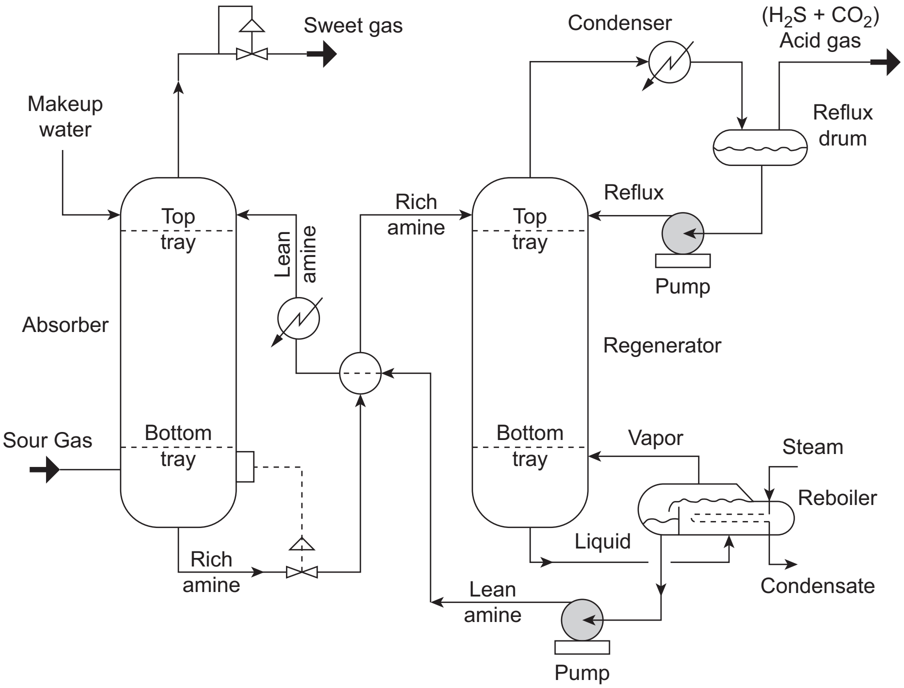

FIG. 8.3 Schematic of the olamine process.

gas specification. Amines are categorized as being primary, secondary and tertiary, depending upon the degree of substitution of the central nitrogen by organic groups. Primary amines react directly with hydrgoen sulfide, carbon dioxide, and carbonyl sulfide (COS). Examples of primary amines includes monoethanolamine (MEA) and the proprietary diglycolamine agent (DGA). Secondary amines react directly with hydrgoen sulfide and carbon dioxide, and react directly with some carbonyl sulfide.

The most common secondary amines is diethanolamine (DEA), while diisopropanolamine (DIPA) is another example of a secondary amine which is not as common anymore in amine treating systems. Tertiary amines react directly with H_2S, react indirectly with CO_2, and react indirectly with little COS. The most common examples of tertiary amines are methyldiethanolamine (MDEA) and activated methyldiethanolamine (sometime referred to as a-MDEA) (Mokhatab et al., 2006; Speight, 2019a). Depending upon the application, special solutions such as mixtures of amines; amines with physical solvents such as sulfolane and piperazine; and amines which have been partially neutralized with an acid such as phosphoric acid may also be used (Bullin, 2003).

Amine absorbers (Fig. 8.3) use counter-current flow through a trayed or packed tower to provide intimate contact between the amine solvent and the sour gas so that the hydrogen sulfide and carbon dioxide can transfer from the gas-phase to the solvent liquid-phase. In tray columns, a liquid level is maintained on each tray by a weir usually 2 or 3 inches high. The gas passes up from underneath the trays through openings in the trays such as perforations, bubble caps, or valves, and disperses into bubbles through the liquid, forming a froth.

The gas disengages from the froth, travels through a vapor space, providing time for entrained amine solution to fall back down to the liquid on the tray, and passes through the next tray above. In packed columns the liquid solvent is dispersed in the gas stream, by forming a film over the packing, providing a large surface area for transfer of hydrogen sulfide and carbon dioxide from the gas to the liquid solvent. The degree of sweetening achieved is largely dependent on the number of trays or the height of packing available in the absorber.

The selection of the amine can have a major impact on the performance of a sweetening unit. It is important to consider all aspects of the amine chemistry and type since the omission of a single issue may lead to operational issues. While many of the operations have focused on the utilization of MDEA over the older generic amines, there are many recent cases where these older generic amines have been the best and, even perhaps, the only choice for recent new plant design (Jenkins and Haws, 2002). MEA and DEA have found the most general application in the sweetening of natural gas streams.

MEA is a stable compound and in the absence of other chemicals suffers no degradation or decomposition at temperatures up to its normal boiling point. MEA reacts with H_2S and CO_2 as follows:

$$2(RNH_2) + H_2S \rightarrow (RNH_3)_2S$$

$$(RNH_3)_2S + H_2S \rightarrow 2(RNH_3)HS$$

$$2(RNH_2) + CO_2 \rightarrow RNHCOONH_3R$$

These reactions are reversible by changing the system temperature. MEA also reacts with carbonyl sulfide (COS) and carbon disulfide (CS_2) to form heat-stable salts that cannot be regenerated.

On the other hand, DEA is a weaker base than MEA and therefore DEA system do not typically suffer the same corrosion problems. DEA reacts with H_2S and CO_2 as follows:

$$2R_2NH + H_2S \rightarrow (R_2NH_2)_2S$$

$$(R_2NH_2)_2S + H_2S \rightarrow 2(R_2NH_2)HS$$

$$2R_2NH + CO_2 \rightarrow R_2NCOONH_2R_2$$

The process flow scheme varies little, regardless of the aqueous amine solution used as the sweetening agent.

The sour gas stream containing hydrogen sulfide and/or carbon dioxide typically enters the plant through an inlet separator (scrubber) to remove any free liquids and/or entrained solids after which the gas stream then enters the bottom of the absorber column in an upward flow through the absorber in intimate counter-current contact with the aqueous amine solution, where the amine absorbs acid gas constituents from the gas stream. Sweetened gas leaving the top of the absorber passes through an outlet separator and then flows to a dehydration unit (and compression unit, if necessary) before being considered ready for sale.

In many units the rich amine solution is sent from the bottom of the absorber to a flash tank to recover hydrocarbon derivatives that may have dissolved or condensed in the amine solution in the absorber. The rich solvent is then preheated before entering the top of the stripper column. The amine-amine heat exchanger serves as heat conservation device and lowers total heat requirements for the process. A part of the absorbed acid gases will be flashed from the heated rich solution on the top tray of the stripper. The remainder of the rich solution flows downward through the stripper in counter-current contact with vapor generated in the reboiler. The reboiler vapor (primarily steam) strips the acid gases from the rich solution. The acid gases and the steam leave the top of the stripper and pass overhead through a condenser, where the major portion of the steam is condensed and cooled for the appropriate re-use.

Lean amine solution from the bottom of the stripper column is pumped through an amine-amine heat exchanger and then through a cooler before being introduced to the top of the absorber column. The amine cooler serves to lower the lean amine temperature to a temperature on the order of 38 °C (100 °F) − a higher temperature will result in excessive losses of the amine through vaporization and also lower acid gas carrying capacity in the solution because of temperature effects.

Molecular sieves are highly selective for the removal of hydrogen sulfide (as well as other sulfur compounds) from gas streams and over continuously high absorption efficiency. They are also an effective means of water removal and thus offer a process for the simultaneous dehydration and desulfurization of gas. Gas that has excessively high-water content may require upstream dehydration, however (Mokhatab et al., 2006; Speight, 2014a, 2019a).

The *molecular sieve process* is similar to the iron oxide process. Regeneration of the bed is achieved by passing heated clean gas over the bed. As the temperature of the bed increases, it releases the adsorbed hydrogen sulfide into the regeneration gas stream. The sour effluent regeneration gas is sent to a flare stack, and up to 2% v/v of the gas seated can be lost in the regeneration process. A portion of the natural gas may also be lost by the adsorption of hydrocarbon components by the sieve (Mokhatab et al., 2006; Speight, 2014a, 2019a).

In this process, unsaturated hydrocarbon components, such as olefins and aromatics, tend to be strongly adsorbed by the molecular sieve. Molecular sieves are susceptible to poisoning by such chemicals as glycols and require thorough gas processing methods before the adsorption step. Alternatively, the sieve can be offered some degree of protection by the use of *guard beds* in which a less expensive catalyst is placed in the gas stream before contact of the gas with the sieve, thereby protecting the catalyst from poisoning. This concept is analogous to the use of guard beds or attrition catalysts in the crude oil industry (Speight, 2000).

In summary, Decisions in selecting a gas treating process can many times be simplified by gas composition and operating conditions. High partial pressures (50 psia) of acid gases enhance the probability of using a physical solvent. The presence of significant quantities of high-boiling hydrocarbon derivatives in the feed discourages using physical solvents. Low partial pressures of acid gases and low outlet specifications generally require the use of amines for adequate treating. Process selection is not easy and a number of variables must be weighed prior to making a process selection. After preliminary assessment, usually requires a study of relevant alternatives.

3.5.2 *Sulfur recovery*

The side stream from acid gas treating units consists mainly of hydrgoen sulfide and/or carbon dioxide. Carbon dioxide is usually vented to the atmosphere but sometimes is recovered for enhanced oil recovery using the carbon dioxide-flood technology. Hydrogen sulfide could be routed to an incinerator or flare, which would convert the hydrgoen sulfide to sulfur dioxide. The release of hydrogen sulfide that can be vented to the atmosphere or flared in the regeneration cycle is severely restricted by environmental regulations.

The disposition of hydrogen sulfide, a toxic gas that originates in crude oils and is also produced in the coking, catalytic cracking, hydrotreating, and hydrocracking, processes, is an issue with many refiners. Burning hydrogen sulfide as a fuel gas component or as a flare gas component is precluded by safety and environmental considerations since one of the combustion products is the highly toxic sulfur dioxide (SO_2), which is also toxic. As described above, hydrogen sulfide is typically removed from the refinery gas streams through an olamine process after which application of heat regenerates the olamine and forms an acid gas stream.

Most of sulfur recovery processes use chemical reactions to oxidize hydrogen sulfide and produce elemental sulfur. These processes are generally based either on the reaction of hydrgoen sulfide and oxygen and or hydrgoen sulfide and sulfur dioxide. Both reactions yield water and elemental sulfur. These processes are licensed and involve specialized catalysts and/or solvents. These processes can be used directly on the produced gas stream. Where large flow rates are encountered, it is more common to contact the produced gas stream with a chemical or physical solvent and use a direct conversion process on the acid gas liberated in the regeneration step.

There are two common methods of sulfur recovery, liquid redox and Claus sulfur recovery processes.

3.5.2.1 Liquid redox process

Liquid redox processes for sulfur recovery are liquid-phase oxidation processes which use a dilute aqueous solution of iron or vanadium to selectively remove hydrogen sulfide by chemical absorption from sour gas streams. These processes can be used on relatively small or dilute hydrogen sulfide stream to recover sulfur from the acid gas stream or, in some cases, they can be used in place of an acid gas removal process. The mildly alkaline lean liquid scrubs the hydrogen sulfide from the inlet gas stream, and the catalyst oxidizes the hydrgoen sulfide to elemental sulfur after which the reduced catalyst is regenerated by contact with air in the oxidizer(s). Sulfur is removed from the solution by flotation or settling, depending on the process.

3.5.2.2 Claus process

The Claus sulfur recovery process is the most widely used technology for recovering elemental sulfur from sour gas. The Claus process is used to recover sulfur from the amine regenerator vent gas stream in plants where large quantities of sulfur are present. However, this process is used to treat gas streams with maximum hydrogen sulfide content on the order of 15% v/v. The chemistry of the units involves partial oxidation of hydrogen sulfide to sulfur dioxide and the catalytically promoted reaction of hydrogen sulfide and sulfur dioxide to produce elemental sulfur. The Claus process involves combustion of approximately one-third of the hydrogen sulfide to sulfur dioxide and then reaction of the sulfur dioxide with the remaining hydrogen sulfide in the presence of a fixed bed of activated alumina, cobalt molybdenum catalyst resulting in the formation of elemental sulfur:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

The first stage of the process converts hydrogen sulfide to sulfur dioxide and to sulfur by burning the acid-gas stream with air in the reaction furnace. This stage provides sulfur dioxide for the next catalytic phase of the reaction. Multiple catalytic stages are provided to achieve a more complete conversion of the hydrogen sulfide and each catalytic stage consists of a gas reheater, a reactor, and a condenser. Condensers are provided after each stage to condense the sulfur vapor and separate it from the main stream. Different process flow configurations are in use to achieve the correct hydrogen sulfide/sulfur dioxide ratio in the conversion reactors.

The sulfur recovery depends upon such things as feed composition, age of the catalyst and number of reactor stages. Typical sulfur recovery efficiencies for Claus plants are 90%–96% for a two-stage plant and 95%–98% for a three-stage plant. Because of equilibrium limitations and other sulfur losses, overall sulfur recovery efficiency in a Claus unit usually does not exceed 98%.

In the past, the off-gas leaving a Claus plant (referred to as tail gas) was burned to convert the unreacted hydrogen sulfided to sulfur dioxide, before discharge to the atmosphere, which has a much higher toxic limit. However, the increasing standards of efficiency required by the pressure from environmental protection has led to the development of a large number of Claus tail gas clean-up (TGCU) units, based on different concepts, in order to remove the last remaining sulfur species. The proper selection tail gas clean-up unit is of considerable importance to operators whereas the choice is made complicated by the different performance levels and life cycle costs. A selection of the most popular tail gas clean-up process is based on the sulfur recovery efficiency and most importantly in terms of the recovery (Gall and Gadelle, 2003).

3.6 Enrichment

The purpose of *enrichment* is to produce natural gas for sale and enriched tank oil. The tank oil contains more low-boiling hydrocarbon liquids than natural crude oil, and the residue gas is drier (leaner, i.e., has lesser amounts of the higher molecular weight hydrocarbon derivatives). Therefore, the process concept is essentially the separation of hydrocarbon liquids from the methane to produce a lean, dry gas.

Crude oil enrichment is used when there is no separate market for low-boiling hydrocarbon liquids or when the increase in API gravity of the crude provides a substantial increase in the price per unit volume as well as volume of the stock tank oil. A very convenient method of enrichment involves manipulation of the number and operating pressures of the gas-oil separators (traps). However, it must be recognized that alteration or manipulation of the separator pressure affects the gas compression operation as well as influences other processing steps.

One method of removing light ends involves the use of a pressure reduction (vacuum) system. Generally, stripping of light ends is achieved at low pressure, after which the pressure of the stripped crude oil is elevated so that the oil acts as an absorbent. The crude oil, which becomes enriched by this procedure, is then reduced to atmospheric pressure in stages or using fractionation (rectification).

There is a wide variety of fuels currently in widespread use of which the simplest in composition is natural gas that consists primarily of methane but includes several other constituents from ethane to butane (collectively known as natural gas liquids) as well as higher boiling hydrocarbon derivatives from pentane to octane (C_8H_{18}) or, in some cases, to dodecane ($C_{12}H_{26}$) decane (collectively known as gas condensate and generally referred to as the C_{5+} fraction). In addition, process gas, biogas, and landfill gas are also gases of interest in this present content.

Information on the composition of natural gas (including the condensate fraction) is generally much more available than the information for liquid fuels. Rarely is the molecular composition of liquid fuels known with any degree of certainty (for example, there are many suppositions that go into describing the molecular composition of, say, fuel oil) because of the complexity of the liquid fuels contain a large (sometime undefinable) number of hydrocarbon species. The most commonly reported composition data are derived from the *ultimate analysis*, which consists of measurements of the elemental composition of the fuel, generally presented as mass fractions (% w/w) of carbon, hydrogen, sulfur, oxygen, nitrogen, and ash, where appropriate as well as the potential for low-boiling (even gaseous) hydrocarbon derivatives (ASTM D2427) (Nadkarni, 2005) which, with suitable choice of the column and instrumental parameters can also include determination of olefin constituents (ASTM D2163).

For example, a test method (ASTM D2427) is available for the determination of C_2 through C_5 hydrocarbon derivatives in gasoline (and by inference low-boiling naphtha, gas condensate, and natural gasoline) by gas chromatography. However, this test method does not cover the determination of cyclic olefin derivatives, diolefin derivaitves, or acetylene derivatives, which are typically minor components in finished gasolines although the presence of acetylene derivaitves in low-boiling naphtha fractions (as well as in gas condensate and natural gasoline) is not considered likely. The concentration of the various constituents as determined by this test method are typically reported as:

Ethylene plus ethane
Propane
Propylene
Iso-butane
n-Butane
Butene-1 plus isobutylene
trans-Butene-2
cis-Butene-2
Iso-pentane
3-Methyl butene-1
n-Pentane
Pentene-1
2-Methyl butene-1
trans-Pentene-2
cis-Pentene-2
2-Methyl butene-2

However, as extensive as the method is for the analysis of the relevant sample, it is not suitable for the analysis of samples that contain significant amounts of material boiling lower than ethylene.

In addition to this aforementioned test method (ASTM D2427), various elemental analytical techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), X-ray fluorescence (XRF), or graphite furnace atomic absorption spectrometry (GFAAS) are used for this purpose.

Another test method can be used for elemental analysis of crude oil products, especially the presence of trace elements in the sample. The method covers the rapid determination of seven elements in distillate crude oil products and describes the procedure for the determination of trace elements in low-boiling and middle distillate crude oil products using inductively coupled plasma mass spectrometry (ICP-MS). Test times approximate a few minutes per test specimen, and quantification for most elements is in the low to sub ng/g (ppb mass) range. High analysis sensitivity can be achieved for some elements that are difficult to determine by other techniques.

The heating value (also called the *heat content* or *calorific value*) is a measure of the heat release during complete combustion and is also reported *with* the ultimate analysis. In addition, the properties that influence the handling and use of a particular fuel are frequently measured − for liquid fuels, the specific gravity or API gravity, viscosity (possibly at several temperatures), flash point (a measure of the temperature at which the fuel is sufficiently volatile to ignite readily), and distillation profiles (fraction vaporized as a function of temperature) may be reported. From these data predictability of behavior in use can be estimated.

On the other hand, natural gas, which is predominantly methane, offers more informative data from which behavior can be predicted with a higher degree of certainty that in the case of the liquid fuels. It is often for this reason, and the often-erroneous assumption that natural gas will behave in the same manner as methane but errors (because of erroneous suppositions) have been encountered during the use of the gas and when the gas is released to the environment. For example, the density of any gas compared to the density of air is the *vapor density* and is a very important characteristic of the constituents of natural gas and natural gas constituents (Chapter 8). The C_{3+} constituents (propane and higher molecular weight gaseous constituents) of raw natural gas have a vapor density that shows that these constituents are heavier than air. Thus, when raw natural gas is inadvertently released into the atmosphere these higher molecular weight constituents will collect in low spots (depressions) in the surface of the Earth and are liable to explosive ignition.

Thus, a statement is often made that *natural gas is lighter than air* (because of the continued insistence by some engineers and scientists that the properties of a mixture are determined by the mathematical average of the properties of the individual constituents of the mixture) is incorrect. Such mathematical bravado and inconsistency of thought is *detrimental to safety* and needs to be qualified by consideration of the available analytical data. It such data are not available, they should be!

In fact, at each stage of natural gas production, wellhead treating, transportation, and processing analysis of the gas by standard test methods is an essential part of the chemistry and technology of natural gas. Use of analytical methods offers vital information related to the behavior of natural gas during recovery, wellhead processing, transportation, gas processing, and use. However, the various purposes to be served by the analytical data are listed, and the necessary accuracy with which each constituent of each type of gas must be known in order to serve each specific purpose is then estimated. These estimates afford the criteria by means of which the suitability of analytical methods and apparatus may be judged, but they are subject to revision when more is known related to the limiting attainable accuracies of the analytical methods.

In general, In general view, the batch and amine processes are used for over 90% of all onshore wellhead applications. Amine processes are preferred when the lower operating cost, the chemical cost for this process is prohibitive, and Justifies the higher equipment cost. The key is the sulfur content of the feed gas where below 20-pound sulfur per day, batch processes are more economical, and over 100-pound sulfur per day amine solutions are preferred (Manning and Thompson, 1991).

Thus, because of the world-wide use of natural gas and the varying composition of gas from different wells, there is a need to apply a series of standard test to the gas in order that it can meet sales specifications (Chapter 9). Natural gas testing includes the analysis of conventional and shale gas, liquefied natural gas, and other hydrocarbon condensates and components. Furthermore, regulation of the environmental practices related to natural gas development can more easily address the regional and state-specific character of the activities, compared to a one-size-fits-all management by level of government or industry. Some of these factors include (i) geology, (ii) hydrology, (iii) climate and climate variations, (iv) topography, (v) industry characteristics, (vi) development history, (vii) state legal structures, (viii) population density, and (ix) local economics. Thus, the regulation of natural gas production is a detailed monitoring of each stage of the development (production, wellhead processing, transportation, gas processing facilities, and sales) through the many controls at the state level.

Because of the world-wide use of natural gas and the varying composition of gas from different wells (even wells within the same reservoir), there is a need to apply a series of standard test to the gas in order that it can meet sales specifications. Natural gas testing includes the analysis of conventional and shale gas, liquefied natural gas, and other hydrocarbon condensates and components as well as biogas and landfill gas. Each aspect of gas technology requires detailed analysis (and thence knowledge) of the properties of the gas and to understand the applicability of the analytical methods, it is helpful for the reader to understand (i) the origin of natural gas, (ii) the production of natural gas, (iii) the transportation of natural gas, (iv) the refining of natural gas, including gas cleaning, and (v) the influence of natural gas on the environment. Consequently, an introduction to the essentials of natural gas formation, production, wellhead processing, transportation, gas processing, and use is presented below.

When biogas is sent to processing for impurity removal, the cleaned gas has characteristics of the biogas are close to the characteristics of as natural gas. In this instance the producer of the biogas can utilize the local gas distribution networks. The gas must be very clean to reach pipeline quality. Water (H_2O), hydrogen sulfide (H_2S) and particulates are removed if present at high levels or if the gas is to be completely cleaned. Carbon dioxide is less frequently removed, but it must also be separated to achieve pipeline quality gas. If the gas is to be used without extensively cleaning, it is sometimes cofired with natural gas to improve combustion. Biogas cleaned up to pipeline quality is called renewable natural gas. In this form the gas can be used in any application in which natural gas is used. The heating value of the raw biogas is on the order of 600 Btu/ft^3 (5340 calories/m^3). The raw gas will burn in an engine, but corrosion can occur unless proper materials of construction are selected.

The previous chapters will serve to introduce the reader to the various aspects of natural gas recovery and processing that are involved in making the gas ready for use by the consumer. The awareness of the various processes involved will assist analysts to design test programs that will produce the needed data for the client. There have also been citations to

ASTM standard test methods that produce data by use of highly selective sensitive analytical equipment, such as the so-called piggy-back technique of gas chromatography/mass spectrometry (GC/MS) combined. As a quality control step, it is may be necessary (on the case of processes gas, biogas, and landfill gas) to derivatize (chemically modify) non-volatile and heat degradable target chemicals prior to analysis by the two most commonly used instrumental methods in gas analysis, gas chromatography (GC) or gas chromatography-mass spectrometry (GC/MS).

In the description of the composition of natural gas, the C_{5+} (condensate) fraction is a relatively narrow boiling range fraction and characterization methods are available that can be used to determine the various properties of this fraction. However, contrary to the C_{5+} fraction of natural gas, the standard test methods applied to this condensate are not the typical standard test methods applied to crude oil liquids but should be selected with discretion from the test methods to be applied to low-boiling naphtha which, even when selectively chosen, may require some modification for application to the condensate.

Gases at atmospheric pressure condition have much larger free space between molecules than do liquids. As a result, the interaction between various like and unlike molecules in a gaseous state is less than the molecular interactions in similar liquid mixtures. Therefore, the role of natural gas composition on properties of gas mixtures is not as evident as in the case of liquids. However, the effect of composition on properties of gas mixtures increases as pressure increases and free space between molecules decreases. The role of composition on properties of dense gases cannot be ignored. Under low-pressure conditions where most gases behave like ideal gases all gas mixtures regardless of their composition have the same molar density at the same temperature and pressure.

Generally, volume and mole fractions are used interchangeably for all types of gas mixtures. Composition of gas mixtures is rarely expressed in terms of weight fraction and this type of composition has very limited application for gas systems. Whenever composition in a gas mixture is expressed only in percentage it should be considered as mole % or volume % (i.e., % v/v).

In all aspects of natural gas analysis (as well as the analysis of other gaseous products and fuels) technology, including the calculation of physical properties, accurate characterization of the gas mixture requires (i) assurance that the correct sampling methods have been used (Chapter 5) (ASTM F307 Standard Practice for Sampling Pressurized Gas for Gas Analysis), (ii) the appropriate type of equipment (ASTM E355 Standard Practice for Gas Chromatography Terms and Relationships) leading to a complete compositional analysis of the mixture with known mole fraction and carbon number of the gas (ASTM D7833 Standard Test Method for Determination of Hydrocarbon derivatives and Non-Hydrocarbon Gases in Gaseous Mixtures by Gas Chromatography) as well as method for calculation of the physical properties (for example: ASTM D3588 Standard Practice for Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels) to assist in the design of the most appropriate gas processing sequence (Zhu et al., 2014; El-Rahman et al., 2017).

The analysis of natural gas to determine not only the presence but also the relative amount of the different constituents is a widely used in natural gas technology. When natural gas is extracted from the sources, the gas is treated in gas treating plants before use as an energy source in industries or households. The hydrogen sulfide, carbon dioxide and other constituents of the gas are removed leave methane as the so-called *residue gas*. The importance of the removal of constituents other than methane can be found in a number of reasons such as (i) the production of added-value products, (ii) the toxicity of hydrogen sulfide, (iii) the penchant for hydrogen sulfide and carbon dioxide to enhance metals corrosion in the presence of water, as well as (iv) the potential for environmental pollution when the gas is use.

https://www.asap.nl/wp-content/uploads/2013/08/sulfer-melt.png. The methods for the measurement of the non-methane constituents are numerous but the choice of the analytical method is dependent on the range and composition of the natural gas as well as on the analytical technology available at the time of choice. Part II present information that will be useful in method selection. Thus, by applying the appropriate standard test methods to the gas (as presented in Part II), it is possible to determine the distribution of the constituents from methane to the constituents of the condensate from which the behavior of the reservoir, including the gas composition from different wells within a reservoir, can be assessed.

4. Tight gas processing

Natural gas, as it is used by consumers, is much different from the natural gas that is brought from the underground tight formation to the wellhead since the natural gas brought to the wellhead, although still composed primarily of methane, is by no means as pure as need to for sale to the consumer. The natural gas commonly exists in mixtures with other hydrocarbon derivatives; principally ethane, propane, butane, and pentanes. In addition, raw natural gas contains water vapor, hydrogen sulfide (H_2S), carbon dioxide, helium, nitrogen, and other compounds.

4.1 Wellhead processing

Processing natural gas typically begins at the wellhead – after leaving the gas well, the first step in processing is removing oil, water and condensates. Heaters and scrubbers are used to prevent the temperature of the gas from dropping too low and remove large-particle impurities, respectively (Manning and Thompson, 1991). Wellhead processing is, in all respects, less complicated than the processing that take place at the natural gas plant where processing, cleaning, refining) is taken to the ultimate step of producing essentially pure methane – the natural gas used by consumers is composed almost entirely of methane.

In many instances pressure relief at the wellhead will cause a natural separation of gas from oil (using a conventional closed tank, where gravity separates the gas hydrocarbon derivatives from the higher boiling crude oil). In some cases, however, a multi-stage gas-oil separation process is needed to separate the gas stream from the crude oil. These *gas-oil separators* are commonly closed cylindrical shells, horizontally mounted with inlets at one end, an outlet at the top for removal of gas, and an outlet at the bottom for removal of oil. Separation is accomplished by alternately heating and cooling (by compression) the flow stream through multiple steps; some water and condensate, if present, will also be extracted as the process proceeds.

If the gas stream requires cooling, there are three types of gas coolers (i) natural convection coolers, (ii) forced convection coolers, and (iii) water coolers. The major factors to be taken into consideration are the sensible heat in the gas, the water vapor content of the gas and its heat of condensation and the effects of fouling of the cooler. Natural convection coolers consist of a simple length of pipe and are simple to use and clean and require no additional energy input. A forced convection cooler is equipped with a fan which forces the cooling air to flow around the gas pipes and is typically much smaller than the natural convection coolers. The disadvantage of the forced convention cooler is the extra energy input required for the fan and the necessity to use gas cooling pipes of small diameters, which can lead to fouling problems. The former can in some cases be offset by using the cooling air supplied by the engine fan.

Water coolers are available in two types, the scrubber and the heat exchanger; where a water scrubber or bubbler is used, the objective is generally to cool and clean the gas in one and the same operation. Scrubbers of many different types exist, but the principle is always the same: the gas is brought in direct contact with a fluid medium (generally water) which is sprayed into the gas stream by means of a suitable nozzle device. The advantage of this system is its small size but the disadvantage is the need for fresh water, increased complexity of maintenance, and additional power consumption resulting from the use of a water pump. It is also possible to cool the gas by means of a water cooled heat exchanger. This is a suitable method in case a source of fresh water is continuously available and the extra investment and power consumption of a suitable water pump can be justified.

At the wellhead, the gas stream is prepared for transportation by using processes for (i) water removal, and (ii) condensate and crude oil removal.

4.1.1 Water removal

Water is a common impurity in gas streams, and removal of water is necessary to prevent condensation of the water and the formation of ice or gas hydrates ($C_nH_{2n+2}.\ xH_2O$). Water in the liquid phase causes corrosion or erosion problems in pipelines and equipment, particularly when carbon dioxide and hydrogen sulfide are present in the gas (Speight, 2014b). The simplest method of water removal (dehydration) is to cool the gas (refrigeration or cryogenic separation) to a temperature at least equal to or (preferentially) below the dew point.

In addition to separating crude oil and some condensate from the wet gas stream, it is necessary to remove most of the associated water. Most of the liquid, free water associated with extracted natural gas is removed by simple separation methods at or near the wellhead. However, the removal of the water vapor that exists in solution in natural gas requires a more complex treatment. This treatment consists of dehydrating the natural gas, which usually involves one of two processes: either absorption, or adsorption. Absorption occurs when the water vapor is taken out by a dehydrating agent whereas adsorption occurs when the water vapor is condensed from the gas stream and collected on the surface.

In a majority of cases, cooling alone is insufficient and, for the most part, impractical for use in field operations. Other more convenient water removal options use (i) *hygroscopic* liquids (e.g., diethylene glycol or triethylene glycol) and (ii) solid adsorbents or desiccants (e.g., alumina, silica gel, and molecular sieves). Ethylene glycol can be directly injected into the gas stream in refrigeration plants.

Water removal from the gas stream at the wellhead is required because of the tendency for the formation of gas hydrates. Process options are available (Mokhatab et al., 2006, Kidnay et al., 2011; Speight, 2014a, 2019a) and choice is dictated by the amount of the water and process efficiency. An example of water removal process is a mechanical refrigeration plants that chill the gas will promote the formation of gas. Cryogenic liquid recovery plants will freeze up (form hydrates) if the gas water content is above 100 parts per million by volume (ppm v/v). The most prevalent solutions to dry the gas are (i) contacting the gas with 99% triethylene glycol to dry the gas, (ii) injecting 80% v/v ethylene glycol into the mechanical refrigeration unit to prevent hydrate formation and (iii) processing the gas in a molecular sieve unit upstream of the cryogenic plant to dry the gas to below 100 ppm v/v.

In addition, heaters and scrubbers are installed, usually at or near the wellhead and serve to remove sand and other particulate matter impurities. The heaters ensure that the temperature of the gas does not drop too low − when natural gas that contains even low quantities of water, natural gas hydrates have a tendency to form at low temperatures (Chapter 1). The gas hydrates are solid or semi-solid compounds with the hydrocarbon derivatives at the center of an ice-like cage and an accumulation of the hydrates can impede the flow of the natural gas through the various pipeline valves and through the gathering systems. To reduce the occurrence of hydrates, small natural gas-fired heating units are may be installed along the gathering pipe wherever it is possible that gas hydrates may form.

While the ethane, propane, butane derivatives, pentane derivatives, and natural gasoline (a mixture of higher molecular weight hydrocarbon derivatives up to approximately C_{10} and sometimes referred to as *gas condensate*) must be removed from natural gas. The natural gas liquids are sold separately and have a variety of different uses; including enhancing oil recovery in oil wells, providing raw materials for oil refineries or petrochemical plants, and as sources of energy.

Thus, while some of the needed processing operations can be accomplished at or near the wellhead (field processing), the complete processing of natural gas takes place at a processing plant and the wellhead-treated natural gas is transported to these processing plants through a network of gathering pipelines, which are small-diameter, low pressure pipes. However, in addition to processing done at the wellhead and at centralized processing plants, some final processing is also sometimes accomplished at *straddle extraction plants*, which are located on major pipeline systems. Although the natural gas that arrives at these straddle extraction plants is already of pipeline quality, in certain instances there may still exist in the gas stream small quantities of natural gas liquids that are extracted at the straddle plants.

Once at the gas processing plant, the natural gas stream is further processed to levels of purity that make the gas suitable for sales to the consumer. To remove the various remaining impurities, the processing sequence typically four main processes: (i) oil and condensate removal, (ii) water removal, (iii) separation of natural gas liquids, and (iv) sulfur and carbon dioxide removal.

The natural-gas-processing facility is a dedicated separations train that begins with the removal of acid gases (carbon dioxide, hydrogen sulfide. and organosulfur compounds) (Fig. 8.4) (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a) there is still the challenge in treating the gas when the H_2S/CO_2 ratio is low along with the desire to meet pipeline specifications in regard to the carbon dioxide content (Weiland and Hatcher, 2012). Elemental sulfur is often recovered from treatment of the off gas stream from this process. The most appropriate technology for removing acid gas depends on the amount in the

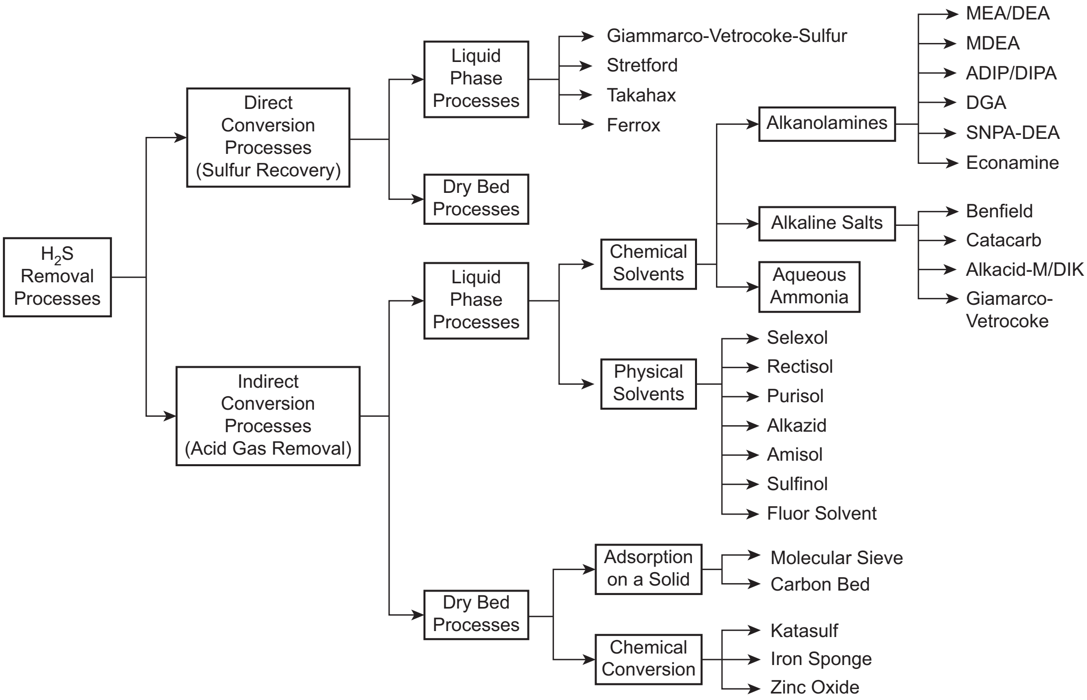

FIG. 8.4 General schematic flow for gas processing.

feed and the desired contaminant level in the product. The most common processes for removing carbon dioxide are amine treating, membranes and molecular sieves.

At some stage of the processing, the gas flow is directed to a unit that contains a series of filter tubes. As the velocity of the stream reduces in the unit, primary separation of remaining contaminants occurs due to gravity. Separation of smaller particles occurs as gas flows through the tubes, where they combine into larger particles which flow to the lower section of the unit. Further, as the gas stream continues through the series of tubes, a centrifugal force is generated which further removes any remaining water and small solid particulate matter.

The amount of particulate matter that is present in the gas depends on the properties of the shale reservoir. Over the past several decades since World War II, a range of dry filters containing wood wool, sisal fiber, glass wool, wood chips soaked in oil, and other types of fibrous or granular material were used for removal of the particulate matter (average particle size below 60 μm), but success was very limited. Wet purifiers such as water and oil scrubbers and bubblers are also effective but only within certain limits.

The most effective process for the removal of particulate matter employs cloth filters but normal cloth filters are very sensitive to the gas temperature and at high temperatures theses filters are likely to char and decompose in the hot gas stream. Another disadvantage is that the filters are subject to a rapid build-up of particulate matter and need frequent cleaning if not used in conjunction with a pre-filtering step.

The disadvantages of using cloth filters can be partly offset by using woven glass wool filter bags as proposed by Nordstrom (33). This material can be used at temperatures up to 300 °C (570 °F). By heating (insulated) filter housing by means of the hot gas stream coming from the gasifier, temperatures above 100 °C (212 °F) can be maintained in the filter, thus avoiding condensation and enhanced pressure drop. If a pre-filtering step consisting of a cyclone and/or an impingement filter is employed. It is possible to keep the service and maintenance intervals within reasonable limits. Electrostatic filters are also known to have very good particle separating properties, and most probably they could also be used to produce a gas of acceptable quality.

Typically, depending upon the process used for water removal, the density differential between the particulate matter and the gas/condensate/oil would also facilitate removal of the particulate matter with the water. Alternatively, a simple filter system may be installed at the wellhead. Such systems use *fabric filters* which are typically designed with non-disposable filter bags. As the gas stream flows through the filter media (typically cotton, polypropylene, Teflon, or fiberglass), particulate matter is collected on the bag surface as a dust cake. Fabric filters are generally classified on the basis of the filter bag cleaning mechanism employed. Fabric filters operate with collection efficiencies up to 99.9%, depending upon the size of the particulate matter particles and the size of the filter orifices.

4.1.2 Condensate removal

In order to process and transport associated natural gas, it must be separated from the any condensate or crude oil in which it is dissolved and which is typically carried using equipment installed at or near the wellhead. In the next step, after water removal, the condensate or crude oil is separated from the gas with a conventional separator which consists of a closed tank that separates the liquids and solids by the force of gravity. When gravity alone does not separate the two, separators use pressure to cool the gas, then moves through a high pressure liquid at a low temperature to knockout any remaining oil and a portion of the water. Typically, the density differential would also facilitate removal of the particulate matter into the condensate/crude oil lay if they have not already been removed during the water-removal process.

However, the actual process used to separate oil from natural gas, as well as the equipment that is used, can vary widely, especially since shale gas not only has a varied composition from reservoir to reservoir but also can vary in computation on a well-by-well basis from the same reservoir. If the natural gas co-exists with crude oil in the same tight reservoir there will be the need to remove the crude oil. Typically, the natural gas can be separated from condensate or crude oil at the wellhead by the use of a separator (Mokhatab et al., 2006, Kidnay et al., 2011; Speight, 2014a, 2019a).

In addition to removing contaminants, shale gas often is produced with natural gas liquids that bring higher value if they are recovered for petrochemical or other uses that exceed their Btu value when left in the natural gas stream. Depending on the inlet gas conditions (such as gas richness, pressure, temperature, and product specifications), the optimum liquid recovery process will be selected. For a production situation that anticipates fairly rich gas and propane-plus recovery, and normally smaller volumes, a suitable choice of process is mechanical refrigeration with injection of ethylene glycol. This process yields high recovery of propane recovery when the gas has five gallons of liquid hydrocarbon derivatives per

1000 ft^3 or better. In situations with lean or rich gas and very small proportions of ethane, a Joule-Thomson process with molecular sieve dehydration is a sensible solution. Finally, situations expecting lean or rich gas, high propane or ethane recovery, and medium to large gas volumes should choose a cryogenic process.

In many cases, the separation of liquid crude oil/condensate from the natural gas is relatively straightforward and the two hydrocarbon streams are then sent (separately) for further processing. The most basic type of separator is a closed tank, where the force of gravity serves to separate the heavier liquids like oil, and the lower-boiling gases, such as natural gas. In more difficult situations, a pressure separator or temperature separator may be employed to separate the liquid and gas streams. These separators are typically used for wells producing high pressure or high temperature natural gas along with light crude oil or gas condensate.

The pressure separators use pressure differentials to cool the wet natural gas and separate the oil and condensate. In the process, wet gas enters the separator, after some cooling has occurred in a heat exchanger. The gas then travels through a high pressure liquid *knockout* vessel which serves to remove any liquids into a low-temperature separator. The gas then flows into this low-temperature separator through a choke mechanism, which expands the gas as it enters the separator and the rapid expansion of the gas allows for the lowering of the temperature in the separator. After removal of the liquids, the dry gas then travels back through the heat exchanger and is warmed by the incoming wet gas. By varying the pressure of the gas in various sections of the separator, it is possible to vary the temperature, which causes the oil and some water to be condensed out of the wet gas stream. This basic pressure-temperature relationship can work in reverse as well, to extract gas from a liquid oil stream, such as a crude oil stream containing dissolved gas from a tight formation reservoir.

The use of tight gas as a fuel and as a source of petrochemical feedstocks will, like the use of crude oil, continue at least for the next three-to-five decades (Speight, 2011). Moreover, it is also predictable that use of natural gas in the transportation sector will increase as increases in travel offset increased efficiency. Consequently, the generation of contaminant-free products there is the need to prepare natural gas for use by a range of domestic and industrial consumers.

4.2 Other aspects

Whatever the tight reservoir from which the natural gas came, once separated from condensate and crude oil (if present), natural gas commonly exists in mixtures with other hydrocarbon derivatives; principally ethane, propane, butane, and pentanes. In addition, raw natural gas contains water vapor, hydrogen sulfide (H_2S), carbon dioxide and may even contain helium, nitrogen, and other compounds. In addition, acid gases corrode refining equipment, harm catalysts, pollute the atmosphere, and prevent the use of hydrocarbon components in petrochemical manufacture. When the amount of hydrogen sulfide is high, it may be removed from a gas stream and converted to sulfur or sulfuric acid.

Because of the variable number of constituents and the variable composition of the gas, there are many variables in treating refinery gas or natural gas. The precise area of application, of a given process is difficult to, define. Several factors (not necessarily in order of importance) must be considered: (i) the types of contaminants in the gas, (ii) the concentrations of contaminants in the gas, (iii) the degree of contaminant removal desired, (iv) the selectivity of acid gas removal required, (v) the temperature of the gas to be processed, (vi) the pressure of the gas to be processed, (vii) the volume of the gas to be processed, (viii) the composition of the gas to be processed, (ix) the carbon dioxide-hydrogen sulfide ratio in the gas, and (x) the desirability of sulfur recovery due to process economics or environmental issues.

In addition to hydrogen sulfide (H_2S) and carbon dioxide (CO_2), natural gas from tight reservoirs may contain other contaminants, such as mercaptans (RSH) and carbonyl sulfide (COS). The presence of these impurities may eliminate some of the sweetening processes since some processes remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes that are not designed to remove (or are incapable of removing) large amounts of acid gases. However, these processes also capable of decreasing the acid gas impurities to very low levels when the acid gases are present in low to medium concentrations in the gas.

Thus, natural gas processing consists of separating all of the various hydrocarbon derivatives and fluids from the pure natural gas, to produce what is known as *pipeline quality* (sometimes referred to as *sales quality*) dry natural gas. Major transportation pipelines usually impose restrictions on the make-up of the natural gas that is allowed into the pipeline. Thus, after the natural gas is released from the tight reservoir produced (brought to the surface), water and condensate (higher-hydrocarbon liquids) are typically removed from the raw natural gas at or near the wellhead. Gathering lines then carry the remaining natural gas to a gas-processing facility that removes other constituents so that the processed gas meets pipeline specifications and so maximum value can be obtained for constituents such as natural gas liquids (NGLs) (Weiland and Hatcher, 2012).

Gas processing is a necessary segment the natural gas value chain insofar as the series of unit processes ensure that the natural gas intended for use is as clean and pure as possible and meets the specifications, of being a clean-burning and environmentally sound energy choice. Once the natural gas has been fully processed, and is ready to be consumed, it must be transported from those areas that produce natural gas, to those areas that require it.

Just as gas processing is necessary segment of the gas value chain, chemical analysis is used to determine the qualitative or quantitative content of a given sample with the help of chemical and physical methods. In fact, the analysis of the chemical and physical properties of natural gas is an essential part of the chemistry and technology of the use natural gas. The data from the of analytical methods (Part II) offers vital information related to the behavior of natural gas during recovery, wellhead processing, transportation, gas processing, and use.

Typically, natural gas is a mixture of low-boiling hydrocarbon gases rich in methane – the methane content of natural gases is usually above 75 % with C_{5+} fraction (i.e. the fraction commonly known as *gas condensate*) less than 1% v/v. If the mole fraction of hydrogen in a natural gas is less than 4 ppm v/v it is called "sweet" gas. Dry gases contain no C5+ and have more than 90 mol% methane. The main difference between natural gas and other reservoir fluids is that the amount of C_{5+} or even C_{5+} in the mixture is quite low and the main components are low-boiling paraffin hydrocarbon derivatives.

Another type of reservoir fluid that is in gaseous phase under reservoir conditions are gas condensate systems (the C_{5+} fraction). The C_{5+} fraction of a mixture should be treated as an undefined fraction and its properties may be determined by a series of standard test methods that are different from the test methods used for various gases as well as the liquid constituents of gas streams. The C_{5+} content is more than that of natural gases and it is on the order of several few percent, while the methane content is less than the methane content of that of natural gas. However, these reservoir fluids generally contain components such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), or nitrogen (N_2). Presence of such compounds affects the properties of the gas mixture.

Major transportation pipelines usually impose restrictions on the make-up of the natural gas that is allowed into the pipeline. That means that before the natural gas can be transported it must be purified. This can commence at the wellhead where efforts are made to remove (at least) water, carbon dioxide and hydrogen sulfur to prevent damage (corrosion) to the pipeline and associated equipment (Speight, 2014b). The goal of this first stage of natural gas processing consists of separating (some or all of) the various hydrocarbon derivatives (C_{2+} as well as natural gasoline) which, depending upon the dew point of the hydrocarbon and the conditions in the pipeline, could separate in the pipeline and cause liquid-blockage.

These associated hydrocarbon derivatives, known as *natural gas liquids* (NGLs) can be very valuable by-products of natural gas processing. The natural gas liquids may undergo further separation at a gas processing plant to be sold separately and have a variety of different uses, including providing raw materials for crude oil refineries or petrochemical plants, and as sources of energy. Also at the wellhead, contaminants such as carbon dioxide and hydrogen sulfide are also separated from the gas steam to produce *pipeline quality* dry natural gas. While the ethane, propane, butane, and pentanes must be removed from natural gas, this does not mean that they are waste products, but they are valuable by-products (Speight, 2014a, 2017).

Briefly, gas processing (Mokhatab et al., 2006; Speight, 2014a, 2019a) consists of separating all of the various hydrocarbon derivatives and any other impurities from the methane (Fig. 8.4). Gas processing is necessary to ensure that the natural gas intended for use is as clean and pure as possible that meets the specifications which guarantee that the gas will the clean-burning and environmentally-sound energy choice. While the necessary pre-processing of natural gas can be accomplished at or near the wellhead (field processing), the complete processing of natural gas takes place at a processing plant, usually located in a natural gas producing region. The extracted natural gas is transported to these processing plants through a network of gathering pipelines, which are small-diameter, low pressure pipes.

A complex gathering system can consist of thousands of miles of pipes, interconnecting the processing plant to upwards of 100 wells in the area. In addition to processing done at the wellhead and at centralized processing plants, some final processing is also sometimes accomplished at *straddle extraction plants*. These plants are located on major pipeline systems and although the natural gas that arrives at these straddle extraction plants is already of pipeline quality, in certain instances there still exist small quantities of natural gas liquids, which are extracted at the straddle plants.

Sulfur and a variety of sulfur containing compounds (such as hydrogen sulfide, H_2S, mercaptans, RSH − also called thiols − and carbonyl sulfide, COS) occur in gases. These compounds are detrimental (especially in the presence of water) by causing corrosion to the pipeline and can cause deactivation of catalysts used in gas-treating systems. The sulfur levels in the natural gas (or, for that matter, in any gas stream) are an important parameter for gas treatment. Therefore, it is essential that sulfur-containing compounds such as hydrogen sulfide (as well acid gases such as carbon dioxide) be removed from a gas stream and converted to more useful products such as sulfur or sulfuric acid (Bartoo, 1985; Mokhatab et al., 2006; Speight, 2014a, 2019a).

To satisfy the chemical principles for the combustion of natural gas, knowledge of the concentration of the various constituents is essential. Natural gas is available in different forms (Chapter 1) and knowledge of gas composition (ASTM D1945) and heating value are important parameters to be met for optimum and economical processing to separate the gas into the individual constituents and ensuring that each constituent meets the necessary sales specifications. In this context, the term concentration describes the amount of a substance, expressed as mass or volume in a unit mass or volume of the gas. Also, the heating value can by presented as Btu/lb (the commonly-used units in the United States) or in units that are consistent with the SI system of units.

Although the processing of natural gas is, in many respects, less complicated than the processing and refining of crude oil, it is equally as necessary before its use by end users. The natural gas used by consumers is composed almost entirely of methane. However, natural gas found at the wellhead, although still composed primarily of methane, is by no means as pure.

Whatever the source of the natural gas, once separated from crude oil (if present) it commonly exists in mixtures with other hydrocarbon derivatives; principally ethane, propane, butane, and pentanes. In addition, raw natural gas contains water vapor, hydrogen sulfide (H_2S), carbon dioxide, helium, nitrogen, and other compounds. In fact, the associated hydrocarbon derivatives (the natural gas liquids) can be very valuable by-products of natural gas processing. Natural gas liquids include ethane, propane, butane, iso-butane, and natural gasoline that are sold separately and have a variety of different uses; including enhancing oil recovery in oil wells, providing raw materials for oil refineries or petrochemical plants, and as sources of energy.

Finally, it is also worthy of note that, because of the variation of gas volume with changes in temperature and changes in pressure, it is necessary to use one of the following alternatives for describing a concentration value: (i) additional specification of gas temperature and pressure values existing during measurement or (ii) conversion of the measured concentration value into the corresponding value at standard zero conditions.

In terms of gas processing (Fig. 8.4), the analysis of natural gas and its constituents (Chapter 10) includes the detection of gases and vapors in connection with control of chemical and metallurgical processes, control of environment and in the field of safety control. A whole class of analytical instruments, which use physical or physico-chemical detecting methods, is available for gas analysis. Although analyzers are considered to be electrical instruments some knowledge of chemistry is required to understand their operating principle and to obtain correct and accurate measuring results.

Process analysis, in contrast to laboratory analysis, includes all continuous measuring methods for real-time determination of physical and chemical properties and concentrations in process streams. Measuring points with continuously operating sampling devices, including the analyzers are located at selected locations spots in a gas processing plant. The difference to laboratory analysis, is where the analyzers are installed in a laboratory at the best operating conditions and where the samples are taken discontinuously from the process and brought to the laboratory. Laboratory analyzers are normally designed for sophisticated measurements and require trained operators.

The results of analysis in gas processing at the wellhead and in gas processing plants (Fig. 8.4) are used for (i) process control by, for example, controlling/monitoring the properties of the raw feedstock and the products by optimizing the process steps, (ii) safety issues, such as the protection of personnel and plant equipment by controlling the plant atmosphere for toxic gas mixtures or for explosive gas mixtures, (iii) product quality control by monitoring the production process steps and controlling the final product specification, and (iv) environmental protection by monitoring the exhaust gases for compliance with the specified limits of the types of pollutants.

Knowledge of those constituents that can have a detrimental effect on the combustion process or, for that matter, on the sales specification must be known and given attention. It is for this reason that gas processing (also called gas processing or gas refining) is an important aspect of natural gas technology along with the relevant analytical test methods for natural gas feedstocks as well as the properties of the separated products.

Using methane as the example, when natural gas is used as a combustible fuel gas, the presence of non-combustible (inert) constitunets reduces the gross and net calorific value of the gas and increases contamination of the furnace walls. Increasing water content raises the water dew point and consumes energy to evaporate water in the flue gas. The sulfur contained in the gas is burnt (oxidized) to sulfur dioxide (SO_2) and sulfur trioxide (SO_3), which, at temperatures below the dew point, may lead to the formation of aggressive sulfurous acid and sulfuric acid:

$$SO_2 + H_2O \rightarrow \underset{\text{Sulfurous acid}}{H_2SO_3}$$

$$SO_3 + H_2O \rightarrow \underset{\text{Sulfuric acid}}{H_2SO_4}$$

$$2SO_2 + 2O_2 + 2H_2O \rightarrow \underset{\text{Sulfuric acid}}{2H_2SO_4}$$

Thus, the compositional analysis of natural gas includes the detection of gases and vapors relating to control of gas processing processes, control of environmental emissions, and in the field of safety control. After production of the natural gas, the analysis starts with transportation (to detect and remove corrosive contaminants) and in the gas processing units where the gas is cleaned of all possible contaminants and prepared for use by domestic and industrial consumers.

In addition, the oxygen required for a natural gas combustion process is supplied as part of the combustion air which consists of nitrogen (N_2), oxygen (O_2), a varying small amounts of carbon dioxide and rare gases as well as a variable content of water vapor. In some processes pure oxygen or an air/oxygen mixture may be used for the combustion. The minimal amount of oxygen required to burn all combustible components completely depends on the fuel composition. The actual volume of air required for the combustion of natural gas can be calculated (i) from the air volume needed for the ideal combustion, depending on the composition of the gas, (ii) the desired excess oxygen value, and (iii) the relative oxygen content of the used air or the air/oxygen mixture. If, however, the ambient air is not dry, the water content must also be considered for correct air volume calculation.

The actual practice of processing natural gas to high quality pipeline gas for the consumer usually involves four main processes to remove the various impurities (i) water removal,

(ii) liquids removal, (iii) enrichment, (iv) fractionation and (v) the process by which hydrogen sulfide is converted to sulfur (the *Claus process*).

The shale gas resources (Chapter 2) represent a major contribution to the resource base of the United States. However, it is important to note that there is considerable variability in the quality of the resources, both within and between gas shale resources. Elevated levels of ethane, propane, carbon dioxide, or nitrogen in certain shale gases are of concern regarding their interchangeability with traditional natural gas supplies. This high level of variability in individual well productivity clearly has consequences with respect to the variability of individual well economic performance.

Gas processing (*gas treating*, *gas refining*) removes one or more components from the recovered (harvested) gas to prepare the gas for use. Gas processing (gas treating, gas refining) usually involves several processes to remove: (i) oil; (ii) water; (iii) elements such as sulfur, helium, and carbon dioxide; and (iv) natural gas liquids (Chapter 6). In addition, it is often necessary to install scrubbers and heaters at or near the wellhead that serve primarily to remove sand and other large-particle impurities. The heaters ensure that the temperature of the natural gas does not drop too low and form a hydrate with the water vapor content of the gas stream (Mokhatab et al., 2006; Speight, 2014a, 2019a).

Gas processing is an instrumental piece of the natural gas value chain and is required to ensure that the natural gas intended for use is as clean and pure as possible, making it the clean burning and environmentally sound energy choice. In the processing sequence, common components removed to meet pipeline, safety, environmental, and quality specifications include hydrogen sulfide, carbon dioxide, nitrogen, hydrocarbon derivatives having a higher molecular weight then methane, and water (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a). Once the natural gas has been fully processed, and is ready to be consumed, it must be transported from those areas that produce natural gas, to those areas that provide a market for natural gas.

Whatever the source (tight shale, tight sandstone, tight carbonate), natural gas needs to be processed before use because of the occurrence of the diluents and contaminants. The processes focus on sulfur removal and carbon dioxide removal. The processes that have been developed to accomplish gas purification vary from a simple once-through wash operation to complex multi-step recycling systems. In many cases, process complexities arise because of the need for recovery of the materials used to remove the contaminants or even recovery of the contaminants in the original, or altered, form. However, process complexities in terms of the choice of the process also arise because of the varying composition of gas from tight formations. In fact, there are many variables in treating natural gas from tight formations and the precise area of application of a given process may be difficult to, define. In addition to hydrogen sulfide and carbon dioxide, gas may contain other contaminants, such as mercaptans (R−SH) and carbonyl sulfide (COS). The presence of these impurities may eliminate some of the sweetening processes since some processes remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes that are not designed to remove (or are incapable of removing) large amounts of acid gases. However, these processes also capable of removing the acid gas impurities to very low levels when the acid gases are there in low to medium concentrations in the gas. Process selectivity indicates the preference with which the process removes one acid gas component relative to (or in preference to) another. For example, some processes remove both hydrogen sulfide and carbon dioxide; other processes are designed to remove hydrogen sulfide only. It is important to consider the process selectivity for, say, hydrogen sulfide removal compared to carbon dioxide removal that ensures minimal concentrations of these components in the product, thus the need for consideration of the carbon dioxide to hydrogen sulfide in the gas stream.

Many chemical processes are available for processing or refining natural gas. However, there are many variables in the choice of process of the choice of refining sequence that dictate the choice of process or processes to be employed. In this choice, several factors must be considered: (i) the types and concentrations of contaminants in the gas, (ii) the degree of contaminant removal desired, (iii) the selectivity of acid gas removal required, (iv) the temperature, pressure, volume, and composition of the gas to be processed, (v) the carbon dioxide-hydrogen sulfide ratio in the gas, and (vi) the desirability of sulfur recovery due to process economics or environmental issues.

In a general processing sense, many chemical processes and physical process are available for processing or refining natural gas (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a). However, there are many variables in the choice of process of the choice of refining sequence that dictate the choice of process or processes to be employed. In this choice, several factors must be considered: (i) the types and concentrations of contaminants in the gas, (ii) the degree of contaminant removal desired, (iii) the selectivity of acid gas removal required, (iv) the temperature, pressure, volume, and composition of the gas to be processed, (v) the carbon dioxide-hydrogen sulfide ratio in the gas, and (vi) the desirability of sulfur recovery due to process economics or environmental issues.

The processes that have been developed to accomplish gas purification vary from a simple once-through wash operation to complex multi-step recycling systems (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a). In many cases, the process complexities arise because of the need for recovery of the materials used to remove the contaminants or even recovery of the contaminants in the original, or altered, form (Kohl and Riesenfeld, 1985; Newman. 1985; Mokhatab et al., 2006). In addition, it is often necessary to install scrubbers and heaters at or near the wellhead that serve primarily to remove sand and other large-particle impurities. The heaters ensure that the temperature of the natural gas does not drop too low and form a hydrate with the water vapor content of the gas stream (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a).

In addition to hydrogen sulfide and carbon dioxide, gas may contain other contaminants, such as mercaptans (also called *thiols*, R—SH) and carbonyl sulfide (COS). The presence of these impurities may eliminate some of the sweetening processes since some processes remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes that are not designed to remove (or are incapable of removing) large amounts of acid gases. However, these processes also capable of removing the acid gas impurities to very low levels when the acid gases are there in low to medium concentrations in the gas.

Process selectivity indicates the preference with which the process removes one acid gas component relative to (or in preference to) another. For example, some processes remove both hydrogen sulfide and carbon dioxide; other processes are designed to remove hydrogen sulfide only. It is very important to consider the process selectivity for, say, hydrogen sulfide removal compared to carbon dioxide removal that ensures minimal concentrations of these components in the product, thus the need for consideration of the carbon dioxide to hydrogen sulfide in the gas stream.

However, the processes applied to gas processing are subject to several variables that must, of necessity be considered: (i) the types of contaminants in the gas, (ii) the concentrations of contaminants in the gas, (iii) the degree of contaminant removal desired, (iv) the selectivity of acid gas removal required, (v) the temperature of the gas to be processed, (vi) the pressure of the gas to be processed, (vii), the volume of the gas to be processed, (viii) the composition of the gas to be processed, (ix) the carbon dioxide-hydrogen sulfide ratio in the gas and (x) the desirability of sulfur recovery due to process economics or environmental issues.

In addition to hydrogen sulfide (H_2S) and carbon dioxide (CO_2), gas may contain other contaminants, such as mercaptans (RSH) and carbonyl sulfide (COS). The presence of these impurities may eliminate some of the sweetening processes since some processes remove large amounts of acid gas but not to a sufficiently low concentration. On the other hand, there are those processes that are not designed to remove (or are incapable of removing) large amounts of acid gases. However, these processes also capable of removing the acid gas impurities to very low levels when the acid gases are there in low to medium concentrations in the gas.

The process units employed to remove the unwanted constituents the gas varies with the composition of the gas stream. For example, acid-gas removal is commonly by absorption of the hydrogen sulfide, carbon dioxide into aqueous solutions od amine derivatives (such as glycolamine, 2-aminoethanol, 2-hydroxy ethylamine, $HOCH_2CH_2NH_2$). This process performs admirably for high-pressure gas streams and those with moderate to high concentrations of the acid-gas components (hydrogen sulfide and carbon dioxide). Physical solvents such as methanol (CH_3OH) or Selexol may also be used in some cases — the Selexol solvent is a mixture of the dimethyl ethers of polyethylene glycol. Removal of acid gases is especially relevant if the tight gas originates from a carbonate ($CaCO_3$) formation.

The Selexol process, unlike the amine-based processes, is a physical solvent, that does not rely on a chemical reaction with the acid gases. Since no chemical reactions are involved, Selexol usually requires less energy than the amine based processes. However, at feed gas pressures below approximately 300 psi, the Selexol solvent capacity (in amount of acid gas absorbed per volume of solvent) is reduced and the amine based processes will usually be superior. In the process, the Selexol solvent dissolves (absorbs) the acid gases from the feed gas at relatively high pressure, usually 300 to 2000 psi. The rich solvent containing the acid gases is then let down in pressure and/or steam stripped to release and recover the acid gases. The Selexol process can operate selectively to recover hydrogen sulfide and carbon dioxide as separate streams, so that the hydrogen sulfide can be sent to either a Claus unit for conversion to elemental sulfur wet sulfuric acid process (WSA process) unit for conversion to sulfuric acid while, at the same time, the carbon dioxide can be sequestered or used for enhanced oil recovery. The Rectisol process, which uses refrigerated methanol as the solvent, is similar in principle to the Selexol. However, if the level of carbon dioxide is high, such as in gas from carbon dioxide flooded reservoirs, membrane technology affords bulk carbon dioxide removal in advance of processing with another method. For minimal amounts of hydrogen sulfide in a gas stream, scavengers can be a cost effective approach to hydrogen sulfide removal.

Gas that becomes saturated with water in the reservoir requires dehydration to increase the heating value of the gas and to prevent pipeline corrosion and the formation of solid hydrates. In most cases, dehydration with a glycol is employed. The water rich glycol can be regenerated by reducing the pressure and applying heat. Another possible dehydration method is use of molecular sieves that contact the gas with a solid adsorbent to remove the water. Molecular sieves can remove the water down to the extremely low levels required for cryogenic separation processes.

Distillation uses the different boiling points of higher molecular weight hydrocarbon derivatives and nitrogen for separation. Cryogenic temperatures, required for separation of nitrogen and methane, are achieved by refrigeration and expansion of the gas through an expander. Removal of the high-boiling hydrocarbon derivatives is dictated by pipeline quality requirements, while deep removal is based on the economics of the production of natural gas liquids (NGLs).

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Gas processing equipment, whether in the field or at processing/treatment plants, assures that these requirements can be met. While in most cases processing facilities extract contaminants and higher molecular weight hydrocarbon derivatives (natural gas liquids) from the gas stream. However, in some cases, the higher molecular weight hydrocarbon derivatives may be blended into the gas stream to bring it within acceptable Btu levels. Whatever the situation, there is the need to prepare the gas for transportation and use in domestic and commercial furnaces. Thus, natural gas processing begins at the wellhead and since the composition of the raw natural gas extracted from producing wells depends on the type, depth, and location of the underground deposit and the geology of the area, processing must offer several options (even though each option may be applied to a different degree) to accommodate the difference in composition of the extracted gas.

In those few cases where pipeline-quality natural gas is actually produced at the wellhead or field facility (Manning and Thompson, 1991), the natural gas is moved directly to the pipeline system. In other instances, especially in the production of non-associated natural gas, field or lease facilities referred to as *skid-mount plants* are installed nearby to dehydrate (remove water) and decontaminate (remove dirt and other extraneous materials) raw natural gas into acceptable pipeline-quality gas for direct delivery to the pipeline system. The *skids* are often specifically customized to process the type of natural gas produced in the area and are a relatively inexpensive alternative to transporting the natural gas to distant large-scale plants for processing.

Gas processing (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a) consists of separating all of the various hydrocarbon derivatives, non-hydrocarbon derivatives (such as carbon dioxide and hydrogen sulfide), and higher molecular weight hydrocarbon derivatives from the methane component (Table 8.4; Fig. 8.4). Major transportation pipelines usually impose restrictions on the make-up of the natural gas that is allowed into the pipeline. That means that before the natural gas can be transported it must be purified. While the ethane, propane, butanes, and pentanes must be removed from natural gas, this does not mean that they are all waste products. Gas processing is necessary to ensure that the natural gas intended for use is clean-burning and environmentally acceptable. Natural gas used by consumers is composed almost entirely of methane but natural gas that emerges from the reservoir at the wellhead is by no means as *pure* methane (Table 8.4) (Chapter 3). Although the processing of natural gas is in many respects less complicated than the processing and refining of crude oil, it is equally as necessary before its use by end users.

Raw natural gas comes from three types of wells: oil wells, gas wells, and condensate wells (Chapter 2 and Chapter 4). *Associated gas* (Chapter 1), i.e., gas from crude oil wells, can exist separate from oil in the formation (free gas), or dissolved in the crude oil (dissolved gas). *Non-associated gas*, i.e., gas from gas wells or condensate wells is *free* natural gas along with a semi-liquid hydrocarbon condensate. Whatever the source of the natural gas, once separated from crude oil (if present) it commonly exists in mixtures with other hydrocarbon derivatives; principally ethane, propane, butane, and pentanes. In addition, raw natural gas contains water vapor, hydrogen sulfide (H_2S), carbon dioxide, helium, nitrogen, and other compounds. In fact, the associated hydrocarbon derivatives (*natural gas liquids*, NGLs) can be very valuable by-products of natural gas processing. Natural gas liquids include ethane, propane, butane, iso-butane, and natural gasoline that are sold separately and have a variety of different uses − including enhancing oil recovery in oil wells, providing raw materials for oil refineries or petrochemical plants, and as sources of energy.

The actual practice of processing natural gas to high quality pipeline gas for the consumer usually involves four main processes to remove the various impurities (i) water removal, (ii) liquids removal, (iii) enrichment, (iv) fractionation and (v) the process by which hydrogen sulfide is converted to sulfur (the *C. process*). Process selectivity indicates the preference with which the process removes one acid gas component relative to (or in preference to) another. For example, some processes remove both hydrogen sulfide and carbon dioxide while other processes are designed to remove hydrogen sulfide only. It is important to consider the process selectivity for, say, hydrogen sulfide removal compared to carbon dioxide removal that ensures minimal concentrations of these components in the product, thus the need for consideration of the carbon dioxide to hydrogen sulfide ratio in the gas stream (Maddox, 1982; Kohl and Riesenfeld, 1985; Newman, 1985; Soud and Takeshita, 1994).

Initially, natural gas receives a degree of cleaning at the wellhead. The extent of the cleaning depends upon the specification that the gas must meet to enter the pipeline system. For example, natural gas from high-pressure wells is usually passed through field separators at the well to remove hydrocarbon condensate and water (Fig. 8.5). Natural gasoline, butane, and propane are usually present in the gas, and gas processing plants are required for the recovery of these liquefiable constituents.

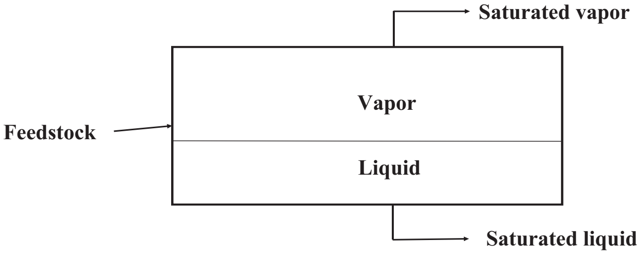


FIG. 8.5 Simplified schematic of a field separator.

An oil/gas separator is a pressure vessel used for separating a wellhead stream into gaseous and liquid components and the separator is installed close to the wellhead and can be divided into horizontal, vertical, or spherical separators. In teams of fluids to be separated, the oil/gas separators can be grouped into gas/liquid two-phase separator or oil/gas/water three-phase separator. In order to meet the various process requirements, the oil/gas separators are normally designed in stages, in which the first stage separator is used for preliminary phase separation, while the second and third stage separator are applied for further treatment of each individual phase (gas, oil and water). Depending on a specific application, oil/gas separators are used to remove dispersed droplets from a bulk gas stream or are designed to remove contaminant gas bubbles from the bulk liquid stream.

4.3 Chemicals from tight gas

If the changes brought about by shale gas take hold in the chemicals industry, they will create a need for specialty steels, reactors, separation columns, pipes, compressors, pumps, valves, fittings, control systems, storage tanks, and other chemical processing equipment, as well as the services of engineering and construction firms.

Given the law of supply and demand, increases in ethylene-based capacity could yield a decline in chemicals pricing. Since chemicals are used in an estimated 90% of all manufactured products, lower chemicals prices could bring about a reduction in costs for US manufacturers. Another possible outcome is that chemical products will increasingly become a substitute for more expensive materials, such as metals, glass, wood, leather, and textiles.

Partial substitution could occur in complex manufactured products. For example, while today automobiles have a 20% chemical content, that percentage could rise as some manufacturers reengineer parts to increase chemical content, thereby decreasing weight and costs. It is also possible that lower energy costs could bring some manufacturing back to the United States. The decision by Dow Chemical to build an ethylene plant in Texas is, in part, based on the competitive advantage low-cost, natural gas-based feedstocks brings to the production of certain products, such as plastics, performance materials, and advanced materials. Likely targets will be relatively simple products such as toothpaste tubes, disposable medical syringes, or pens that can be produced on high-speed lines with robotics, requiring little labor. In the electronic device industry, we are seeing the manufacturing of more demanding products, such as touch-sensitive screens, higher-strength films, mobility devices, and miniaturized components, return to the United States. Additionally, supplying US customers with US products simplifies the long and costly supply chain.

All of these scenarios present challenges and opportunities for manufacturing companies. We have seen the changes in natural gas prices and how those changes flow through the chemicals industry. [Fig. 8.6 illustrates the potential ethane impact on manufacturing.] Whether these opportunities are realized will depend on how downstream manufacturers will be positioned to capture the cost-saving opportunities. Successful manufacturing companies are already reexamining their strategies, product innovation portfolio, supply chain planning, and other areas. Some of the changes they face might be as dramatic as the events now unfolding in the chemicals industry.

5. Product evaluation

The goal of processing tight gas is to separate the methane from the other constituents (ethane, propane, and butane) each of which finds use in the petrochemical industry.

It is the purpose of this section to present to the reader a brief introduction to the tight gas constituents that will be used for the production of chemicals. The detailed chemical and physical and properties of the methane (CH_4), ethane, propane, and butene and the route by which these gas are used in the petrochemical industry is provided elsewhere (Speight, 2019c).

5.1 Methane

Methane (CH_4) is the simplest alkane, and the principal component of tight gas and is colorless and naturally odorless, and burns efficiently without many by products. It is also known as marsh gas or methyl hydride and is easily ignited. The vapor is lighter than air (Table 8.7). Under prolonged exposure to fire or intense heat the containers may rupture in a violent explosion.

The preparation of chemicals and chemical intermediates from methane should not be restricted to those described here but should be regarded as some of the building blocks of the petrochemical industry (Speight, 2019c). In addition to methane being the major constituent of tight gas, the products of the gasification of carbonaceous feedstocks also contain methane. The commonly accepted approach to the synthesis of methane from the carbonaceous feedstock is the catalytic reaction of hydrogen and carbon monoxide:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

A variety of metals have been used as catalysts for the methanation reaction; the most common, and to some extent the most effective methanation catalysts, appear to be nickel and ruthenium, with nickel being the most widely used. The synthesis gas must be desulfurized before the methanation step since sulfur compounds will rapidly deactivate (poison) the catalysts. Also, the composition of the products of gasification processes are varied insofar as the gas composition varies with the feedstock and the system employed. It is emphasized that the gas product must be first freed from any pollutants such as particulate matter and sulfur compounds before further use, particularly when the intended use is a water gas shift or methanation (Mokhatab et al., 2006; Speight, 2013, 2014a). Methane is a major raw material for many chemical processes and the potential number of chemicals that can be produced

TABLE 8.7 Properties of methane.

Chemical formula	CH_4
Molar mass	16.04 g mol^{-1}
Appearance	Colorless gas
Odor	Odorless
Density	• 0.656 g/L (gas, 25 °C, 1 atm); 0.716 g/L (gas, 0 °C, 1 atm); 0.42262 g cm^{-3} (liquid, −162 °C)
Liquid density	• 0.4226
Vapor density (air = 1)	• 0.55
Melting point	−182.5 °C; −296.4 °F; 90.7 K
Boiling point	−161.49 °C; −258.68 °F; 111.66 K
Solubility in water	22.7 mg L^{-1}
Solubility	Soluble in ethanol, diethyl ether, benzene, toluene, methanol, acetone
Flash point	−188 °C (−306.4 °F; 85.1 K)
Autoignition temperature	537 °C (999 °F; 810 K)
Explosive limits	4.4%—17% v/v in air

from methane is almost limitless (Speight, 2019c). Indeed, methane can be converted to a wide variety of chemicals, in addition to serving as a source of synthesis gas. This leads to a wide variety of chemicals which involve chemistry (i.e., the chemistry of methane and other one-carbon compounds).

In the chemical industry, methane is the feedstock of choice for the production of hydrogen, methanol, acetic acid, and acetic anhydride. To produce any of these chemicals, methane is first made to react with steam in the presence of a nickel catalyst at high temperatures (700—1100 °C, 1290 to 2010 °F):

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

The synthesis gas is then reacted in various ways to produce a wide variety of products.

In addition, acetylene is prepared by passing methane through an electric arc. When methane is made to react with chlorine (gas), various chloro-methane derivatives are produced: chloromethane (CH_3Cl), dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4). However, the use of these chemicals, however, is declining − acetylene may be replaced by less costly substitutes, and the chloro-methane derivatives are used less often because of health and environmental concerns.

It must be recognized that there are many other options for the formation of chemical intermediates and chemicals from methane by indirect routes, i.e. where other compounds are prepared from the methane which are then used as further sources of petrochemical products.

In summary, methane is an important source of petrochemical intermediates and solvents.

5.2 Ethane

Ethane (C_2H_6) is a two-carbon alkane that, at standard temperature and pressure, is a colorless, odorless gas. Ethane is isolated on an industrial scale from natural gas and as a byproduct of petroleum refining (Table 8.8). Its chief use is as petrochemical feedstock for ethylene production, usually by pyrolysis (Vincent et al., 2008):

$$CH_3CH_3 \rightarrow CH_2{=}CH_2 + H_2$$

In terms of the hydrocarbon constituents, ethane is the second-largest component of tight gas after methane. Natural gas from different gas fields varies in ethane content from less than 1% to more than 6% v/v. Prior to the 1960s, ethane and higher molecular weight gases were not separated from the methane component of natural gas, but simply burnt along with the methane as a fuel. Currently, ethane is an important petrochemical feedstock, and it is separated from the other components of natural gas in most gas processing plants. Ethane can also be separated from petroleum gas, a mixture of gaseous hydrocarbon derivatives that arises as a byproduct of petroleum refining.

The main source for ethane is the fraction known as gas liquids, which are the higher molecular weight hydrocarbon derivatives separate from tight gas during processing operations (Mokhatab et al., 2006; Kidnay et al., 2011; Speight, 2014a, 2019a). Approximately 40% of the available ethane is recovered for chemical use. The only large consumer of ethane is the steam cracking process for ethylene production.

Ethane is most efficiently separated from methane by liquefying it at cryogenic temperatures. Various refrigeration strategies exist: the most economical process presently in wide use employs turbo-expansion, and can recover over 90% of the ethane in natural gas. In this process, chilled gas expands through a turbine; as it expands, its temperature drops to

TABLE 8.8 Properties of ethane.

Chemical formula	C_2H_6
Molar mass	30.07 g mol^{-1}
Appearance	Colorless gas
Odor	Odorless
Density	• 1.3562 mg cm^{-3} (at 0 °C), 0.5446 g cm^{-3} (at 184 K)
Liquid density	• 0.446 @ 0 °C
Vapor density (air = 1)	• 1.05
Melting point	−182.8 °C; −296.9 °F; 90.4 K
Boiling point	−88.5 °C; −127.4 °F; 184.6 K
Flash point	−94.4 °C, 137.9 °F
Solubility in water	56.8 mg L^{-1}
Explosive limits	3–12% v/v in air

about −100 °C (212 °F). At this low temperature, gaseous methane can be separated from the liquefied ethane and heavier hydrocarbon derivatives by distillation. Further distillation then separates ethane from the propane and the higher molecular weight hydrocarbon derivatives.

5.3 Propane

Propane is produced as a by-product of two other processes: (i) gas processing and (ii) petroleum refining (Table 8.9). The processing of natural gas involves removal of butane, propane, and large amounts of ethane from the raw gas, to prevent condensation of these volatiles in natural gas pipelines. Additionally, crude oil refineries produce some propane as a by-product of cracking processes (Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017). Propane can also be produced as a biofuel by the thermal conversion of various types of biomass (Speight, 2011).

Propane is produced from both crude oil refining and gas processing. Propane is not produced for its own sake, but is a by-product of these two other processes. The gas plant production of propane primarily involves extracting materials such as propane and butane from natural gas to prevent these liquids from condensing and causing operational problems in natural gas pipelines. Similarly, when oil refineries make major products such as motor gasoline, diesel and heating oil, some propane is produced as a by-product of those processes.

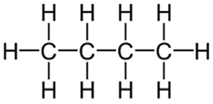
Propane has a wide variety of uses worldwide including small domestic heating applications to large industrial and manufacturing processes. Some of the more common uses of propane are for residential & commercial heating and cooking, motor fuel use in vehicles, irrigation pumps, and power generation, agricultural crop drying and weed control, and as a raw material in the petrochemical industry to make things such as plastics, alcohol, fibers and cosmetics.

TABLE 8.9 Properties of propane.

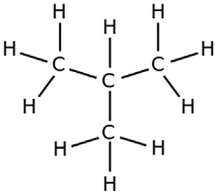
Chemical formula	C_3H_8
Molar mass	44.10 g mol^{-1}
Appearance	Colorless gas
Odor	Odorless
Density	2.0098 kg/m^3 (at 0 °C, 101.3 kPa)
Liquid density	0.493 @ 25 °C
Vapor density (air = 1)	2.05
Melting point	−187.7 °C; −305.8 °F; 85.5 K
Boiling point	−42.25 to −42.04 °C; −44.05 to −43.67 °F
Flash point	−104 °C, −155 °F
Solubility in water	47 mg L^{-1} (at 0 °C)
Explosive limits	2.3–9.5% v/v in air

5.4 Butane isomers

Like propane, butane isomers can be obtained from natural gas liquids and from refinery gas streams. The C4 acyclic paraffin consists of two isomers: n butane and isobutane (2-methylpropane). The physical as well as the chemical properties of the two isomers are quite different due to structural differences. There are two isomers of butane:



n-Butane.



iso-Butane.

In the IUPAC system of nomenclature, however, the name butane refers only to the n-butane isomer ($CH_3CH_2CH_2CH_3$). Butane derivatives are highly flammable, colorless, easily liquefied gases that quickly vaporize at room temperature.

If present, the butane isomers present in tight gas can be separated from the large quantities of lower-boiling gaseous constituents, such as methane and ethane, by absorption in a light oil. The butane thus obtained can be stripped from the absorbent along with propane and marketed as liquefied petroleum gas that meets the required specifications or they can be separated from the propane and then from each other by fractional distillation: *n*-butane boils at −0.5 °C (31.1 °F) (Table 8.10); isobutane boils at −11.7 °C (10.9 °F) (Table 8.11). Butane derivaitves that are formed by catalytic cracking and other refinery processes can be recovered by absorption into a light oil (Parkash, 2003; Gary et al., 2007; Speight, 2007; 2014a; Hsu and Robinson, 2017; Speight, 2017).

Commercially, *n*-butane can be added to gasoline to increase its volatility (as an aid to ignition) in cold climates. Transformed to isobutane in a refinery process known as isomerization, it can be reacted with certain other hydrocarbon derivatives such as butylene to form valuable high-octane constituents of gasoline.

Like propane, n-butane is mainly obtained from natural gas liquids. It is also a by-product from different refinery operations. Currently, the major use of n-butane is to control the vapor pressure of product gasoline. Due to new regulations restricting the vapor pressure of gasoline, this use is expected to be substantially reduced. Surplus n-butane could be isomerized to isobutane, which is currently in high demand for producing isobutene. Isobutene is a

TABLE 8.10 Properties of n-Butane.

Chemical formula	C_4H_{10}
Molar mass	58.12 g mol^{-1}
Appearance	Colorless gas
Odor	Gasoline-like or natural gas-like
Density	2.48 kg/m^3 (at 15 °C, 59 °F)
Liquid density	0.573 @ 25 °C
Vapor density (air = 1)	2.1
Melting point	−140 to −134 °C; −220 to −209 °F
Boiling point	−1 to 1 °C; 30 to 34 °F
Solubility in water	61 mg L^{-1} (at 20 °C, 68 °F)
Explosive limits	1.9—8.5% v/v in air

TABLE 8.11 Properties of iso-Butane.

Chemical formula	C_4H_{10}
Molar mass	58.12 g mol^{-1}
Appearance	Colorless gas
Odor	Odorless
Density	2.51 kg/m^3 (at 15 °C, 100 kPa)
Liquid density	0.551 @ 25 °C
Vapor density	2.01
Melting point	−159.42 °C (−254.96 °F)
Boiling point	−11.7 °C (10.9 °F)
Solubility in water	48.9 mg L^{-1} (at 25 °C, 77 °F)
Explosive limits	1.8—8.4% in air

precursor for methyl and ethyl tertiary butyl ethers, which are important octane number boosters. Another alternative outlet for surplus n-butane is its oxidation to maleic anhydride. Almost all new maleic anhydride processes are based on butane oxidation. n-Butane has been the main feedstock for the production of butadiene. However, this process has been replaced by steam cracking hydrocarbon derivatives, which produce considerable amounts of by-product butadiene.

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CHAPTER

9

Analysis of oil from tight formations

1. Introduction

By way of recall (Chapter 1), tight oil is another type of crude oil which various from a gas condensate-type liquid to a highly-volatile liquid (McCain, 1990; Dandekar, 2013; Speight, 2014a, 2016; Terry and Rogers, 2014). Tight oil refers to the oil preserved in tight sandstone or tight carbonate rocks with low matrix permeability – in these reservoirs, the individual wells generally have no natural productivity or their natural productivity is lower than the lower limit of industrial oil flow, but industrial oil production can be obtained under certain economic conditions and technical measures. Such measures include acid fracturing, multi-stage fracturing, horizontal wells, and multi-lateral wells (Akrad et al., 2011; Speight., 2016).

The term *light tight oil* is also used to describe oil from shale reservoirs and tight reservoirs because the crude oil produced from these formations is light crude oil. The term *light crude oil* refers to low-density crude oil that flows freely at room temperature and these light oils have a higher proportion of light hydrocarbon fractions resulting in higher API gravities (between 37° and 42°) (Speight, 2014a). However, the crude oil contained in shale reservoirs and in tight reservoirs will not flow to the wellbore without assistance from advanced drilling (such as horizontal drilling) and fracturing (hydraulic fracturing) techniques. There has been a tendency to refer to this oil as *shale oil*. This terminology is incorrect insofar as it is confusing and the use of such terminology should be discouraged as illogical since shale oil has (for decades, even centuries) been the name given to the distillate produced from oil shale by thermal decomposition (Chapter 11). There has been the recent (and logical) suggestion that shale oil can be referred to as *kerogen oil* (IEA, 2013).

The challenges associated with the production of crude oil from shale formations are a function of the compositional complexity and the varied geological formations where they are found. These oils are light, but they often contain high proportions of waxy constitunets and, for the most part, reside in oil-wet formations. These phenomena create some of the predominant difficulties associated with crude oil extraction from the shale formations, and include: (i) scale formation, (ii) salt deposition, (iii) paraffin wax deposits, (iv) destabilized asphaltene constituents, (v) equipment corrosion, and (vi) bacteria growth. Thus, multicomponent chemical additives are added to the stimulation fluid to control these problems.

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The most notable tight oil plays in North America include the Bakken shale, the Niobrara formation, the Barnett shale, the Eagle Ford shale, and the and the Miocene Monterey play of the San Joaquin Basin (California) in the United States, and the Cardium play (Alberta) in Canada. In many of these tight formations, the existence of large quantities of oil has been known for decades and efforts to commercially produce those resources have occurred sporadically with typically disappointing results. However, starting in the mid-decade of the current century, advancements in well drilling and stimulation technologies combined with high oil prices have turned tight oil resources into one of the most actively explored and produced targets in North America.

Furthermore, of the tight oil plays, perhaps the best understood is the Bakken which straddles the border between Canada and the US in North Dakota, Montana, and Saskatchewan. Much of what is known related to the exploitation of tight oil resources comes from industry experiences in the Bakken and the predictions of future tight oil resource development described in this study are largely based on that knowledge. He Bakken tight oil play historically includes three zones, or members, within the Bakken Formation. The upper and lower members of the Bakken are organic rich shales which serve as oil source rocks, while the rocks of the middle member may be siltstone formations, sandstone formations, or carbonate formations that are also typically characterized by low permeability and high oil content. Since 2008 the Three Forks Formation, another tight oil-rich formation which directly underlies the lower Bakken shale, has also yielded highly productive oil wells. Drilling, completion, and stimulation strategies for wells in the Three Forks Formation are similar to those in the Bakken and the light, sweet crude oil that is produced from both plays has been geochemically determined to be essentially identical. Generally, the Three Forks Formation is considered to be part of the Bakken play, though the authors of published works will sometimes refer to it as the Bakken-Three Forks play.

Other known tight formations (on a worldwide basis) include the R'Mah Formation in Syria, the Sargelu Formation in the northern Persian Gulf region, the Athel Formation in Oman, the Bazhenov formation and Achimov Formation in West Siberia, Russia, the Coober Pedy in Australia, the Chicontepex formation in Mexico, and the Vaca Muerta field in Argentina (US, 2011; 2013, 2014). However, tight oil formations are heterogeneous and vary widely over relatively short distances. Thus, even in a single horizontal drill hole, the amount of oil recovered may vary as may recovery within a field or even between adjacent wells. This makes evaluation of *shale plays* and decisions regarding the profitability of wells on a particular lease difficult and a tight reservoir which contains only crude oil (without natural gas as the pressurizing agent) cannot be economically produced (US, 2011; 2013).

In terms of refining, although tight oil is considered sweet (low sulfur content) and amenable to refinery options, this is not always the case. Hydrogen sulfide gas, which is flammable and poisonous, comes out of the ground with the crude oil and must be monitored at the drilling site as well as during transportation. Amine-based hydrogen sulfide scavengers are added to the crude oil prior to transport to refineries. However, mixing during transportation due to movement, along with a change in temperature that raises the vapor pressure of the oil, can cause the release of entrained hydrogen sulfide during offloading, thereby creating a safety hazard. For example, such crude that is loaded on railcars in winter and then transported to a warmer climate becomes hazardous clue to the higher vapor pressure. The shippers and receivers of the oil should be aware of such risks.

Paraffin waxes are present in tight oil and remain on the walls of railcars, tank walls, and piping. The waxes are also known to foul the preheat sections of crude heat exchangers (before they are removed in the crude desalter). Paraffin waxes that stick to piping and vessel walls can trap amines against the walls which can create localized corrosion (Speight, 2014c). *Filterable solids* also contribute to fouling in the crude preheat exchangers and a tight crude can contain over seven times more filterable solids than a traditional crude oil. To mitigate filter plugging, the filters at the entrance of the refinery require automated monitoring because they need to capture large volumes of solids. In addition, wetting agents are added to the desalter to help capture excess solids in the water, rather than allowing the undesired solids to travel further downstream into the process.

In many refineries, *blending two or more crude oils* as the refinery feedstock is now standard operating procedure which allows the refiner to achieve the right balance of feedstock qualities. However, the blending of the different crude oils may cause problems if the crude oils being mixed are incompatible (Chapter 17) (Mushrush and Speight, 1995; Speight, 2014). When crude oils are incompatible, the is increased deposition of the asphaltene constituents (Speight, 2014) which accelerates fouling in the heat exchanger train downstream of the crude desalter (Speight, 2014c). Accelerated fouling increases the amount of energy that must be supplied by the crude fired heater, which limits throughput when the fired heater reaches its maximum duty and may also necessitate an earlier shutdown for cleaning.

Mixing stable crude oil blends with asphaltic and paraffinic oils creates the potential for precipitating the unstable asphaltene constituents — a high content of paraffinic naphtha in tight oils also creates favorable conditions for precipitation of the asphaltene constitunets (Speight, 2014a, 2014c). It should be noted that the ratio of crude oils in a blend may have an impact on crude incompatibility. For example, a low amount of tight oil in a blend may not cause accelerated fouling whereas a blend containing a higher amount of tight oil may cause accelerated fouling. The key is the separation of any constituents that can cause fouling (Speight, 2014c).

While crude oil from tight shale formations is characterized by a low content)if any) of residuum and low-sulfur content, there can be a significant proportion of wax constituents in the oil. These constituents may exhibit a broad distribution of the molecular weight. For example, paraffin carbon chains of C_{10} to C_{60} have been found and some tight crude oil may even have hydrocarbon carbon chains (wax) up to C_{72}. While this may be a relief from recovery of high-asphaltene heavy (high density, low API gravity) oils, the joy is short-lived and the deposition of waxy constituents can cause as many problems as asphaltene incompatibility. To control deposition and plugging in formations due to paraffin, a variety of wax dispersants are available for use. In upstream applications, the paraffin wax dispersants are applied as part of multifunctional additive packages where, for convenience, asphaltene stability and corrosion control can also be addressed simultaneously. Scale deposits of calcite, carbonates and silicates must also be controlled during production or plugging problems arise. A wide range of scale additives is available. These additives can be highly effective when selected appropriately. Depending on the nature of the well and the operational conditions, a specific chemistry is recommended or blends of products are used to address scale deposition.

Oil from tight shale formation is characterized by low-asphaltene content, low-sulfur content and a significant molecular weight distribution of the paraffinic wax content (Speight, 2104a, 2015). Paraffin carbon chains of C_{10} to C_{60} have been found, with some shale oils containing carbon chains up to C_{72}. To control deposition and plugging in formations due to paraffin derivatives, the dispersants are commonly used. In upstream applications, these paraffin dispersants are applied as part of multifunctional additive packages where asphaltene stability and corrosion control are also addressed simultaneously (Speight, 2014a, 2014b; 2014c, 2015). In addition, scale deposits of calcite ($CaCO_3$), other carbonate minerals (minerals containing the carbonate ion, CO_3^{2-}), and silicate minerals (minerals classified on the basis of the structure of the silicate group, which contains different ratios of silicon and oxygen) must be controlled during production or plugging problems arise. A wide range of scale additives is available which can be highly effective when selected appropriately. Depending on the nature of the well and the operational conditions, a specific chemistry is recommended or blends of products are used to address scale deposition.

While the basic approach toward developing a tight oil play are expected to be similar from area to area, the application of specific strategies, especially with respect to well completion and stimulation techniques, will almost certainly differ from play to play, and often even within a given play. The differences depend on the geology (which can be very heterogeneous, even within a play) and reflect the evolution of technologies over time with increased experience and availability.

This chapter presents the analytical methods that can be applied to tight oil as a refinery feedstock. The test methods that are suitable for application of the four predominant product fractions of tight oil: (i) naphtha, (ii) kerosene, and (iii) gas oil, and (iv) resid ra presented elsewhere (Chapter 10). For the most part, tight oil is not generally recognized as having a residuum and if the test methods for the determination of the proeprties of the resid are required, the methods are presented in detail elsewhere (Speight, 2014; 2015).

2. Tight oil

Formations, such as shale formations, that contain crude oil (tight oil) are heterogeneous and vary widely over relatively short distances. As a consequence, the oil extracted from such reservoirs must be expected to vary in composition and properties. Thus, the evaluation of tight oil is an important aspect of the pre-refining examination of the oil as a refinery feedstock as well as for direct use of the oil as a fuel.

Evaluation, in this context, is the determination of the physical and chemical characteristics of crude oil, heavy oil, and tar sand bitumen since the yields and properties of products or factions produced from these feedstocks vary considerably and are dependent on the concentration of the various types of hydrocarbon derivatives as well as the amounts of the heteroatom compounds (i.e., molecular constituents contacting nitrogen and/or oxygen and/or sulfur and/or metals). Some types of feedstocks have economic advantages as sources of fuels and lubricants with highly restrictive characteristics because they require less specialized processing than that needed for production of the same products from many types of crude oil. Others may contain unusually low concentrations of components that are desirable fuel or lubricant constituents, and the production of these products from such crude oils may not be economically feasible.

Since tight oil exhibits a wide range of physical properties, it is not surprising the behavior of various feedstocks in these refinery operations is not simple. The atomic ratios from ultimate analysis can give an indication of the nature of a feedstock and the generic hydrogen requirements to satisfy the refining chemistry, but it is not possible to predict with any degree of certainty how the feedstock will behave during refining. Any deductions made from such data are pure speculation and are open to much doubt.

For example, the content of the oil that can be distilled at atmospheric pressure may approach 80% v/v of the tight oil while the amount of residuum may be as low as 5% v/v. In addtion, the wax content of tight oil may be high − resulting from a high content of n-paraffin derivatives. Thus, blending of tight oil and/or products derived from tight oil or requires attention because of the potential for incompatibility of the constituents of the blend (Chapter 17). Also, safety precautions must be taken during all stages of the handling of tight oil because of a high content of methane-to-butane (CH_4, C_2H_6, C_3H_8, C_4H_{10}) hydrocarbons (Olsen, 2015).

Most refineries process many different crudes and the coastal refineries of the United States may process 50 or more different crude oils over the course of a year (Olsen, 2015). Each crude oil requires slightly different processing conditions in the major process units. Typically, a refinery is designed to process crude oil of a particular composition and produce products with specified properties, with some flexibility based on the capabilities of equipment such as pumps, heat exchangers, and the particular catalysts within the reactors. Refiners try to match the crude oil composition to the configuration of the refinery, usually by blending two or more crude oils, if a single crude oil with the required composition is not available or economical.

Recall (Chapter 1, Chapter 10), the American Petroleum Institute (API) gravity is a specific gravity scale developed by the oil industry to classify crude oils and other petroleum liquids based on their relative densities. It is expressed in degrees (°API), and is an inverse measure of the relative density of a petroleum product and the density of water. Light crude oil has an API gravity higher than 31° API, medium crude oil has an API gravity between 20° and 31°, and heavy crude has an API gravity below 20°. Tight oils have an API gravity on the order of 40−45° and with a sulfur content less than 0.5% w/w fall into the light and sweet (low-sulfur) category.

Hydroprocessing of naphtha from tight oil is often necessary to increase octane number as well as the octane number of the middle distillates to attain the necessary cold flow properties that are required for diesel fuel. In addition, hydroprocessing of the residuum from tight oil yields additional naphtha and middle distillates. Because of a great variability in properties, the pre-treatment of the tight oil feedstocks of feeds may be necessary to minimize any potential adverse effects on catalysts. Hydroisomerization is the principal reaction during the hydroprocessing of the atmospheric distillates while hydrocracking and ring opening are the principal reactions during the hydroprocessinf of resids from tight oil.

In addition, the chemical composition of a feedstock is also an indicator of refining behavior (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2015; Hsu and Robinson, 2017; Speight, 2017). Whether the composition is represented in terms of compounds types or in terms of generic compound classes, it can enable the refiner to determine the nature of the reactions. Hence, chemical composition can play a large part in determining the nature of the products that arise from the refining operations. It can also play a role in determining the means by which a particular feedstock should be processed (Parkash, 2003; Gary et al., 2007; Speight, 2014; Hsu and Robinson, 2006; Speight, 2017).

Therefore, the judicious choice of a crude oil to produce any given product is just as important as the selection of the product for any given purpose. Thus, initial inspection of the nature of the tight oil will provide deductions related to the most logical means of refining. Indeed, careful evaluation of tight oil from physical property data is a major part of the initial study of any tight oil destined as a refinery feedstock. Proper interpretation of the data resulting from the inspection of crude oil requires an understanding of their significance.

Tight oil exhibits a wide range of physical properties and several relationships can be made between various physical properties (Speight, 2001). Whereas the properties such as viscosity, density, boiling point, and color of tight oil may vary widely, the ultimate or elemental analysis varies, as already noted, over a narrow range for a large number of tight oil samples. The carbon content is relatively constant, while the hydrogen and heteroatom contents are responsible for the major differences between tight oil. Coupled with the changes brought about to the feedstock constituents by refinery operations, it is not surprising that tight oil characterization is a monumental task.

Although it is possible to classify refinery operations using the three general terms: (1) separation, (2) conversion, and (3) finishing, the chemical composition of a feedstock is a much truer indicator of refining behavior. Whether the composition is represented in terms of compounds types or in terms of generic compound classes, it can enable the refiner to determine the nature of the reactions. Hence, chemical composition can play a large part in determining the nature of the products that arise from the refining operations. It can also play a role in determining the means by which a particular feedstock should be processed (Wallace et al., 1988; Wallace et al., 1988; Speight, 2001, 2014a, 2017; Parkash, 2003; Gary et al., 2007, 2015; Hsu and Robinson, 2017).

The physical and chemical characteristics of crude oils and the yields and properties of products or factions prepared from them vary considerably and are dependent on the concentration of the various types of hydrocarbon derivatives and minor constituents present. Some types of tight oil have economic advantages as sources of fuels and lubricants with highly restrictive characteristics because they require less specialized processing than that needed for production of the same products from many types of crude oil. Others may contain unusually low concentrations of components that are desirable fuel or lubricant constituents, and the production of these products from such crude oils may not be economically feasible.

Evaluation of tight oil for use as a feedstock usually involves an examination of one or more of the physical properties of the material. By this means, a set of basic characteristics can be obtained that can be correlated with utility. The physical properties of tight oil and tight oil products are often equated with those of the hydrocarbon derivatives for although tight oil is indeed a very complex mixture, there is gasoline, produced by nondestructive distillation, in which fewer than a dozen hydrocarbon derivatives make up at least 50% of the material (Speight, 2014a, 2015).

To satisfy specific needs with regard to the type of tight oil to be processed, as well as to the nature of the product, most refiners have, through time, developed their own methods of tight oil analysis and evaluation. However, such methods are considered proprietary and are not normally available. Consequently, various standards organizations, such as the American

Society for Testing and Materials in North, which has devoted considerable time and effort to the correlation and standardization of methods for the inspection and evaluation of tight oil and tight oil products. A complete discussion of the large number of routine tests available for tight oil fills an entire book (Speight, 2015). However, it seems appropriate that in any discussion of the physical properties of crude oil and crude oil products reference be made to the corresponding test, and accordingly, the various test numbers have been included in the text.

Typical of the crude oil from tight formations (*tight oil – tight light oil, and tight shale oil* have been suggested as alternate terms) is the Bakken crude oil which is a light highly volatile crude oil. Briefly, Bakken crude oil is a light sweet (low-sulfur) crude oil that has a relatively high proportion of volatile constituents. The production of the oil also yields a significant amount of volatile gases (including propane and butane) and low-boiling liquids (such as pentane and natural gasoline), which are often referred to collectively as (low-boiling or light) naphtha. By definition, natural gasoline (sometimes also referred to as *gas condensate*) is a mixture of low-boiling liquid hydrocarbon derivatives isolate from crude oil and natural gas wells suitable for blending with light naphtha and/or refinery gasoline (Mokhatab et al., 2006; Speight, 2014a). Because of the presence of low-boiling hydrocarbon derivatives, low-boiling naphtha (*light naphtha*) can become extremely explosive, even at relatively low ambient temperatures. Some of these gases may be burned off (flared) at the field well-head, but others remain in the liquid products extracted from the well (Speight, 2014a).

Oil from tight shale formation is characterized by low-asphaltene content, low-sulfur content and a significant molecular weight distribution of the paraffinic wax content (Speight, 2014a, 2015a). Paraffin carbon chains of C_{10} to C_{60} have been found, with some shale oils containing carbon chains up to C_{72}. Finally, the properties of tight oil are highly variable. Density and other properties can show wide variation, even within the same field. The Bakken crude is light and sweet with an API of 42° and a sulfur content of 0.19% w/w. Similarly, Eagle Ford is a light sweet feed, with a sulfur content of approximately 0.1% w/w and with published API gravity between 40° API and 62° API.

It is the purpose of this chapter to present an outline of the tests that may be applied to crude oil, heavy oil, and tar sand bitumen as well as too their respective products or even crude oil product as well as the resulting chemical properties and physical properties from which a feedstock or product can be evaluated (Speight, 2014a, 2015). For this purpose, data relating to various chemical physical properties have been included as illustrative examples, but theoretical discussions of the physical properties of hydrocarbon derivatives were deemed irrelevant and are omitted. For the most part, and to forgo the potential for repetition, the test methods employed to determine the properties of naphtha can be applied to the determination of the properties of tight oil.

3. Crude oil assay

Crude oil exhibits wide variations in composition and properties, and these occur not only in crude oil from different fields but also in oils taken from different production depths in the

TABLE 9.1 Suggested analytical inspections for conventional crude oil compared to the requirements for heavy feedstocks.

Crude oil	*Heavy feedstocks/resids*
Composition	Composition
Carbon, % w/w	Carbon, % w/w
Hydrogen, % w/w	Hydrogen, % w/w
Sulfur, % w/w	Sulfur, % w/w
Nitrogen, % w/w	Nitrogen, % w/w
	Nickel, ppm
	Vanadium, ppm
	Iron, ppm
	Ash, % w/w
Wax content	
	Asphaltenes, %w/w
	Resins, % w/w
	Aromatics, % w/w
	Saturates, % w/w
Physical properties	Physical properties
Carbon residue, % w/w[a]	Carbon residue, % w/w
Density/specific gravity/API gravity	Density/specific gravity/API gravity
Distillation profile	Distillation profile
Pour point	Pour point
Viscosity	Viscosity
Wax appearance point	

[a] *of the residuum*

same well. Historically, physical properties such as boiling point, density (gravity), and viscosity have been used to describe crude oil but the needs are even more extensive as increased amounts of viscous feedstocks are introduced into refineries (Table 9.1).

Crude oil analysis involves not only determining the composition of the material under investigations but, more appropriately, determining the suitability of the crude oil for refining or the product for use. In this sense, the end product of crude oil analysis or (testing) is a series of data that allow the investigator to *specify* the character and quality of the material under investigation. Thus, a series of specifications are determined for crude oil and its products.

Because of the differences in crude oil composition, the importance of the correct sampling of crude oil that contains low-boiling hydrocarbon derivatives cannot be over-estimated.

Properties such as specific gravity, distillation profile, vapor pressure, hydrogen sulfide content, and octane number of gasoline are affected by the low-boiling hydrocarbon content so that suitable cooling or pressure sampling methods have to be used and care taken during the subsequent handling of the oil in order to avoid the loss of any volatile constituents. In addition, adequate records of the circumstances and conditions during sampling have to be made. For example, sampling from oilfield separators, the temperatures and pressures of the separation plant, and the atmospheric temperature should be noted.

Hence, the production of data focuses on (i) measurement, (ii) accuracy, (iii) precision, and (iv) method validation. All of which depend upon the sampling protocols that were used to obtain the sample. Without strict sampling protocols, variation and loss of accuracy (or precision) must be anticipated. For example, correct sampling of the product in storage or carrier tanks is important in order to obtain a representative sample for the laboratory tests which are essential in converting measured quantities to the standard volume.

Elemental analyses of crude oil show that it contains mainly carbon and hydrogen. Nitrogen, oxygen, and sulfur (heteroelements) are present in smaller amounts and also trace elements such as vanadium, nickel etc. Of the heteroelements, sulfur is the most important. The mixture of hydrocarbon derivatives is highly complex. Paraffinic, naphthenic, and aromatic structures can occur in the same molecule and the complexity increases with boiling range. The attempted classification of crude oils in terms of these three main structural types has proved inadequate.

3.1 Assay

An assay, as the term is used in the crude oil industry, is the application of a series of test to crude oil, heavy oil, extra heavy oil, or tar sand bitumen that present data upon which the character and processability of the feedstock can be estimated (Table 9.1). Since crude oil is a naturally occurring mixture of hydrocarbon derivatives, generally in a liquid state, that may also include compounds of sulfur, nitrogen, oxygen, metals, and other elements (ASTM D4175). Consequently, it is not surprising that crude oil can vary in composition properties and produce wide variations in refining behavior as well as product properties. Thus, a feedstock assay is a necessary preliminary step before refining.

The crude oil being processed in refineries is becoming increasingly heavier (higher amounts of residuum) and higher sulfur content) (Speight, 1999; 2002 and references cited therein). Market demand (*market pull*) dictates that *residua* must be upgraded to higher value products (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017; Hsu and Robinson, 2017). In short, the value of crude oil depends upon its quality for refining and whether or not a product slate can be obtained to fit market demand.

Thus, process units in a refinery require analytical test methods that can adequately evaluate feedstocks and monitor product quality. In addition, the high sulfur content of crude oil and regulations limiting the maximum sulfur content of fuels makes sulfur removal a priority in refinery processing. Here again, analytical methodology is key to the successful determination of the sulfur compound-types present and their subsequent removal.

Upgrading residua involves processing (usually conversion) into a more salable, higher valued product. Improved characterization methods are necessary for process design, crude oil evaluation, and operational control. Definition of the boiling range and the hydrocarbon-type distribution in high-boiling distillates and in residua is increasingly important. Feedstock analysis to provide a quantitative boiling range distribution (that accounts for non-eluting components) as well as the distribution of hydrocarbon types in gas oil and higher boiling materials is important in evaluating feedstocks for further processing.

Sulfur reduction processes are sensitive to both amount and structure of the sulfur compounds being removed. Tests that can provide information about both are becoming increasingly important and analytical tests that provide information about other constituents of interest (e.g., nitrogen, organometallic constituents) are also valuable and being used for characterization.

But before emerging into the detailed aspects of crude oil analysis, it is necessary to understand the nature and character of crude oil as well as the methods used to produce crude oil products. This will present to the reader the background that is necessary to understand crude oil and the processes used to convert it to products. The details of the chemistry are not presented here and can be found elsewhere (Speight, 2014a, 2017).

Elemental analyses of crude oil shows that the major constituents are carbon and hydrogen with smaller amounts of sulfur (0.1−8% w/w), nitrogen (0.1−1.0% w/w), and oxygen (0.1−3% w/w) and trace elements such as vanadium, nickel, iron, and copper present at the part-per-million (ppm) level. Of the non-hydrocarbon (heteroelements) elements, sulfur is the most abundant and often considered the most important by refiners. However, nitrogen and the trace metals also have deleterious effects on refinery catalysts and should not be discounted because of relative abundance. Process units that have, for example, a capacity of 50,000 bbl/day and which are in operation continuously can soon reflect the presence of the trace elements. The effects of oxygen, which also has an effect on refining catalysts, has received somewhat less study than the other heteroelements but remains equally important in refining.

Petroleum suitability for refining (to produce a slate of predetermined products) is determined by application of a series of analytical methods (Speight, 2014a) that provide information that is sufficient to assess the potential quality of the crude oil as a feedstock and also to indicate whether any difficulties might arise in handling, refining, or transportation. Such information may be obtained either by: (i) a preliminary assay of crude oil or by (ii) a full assay of crude oil that involves presentation of a true boiling point curve and the analysis of fractions throughout the full range of crude oil.

Moreover, the suitability of a crude oil product for a specific use cannot be assumed and the suitability must be determined by a sequence of analytical test data which must be in agreement with (or within the range of) the data presented as part of the specifications. Thus, an efficient assay is derived from a series of test data that give an accurate description of crude oil quality and crude oil product quality and allow an indication of its behavior during refining or service. The first step is, of course, to assure adequate (correct) sampling by use of the prescribed protocols (ASTM D4057).

Thus, analyses are performed to determine whether each batch of crude oil received at the refinery or each batch of the product is suitable for refining purposes or for the designated use. The tests are also applied to determine if there has been any contamination during storage or transportation that may increase the processing difficulty (cost). The information required is generally specific to a particular refinery and is also a function of refinery operations and desired product slate.

To obtain the necessary information, two different analytical schemes are commonly used and these are: (i) an inspection assay and (ii) a comprehensive assay.

Inspection assays usually involve determination of several key bulk properties of the sample (such as API gravity, sulfur content, pour point, and distillation range) as a means of determining if *major* changes in characteristics have occurred since the last comprehensive assay was performed. For example, a more detailed inspection assay might consist of the following tests: API gravity (or density or relative density), sulfur content, pour point, viscosity, salt content, water and sediment content, trace metals (or organic halides). The results from these tests − as well as the archived data from a comprehensive assay − provide an estimate of any changes that have occurred in the crude oil that may be critical to refinery operations. Inspection assays are routinely performed on all crude oils received at a refinery.

On the other hand, the comprehensive (or full) assay is more complex (as well as time-consuming and costly) and is usually only performed only when a new field comes on stream, or when the inspection assay indicates that significant changes in the composition of the crude oil have occurred. Except for these circumstances, a comprehensive assay of a particular crude oil stream may not (unfortunately) be updated for several years.

The amount of the individual low-boiling hydrocarbon derivatives in crude oil (methane to butane or pentane) is often included as part of the preliminary assay. For safety reasons, it is essential to know the content of low-boiling hydrocarbon derivatives in crude oil prior to handling and shipping the crude oil. For example, Bakken crude oil is a low-boiling sweet (low-sulfur) crude oil that has a relatively high proportion of volatile constituents. The production of the oil yields not only crude oil but also a significant amount of volatile gases (including propane and butane) and low-boiling liquids (such as pentane and natural gasoline), which are often referred to collectively as (low-boiling or low-boiling) naphtha. By definition, natural gasoline (sometime also referred to as *gas condensate*) is a mixture of low-boiling liquid hydrocarbon derivatives isolate from crude oil and natural gas wells suitable for blending with low-boiling naphtha and/or refinery gasoline (Mokhatab et al., 2006; Speight, 2014a, 2019). Because of the presence of low-boiling hydrocarbon derivatives, low-boiling naphtha can become extremely explosive, even at relatively low ambient temperatures. Some of these gases may be burned off (flared) at the field well-head, but others remain in the liquid products extracted from the well (Speight, 2014a).

Although one of the more conventional distillation procedures might be employed, the determination of low-boiling hydrocarbon derivatives in crude oil is best is carried out using a gas chromatographic method (ASTM D2427).

Crude oil assays often include nickel and vanadium contents due to the detrimental effects of these metals on catalysts used in cracking and desulphurization processes. Knowledge of the metal content of a feedstock or product (ASTM D5185) can provide information on both the potential problem that can occur during refining as well as the performance of a metal-containing product.

3.2 Specifications

A *feedstock specification* or *product specification* is the data that give adequate control of feedstock behavior in a refinery or product quality. More accurately, the specifications are derived from the set of tests and data limits applicable to the crude oil or to a finished product in order to ensure that every batch is of satisfactory and consistent quality at release for sales. The specifications should include all critical parameters in which variations would be likely to affect the safety and in-service use of the product − they are, in fact, part of the assay.

Often, the specifications against which a finished product is tested before release for sale are referred to as the *batch release specifications*. These are the product data against which the finished product is tested to ensure satisfactory quality. If the product should be in-service before a certain date, the purchases will be advised (by law) through a note on the product of the *expiry specifications* and the product, if tested at any time within the functional life period must comply with the requirements in the expiry specifications.

In terms of the whole crude oil, a specification offers the luxury of *predictability* of feedstock behavior in a refinery or *predictability* of product quality (therefore, product behavior) relative to market demand. Ultimately, feedstock behavior and/or product quality is judged by the by an assessment of performance. And it is *performance* that is the ultimate criterion of quality. It is therefore necessary to determine those properties, the values of which can be established precisely and relatively simply by inspection tests in a control laboratory, that correlate closely with the important performance properties.

The value of crude oil to a refiner depends upon its quality and whether he can economically obtain a satisfactory product pattern that matches market demand (*market pull*). In the main, the refiner is not concerned with the actual chemical nature of the material but in methods of analysis which would provide information sufficient to assess the potential quality of the oil, to supply preliminary engineering data, and also to indicate whether any difficulties might arise in handling, refining, or transporting crude oil or its products. Such information may be obtained in one of two ways: (i) inspection data from a preliminary assay, and (ii) inspection data from a full assay, which involves the derivation of a true boiling point curve and the analysis of fractions and product blends throughout the full range of the crude oil.

The *preliminary assay* provides general data on the oil and is based on simple tests such as distillation range, water content, specific gravity, and sulfur content that enable desirable or undesirable features to be noted. This form of assay requires only a small quantity of sample and is therefore particularly useful for the characterization of oilfield samples produced from cores, drill stem tests or seepages.

The tests in the preliminary assay are relatively simple and can be completed in a short time and generally on a routine basis. This assay gives a useful general picture of the quality of crude oil but it does not cover the work necessary to provide adequate data, for example, for the design of refinery equipment, nor does it produce a sufficient quantity of the various products from the crude so that they can be examined for quality. A *full assay* of crude oil is based on a true boiling point distillation of the crude, and sufficient data are obtained to assess the yields and properties of the straight run products, covering low-boiling hydrocarbon derivatives, middle and high-boiling distillate, lubricants, residual fuel oil, and residuum. Often, both the middle-ground is reached between the preliminary assay and the full assay but the requirements may also be feedstock dependent (Table 9.1).

Sometimes the inspection tests attempt to measure these properties, for example the carbon residue of a feedstock that is an approximation of the amount of the thermal coke that will be formed during refining. Or, a research octane number test that was devised to measure performance of motor fuel. In other cases the behavior must be determined indirectly from a series of test results.

The carbon residue of crude oil and crude oil products serve as an indication of the propensity of the sample to form carbonaceous deposits (thermal coke) under the influence of heat.

Tests for Conradson carbon residue (ASTM D189, IP 13), the Ramsbottom carbon residue (ASTM D524, IP 14), the microcarbon carbon residue (ASTM D4530, IP 398), and asphaltene content (ASTM D893, ASTM D2007, ASTM D3279, ASTM D4124, ASTM D6560, IP 143) are sometimes included in inspection data on crude oil. The data give an indication of the amount of coke that will be formed during thermal processes as well as an indication of the amount of high boiling constituents in crude oil.

The determination of the *carbon residue* of crude oil or a crude oil product is applicable to relatively nonvolatile samples that decompose on distillation at atmospheric pressure. Samples that contain ash-forming constituents will have an erroneously high carbon residue, depending upon the amount of ash formed. All three methods are applicable to relatively non-volatile crude oil products that partially decompose on distillation at atmospheric pressure. Crude oils having a low carbon residue may be distilled to a specified residue and the carbon residue test of choice then applied to the residue.

In the Conradson carbon residue test (ASTM D189, IP 13), a weighed quantity of sample is placed in a crucible and subjected to destructive distillation for a fixed period of severe heating. At the end of the specified heating period, the test crucible containing the carbonaceous residue is cooled in a desiccator and weighed and the residue is reported as a percentage (% w/w) of the original sample (Conradson carbon residue).

In the Ramsbottom carbon residue test (ASTM D524, IP 14), the sample is weighed into a glass bulb that has a capillary opening and is placed into a furnace (at 550 °C, 1020 °F). The volatile matter is distilled from the bulb and the non-volatile matter that remains in the bulb cracks to form thermal coke. After a specified heating period, the bulb is removed from the bath, cooled in a desiccator, and weighed to report the residue (Ramsbottom carbon residue) as a percentage (% w/w) of the original sample.

In the microcarbon residue test (ASTM D4530, IP 398), a weighed quantity of the sample placed in a glass vial is heated to 500 °C (930 °F) under an inert (nitrogen) atmosphere in a controlled manner for a specific time and the carbonaceous residue [*carbon residue (micro)*] is reported as a percent (% w/w) of the original sample.

The data produced by the microcarbon test (ASTM D4530, IP 398) are equivalent to those by Conradson Carbon method (ASTM D189 IP 13). However, this microcarbon test method offers better control of test conditions and requires a smaller sample. Up to twelve samples can be run simultaneously. This test method is applicable to crude oil and to crude oil products that partially decompose on distillation at atmospheric pressure and is applicable to a variety of samples that generate a range of yields (0.01% w/w to 30% w/w) of thermal coke.

As noted, in any of the carbon residue tests, ash-forming constituents (ASTM D482) or nonvolatile additives present in the sample will be included in the total carbon residue reported leading to higher carbon residue values and erroneous conclusions about the coke-forming propensity of the sample.

The asphaltene fraction (ASTM D893, ASTM D2007, ASTM D3279, ASTM D4124, ASTM D6560, IP 143) is the highest molecular weight and most complex fraction in crude oil.

The yield of the asphaltene fraction gives an indication of the amount of coke that can be expected during processing (Speight, 2014a, 2017).

In any of the methods for the determination of the asphaltene content, the crude oil or product (such as asphalt) is mixed with a large excess (usually >30 vol hydrocarbon per volume of sample) low-boiling hydrocarbon such as *n*-pentane or *n*-heptane. For an extremely viscous sample, a solvent such as toluene may be used prior to the addition of the low-boiling hydrocarbon but an additional amount of the hydrocarbon (usually >30 vol hydrocarbon per volume of solvent) must be added to compensate for the presence of the solvent. After a specified time, the insoluble material (the asphaltene fraction) is separated (by filtration) and dried. The yield is reported as percentage (% w/w) of the original sample.

It must be recognized that, in any of these tests, different hydrocarbon derivatives (such as *n*-pentane or *n*-heptane) will give different yields of the asphaltene fraction and if the presence of the solvent is not compensated by use of additional hydrocarbon the yield will be erroneous. In addition, if the hydrocarbon is not present in large excess, the yields of the asphaltene fraction will vary and will be erroneous (Speight, 1999).

The *precipitation number* is often equated to the asphaltene content but there are several issues that remain obvious in its rejection for this purpose. For example, the method to determine the precipitation number (ASTM D91) advocates the use of naphtha for use with black oil or lubricating oil and the amount of insoluble material (as a % v/v of the sample) is the precipitating number. In the test, 10 mL of sample is mixed with 90 mL of ASTM-specified precipitation naphtha (that may or may not have a constant chemical composition) in a graduated centrifuge cone and centrifuged for 10 min at 600–700 rpm. The volume of material on the bottom of the centrifuge cone is noted until repeat centrifugation gives a value within 0.1 mL (the precipitation number). Obviously, this can be substantially different from the yield of the asphaltene fraction.

For clarification, it is necessary to understand the basic definitions that are used to define the density of crude oil. This, the *density* is the mass of liquid per unit volume at 15 °C, whereas the *relative density* is the ratio of the mass of a given volume of liquid at 15 °C to the mass of an equal volume of pure water at the same temperature, and the *specific gravity* is the same as the relative density and the terms are used interchangeably.

Density (ASTM D1298, IP 160) is an important property of crude oil products since crude oil and especially crude oil products are usually bought and sold on that basis or if on volume basis then converted to mass basis via density measurements. This property is almost synonymously termed as density, relative density, gravity, and specific gravity, all terms related to each other. Usually a hydrometer, pycnometer or more modem digital density meter is used for the determination of density or specific gravity (ASTM 2013; Speight, 2014a).

In the most commonly used method (ASTM D1298, IP 160), the sample is brought to the prescribed temperature and transferred to a cylinder at approximately the same temperature. The appropriate hydrometer is lowered into the sample and allowed to settle and, after temperature equilibrium has been reached, the hydrometer scale is read and the temperature of the sample is noted.

Although there are many methods for the determination of density due to the different nature of crude oil itself and the different products, one test method (ASTM D5002) is used for the determination of the density or relative density of crude oil that can be handled in a normal fashion as liquids at test temperatures between 15 and 35 °C (59 and 95 °F). This test method applies to crude oil oils with high vapor pressures provided appropriate precautions are taken to prevent vapor loss during transfer of the sample to the density analyzer. In the method, approximately 0.7 mL of crude oil sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in mass of the tube is used in conjunction with calibration data to determine the density of the sample.

Another test determines density and specific gravity by means of a digital densimeter (ASTM D4052, IP 365). In the test, a small volume (approximately 0.7 mL) of liquid sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample. The test is usually applied to of crude oil, crude oil distillates, and crude oil products that are liquids at temperatures between 15 and 35 °C (59 and 95 °F) that have vapor pressures below 600 mm Hg and viscosities below about 15,000 cSt at the temperature of test. However, the method should not be applied to samples so dark in color that the absence of air bubbles in the sample cell cannot be established with certainty.

Accurate determination of the density or specific gravity of crude oil is necessary for the conversion of measured volumes to volumes at the standard temperature of 15.56 °C (60 °F) (ASTM D1250, IP 200). The specific gravity is also a factor reflecting the quality of crude oils.

The accurate determination of the API gravity of crude oil and its products is necessary for the conversion of measured volumes to volumes at the standard temperature of 60 °F (15.56 °C). Gravity is a factor governing the quality of crude oils. However, the gravity of a crude oil product is an uncertain indication of its quality. Correlated with other properties, gravity can be used to give approximate hydrocarbon composition and heat of combustion. This is usually accomplished through use of the API gravity that is derived from the specific gravity:

$$\text{API gravity, API} = (141.5/\text{sp gr } 60/60^{\circ}\text{F}) - 131.5$$

The API gravity is also is also an important measure for estimating the quality and refinability of crude oil.

API gravity or density or relative density, can be determined using one of two hydrometer methods (ASTM D287, ASTM D1298). The use of a digital analyzer (ASTM D5002) is finding increasing popularity for the measurement of density and specific gravity.

In the method (ASTM D287), the API gravity is determined using a glass hydrometer for crude oil and crude oil products that are normally handled as liquids and that have a Reid vapor pressure of 26 psi (180 kPa) or less. The API gravity is determined at 15.6 °C (60 °F), or converted to values at 60 °F, by means of standard tables. These tables are not applicable to nonhydrocarbon derivatives or essentially pure hydrocarbon derivatives such as the aromatics.

This test method is based on the principle that the gravity of a liquid varies directly with the depth of immersion of a body floating in it. The API gravity is determined using a hydrometer by observing the freely floating API hydrometer and noting the graduation nearest to the apparent intersection of the horizontal plane surface of the liquid with the vertical scale of the hydrometer, after temperature equilibrium has been reached. The temperature of the sample is determined using a standard test thermometer that is immersed in the sample or from the thermometer that is an integral part of the hydrometer (thermohydrometer).

4. Chemical and physical properties

The world of crude is changing due to the appearance of significant supplies of tight oil and other highly variable feedstock. In addition to becoming increasingly abundant as compared to traditional feedstock, these opportunity crudes may be discounted and so cannot be ignored. Because their properties are so variable, an old-style crude assay does not make sense. Hence, the need is for real-time analysis to provide the data for *ad-hoc* blending of crude supplies and intelligent process control. Together these can make a solution. Given the reality of the world refineries face today, it is important that such optimization solutions be implemented. It is also important that when this is done, it must be backed by deep expertise, as this is the best way to successfully handle a complex and changing situation.

Because of the influx of light sweet crude oil from tight formations, the nature of crude is changing and the refining industry must change with it. At one time, oil wells could be adequately characterized by a crude assay that would change only slowly with time and, thus, refineries could count on fairly stable feedstock. That is no longer the case, with the arrival of light sweet crude oil from tight formations has been the driver in a wider variability of refinery feedstocks. Dealing with this situation requires three components: (i) an ability to do accurate, on-the fly, rapid analysis, (ii) the capability to adjust feedstock blending as needed, and (iii) smart process control to achieve the best possible processing.

The chemical composition of crude oil and crude oil products is complex (Chapter 1) which makes it essential that the most appropriate analytical methods are selected from a comprehensive list of methods and techniques that are used for the analysis of samples (Dean, 1998; Miller, 2000; Budde, 2001; Speight, 2001, 2014a, 2005; Speight and Arjoon, 2012). Furthermore, samples may be disturbed during sampling, storage and pre-treatment. Also, most laboratory experiments impose steady environmental conditions while in an outdoor climate these conditions show dynamic behavior (Speight and Arjoon, 2012). However, the manner in which the corrections are applied must be beyond reproach or claims of falsification of the data will be the most likely result (Speight and Foote, 2011).

In the early days of crude oil processing there was not the need to understand the character and behavior of crude oil in the detail that is currently required. Refining was relatively simple and involved distillation of the valuable kerosene fraction that was then sold as an illuminant. After the commercialization of the internal combustion engine, the desired product became gasoline and it was also obtained by distillation. Even when crude oil that contained little natural gasoline was used, cracking (i.e. thermal decomposition with simultaneous removal of distillate) became the *modus operandi*.

However, with the startling demands on the crude oil industry during, and after World War II, and the emergence of the age of petrochemicals and plastics, the crude oil industry needed to produce materials not even considered as products in the decade before the war. Thus, crude oil refining took on the role of technological innovator as new and better processes were invented and advances in the use of materials for reactors were developed. In addition, there became a necessity to find out more related to crude oil so that refiner might be able to enjoy the luxury of predictability and plan a product slate that was based on market demand. A difficult task when the character of the crude oil was unknown! The idea that crude oil refining should be a *hit and miss* affair was not acceptable.

The processing of crude oil requires not only knowledge of its chemical and physical properties but also knowledge of its chemical and physical reactivity. The former is dealt with in this chapter the latter, because of the structure of crude oil, is dealt with elsewhere in this book (Chapter 18). Because crude oil varies markedly in its properties and composition according to the source, it also varies in its chemical and physical reactivity. Thus, knowledge of crude oil reactivity is required for optimization of existing processes as well as for the development and design of new processes.

For example, valuable information can be obtained from the true boiling point (TBP) curve which is a function of percent weight distilled and temperature, that is, a boiling point distribution (Speight, 2001, 2014a). However, the boiling range does not convey much detail related to the chemical reactivity of crude oil. In addition to the boiling point distribution, it is possible to measure bulk physical properties, such as specific gravity and viscosity that have assisted in the establishment of certain empirical relationships for crude oil processing from the *true boiling point* curve. Many of these relationships include assumptions that are based on experience with a range of feedstocks. However, the chemical aspects of refining feedstocks that contain different proportions of chemical species emphasizes the need for more definitive data that would enable more realistic predictions to be made of crude oil behavior in refinery operations.

Thus, this chapter presents some of the methods that are generally applied to study the makeup of the feedstock in terms of chemical structures as well as methods that might be preferred for refining. There are, of course, many analytical methods the can be applied to the analysis of crude oil and crude oil products but they vary with sample condition and composition. More specifically, this chapter deals with the more common methods used to define chemical and physical properties of the sample. Any of the methods described herein might also be applied to the analysis of sample for environmental purposes. However, methods for analytical purpose are not intended to be the focus of this text and are described elsewhere (Speight, 2005; Speight and Arjoon, 2012).

Also, this section is a general follow-on from the following chapter (Chapter 10) in which three fractions of tight oil (naphtha, kerosene, and gas oil) were used as possible examples of separate refinery feedstocks and were described in terms of analytical test methods and presents some of the methods that are generally applied to study the makeup of the feedstock in terms of chemical structures as well as methods that might be preferred for refining. There are, of course, many analytical methods the can be applied to the analysis of crude oil and crude oil products but they vary with sample condition and composition. More specifically, this chapter deals with the more common methods used to define chemical and physical properties of the sample. Furthermore, any of the methods described herein might also be applied to the analysis of sample for environmental purposes (Chapter 18).

4.1 Sampling

The composition of any reservoir fluid is determined by acquiring a representative sample of the fluid. Surface samples can be obtained relatively easily by collecting liquid and gas samples from test or production separators after which the samples are recombined in a laboratory. However, the result can be (or more than likely be) unrepresentative of reservoir conditions, particularly when sampling from a gas-condensate reservoir. Some examples of potential problems include (1) recombining the gas and liquid samples at an incorrect ratio, changing production conditions prior to or during sampling and commingling samples from different zones where the samples have different properties. If the liquid content is low when acquiring surface samples, a small loss of the liquid in production tubulars or separators will render the condensate sample unrepresentative of the formation fluid.

On the other hand, samples can also be collected downhole from wellbore fluids in gas-condensate reservoirs or in volatile crude oil reservoirs (such as oil held in tight formations and in shale formations) (Table 9.2), which is practical if the wellbore flowing pressure is above the dew-point pressure, but it is generally not recommended if the pressure anywhere in the tubing is lower than the dew point pressure. If there is two-phase flow in the wellbore, any liquid forming in the tubing during or prior to the sampling may segregate to the bottom of the tubing string-where a bottomhole sampler collects fluids-potentially resulting in an unrepresentative sample with too much of the heavier components. In the case of a highly volatile crude oil (such as the Bakken crude oil) this would give anomalous data which would indicate that the crude is not as volatile (and less dangerous) than it actually is.

In fact, as a result of the complexity (and variation in the composition) of petroleum and the conditions in the reservoir (or deposit), the importance of the correct *sampling* cannot be overstressed (Wallace et al., 1988; Speight, 2014; 2015). Properties such as elemental analysis, metals content, density (specific gravity), and viscosity (to mention only a few properties) are affected by the homogeneity (or heterogeneity) of the sample. In addition, adequate records of the circumstances and conditions during sampling have to be made, for example, in sampling from oilfield separators, the temperatures and pressures of the separation plant and the atmospheric temperature would be noted. An accurate sample handling and storage log should be maintained and should include information such as: (i) the precise source

TABLE 9.2 Typical properties of fluids occurring in tight formations and shale formations.

Constituents (%v/v)	Dry Gas	Wet Gas	Condensate	Volatile Oil[a]
CO_2	0.10	1.41	2.37	1.82
N_2	2.07	0.25	0.31	0.24
C_1	86.12	92.46	73.19	57.60
C_2	5.91	3.18	7.80	7.35
C_3	3.58	1.01	3.55	4.21
Butanes (C_4)	1.72	0.52	2.16	2.84
Pentanes (C_5)	0.50	0.21	1.32	1.48
Hexanes (C_{6+})		0.14	1.09	1.92
Heptanes (C_{7+})		0.82	8.21	22.57

[a] *Representative of Crude Oil from Tight Formations and Tight Shale Formations.*

of the sample, i.e. the exact geographic location or locale from which the sample was obtained, (ii) a description of the means by which the sample was obtained, (iii) the protocols that have been used to store the sample, (iv) chemical analyses, such as elemental composition, (v) physical property analyses, such as API gravity, pour point, and distillation profile, (vi) the standard test methods used to determine the properties in items 4 and 5, and (vii) the number of times that the samples have been retrieved from storage to extract a portion, i.e. indications of the exposure of the sample to the air or to oxygen. Attention to factors such as these enables standardized comparisons to be made when subsequent samples are taken from the stored material.

However, before this occurs there are several protocols involved in initial isolation and cleanup of the sample. In fact, considerable importance attaches to the presence of *water* or *sediment* in crude oil (ASTM D1796, ASTM D4007) for they lead to difficulties during transportation and during refining, e.g. corrosion of pipelines and equipment, uneven running on the distillation unit, blockages in heat exchangers and adverse effects on product quality. Typically, the *sediment* consists of finely divided solids that may be dispersed in the oil or carried in water droplets. The solids may be drilling mud or sand or scale picked up during the transport of the oil, or may consist of chlorides derived from evaporation of brine droplets in the oil. In any event, the sediment can lead to serious plugging of the equipment, corrosion due to chloride decomposition, and a lowering of residual fuel quality.

Water may be found in the crude either in an emulsified form or in large droplets and can cause flooding of distillation units and excessive accumulation of sludge in tanks. The quantity is generally limited by pipeline companies and by refiners, and steps are normally taken at the wellhead to reduce the water content as low as possible. However, water can be introduced during shipment and, in any form, water and sediment are highly undesirable in a refinery feedstock and the relevant tests are regarded as important in crude oil quality examinations. Prior to assay it is sometimes necessary to separate the water from a crude oil sample and this is usually carried out by one of the procedures described in the preliminary distillation of crude oil. In addition, some crude oils and heavy oils forms persistent (difficult-to-break) emulsions which can interfere during testing wax-bearing crude oils for sediment and water insofar as wax suspended in the sample (unless brought into solution prior to the test) will be recorded as sediment.

There is a great variation in the *salt content* of crude oil depending mainly on the source, and possibly on the producing wells or zones within a reservoir or field. In addition, at the refinery, salt water introduced during shipment by tanker may have contributed to this total salt content. These salts have adverse effects on refinery operations especially in increasing maintenance following corrosion in crude units and heat exchangers. It is common practice to monitor wells in a producing field for high salt content, and it is also general practice to desalt the crude at the refinery. The determination of the salt content of crude oil is often made, but as with water and sediment tests, careful sampling is necessary.

4.2 Chemical and physical analyses

The importance of chemical and physical properties is dependent upon the purity of the crude oil or crude oil. In the strictest sense, crude oil and crude oil products are complex chemical mixtures. These mixtures contain hydrocarbon derivatives and non-hydrocarbon compounds that confer properties on the mixture that may not be reflected in the composition. Therefore, it is necessary to apply various text methods to crude oil and crude oil products to determine if the material is suitable for processing and (in the case of the products) for sale with a designated use in mind. The more common tests are introduced in the following sub-sections − these tests are presented in alphabetical order with no preference given to any particular test method.

4.2.1 Boiling point distribution

In the crude oil refining industry, boiling range distribution data are used (i) to assess crude oil crude quality before purchase, (ii) to monitor crude oil quality during transportation, (iii) to evaluate crude oil for refining, and (iv) to provide information for the optimization of refinery processes.

Traditionally, boiling range distributions of the various fractions have been determined by distillation. Yield-on-crude data are still widely reported in the crude oil assay literature, providing information on the yield of specific fractions obtained by distillation. To some extent in the laboratory, atmospheric and vacuum distillation techniques have largely been replaced by *simulated* distillation methods, which use low resolution gas chromatography and correlate retention times to hydrocarbon boiling points.

The distillation tests give an indication of the types of products and the quality of the products that can be obtained from the crude oil and the tests are used to compare different crude oil through the yield and quality of the 300 °C (570 °F) residuum fraction. For example, the waxiness or viscosity of this fraction gives an indication of the amount, types, and quality of the residual fuel that can be obtained from the crude oil. In this respect, the determination of the aniline point (ASTM D611, IP 2) can be used to determine the aromatic or aliphatic character of crude oil. Although not necessarily the same as the wax content, correlative relationships can be derived from the data.

The basic method of distillation (ASTM D86) is one of the oldest methods in use since the distillation characteristics of hydrocarbon derivatives have an important effect on safety and performance, especially in the case of fuels and solvents. The boiling range gives information on the composition, the properties, and the behavior of crude oil and derived products during storage and use. Volatility is the major determinant of the tendency of a hydrocarbon mixture to produce potentially explosive vapors. Several methods are available to define the distillation characteristics of crude oil and its various crude oil products. In addition to these physical methods, other test methods based on gas chromatography are also used to derive the boiling point distribution of a sample (ASTM D2887, ASTM D3710, ASTM D6352).

In the preliminary assay of crude oil the method of distillation is often used to give a rough indication of the boiling range of the crude (ASTM D2892, IP 123). The test method is used for the distillation of stabilized (gases-removed) crude oil to a final cut temperature of up to 400 °C (750 °F) *atmospheric equivalent temperature* (AET). The crude oil is heated and separated by the distillation column into lower-boiling products such as; naphtha and kerosene. The distillate and the residuum can be further examined by tests such as specific gravity (ASTM D1298, IP 160), sulfur content (ASTM D129, IP 61) and viscosity (ASTM D445, IP 71). In fact using a method (ASTM D2569) developed for the determining the distillation characteristics of pitch allows further detailed examination of residua.

In addition to the whole crude oil tests performed as part of the inspection assay, a comprehensive or full assay requires that the crude be fractionally distilled and the fractions characterized by the relevant tests. Fractionation of the crude oil begins with a true boiling point (TBP) distillation employing a fractionating column having an efficiency of 14–18 theoretical plates and operated at a reflux ratio of 5: 1 (ASTM D2892). The TBP distillation may be used for all fractions up to a maximum cut point of about 350 °C atmospheric equivalent temperature (AET) but or low residence time in the still (or reduced pressure) is needed to minimize cracking.

It is often useful to extend the boiling point data to higher temperatures than are possible in the fractionating distillation method previously described, and for this purpose a vacuum distillation in a simple still, with no fractionating column (ASTM D1160) can be carried out. This distillation, which is done under fractionating conditions equivalent to one theoretical plate, allows the boiling point data to be extended to approximately 600 °C (1,110 °F) with many crude oils. This method gives useful comparative and reproducible results that are often accurate enough for refinery purposes, provided significant cracking does not occur.

Usually seven fractions provide the basis for a reasonably thorough evaluation of the distillation properties of the feedstock: (i) gas, boiling range: <15.6 °C/60 °F, (ii) gasoline (low-boiling naphtha), boiling range: 15.6 to 150 °C/60 to 300 °F, (iii) kerosene (medium naphtha), boiling range: 150–230 °C/300 to 450 °F, (iv) gas oil, boiling range: 230–345 °C/450 to 650 °F, (v) low-boiling vacuum gas oil boiling range: 345–370 °C/650 to 700 °F, (vi) high-boiling vacuum gas oil, boiling range: 370–565 °C/700 to 1050 °F, and (vii) residuum, boiling range: >565 °C/1050 °F. From five to fifty liters of crude oil are necessary to complete a full assay, depending on the number of cuts to be taken and the tests to be performed on the fractions.

A more recent test method (ASTM D5236) is seeing increasingly more use and appears to be the method of choice for crude assay vacuum distillations. The method employs a vacuum pot still with a low pressure drop entrainment separator operated under total takeoff conditions. The reduced pressure allows volatilization at a lower temperature than under atmospheric conditions, thus allowing temperatures up to 565 °C (1050 °F) for most samples and which avoids thermal decomposition (cracking) of the oil (caused by prolonged exposure to temperatures in excess of above 350 °C, 650 °F). The test method applies to the higher boiling fractions of crude oil that are in the gas oil and lubricating oil range as well as heavy crude oils and residua.

ASTM D2887 (Standard Test Method for Boiling Range Distribution of Crude oil Fractions by Gas Chromatography) and ASTM D3710 (Standard Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography) use external standards composed of n-alkanes. ASTM D5307 (Standard Test Method for Determination of Boiling Range Distribution of Crude Petroleum oil by Gas Chromatography) is very similar to ASTM D2887 but requires two determinations to be made with each sample, one of which uses an internal standard. The amount of material boiling above 540 °C (above 1000 °F) (reported as residue) is calculated from the differences between the two determinations.

Wiped-wall or thin-film molecular stills can also be used to separate the higher boiling fractions under conditions that minimize cracking. In these units, however, cut points cannot be directly selected, because vapor temperature in the distillation column cannot be measured accurately under operating conditions. Instead, the wall (film) temperature, pressure, and feed rate that will produce a fraction with a given end point are determined from in-house correlations developed by matching yields between the wiped-wall distillation and the conventional distillation (ASTM D1160, ASTM D5236). And wiped-wall stills are often used because they allow higher end points and can easily provide sufficient quantities of the fractions for characterization purposes.

From the point of view of crude oil and crude oil product analysis for environmental purposes, boiling range distributions provide an indication of volatility and component distribution. In addition, boiling range distribution data is also useful for the development of equations for predicting evaporative loss (Speight, 2005; Speight and Arjoon, 2012).

4.2.2 Density, specific gravity, and API gravity

Density is the mass per unit volume of a substance. It is most often reported for oils in units of g/mL or g/cm^3, and less often in units of kg/m$^{3.}$ Density is temperature-dependent. It is an important property of crude oil and crude oil products as it gives the investigator(s) indications of whether or not the contaminant(s) will float on water.

Two density-related properties of crude oil and crude oil products are often used: (i) specific gravity and (ii) American Petroleum Institute (API) gravity. Specific gravity (*relative density*) is the ratio, at a specified temperature, of the oil density to the density of pure water. The API gravity scale (presented as $^{\text{o}}$API) arbitrarily assigns an API gravity of 10$^{\text{o}}$ to pure water. Thus:

$$\text{API} = [141.5 / (\text{specific gravity at } 15.6\,^{\circ}\text{C}) - 131.5]$$

The scale is commercially important for an arbitrary ranking of crude oil quality − heavy oil typically has an API gravity less than 20°; medium crude oil typically has an API gravity in the range 20–35 °API; light oil typically has an API gravity on the order of 35–45° API while, on the other hand, gas condensate and liquid crude oil products can have an API gravity up to 65$^{\text{o}}$.

Crude oil (unless it is a specific heavy oil) and crude oil products (unless it is a residual fuel oil or asphalt) will float on water if the density of the crude oil or crude oil product is less than that of the water. This behavior is typical of all crude oils and distillate products for both salt and fresh water. Some heavy oils, tar sand bitumen, and residual fuel oils may have densities greater than 1.0 g/mL and their buoyancy behavior varies depending on the salinity and temperature of the water (Speight, 2009).

4.2.3 Emulsion formation

A water-in-oil emulsion is a stable dispersion of small droplets of water in oil. When formed from crude oils spilled at sea, these emulsions can have very different characteristics from their parent crude oils. This has important implications for the fate and behavior of the oil and its subsequent cleanup. It is desirable, therefore, to determine if oil is likely to form an emulsion, and if so, whether that emulsion is stable, and the physical characteristics of the emulsion.

In an older test method, the tendency for a crude oil to form a water-in-oil emulsion was measured using a method based on the rotating flask apparatus (Mackay and Zagorski, 1982). All numerical values (mostly ones or zeroes) based on this method have subsequently been reduced to *yes* or *no*, respectively, and indicate the formation (or not) of an emulsion that remained stable 24 h after settling. In a newer variation, the reproducibility is considerably improved and several parameters (i) the water-to-oil ratio, (ii) the fill volume, and (iii) the orientation of the vessels were found to be important parameters affecting emulsion formation.

However, such effects are not lasting. Emulsion formation and behavior is influenced by the oxidation of crude oil constituents (Speight, 2014a). The inclusion of polar functions such as hydroxyl groups (—OH) or carbonyl groups (>C=O) (a result of the oxidation process) causes an increase in the density of the emulsion (relative to the original unoxidized crude oil) and with an increased propensity to form emulsions. As a result, the emulsion and sinks to various depths or even to the seabed, depending on the extent of the oxidation and the resulting density. This may give the erroneous appearance (leading to erroneous deductions with catastrophic consequences) that the crude oil spill (as evidenced from the crude oil remaining on the surface of the water) is less than it actually was. The so-called *missing* oil will undergo further chemical changes and eventually reappear on the water surface or on a distant beach.

4.2.4 Evaporation

Evaporation is the removal of the lower-boiling constituents from crude oil or a crude oil product usually under ambient conditions or, in the current context, under the conditions prevalent at the spill site. The rate of evaporation and loss of oil constituents are of importance for all volatile constituents of crude oil and crude oil products. While standard test methods such as those designated for distillation and vapor pressure determination are often used to determine evaporation properties (ASTM, 2019), test methods for determining evaporation loss are available for higher boiling crude oil products (ASTM D972: Standard Test Method for Evaporation Loss of Lubricating Greases and Oils; ASTM D2595: Standard Test Method for Evaporation Loss of Lubricating Greases Over Wide-Temperature Range). Although not necessarily applicable to crude oil and crude oil products in general, evaporation loss data can be obtained at any temperature in the range from 93 to 315 °C (200 and 600 °F). Viscous samples can be analyzed using a water vaporizer accessory that heats the sample in the evaporation chamber, and the vaporized water is carried into the Karl Fischer titration cell by a dry inert carrier gas.

Crude oil and crude oil products evaporate at a logarithmic rate with respect to time (Fingas, 1998). This is attributed to the overall logarithmic appearance of many components evaporating at different linear rates. Crude oil products with fewer constituents (such as diesel fuel) evaporate at a rate which is square root with respect to time, which is a result of the number of components evaporating. The evaporation process, as evidence by crude oil and crude oil products is not strictly boundary-layer regulated, which is largely a result of the high saturation concentrations of oil components in air and is associated with a high boundary-layer regulated rate. Some volatile crude oils and crude oil products show some effect of boundary-layer regulation at the start of the evaporation process, but after several minutes, evaporation slows because of the loss of the more volatile components, at which point evaporation ceases to be boundary-layer regulated.

It must also be recognized that as evaporation occurs the density and viscosity of the residual crude oil or residual crude oil product increase thereby causing behavioral changes in the contaminant. Such changes could be reflected in an increase in adhesion of the contaminant constituents to the soil or rock.

4.2.5 Fire point and flash point

The *fire point* is the lowest temperature, corrected to one atmosphere pressure (14.7 psi), at which the application of a test flame to the crude oil or crude oil product sample surface causes the vapor of the oil to ignite and burn for at least 5 s. At any time after a spill of crude oil or a crude oil product, fire should always be considered an imminent hazard. Related to fire point, the flash point is a measure of the tendency of the crude oil or a crude oil product to form a flammable mixture with air under controlled laboratory conditions. It is only one of a number of properties that should be considered in assessing the overall flammability hazard of a spilled material (ASTM D92). The ignition temperature (sometimes called the *autoignition temperature*) is the minimum temperature at which the material will ignite without a spark or flame being present. The method of measurement is given by ASTM E659 (Standard Test Method for Autoignition Temperature of Liquid Chemicals). Also related to fire point, the flammability limits of vapor in air is an expression of the percent concentration in air (by volume) is given for the lower and upper limit. These values give an indication of relative flammability. The limits are sometimes referred to as *lower explosive limit* (LEL) and *upper explosive limit* (UEL).

The *flash point* of crude oil or a crude oil product is the temperature to which the sample must be heated to produce a vapor/air mixture above the liquid fuel that is ignitable when exposed to an open flame under specified test conditions. In North America, flash point is used as an index of fire hazard and is an extremely important factor in relation to the safety of spill cleanup operations. Gasoline and other low-boiling liquid fuels can be ignited under most ambient conditions and therefore pose a serious hazard when spilled. Many freshly spilled crude oils also have low flash points until the lower boiling components have evaporated or dispersed.

There are several ASTM methods for measuring the flash point (ASTM D56, ASTM D93 are among the most commonly used. The minimum flash point that can be determined (ASTM D93) is 10 °C (50 °F). On method (ASTM D56) is intended for liquids with a viscosity less than 9.5 cSt at 25 °C (77 °F). The flash point and fire point of lubricating oil is determined by a separate method (ASTM D92).

4.2.6 Fractionation

Rather than quantifying a complex total crude oil hydrocarbon mixture as a single number, crude oil fractionation methods break the mixture into discrete fractions, thus providing data that can be used in a risk assessment and in characterizing product type and compositional changes such as may occur during weathering (oxidation). The fractionation methods can be used to measure both the volatile constituents and the extractable constituents.

In contrast to traditional methods for total crude oil hydrocarbon derivatives that report a single concentration number for complex mixtures, the fractionation methods report separate concentrations for discrete aliphatic and aromatic fractions. The available crude oil fraction methods are GC-based and are thus sensitive to a broad range of hydrocarbon derivatives. Identification and quantification of aliphatic and aromatic fractions allows one to identify crude oil products and evaluate the extent of product weathering. These fraction data also can be used in risk assessment.

4.2.7 *Metals content*

Crude oil, as recovered from the reservoir, contains metallic constituents but also pick up metallic constituents during recovery, transportation, and storage. Even trace amounts of these metals can be deleterious to refining processes, especially processes where catalysts are used. Trace components, such as metallic constituents, can also produce adverse effects in refining either (i) by causing corrosion, or (ii) by affecting the quality of refined products.

Hence, it is important to have test methods that can determine metals, both at trace levels and at major concentrations. Thus, test methods have evolved that are used for the determination of specific metals as well as for the multi-element methods determination using techniques such as atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, and X-ray fluorescence spectroscopy.

Nickel and vanadium along with iron and sodium (from the brine) are the major metallic constituents of crude oil. These metals can be determined by atomic absorption spectrophotometric methods (ASTM D5863, IP 285, IP 465), wave length-dispersive X-ray fluorescence spectrometry (IP 433), and inductively coupled plasma emission spectrometry (ICPAES). Several other analytical methods are available for the routine determination of trace elements in crude oil, some of which allow direct aspiration of the samples (diluted in a solvent) instead of the time-consuming sample preparation procedures such as wet ashing (acid decomposition) or flame or dry ashing (removal of volatile/combustible constituents) (ASTM D5863). Among the techniques used for trace element determinations are conductivity (IP 265), flameless and flame atomic absorption (AA) spectrophotometry (ASTM D5863) and inductively coupled argon plasma (ICP) spectrophotometry (ASTM D5708).

Inductively coupled argon plasma emission spectrophotometry (ASTM D5708) has an advantage over atomic absorption spectrophotometry (ASTM D4628, ASTM D5863) because it can provide more complete elemental composition data than the atomic absorption method. Flame emission spectroscopy is often used successfully in conjunction with atomic absorption spectrophotometry (ASTM D3605). X-ray fluorescence spectrophotometry (ASTM D4927, ASTM D6443) is also sometimes used but matrix effects can be a problem.

The method to be used for the determination of metallic constituents in crude oil is often a matter of individual preference.

4.2.8 *Pour point*

The pour point of crude oil or a crude oil product is the lowest temperature at which the oil will just flow, under standard test conditions (ASTM D97). The failure to flow at the pour point is usually attributed to the separation of waxes from the oil, but can also be due to the effect of viscosity in the case of very viscous oils. Also, particularly in the case of residual fuel oils, pour points may be influenced by the thermal history of the sample, that is, the degree and duration of heating and cooling to which the sample has been exposed.

In the original (and still widely used) test for pour point (ASTM D97, IP 15), a sample is cooled at a specified rate and examined at intervals of 3 °C (5.4 °F) for flow characteristics. The lowest temperature at which the movement of the oil is observed is recorded as the pour point. A later test method (ASTM D5853) covers two procedures for the determination of the pour point of crude oils down to -36 °C (-33 °F). One method provides a measure of the maximum (upper) pour point temperature. The second method measures the minimum (lower) pour point temperature. In the methods, the test specimen is cooled (after preliminary heating) at a specified rate and examined at intervals of 3 °C (5.4 °F) for flow characteristics. Again, the lowest temperature at which movement of the test specimen is observed is recorded as the pour point.

In any determination of the pour point, crude oil that contains wax produces an irregular flow behavior when the wax begins to separate. Such crude oil possesses viscosity relationships that are difficult to predict in pipeline operation. In addition, some waxy crude oil is sensitive to heat treatment that can also affect the viscosity characteristics. This complex behavior limits the value of viscosity and pour point tests on waxy crude oil. However, laboratory pumpability tests (ASTM D3829, ASTM D7528) are available that give an estimate of minimum handling temperature and minimum line or storage temperature.

From the transportation or spill response points of view, it must be emphasized that the tendency of the oil to flow will be influenced by the size and shape of the container, the head of the oil, and the physical structure of the solidified oil. The pour point of the oils is therefore an indication, and not an exact measure, of the temperature at which flow ceases (Dyroff, 1993).

4.2.9 Salt content

The salt content of crude oil is highly variable and results principally from production practices used in the field and, to a lesser extent, from its handling aboard tankers bringing it to terminals. The bulk of the salt present will be dissolved in coexisting water and can be removed in desalters, but small amounts of salt may be dissolved in the crude oil itself. Salt may be derived from reservoir or formation waters, or from other waters used in secondary recovery operations. Aboard tankers, ballast water of varying salinity may also be a source of salt contamination.

Salt in crude oil may be deleterious in several ways. Even in small concentrations, salts will accumulate in stills, heaters, and exchangers leading to fouling that requires expensive cleanup. More importantly, during flash vaporization of crude oil certain metallic salts can be hydrolyzed to hydrochloric acid according to the following reactions:

$$2\mathrm{NaCl} + \mathrm{H_2O} \rightarrow 2\ \mathrm{HCl} + \mathrm{Na_2O}$$

$$\mathrm{MgCl_2} + \mathrm{H_2O} \rightarrow 2\ \mathrm{HCl} + \mathrm{MgO}$$

The hydrochloric acid evolved is extremely corrosive, necessitating the injection of a basic compound, such as ammonia, into the overhead lines to minimize corrosion damage. Salts and evolved acids can also contaminate both overhead and residual products, and certain metallic salts can deactivate catalysts. Thus, knowledge of the content of salt in crude oil is important in deciding whether or not and to what extent the crude oil needs desalting.

The salt content is determined by potentiometric titration in a non-aqueous solution in which the conductivity of a solution of crude oil in a polar solvent is compared to that of a series of standard salt solutions in the same solvent (ASTM D3230). In the method, the sample is dissolved in a mixed solvent and placed in a test cell consisting of a beaker and two parallel stainless steel plates. An alternating voltage is passed through the plates and the salt content is obtained by reference to a calibration curve of the relationship of salt content of known mixtures to the current.

It is necessary, however, to employ other methods, such as atomic absorption, inductively coupled argon plasma spectrophotometry, and ion-chromatography to determine the composition of the salts present. A method involving application of extraction and volumetric titration is also used (IP 77).

4.2.10 Sulfur content

Sulfur is present in crude oil as sulfides, thiophene derivatives, benzothiophene derivatives, and dibenzothiophene derivatives. In most cases, the presence of sulfur is detrimental to the processing since sulfur can act as catalytic poisons during processing.

The sulfur content of crude oil is an important property and varies widely within the rough limits 0.1% w/w to 3.0% w/w and a sulfur content up to 8.0% w/w has been noted for tar sand bitumen. Compounds containing this element are among the most undesirable constituents of crude oil since they can give rise to plant corrosion and atmospheric pollution. Crude oil can evolve hydrogen sulfide during distillation as well as low boiling sulfur compounds.

Hydrogen sulfide may be evolved during the distillation process either from free hydrogen sulfide in the feedstocks or because of low-temperature thermal decomposition, of sulfur compounds; the latter is less likely than the former. Generally, however, the sulfur compounds concentrate in the distillation residue (Speight, 2000), the volatile sulfur compounds in the distillates being removed by such processes as hydrofining and caustic washing (Speight, 1999). The sulfur content of fuels obtained from crude oil residua and the atmospheric pollution arising from the use of these fuels is an important factor in crude oil utilization, so that the increasing insistence on a low sulfur content fuel oil has increased the value of low sulfur crude oil.

Sulfur compounds contribute to corrosion of refinery equipment and poisoning of catalysts, cause corrosiveness in refined products, and contribute to environmental pollution as a result of the combustion of fuel products. Sulfur compounds may be present throughout the boiling range of crude oils although, as a rule, they are more abundant in the higher boiling fractions. In some crude oils, thermally labile sulfur compounds can decompose on heating to produce hydrogen sulfide that is corrosive and toxic.

A considerable number of tests are available to estimate the sulfur in crude oil or to study its effect on various products. Hydrogen sulfide dissolved in crude oil is normally determined by absorption of the hydrogen sulfide in a suitable solution that is subsequently analyzed chemically (Doctor method) (ASTM, D4952, IP 30) or by the formation of cadmium sulfate (IP 103).

The Doctor test measures the amount of sulfur available to react with metallic surfaces at the temperature of the test. The rates of reaction are metal type, temperature, and time dependent. In the test, a sample is treated with copper powder at 150 °C (300 °F). The copper powder is filtered from the mixture. Active sulfur is calculated from the difference between the sulfur contents of the sample (ASTM D129) before and after treatment with copper.

Sulfur that is chemically combined as an organic constituent of crude is usually estimated by oxidizing a sample in a bomb and converting the sulfur compounds to barium sulfate that is determined gravimetrically (ASTM D129, IP 61). This method is applicable to any sample of sufficiently low volatility (e.g., a residuum or tar sand bitumen) that can be weighed accurately in an open sample boat and that contains at least 0.1 % sulfur. In the method, the sample is oxidized by combustion in a pressure vessel (bomb) containing oxygen under pressure. The sulfur in the sample is converted to sulfate, and from the bomb washings is gravimetrically determined as barium sulfate. However, the method is not applicable to samples containing elements that give residues, other than barium sulfate, which are insoluble in dilute hydrochloric acid and would interfere in the precipitation step. In addition, the method is also subject to inaccuracies that arise from interference by the sediment inherently present in crude oil.

Until recently, one of the most widely used methods for determination of total sulfur content has been combustion of a sample in oxygen to convert the sulfur to sulfur dioxide, which is collected and subsequently titrated iodometrically or detected by non-dispersive infrared (ASTM D1552). This method is particularly applicable to heavier oil and fractions such as residua that boil above 175 °C (350 °F) and contain more than 0.06% w/w sulfur. In addition, the sulfur content of crude oil coke containing up to 8% w/w/sulfur can be determined.

In the iodate detection system, the sample is bummed in a stream of oxygen at a sufficiently high temperature to convert the sulfur to sulfur dioxide. The combustion products are passed into an absorber that contains an acidic solution of potassium iodide and starch indicator. A faint blue color is developed in the absorber solution by the addition of standard potassium iodate solution and as combustion proceeds, bleaching the blue color, more iodate is added. From the amount of standard iodate consumed during the combustion, the sulfur content of the sample is calculated.

In the infrared detection system, the sample is weighed into a special ceramic boat that is then placed into a combustion furnace at 1370 °C (2,500 °F) in an oxygen atmosphere. Moisture and dust are removed using traps and the sulfur dioxide is measured with an infrared detector.

Other methods such as the lamp combustion method (ASTM D1266, IP 107) and the Wickbold combustion method (IP 243) are used for the determination of sulfur in crude oil and as trace quantities of total sulfur in crude oil products and is related to various other methods (ASTM D2384, ASTM D2784, ASTM D4045).

In the lamp method (ASTM D1266, IP 107), a sample is burned in a closed system using a suitable lamp and an artificial atmosphere composed of 70% carbon dioxide and 30% oxygen to prevent formation of nitrogen oxides. The sulfur oxides are absorbed and oxidized to sulfuric acid (H_2SO_4) by means of hydrogen peroxide (H_2O_2) solution that is then flushed with air to remove dissolved carbon dioxide. Sulfur as sulfate in the absorbent is determined acidimetrically by titration with standard sodium hydroxide (NaOH) solution. Alternatively, the sample can be burned in air and the sulfur as sulfate in the absorbent be determined by gravimetrically barium sulfate ($BaSO_4$) after precipitation. If the sulfur content of the sample is less than 0.01% w/w, it is necessary to determine sulfur in the absorber solution turbidimetrically as barium sulfate.

The older, classical techniques for sulfur determination are being supplanted by two instrumental methods (ASTM D2622, ASTM D4294, IP 447). In the former method (ASTM D2622), the sample is placed in an X-ray beam, and the peak intensity of the sulfur Kα line at 5.373Å is measured. The background intensity, measured at 5.190Å is subtracted from the peak intensity and resultant net counting rate is then compared to a previously prepared calibration curve or equation to obtain the sulfur concentration in % w/w.

The latter method (ASTM D4294, IP 477) employs energy-dispersive X-ray fluorescence spectroscopy and has slow-boilingly better repeatability and reproducibility than the high temperature method and is adaptable to field applications but can be affected by some commonly present interferences such as halides. In the method, the sample is placed in a beam emitted from an X-ray source. The resultant excited characteristic X radiation is measured, and the accumulated count is compared with counts from previously prepared calibration standard to obtain the sulfur concentration. Two groups of calibration standards are required to span the concentration range, one standard ranges from 0.015 to 0.1% w/w sulfur, and the other from 0.1 to 5.0% w/w sulfur.

4.2.11 Surface tension and interfacial tension

Interfacial tension is the force of attraction between the molecules at the interface of two fluids. At the air/liquid interface, this force is often referred to as surface tension. The SI units for interfacial tension are milli-newtons per meter (mN/m). These are equivalent to the former units of dynes per centimeter (dyne/cm). The surface tension of crude oil (or a crude oil product), together with its viscosity, affects the rate at which an oil spill spreads.

Air/oil and oil/water interfacial tensions can be used to calculate a spreading coefficient which gives an indication of the tendency for the oil to spread. It is defined as:

$$\text{Spreading coefficient} = S_{WA} - S_{OA} - S_{WO}$$

S_{WA} is water/air interfacial tension, S_{OA} is oil/air interfacial tension, and S_{WO} is water/oil interfacial tension.

A single test method (ASTM D971) is applicable to the measurement of oil/water interfacial tensions. Unlike manually operated ring tensiometers, the maximum deformation of the lamella is detected electronically, and occurs before the ring pulls completely through the interface. This results in interfacial tension that is somewhat lower than that measured manually. Unlike density and viscosity, which show systematic variations with temperature and degree of evaporation, interfacial tensions of crude oils and oil products show no such correlations.

4.2.12 Viscosity

Viscosity is a measure of the resistance of a fluid to flow; the lower the viscosity of a fluid, the more easily it flows. Like density, viscosity is affected by temperature. As temperature decreases, viscosity increases. Viscosity is a very important property of oils because it affects the rate at which spilled oil will spread, the degree to which it will penetrate shoreline substrates, and the selection of mechanical spill countermeasures equipment.

Viscosity measurements may be absolute or relative (sometimes called ‘apparent’). Absolute viscosities are those measured by a standard method, with the results traceable to fundamental units. Absolute viscosities are distinguished from relative measurements made with instruments that measure viscous drag in a fluid, without known and/or uniform applied shear rates (Schramm, 1992). An important benefit of absolute viscometry is that the test results are independent of the particular type or make of viscometer used. Absolute viscosity data can be compared easily between laboratories worldwide.

Modern rotational viscometers are capable of making absolute viscosity measurements for both Newtonian and non-Newtonian fluids at a variety of well controlled, known, and/or uniform shear rates. Unfortunately, no ASTM standard method exists that makes use of these viscometers. Nonetheless, these instruments are in widespread use in many industries.

There are standard test methods for measuring the viscosity of oils (such as ASTM D445 and ASTM D4486) make use of glass capillary kinematic viscometers and will produce absolute measurements in units of centistokes (cSt) only for oils that exhibit Newtonian flow behavior (viscosity independent of the rate of shear). Although now obsolete, at one time the crude oil industry relied on measuring kinematic viscosity with the Saybolt viscometer and expressing kinematic viscosity in Saybolt Universal Seconds (SUS) or Saybolt Furol Seconds (SFS). Occasionally, Saybolt viscosities are still reported in the literature using the official equations relating SUS and SFS to kinematic viscosity (ASTM D2161).

In the test method (ASTM D445), the time for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled temperature is measured in seconds. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer. Conversion of the kinematic viscosity in centistokes (cSt) at any temperature to Saybolt Universal viscosity in Saybolt Universal seconds (SUS) at the same temperature and for converting kinematic viscosity in centistokes at 122 and 210 °F to Saybolt Furol viscosity in Saybolt Furol seconds (SFS) at the same temperatures (ASTM D2161).

The *viscosity index* (ASTM D2270, IP 226) is a widely used measure of the variation in kinematic viscosity due to changes in the temperature of crude oil between 40 °C and 100 °C (104 °F and 212 °F). For crude oils of similar kinematic viscosity, the higher the viscosity index the smaller is the effect of temperature on its kinematic viscosity. The accuracy of the calculated viscosity index is dependent only on the accuracy of the original viscosity determination.

4.2.13 Water and sediment

Considerable importance is attached to the presence of water or sediment in crude oil for they lead to difficulties in the refinery, e.g. corrosion of equipment, uneven running on the distillation unit, blockages in heat exchangers and adverse effects on product quality.

The water and sediment content of crude oil, like salt, results from production and transportation practices. Water, with its dissolved salts, may occur as easily removable suspended droplets or as an emulsion. The sediment dispersed in crude oil may be composed of inorganic minerals from the production horizon or from drilling fluids, and scale and rust from pipelines and tanks used for oil transportation and storage. Usually water is present in far greater amounts than sediment but, collectively, it is unusual for them to exceed one percent of the crude oil on a delivered basis. Like salt, water and sediment can foul heaters, stills, and exchangers and can contribute to corrosion and to deleterious product quality. Also, water and sediment are principal components of the sludge that accumulates in storage tanks and must be disposed of periodically in an environmentally acceptable manner. Knowledge of the water and sediment content is also important in accurately determining net volumes of crude oil in sales, taxation, exchanges, and custody transfers.

The sediment consists of finely divided solids that may be drilling mud or sand or scale picked up during the transport of the oil, or may consist of chlorides derived from evaporation of brine droplets in the oil. The solids may be dispersed in the oil or carried in water droplets. Sediment in crude oil can lead to serious plugging of the equipment, corrosion due to chloride decomposition, and a lowering of residual fuel quality.

Water may be found in the crude either in an emulsified form or in large droplets and can cause flooding of distillation units and excessive accumulation of sludge in tanks. Refiners generally limit the quantity, and although steps are normally taken at the oilfield to reduce the water content as low as possible, water may be later introduced during shipment. In any form, water and sediment are highly undesirable in a refinery feedstock and the relevant tests involving distillation (ASTM D95, ASTM D4006, IP 74, IP 358), centrifuging (ASTM D4007), extraction (ASTM D473, IP 53), and the Karl Fischer titration (ASTM D4377, ASTM D4928, IP 356, IP 386, IP 438, IP 439) are regarded as important in crude oil quality examinations.

Prior to the assay it is sometimes necessary to separate the water from a crude oil sample. Certain types of crude oil, notably heavy oil, often form persistent emulsions that are difficult to separate. On the other hand, testing wax-bearing crude oil for sediment and water care has to be taken to ensure that wax suspended in the sample is brought into solution prior to the test otherwise it will be recorded as sediment.

The Karl Fischer test method (ASTM D1364, ASTM D6304) covers the direct determination of water in crude oil. In the test, the sample injection in the titration vessel can be performed on a volumetric or gravimetric basis. Viscous samples can be analyzed using a water vaporizer accessory that heats the sample in the evaporation chamber, and the vaporized water is carried into the Karl Fischer titration cell by a dry inert carrier gas.

Water and sediment in crude oil can be determined simultaneously (ASTM D4007) by the centrifuge method. Known volumes of crude oil and solvent are placed in a centrifuge tube and heated to 60 °C (140 °F). After centrifugation, the volume of the sediment-and-water layer at the bottom of the tube is read. For crude oil that contains wax, a temperature of 71 °C (160 °F) or higher may be required to completely melt the wax crystals so that they are not measured as sediment.

Sediment is also determined by an extraction method (ASTM D473, IP 53) or by membrane filtration (ASTM D4807). In the former method (ASTM D473, IP 53), An oil sample contained in a refractory thimble is extracted with hot toluene until the residue reaches a constant mass. In the latter test, the sample is dissolved in hot toluene and filtered under vacuum through a 0.45 μm porosity membrane filter. The filter with residue is washed, dried, and weighed.

4.2.14 *Other properties*

The inspection assay tests discussed above are not exhaustive but are the ones most commonly used and provide data on the impurities present as well as a general idea of the products that may be recoverable. Other properties that are determined on an as needed basis include, but are not limited to, the following: (i) wax content, (ii) vapor pressure − Reid method, (iii) total acid number, which is rapidly become essential in terms of the data relating to the content of acidic species in crude oil and crude oil products (Speight, 2014b), (iv) chloride content, and as the occasion demands (v) the *aniline point* (or *mixed aniline point*.

Not every type of crude oil contains significant amounts of wax constituents. However, crude oil with high *wax content* presents difficulties in handling and pumping as well as producing distillate and residual fuels of high pour point and lubricating oils that are costly to dewax. All the standard methods for the determination of the wax involve precipitating the wax from solvents such as methylene chloride or acetone under specified conditions of solvent/oil ratio and temperature. Measurements such as these give comparative results that are often useful in characterizing the wax content of crude oil, or for investigating factors involved in flow problems. On the other hand, the cloud point (ASTM D2500, ASTM D5772, ASTM D7397, ASTM D7689), which is often used to indicate the temperature at which wax deposits from oil, may be determined by cooling of a sample under prescribed conditions with stirring. The temperature at which the wax first appears is the wax appearance point.

The Reid vapor pressure test method (ASTM D323, IP 69) measures the vapor pressure of volatile crude oil. The Reid vapor pressure differs from the true vapor pressure of the sample due to some small sample vaporization and the presence of water vapor and air in the confined space.

The *acid number* is the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample that is required to titrate a sample in this solvent to a green/green-brown end point, using p-naphtholbenzein indicator solution. The *strong acid number* is the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample in the solvent from its initial meter reading to a meter reading corresponding to a freshly prepared non-aqueous acidic buffer solution or a well-defined inflection point as specified in the test method (ASTM D664, IP 177).

To determine the acid number by the color indictor method (ASTM D974, IP 139), the sample is dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water, and the resulting single-phase solution is titrated at room temperature with standard alcoholic base or alcoholic acid solution, respectively, to the end point indicated by the color change of the added p-naphtholbenzein solution (orange in acid and green-brown in base). To determine the strong acid number, a separate portion of the sample is extracted with hot water and the aqueous extract is titrated with potassium hydroxide solution, using methyl orange as an indicator.

To determine the acid number by the potentiometric titration method (ASTM D664, IP 177), the sample is dissolved in a mixture of toluene and iso-propyl alcohol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide using a glass indicating electrode and a calomel reference electrode. The meter readings are plotted manually or automatically against the respective volumes of titrating solution and the end points are taken only at well-defined inflections in the resulting curve. When no definite inflections are obtained, end points are taken at meter readings corresponding to those found for freshly prepared non-aqueous acidic and basic buffer solutions.

The acid numbers obtained by this color-indicator test method (ASTM D974, IP 139) method mayor may not be numerically the same as those obtained by potentiometric titration method (ASTM D664, IP 177). In addition, the color of the crude oil sample can interfere with observation of the end point when the color indictor method is used. Determination of the acid number is more appropriate for high acid crude oils, heavy oils, and tar sand bitumen (which are often high in acid content), and various crude oil products (Speight, 2014b).

The test method for the determination of the acid number by the color indicator titration method (ASTM D3339, IP 431) measures the acid number of oils obtained from laboratory oxidation test (ASTM D943) using smaller amounts of samples than those used in other acid number tests (ASTM D664, ASTM D974, IP 139, IP 177).

In this test, the sample is dissolved in a solvent mixture of toluene, isopropyl alcohol, and a small amount of water and the solution is titrated at room temperature under a nitrogen atmosphere with standard potassium hydroxide (KOH) in isopropyl alcohol to the stable green color of the added indicator p-naptholbenzein. Dark colored crude oils (and crude oil products) are more difficult to analyze by this method because of the difficulty in detecting color change. In such cases, the potentiometric titration method (ASTM D664, IP 177) may be used if sufficient sample is available.

They acid numbers will not provide the data essential to determining whether a single crude oil (or a blend of the crude oil crude oil with other crude oils) will yield the desired product slate. Such data can only be generated when a comprehensive assay of the crude oil (and its partners in the blending) is performed and the data from several tests are taken in relation to each other.

The chloride content of crude oil (ASTM D4929) is, like the total acid content, also a must have – especially at the wellhead and after the desalting operation. Just as *high acid crude oils* cause corrosion in the refinery, overhead corrosion is caused by the mineral salts, magnesium, calcium and sodium chloride which are hydrolyzed to produce volatile hydrochloric acid, causing a highly corrosive condition in the overhead exchangers (Speight, 2014c). Therefore these salts present a significant contamination in opportunity crude oils.

Finally, the *aniline point* (or *mixed aniline point*) (ASTM D611, IP 2) has been used for the characterization of crude oil although it is more applicable to pure hydrocarbon derivatives and in their mixtures and is used to estimate the aromatic content of mixtures. Aromatics exhibit the lowest aniline points and paraffins the highest aniline points. Cycloparaffins and olefins exhibit values between these two extremes. In any hydrocarbon homologous series the aniline point increases with increasing molecular weight.

Yield-on-crude data are still widely reported in the crude oil assay literature, providing information on the yield of specific fractions obtained by distillation (ASTM D86; ASTM D1160). However, to some extent in the laboratory, atmospheric and vacuum distillation techniques have largely been replaced by *simulated* distillation methods, which use low resolution gas chromatography and correlate retention times to hydrocarbon boiling points (ASTM D2887) which typically use external standards such as n-alkanes.

4.3 Chromatographic analyses

Crude oil group analyses are conducted to determine amounts of the crude oil compound classes (e.g., saturate constituents, aromatic constituents, and polar constituents such as the resin constituents) present in crude oil-contaminated samples. This type of measurement is sometimes used to identify fuel type or to track plumes. It may be particularly useful for higher boiling products, such as asphalt. Group type test methods include multidimensional gas chromatography (not often used for environmental samples), high performance liquid chromatography (HPLC), and thin layer chromatography (TLC) (Miller, 2000; Patnaik, 2004; Speight, 2005; Speight and Arjoon, 2012).

Test methods that analyze individual compounds (e.g., benzene-toluene-ethylbenzene-xylene mixtures and polynuclear aromatic hydrocarbon derivatives) are generally applied to detect the presence of an additive or to provide concentration data needed to estimate environmental and health risks that are associated with individual compounds. Common constituent measurement techniques include gas chromatography with second column confirmation, gas chromatography with multiple selective detectors and gas chromatography with mass spectrometry detection (GC/MS) (Speight, 2005; Speight and Arjoon, 2012).

4.3.1 Gas chromatography

Gas chromatography (GC), which is based on the principle of a stationary phase and a mobile phase, remains a primary technique for determining hydrocarbon distribution in crude oil products through the identification of individual hydrocarbon derivatives. Although a measure of purity by gas chromatography is often sufficient for many purposes, it is not always sufficient for measuring absolute purity − not all possible impurities will pass through the chromatographic column, and not all those that do will be measured by the detector. Absolute purity is best measured by distillation range or freeze or solidification points. Despite this disadvantage, the technique is still widely used technique and is the basis of many current standard test methods for the determination and measurement of hydrocarbon derivatives in crude oil products. When classes of hydrocarbon derivatives such as olefins need to be measured, techniques such as bromine index are used (ASTM D1492, ASTM D2710, ASTM D5776).

Briefly, *gas-liquid chromatography* (GLC) is a method for separating the volatile components of various mixtures (Fowlis, 1995; Grob, 1995). It is, in fact, a highly efficient fractionating technique, and it is ideally suited to the quantitative analysis of mixtures when the possible components are known and the interest lies only in determining the amounts of each present. In this type of application gas chromatography has taken over much of the work previously done by the other techniques; it is now the preferred technique for the analysis of hydrocarbon gases, and gas chromatographic in-line monitors are having increasing application in refinery plant control. Gas-liquid chromatography is also used extensively for individual component identification, as well as percentage composition, in the gasoline boiling range.

The mobile phase is the carrier gas, and the gas selected has a bearing on the resolution. Nitrogen has very poor resolution ability, while helium or hydrogen are better choices with hydrogen being the best carrier gas for resolution. However, hydrogen is reactive and may not be compatible with all sets of target analytes. There is an optimum flow rate for each carrier gas to achieve maximum resolution. As the temperature of the oven increases, the flow rate of the gas changes due to thermal expansion of the gas. Most modern gas chromatographs are equipped with constant flow devices that change the gas valve settings as the temperature in the oven changes, so changing flow rates are no longer a concern. Once the flow is optimized at one temperature it is optimized for all temperatures.

4.3.2 Gas chromatography-mass spectrometry

A gas chromatography-mass spectrometry system is used to measure concentrations of target volatile and semi-volatile crude oil constituents. It is not typically used to measure the amount of total crude oil hydrocarbon derivatives. The advantage the technique is the high selectivity, or ability to confirm compound identity through retention time and unique spectral pattern. The method is used for identification and quantification of the constituents of crude oil fractions and crude oil products.

To reduce the possibility of false positives, the intensities of one-to-three selected ions are compared to the intensity of a unique target ion of the same spectrum. The sample ratios are compared to the ratios of a standard. If the sample ratios fall within a certain range of the standard, and the retention time matches the standard within specifications, the analyte is considered present. Quantification is performed by integrating the response of the target ion only.

Mass spectrometers are among the most selective detectors, but they are still susceptible to interferences. Isomers have identical spectra, while many other compounds have similar mass spectra. Heavy crude oil products can contain thousands of major components that are not resolved by the gas chromatograph. As a result, multiple compounds are simultaneously entering the mass spectrometer. Different compounds may share many of the same ions, confusing the identification process. The probability of misidentification is high in complex mixtures such as crude oil products.

4.3.3 High performance liquid chromatography

A high performance liquid chromatography (HPLC) system can be used to measure concentrations of target semi-volatile and non-volatile crude oil constituents. The system only requires that the sample be dissolved in a solvent compatible with those used in the separation. The detector most often used in crude oil environmental analysis is the fluorescence detector. These detectors are particularly sensitive to aromatic molecules, especially polynuclear aromatic hydrocarbon derivatives. An ultraviolet detector may be used to measure compounds that do not fluoresce.

In the method, polynuclear aromatic hydrocarbon derivatives are extracted from the sample matrix with a suitable solvent, which is then injected into the chromatographic system. Usually the extract must be filtered because fine particulate matter can collect on the inlet frit of the column, resulting in high back-pressures and eventual plugging of the column. For most hydrocarbon analyses, reverse phase high performance liquid chromatography (i.e., using a nonpolar column packing with a more polar mobile phase) is used. The most common bonded phase is the octadecyl (C18) phase. The mobile phase is commonly aqueous mixtures of either acetonitrile or methanol.

After the chromatographic separation, the analytes flow through the cell of the detector. A fluorescence detector shines light of a particular wavelength (the excitation wavelength) into the cell. Fluorescent compounds absorb light and reemit light of other, higher wavelengths (emission wavelengths). The emission wavelengths of a molecule are mainly determined by its structure. For polynuclear aromatic hydrocarbon derivatives, the emission wavelengths are mainly determined by the arrangement of the rings and vary greatly between isomers.

Some of the polynuclear aromatic hydrocarbon derivatives (such as phenanthrene, pyrene, and benzo (g,h,i)perylene, are commonly seen in products boiling in the middle to high-boiling distillate range. In a method for their detection and analysis (EPA 8310) an octadecyl column and an aqueous acetonitrile mobile phase are used. Analytes are excited at 280 nm and detected at emission wavelengths of >389 nm. Naphthalene, acenaphthene, and fluorene must be detected by a less-sensitive UV detector because they emit light at wavelengths below 389 nm. Acenaphthylene is also detected by UV detector.

The methods using fluorescence detection will measure any compounds that elute in the appropriate retention time range and which fluoresce at the targeted emission wavelength(s) (Falla Sotelo et al., 2008). In the case of one method (EPA 8310), the excitation wavelength excites most aromatic compounds. These include the target compounds and also many aromatics derivatives, such as alkyl aromatic derivatives, phenol derivatives, aniline derivatives, and heterocyclic aromatic compounds containing various structures — examples are pyrrole (such as indole and carbazole derivatives), pyridine (such as quinoline and acridine derivatives), furan (such as benzofuran and naphthofuran derivatives), and thiophene (such as benzothiophene and naphthothiophene derivatives) structures. In crude oil samples, alkyl polynuclear aromatic hydrocarbon derivatives are strong interfering compounds. For example, there are five methyl phenanthrene derivatives and more than 20 dimethyl phenanthrene derivatives. The alkyl substitution does not significantly affect either the wavelengths or intensity of the phenanthrene fluorescence. For a very long time after the retention time of phenanthrene, the alkyl phenanthrene derivatives will interfere, affecting the measurements of all later-eluting target polynuclear aromatic derivatives.

Interfering compounds will vary considerably from source to source and samples may require a variety of cleanup steps to reach required method detection limits. The emission wavelengths used (EPA 8310) are not optimal for sensitivity of the small ring compounds. With modern electronically-controlled monochromator, wavelength programs can be used which tune excitation and emission wavelengths to maximize sensitivity and/or selectivity for a specific analyte in its retention time window.

4.3.4 Thin layer chromatography

In the environmental; field, thin layer chromatography (TLC) is best used for screening analyses and characterization of semi-volatile and non-volatile crude oil products. The precision and accuracy of the technique is inferior to other methods (Speight, 2005; Speight and Arjoon, 2012) but when speed and simplicity are desired, thin layer chromatography may be a suitable alternative. For characterizations of crude oil products such as asphalt, the method has the advantage of separating compounds that are too high boiling to pass through a gas chromatograph. While thin layer chromatography does not have the resolving power of a gas chromatograph, it is able to separate different classes of compounds. Thin layer chromatography analysis is fairly simple and, since the method does not give highly accurate or precise results, there is no need to perform the highest quality extractions.

In the method, soil samples are extracted by shaking or stirring with the solvent. Water samples are extracted by shaking in a separatory funnel. If there is the potential for the presence of compounds that interfere with the method and make the data suspect, silica gel can be added to clean the extract. Sample extract aliquots are placed close to the bottom of a glass plate coated with a stationary phase. The most widely used stationary phases are made of an organic hydrocarbon moiety bonded to a silica backbone.

For the analysis of crude oil hydrocarbon derivatives, a moderately polar material stationary phase works well. The plate is placed in a sealed chamber with a solvent (mobile phase). The solvent travels up the plate carrying compounds present in the sample. The distance a compound travels is a function of the affinity of the compound to the stationary phase relative to the mobile phase. Compounds with chemical structure and polarity similar to the solvent pass readily into the mobile phase. For example, the saturated hydrocarbon derivatives seen in diesel fuel travel readily up a plate in a hexane mobile phase. Polar compounds such as ketones or alcohols travel a smaller distance in hexane than saturated hydrocarbon derivatives.

After a plate has been exposed to the mobile phase solvent for the required time, the compounds present can be viewed by several methods. Polynuclear aromatic hydrocarbon derivatives, other compounds with conjugated systems, and compounds containing heteroatoms (nitrogen, oxygen, or sulfur) can be viewed with long wave and short wave ultraviolet light. The unaided eye can see other material or the plates can be developed in iodine. Iodine has an affinity for most crude oil compounds, including the saturated hydrocarbon derivatives, and stains the compounds a reddish/brown color.

The method is considered to be a qualitative and useful tool for rapid sample screening. Limitations of the method center on its moderate reproducibility, detection limits, and resolving capabilities. Variability between operators can be as high as 30%. Detection limits (without any concentration of the sample extract) are near 50 ppm (mg/kg) for most crude oil products in soils. When the aromatic content of a sample is high, as with bunker C fuel oil, the detection limit can be near 100 ppm. It is often not possible to distinguish between similar products such as diesel and jet fuel. As with all chemical analyses, quality assurance tests should be run to verify the accuracy and precision of the method.

4.4 Spectroscopic analyses

The chemical composition of a feedstock has always been considered to be a valuable indicator of refining behavior. Whether or not it is the ultimate indicator of refining behavior remains to be seen and is audience dependent! More than likely, chemical composition studies truly complement physical property and physical behavior studies and the true picture is a combination of all of these studies.

However, the chemical composition of a feedstock is represented in terms of compounds types and/or in terms of generic compound classes thus allowing the analytical chemist, the process chemist, the process engineer, and the refiner to determine the nature of the reactions. Hence, chemical composition can play a large part in determining the nature of the products that arise from the refining operations. It can also play a role in determining the means by which a particular feedstock should be processed (Wallace et al., 1988; Speight, 2000). However, proper interpretation of the data resulting from the composition studies requires an understanding of chemical structures, their significance, and an open mind!

The physical and chemical characteristics of crude oils and the yields and properties of products or factions prepared from them vary considerably and are dependent on the concentration of the various types of hydrocarbon derivatives and minor constituents present. Some types of crude oil have economic advantages as sources of fuels and lubricants with highly restrictive characteristics because they require less specialized processing than that needed for production of the same products from many types of crude oil. Others may contain unusually low concentrations of components that are desirable fuel or lubricant constituents, and the production of these products from such crude oils may not be economically feasible.

Spectroscopic studies have played an important role in the evaluation of crude oil and of crude oil products for the last three decades and many of the methods are now used as standard methods of analysis for refinery feedstocks and products. Application of these methods to feedstocks and products is a natural consequence for the refiner.

The methods include the use of *mass spectrometry* to determine the (i) hydrocarbon types in middle distillates (ASTM D2425); (ii) hydrocarbon types of gas oil saturate fractions (ASTM D2786); and (iii) hydrocarbon types in low-olefin gasoline (ASTM D2789); (d) aromatic types of gas oil aromatic fractions (ASTM D3239. *Nuclear magnetic resonance spectroscopy* has been developed as a standard method for the determination of hydrogen types in aviation turbine fuels (ASTM D3701). *X-ray fluorescence spectrometry* has been applied to the determination of the analysis of selected elements (nitrogen, sulfur, nickel, and vanadium) as well as to the determination of sulfur in various crude oil products (ASTM D2622, ASTM D4294).

Infrared spectroscopy is used for the determination of benzene in motor and/or aviation gasoline while ultraviolet spectroscopy is employed for the evaluation of mineral oils (ASTM D2269) and for determining the naphthalene content of aviation turbine fuels (ASTM D1840). Other techniques include the use of *flame emission spectroscopy* for determining trace metals in gas turbine fuels (ASTM D3605) and the use of *absorption spectrophotometry* for the determination of the alkyl nitrate content of diesel fuel (ASTM D4046). *Atomic absorption* has been employed as a means of the analysis of metals (ASTM D1971, ASTM D4698, ASTM D5056), for the manganese content of gasoline (ASTM D3831) as well as for determining the barium, calcium, magnesium, and zinc contents of lubricating oils (ASTM D4628). *Flame photometry* has been employed as a means of measuring the lithium/sodium content of lubricating greases and the sodium content of residual fuel oil (ASTM D1318).

Nowhere is the contribution of spectroscopic studies more emphatic than in application to the delineation of structural types in the heavier feedstocks. This has been necessary because of the unknown nature of these feedstocks by refiners. One particular example is the *n.d.M. method* (ASTM D3238) that is designed for the carbon distribution and structural group analysis of crude oil and crude oil products. Later investigators have taken structural group analysis several steps further than the n.d.M. method.

It is also appropriate at this point to give a brief description of other methods that are used for the identification of the constituents of crude oil. Although useful information related to the composition of high molecular weight crude oil fractions is provided by the right combination of separation and analytical methods, spectroscopic methods can also be applied to the problems of characterization and identification. For example, information related to the nature of polar functional groups or the elucidation of the way vanadium and nickel are bound to the molecules is available from a variety of spectroscopy techniques, as well as by use of a variety of chemical techniques (Speight, 2001, 2014a).

It is not intended to convey here that any one of these methods can be used for complete characterization and identification of the high molecular weight crude oil constituents. Even though any one of these methods may fall short of complete acceptability as a method for the characterization of individual constituents of feedstocks, they can be used as methods by which an overall evaluation of the feedstock may be obtained in terms of molecular types. This is especially true when the methods are used in conjunction with each other.

4.4.1 Infrared spectroscopy

Infrared spectroscopy is a well-established method that was developed for comparative, semi-quantitative analysis leading to the present quantitative analysis (ASTM E168, ASTM E204, ASTM E334, ASTM E1252). Infrared spectra are displayed either as percent transmittance or as absorptivity versus frequency (cm-^{1}). Transmittance, T, defined as the ratio of transmitted light over incident light, or percent transmittance, usually shows more detail over the entire range and is generally the preferred display. Absorbance, A, on the other hand, is proportional to the concentration and is, therefore, used for quantitative measurements.

Infrared spectroscopy is a simple procedure and is one of several techniques that can provide quick information related to the distribution of several structural and functional groups (Drews, 1998; Nadkarni, 2011; Rand, 2003). In combination with nuclear magnetic resonance spectroscopy, it will provide quick yet fairly detail on the distribution of carbon-hydrogen groups. However, in the context of high molecular weight crude oil fractions, conventional infrared spectroscopy yields information related to the functional features of various crude oil constituents. For example, infrared spectroscopy will aid in the identification of imino functions (=N−H) and hydroxyl (−O−H) functions, as well as the nature of the various carbonyl (-C=O) functions.

In the older, infrared spectroscopy, light is refracted by a prism or a grating and scanned by a moving slit that takes several minutes for one measurement. In Fourier Transform infrared (FIR) spectroscopy, the entire spectrum is obtained by an interferometer in a fraction of a second. Thus, several hundred measurements can be taken in a matter of minutes and averaged by computer. This multiplexing leads to greatly increased (approximately 100-fold) sensitivity and precision over those achievable with dispersive instruments.

Thus, with the recent progress of *Fourier transform infrared (FTIR) spectroscopy*, quantitative estimates of the various functional groups can also be made. This is particularly important for application to the higher molecular weight solid constituents of crude oil (i.e. the asphaltene fraction) and for group-type analysis. It is also possible to derive structural parameters from infrared spectroscopic data and these are (i) saturated hydrogen to saturated carbon ratio; (ii) paraffinic character; (iii) naphthenic character; (iv) methyl group content; and (v) paraffin chain length. In conjunction with proton magnetic resonance (see next section), structural parameters such as the fraction of paraffinic methyl groups to aromatic methyl groups can be obtained.

The newer diffuse reflectance infrared (DRIR) techniques seem to give equally good spectra as obtained in conventional ways from solutions in cells or from potassium bromide (KBr) pellets. Another synonym for this technique is DRIFT (for diffuse reflectance infrared Fourier transform). The sample is deposited from solution onto finely ground potassium bromide in a small cup that is placed into a diffuse reflectance accessory after removal of the solvent in a vacuum oven. A related technique, variable angle specular reflectance, allows rotation of the sample holder for optimization.

In the field of the analysis of the high molecular weight crude oil constituents, infrared spectroscopy has been mostly employed for measuring oxygen- and nitrogen-containing groups and for evaluating shifts in certain bands due to aggregation or other interactions such as carboxylic acid derivatives, phenol derivatives, carbazole derivatives, cyclic amides, as well as pyridine and acridine derivatives among the bases. In the lower-boiling crude oil fractions, parts of the hydrocarbon skeleton can be assessed by infrared spectroscopy. Specifically, the alkyl substitution of aromatic rings can be determined from the out-of-plane carbon-hydrogen deformation bands.

4.4.2 Mass spectrometry

Mass spectrometry furnishes the molecular weight and chemical formula of compounds and their relative amounts in a mixture and offers non-destructive examination of the sample (ASTM D2425, ASTM D2650, ASTM D2786, ASTM D2789, ASTM D3239, ASTM E1316). The technique can also provide important information related to the molecular structure. The earliest and most common type of mass spectrometry, electron impact mass spectrometry (El-MS), gives a fragmentation pattern displaying both parent ion peaks and fragment ion peaks, characteristic of each molecular type.

Fragmentation is frequently employed to differentiate between isomers of pure compounds and of molecules in fairly Simple mixtures. However, it is usually avoided with such complex samples as high molecular weight crude oil fractions, which are composed of such a multitude of closely related compounds that their fragmentation patterns are non-distinctive and cannot be readily interpreted.

Mass spectrometry can play a key role in the identification of the constituents of feedstocks and products either in the laboratory or online (ASTM D2425; ASTM D2786; ASTM D2789; ASTM D3239). The principal advantages of mass spectrometric methods are (i) high reproducibility of quantitative analyses; (ii) the potential for obtaining detailed data on the individual components and/or carbon number homologues in complex mixtures; and (iii) a minimal sample size is required for analysis. The ability of mass spectrometry to identify individual components in complex mixtures is unmatched by any modern analytical technique. Perhaps the exception is gas chromatography.

However, there are disadvantages arising from the use of mass spectrometry and these are: (i) the limitation of the method to organic materials that are volatile and stable at temperatures up to 300 °C (570 °F); and (ii) the difficulty of separating isomers for absolute identification. The sample is usually destroyed, but this is seldom a disadvantage.

Nevertheless, in spite of these limitations, mass spectrometry does furnish useful information related to the composition of feedstocks and products even if this information is not as exhaustive as might be required. There are structural similarities that might hinder identification of individual components. Consequently, identification by type or by homologue will be more meaningful since similar structural types may be presumed to behave similarly in processing situations. Knowledge of the individual isomeric distribution may add only a little to an understanding of the relationships between composition and processing parameters.

Mass spectrometry should be used discriminately where a maximum amount of information can be expected. The heavier nonvolatile feedstocks are for practical purposes, beyond the useful range of routine mass spectrometry. At the elevated temperatures necessary to encourage volatility, thermal decomposition will occur in the inlet and any subsequent analysis would be biased to the low molecular weight end and to the lower molecular products produced by the thermal decomposition.

High-voltage electron impact mass spectrometry (HVEI-MS or EI-MS) can cause repeated fragmentation of daughter ions. Considering the repeated fragmentation of even the simplest hydrocarbon derivatives and the fact that the higher molecular weight fractions of crude oil contains such a broad range of molecular weight species (Speight, 2001, 2014a), the patterns obtained from crude oil fractions are so complex as to almost defy interpretation. Thus, non-fragmenting mass spectrometric methods are preferred.

For high molecular weight crude oil fractions, the use of non-fragmenting mass spectrometry (NF-MS) methods is now preferred. These methods, also called *soft ionization* methods, produce predominantly parent ion (molecular ion) peaks and, thus, much simpler spectra than methods producing fragments. By rendering the molecular weight of each compound in a sample, and reasonably well its abundance, non-fragmenting mass spectrometry also can be used to determine the molecular-weight distribution, i.e., the molar mass profile of a sample.

Indeed, the great advantage of *non-fragmenting mass spectrometry* is the relative simplicity of the spectra. A disadvantage is the relatively low signal intensity of the ions. With *low-voltage electron impact ionization*, the number of parent ions formed increases rapidly as the ionizing voltage increases above the ionizing potential of the molecules in the sample. Thus, higher voltage gives a more intense signal (up to approximately 20–40 eV, depending on compound type). However, the higher ionizing voltage transfers more energy to the sample molecules and causes fragmentation to increase. The surplus energy transferred to the molecule in excess of the ionizing potential is equilibrated and dissipated in various ‘ways, for example, by increasing the internal energy of the molecule or by breaking atomic bonds.

Thus, the challenge in *non-fragmenting mass spectrometry* is to maximize the number of parent ions and, at the same time, maintain the number of fragment ions at acceptable levels. Paraffins are highly susceptible to fragmentation; an ionizing voltage high enough to generate a good parent ion spectrum also breaks many (paraffinic) carbon-carbon bonds, producing a significant number of fragment ions.

4.4.3 Nuclear magnetic resonance

Nuclear magnetic resonance has frequently been employed for general studies of hydrogen types in crude oil and crude oil products (ASTM D4808) as well as for the structural studies of crude oil constituents (ASTM E386; Speight, 1994). The technique has recently been adapted to measure the hydrogen content of fuels and other crude oil products (ASTM D3701, ASTM D4808). In fact, *proton magnetic resonance* (PMR) studies (along with infrared spectroscopic studies) were, perhaps, the first studies of the modern era that allowed structural inferences to be made related to the polynuclear aromatic systems that occur in the high molecular weight constituents of crude oil.

Thus, nuclear magnetic resonance (NMR) methods have gained a prominent place in the compositional and structural analysis of crude oil fractions (Speight, 1994). In its basic applications, NMR is fast and relatively inexpensive. Because of its convenience, speed, and greater wealth of detailed information, particularly from ‘^{3}C NMR, it has displaced the n-d-M and related methods in most laboratories (Speight, 2001, 2014a). Nuclear magnetic resonance presents a direct measure of the aromatic and aliphatic carbon as well as hydrogen distribution. Beyond these results, both carbon and hydrogen in various structural groupings in a molecule can be determined. Thus, proton (^{1}H) and carbon-13 (^{13}C) nuclei are the most common ones used in nuclear magnetic resonance spectroscopy; nitrogen (^{15}N and ^{14}N) and sulfur (^{33}S) have been employed on occasion with crude oil fractions for special applications.

Proton magnetic resonance has been widely employed in the structural analysis of crude oil fractions. It is a relatively inexpensive technique that allows measurement of hydrogen atoms in aromatic and aliphatic groups, even allowing differentiation between hydrogen attached to next to an aromatic ring (α-position) and those farther removed from the ring. Atoms in single-ring and multi-ring aromatic compounds as well as those in olefin locations can also be identified.

Only a small amount (<10 mg) of the sample is required, dissolved in a solvent such as deutero-chloroform (CD_3Cl), contained in a glass tube (5 mm diameter) and placed in a highly homogeneous magnetic field where it is surrounded by one or more coils. The coils serve to subject the sample to a weak radio-frequency (RF) field. The hydrogen nuclei of the sample can be visualized as magnets and when the radio frequency is equal to the processing frequency, resonance occurs between the two, and the spin resonance is detected by a receiver coil. The position of a sample resonance with that of tetramethylsilane (TMS) as a reference difference is reported as *chemical shift*, δ, which is a dimensional number that is expressed in terms of parts per million (ppm) difference from the reference (TMS).

Quantitative accuracy of proton magnetic resonance for aromatic and aliphatic hydrogen is approximately 1% for distillates and 2–3% for residua; that for the distinction of aliphatic hydrogen atoms a to an aromatic ring from those β and farther away from the ring is somewhat lower. Methyl (CH_3), methylene (CH_2), and methine (CH) hydrogen can ordinarily not be distinguished except for methyl hydrogen γ or farther away from aromatic rings. Even this methyl peak is sometimes difficult to quantify because of interference by naphthenic methine and methylene hydrogen.

Protons attached to single-ring and multi-ring aromatic compounds can usually be distinguished with reasonable accuracy, especially when the sample concentration is 2% or less. At such low concentrations, the dividing line between these protons is at 7.25 ppm. In the spectra of samples with high boiling point, much of the detail is lost and differentiation between group-types is difficult.

Thus, in general, the proton (hydrogen) types in crude oil fractions can be subdivided into three types: (i) aromatic ring hydrogen, (ii), aliphatic hydrogen adjacent to an aromatic ring, and (iii) aliphatic hydrogen remote from an aromatic ring. In other cases, five types of hydrogen locations are identified: (i) aromatic hydrogen, (ii) substituted hydrogen next to an aromatic ring, (iii) naphthene hydrogen, (iv) methylene hydrogen; and (v) terminal methyl hydrogen remote from an aromatic ring. Other ratios are also derived from which a series of structural parameters can be calculated.

However, it must be remembered that the structural details of the carbon backbone obtained from proton spectra are derived by inference but it must be recognized that protons at peripheral positions can be obscured by intermolecular interactions. This, of course, can cause errors in the ratios that can have a substantial influence on the outcome of the calculations (Ebert et al., 1987; Ebert, 1990).

It is in this regard that *carbon-13 magnetic resonance* (CMR) can play a useful role. Since carbon magnetic resonance deals with analyzing the carbon distribution types, the obvious structural parameter to be determined is the is aromaticity, f_a. A direct determination from the various carbon type environments is one of the better methods for the determination of aromaticity. Thus, through a combination of proton and carbon magnetic resonance techniques, refinements can be made on the structural parameters and, for the solid state high resolution CMR technique, additional structural parameters can be obtained.

The basic instrumentation for carbon-13 magnetic resonance is the same as that for proton magnetic resonance except that there are two radio-frequency fields orthogonal (at right angles) to the main magnetic field, one for observing the carbon-13 nuclei and the other for decoupling the proton nuclei. The low abundance of carbon-13 isotopes (1.1%) and the lower gyromagnetic ratio of the carbon-13 nucleus make the signal weaker by more than two orders of magnitude and, moreover, the nuclei have longer relaxation times. The effect is that, even with Fourier transform (FT) data acquisition, carbon-13 magnetic resonance measurements can hours to perform.

In contrast to proton magnetic resonance spectroscopy, the peak areas arising from the carbon-13 nuclei in different molecular positions ordinarily are not proportional to their concentration. Quantitative measurements require that two effects must be overcome: (i) the different relaxation times of the carbon-13 nuclei in different chemical groups, and (ii) the nuclear Overhauser enhancement (NOE). The latter effect refers to the rise in signal intensity when C–H coupled protons are saturated by the decoupling field.

One way to do this is to add a small amount of a paramagnetic relaxation reagent, such as trisacetylacetonatochromium (III), $Cr(AcAc)_3$, which changes the dominant relaxation mechanism into one involving the interaction between unpaired electrons and $^{\prime 3}C$ nuclei. It also reduces the long relaxation times of some carbons.

In its simplest form, carbon-13 magnetic resonance can distinguish between aliphatic and aromatic carbon. In the aliphatic region of crude oil ^{13}C NMR spectra, several sharp peaks stand out and are used for quantitative. The most prominent peak is usually that at 29.7 ppm. It is attributed to methylene (CH_2) carbon atoms in long alkyl chains, positioned four or more carbons ($>\gamma$) away from an aromatic ring and from terminal methyl CH_3) groups.

Normally, the absorption of 29.5–30.3 ppm an estimation of the amount of carbon atoms in long alkyl chains ($>C_5$). Because this band represents methylene (CH_2) groups two or more carbons away from an aromatic ring and a terminal group, there must be four more carbons per chain than indicated by the area under these peaks. The *number of long chains* (n_{CH2}) can be estimated from the peaks at 14.2 ppm (ω-CH_3) and at 28.1 ppm (CH_2) next to a terminal branch point, i.e., a methane (CH) group. On the one hand, the peak at 14.2 ppm gives results too high for this purpose because it also indicates CH_3 groups from chain branches. Subtracting half of the 37.6-ppm peak area (CH_2 next to CH groups inside a chain) corrects for this feature. On the other hand, the peak at 14.2 ppm does not cover twin CH_3 groups (as in an isopropyl group). This is why the 28.1 peak (CH next to two terminal methyl groups is needed. Thus,

$$n_{\mathrm{CH2long\ chains}} = A(14.2) - 1/2A(37.6) + 1/3A(28.1)$$

The number of methylene groups in long chains is the sum of the by the peak at 29.7 ppm, the number of methylene groups at the two ends, i.e., six times the number of long chains for each of the two ends (Fig. 5.8), and the number close to branch points inside the chain, namely, those next to them and one carbon atom removed, on both sides of the CH group. Thus, the total numbers is:

$n_{CH2} = C\ (29.7) + 6n_{\mathrm{CH2long\ chains}} + 4C\ (37.6)$.

The number of methine (CH) groups in long chains can be estimate from the absorbance at 37.6 ppm and at 39.5 ppm. The peak at 37.6 ppm represents methylene groups next to methane carbon and thus does not represent a direct measurement of the methane groups. Thus:

$$n_{\text{CHlong chains}} = 1/2C(37.6) + C(39.5)$$

The methyl groups give rise to at least four peaks in carbon-13 spectra, namely the peaks at 11.5, 14.2, 19.5, and 22.7 ppm. The peak 22.7 ppm represents twin methyl groups as in an isopropyl group and it also has a contribution from a methylene group next to a methyl group and does not need to be represented again by a contribution to the equation from the peak at 14.2 ppm. Thus.

$$n_{\text{CH3long chains}} = C(11.5) + C(19.5) + C(22.7)$$

The final estimate for carbon atoms in long chains is then the sum of the three types. The average length of long chains derives from dividing the number of carbon atoms in long chains by the number of long chains. Remembering, of course, that averages derived from magnetic resonance spectra can be very misleading if the data are interpreted too literally (Speight, 2014a).

The methyl group (CH_3) gives rise to several peaks depending on its position in the molecule. A peak at 14.2 ppm signals such a group positioned at the end of an unbranched chain segment of at least two or three methylene (CH_2) groups. A methyl group next to a branch point (methine group, CH) at the end of a chain with at least two methylene groups produces a peak at 22.7 ppm. Farther away from the end of the chain, such a group gives a peak at or near 19.8 ppm. The methyl group at the end is also affected by these branch points (Fig. 5.8).

Naphthenic carbon in high molecular weight crude oil fractions usually occupies so many slightly different positions that the peaks are unresolved and form a broad hump in the range 25–60 ppm, under the generally well-resolved paraffinic peaks.

The evaluation of the hump is the only direct method for the determination of naphthenic methylene and methane (CH_n) groups. However, its measurement may not always be reliable. In very high-boiling crude oil samples, such as asphaltene constituents, the paraffin-type resonance may be only partly resolved. Although this leads mainly to broader peaks, the overlap may in some cases add to the hump and, thus, cause erroneously high results for naphthenic carbon. The aromatic region of the ^{13}C NMR spectrum can be evaluated by conventional integration of the peaks due to the main aromatic group types.

Thus, proton and carbon-13 magnetic resonance spectroscopic techniques offer the potential information related to the molecular types in the non-volatile fractions of crude oil. The techniques have, by the application of the estimation of peak areas and further application of mathematical methods have been used to obtain information related to *structural parameters* that are then converted to *average structures*.

In most cases the average structure of such complex mixtures as crude oil fractions is not the same as a representative structure. As already noted, average structures derived from magnetic resonance spectra can be very misleading if the data are interpreted too literally (Speight, 2014a). Even though the average structures may always be questions, one must also treat with some caution the structural parameters since they have been derived using assumptions that themselves are subject to debate.

4.4.4 Ultraviolet spectroscopy

The ultraviolet–visible (UV–Vis) spectrum, although not as specific for chemical group types as infrared spectroscopy and nuclear magnetic resonance spectroscopy, can distinguish between aromatic compounds with different ring numbers and configurations (e.g., ASTM D1840, ASTM D2269). The patterns are not distinct enough to recognize or distinguish these compounds in complex mixtures, but they can be useful for their identification in narrow fractions.

Ultraviolet–visible spectroscopy (ASTM E169) can be employed as a detector for the fractionation of crude oil samples, for example, for the chromatographic separation and/or identification of aromatics by ring number, especially in combination with a technique such as liquid chromatography (Speight, 1986). Thus, ultraviolet–visible spectroscopy lends itself to studies of refining processes as an online detector.

4.4.5 X-ray diffraction

X-ray diffraction had been used for the determination of the fraction of aromatic carbon (f_a) in crude oil constituents. This ratio can also be conveniently and precisely obtained by carbon-13 nuclear magnetic resonance spectroscopy as well as by infrared spectroscopy. The determination of the fraction of carbon that is aromatic may be in error (Ebert, 1990) since X-ray diffraction data can be very misleading (Ebert et al., 1984), especially when the data are used to translate geometric data-measurements of (aromatic) sheet diameter -into structural information. On the one hand, not all aromatic atoms contribute to the stack diameter seen by x-ray diffraction,whereas, on the other hand, non-aromatic atoms such as hydroaromatic carbons and other substituents on aromatic rings may contribute to the diffraction pattern. Thus, the interpretation of these measurements is quite arbitrary.

Extended x-ray absorption fine structure (EXAFS) and *x-ray absorption near-edge structure* (XANES) spectroscopy are tools for the investigation of the immediate chemical environment of x-ray absorbing elements such as metals and sulfur. X-ray absorption near-edge structure and x-ray photoelectron spectroscopy (XPS) have been applied to the determination of sulfur compounds as well as nickel and vanadium in crude oil samples.

4.5 Molecular weight

The molecular weight (formula weight) of a compound is the sum of the atomic weights of all the atoms in a molecule and can be determined by a variety of methods. Crude oil, being a complex mixture of (at least) several thousand constituents requires qualification of the molecular weight as either (i) number average molecular weight or (ii) weight average molecular weight.

The *number average molecular weight* is the ordinary arithmetic mean or average of the molecular weights of the individual constituents. It is determined by measuring the molecular weight of *n* molecules, summing the weights, and dividing by *n*. The *weight average molecular weight* is a way of describing the molecular weight of a complex mixture such as crude oil even if the molecular constituents are not of the same type and exist in different sizes. Molecular weight is often used in refineries to provide mass-average or number-average measurements. Consequently a number of methods are available to measure molecular weight of crude oil and crude oil products.

Molecular weight may be calculated from viscosity data (ASTM D2502). The test method requires viscosity data from different temperatures, typically at 37.8 °C and 98.9 °C (100 and 210 °F. The method is generally applicable to a variety of crude oil fraction and products but the number is an average number and applicable to those fraction or products with a molecular weight in the range 250–700. Samples with unusual composition, such as aromatic-free white mineral oils, or oils with very narrow boiling range, may give atypical or questionable results. For samples with higher molecular weight (up to 3000 or more) with unusual composition or for polymers another test method is recommended (ASTM D2503). This method uses a vapor pressure osmometer to determine the molecular weight of the sample. Low boiling samples may not be suitable – the vapor pressure of the constituents of the sample can interferes with the method.

A third method (ASTM D2878) developed for measuring the molecular weight of lubricating oil provides a procedure to calculate these properties from test data on evaporation. The procedure is based on the test method for measuring the evaporation loss of lubricating greases and other high-boiling crude oil products (ASTM D972). In the procedure, the sample is partly evaporated at a temperature of 250–500 °C (480–930 °F). However, fluids that are unstable in this temperature range are not suitable for submission to this test method.

If the molecular weight determination involves use of a solvent, it is recommended that to negate concentration effects and temperature effects the molecular weight determination be carried out at three different concentrations at three different temperatures. The data for each temperature are then extrapolated to zero concentration and the zero concentration data at each temperature are then extrapolated to room temperature (Speight, 2001, 2014a). Furthermore, each method of molecular weight determination has proponents and opponents because of assumptions made in the use of the method or because of the mere complexity of the sample and the nature of the inter- and intra-molecular interactions.

Methods for molecular weight measurement are also included in other more comprehensive standards and there are several indirect methods have been proposed for the estimation of molecular weight by correlation with other, more readily measured physical properties. They are satisfactory when dealing with the conventional type of crude oils or their fractions and products when approximate values are desired.

4.6 The future

In the crude oil industry, as in other chemical industries, the importance of feedstock and product analyses continues to grow. Instrumental and automated methods are replacing chemical and physical methods in the laboratories.

More stringent product requirements related not only to product performance but also environmental issues, advanced catalytic processing techniques, and improved feedstock purification for specific downstream processes are driving the limits of impurities into the less than parts-per-million range – in some cases into the parts-per-billion range. Efforts to provide quantitative analyses at this level continue. As refinery feedstocks, product distributions, and methodologies change, efforts to improve analytical methods based on current instrumental technology will continue to go hand-in-hand with refinery evolution.

With the passage of time since the 1960s, the crude oils being processed in refineries are on average becoming increasingly heavier (more residuum) and more sour (higher sulfur content). In addition, refinery economics dictate that the *bottom of the barrel* (residuum) must be upgraded to higher value products. To produce a viable product slate with these crudes, refiners must add to or expand existing treatment and processing options. The high sulfur content of crude coupled with government regulations limiting the maximum sulfur content of fuels makes sulfur removal a priority in refinery processing. This is not the only answer − fuels containing aromatic constituents can, and often do, emit black fumes when traveling under a load or moving up an incline. New treatment and process units in the refinery usually translate into a need for new analytical test methods that can adequately evaluate feedstocks and monitor product quality.

Desulfurization processes (hydrodesulfurization processes) in a refinery use catalyst that are sensitive to (i) the amount of sulfur and (ii) the structure of the sulfur compounds being removed and test methods that can provide data related to both of the sulfur-related issues are continuing and will continue to increase in importance. Extension of these types of analyses are combining the separation power of gas chromatography with sulfur-selective detectors to provide data on the boiling range distribution of the sulfur compounds and the molecular types of sulfur compounds that occur within a specific boiling range. Work on extending this type of analysis to the higher boiling ranges is also being used for characterization.

Specific to the *bottom of the barrel* upgrading and the production of quality products, involves taking more (all, if possible) of the residuum and producing more salable, higher value, on-specification products. As this form of upgrading expands, improved test methods and characterization techniques are necessary for (i) feedstock evaluation, (ii) process design, and (iii) predictability of yields of the product yields and character of the product.

In particular, there is a need to continue development of text methods that define the boiling range and distribution of the molecular-types. The boiling range distribution of high-boiling distillates and residua are, for example, increasingly being carried out by high-temperature simulated distillation (HTSD) using gas chromatography as the operational technique. The distributions of hydrocarbon types in gas oil and heavier materials are important in evaluating them as feedstocks for further processing.

The goal for any such method is automated, instrumental analyses as the option of choice when developing new methods and the trend to automation appears to be increasing. Reduction in analytical time as well as improving the quality of test results (eliminating dependency on the manual skills of the analyst) is needed to fulfill the required levels of accuracy and precision. Moved ahead by advances in technology, it is necessary that the analytical challenges of the refining industry.

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CHAPTER

10

Processing oil from tight formations

1. Introduction

Tight oil, sometimes referred to as light tight oil, is a crude oil from shales or other low-permeability geologic formations (Chapter 1). Permeability is a measure of a geologic formation to allow fluid, such as oil or gas, to move through it. Obtaining tight oil from shales requires hydraulic fracturing, often using the same horizontal well technology that is employed in the production of shale gas.

Tight oil is found throughout the world, as shown in (Chapter 2). However, the United States, Canada, China, and Argentina are currently the only four countries in the world that are producing commercial volumes of either natural gas from shale formations (shale gas) or crude oil from tight formations (tight oil). The United States is by far the leading producer of both shale gas and tight oil; Canada is the only other country to produce both shale gas and tight oil.

Tight oils are considered opportunity crudes because they are typically less expensive than crude oils produced by traditional drilling methods. Processing these cheaper crudes offers the refiner economic incentives but tights oils do come with their own set of unique challenges. Although tight oils have many physical properties in common, but the characteristics that differentiate them from one another are, in many cases, the root cause of a variety of processing challenges.

By way of recall, *opportunity crude oils* are either new crude oils with unknown or poorly understood properties relating to processing issues or are existing crude oils with well-known properties and processing concerns (Chapter 1). Opportunity crude oils are often, but not always, heavy crude oils but in either case are more difficult to process due to high levels of solids (and other contaminants) produced with the oil, high levels of acidity, and high viscosity. These crude oils may also be incompatible with other oils in the refinery feedstock blend and cause excessive equipment fouling when processed either in a blend or separately (Speight, 2015b).

Most refineries process many different crude oils and each crude oil requires slightly different processing conditions in the major process units (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017; Hsu and Robinson, 2017). Typically, a refinery is designed to process crude oil of a particular composition and produce products with specified properties, with some flexibility based on the capabilities of the equipment and the particular catalysts within

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the reactors. For maximum productivity and overall refinery efficiency, refiners try to match the crude oil composition to the configuration of the refinery, usually by blending two or more crude oils, if a single crude oil with the required composition is not available or economical. In fact, in many refineries, the days of the refinery accepting only one crude oil are now of historical practice rather than of current practice.

By way of comparison, using a general method of identification rather than a classification method, conventional low-density (light) crude oil has an API gravity in excess of 30°, medium crude between 20 and 30° API, and heavy crude has an API gravity below 20° API. Low-sulfur crude oil (typically referred to as sweet crude oil) contains less than 0.5% w/w sulfur while sour crude oil contains sulfur in excess of 0.5% w/w. Tight oils are typically lower density (light) and low-sulfur (sweet) crude oils and particularly noteworthy is high API gravity that is in excess of 40° API.

Generally, unconventional tight oil resources are found at considerable depths in tight sedimentary rock formations (tight shale formations, tight siltstone formations, tight sandstone formations, and tight carbonate formations) that are characterized by very low permeability (Chapter 1, Chapter 2, Chapter 3). These tight formations scattered thought North America and other parts of the world have the potential to produce considerable reserves of crude oil (*tight oil*) (US EIA, 2011; US EIA, 2013; Deepak et al., 2014).

Briefly and for reference, a shale play is a defined geographic area containing an organic-rich fine-grained sedimentary rock that underwent physical and chemical compaction during diagenesis to produce the following characteristics: (i) clay to silt sized particles, (ii) high % of silica, and sometimes carbonate minerals, (iii) thermally mature, (iv) hydrocarbon-filled porosity − on the order of 6%−14%, (v) low permeability − on the order of <0.1 mD, (vi) large areal distribution, and (vii) fracture stimulation required for economic production. The crude oils found in such reservoirs are typically light (low-density) crude oils (high API gravity) with a low sulfur content (Fig. 10.1).

In a conventional crude oil reservoir (for example, a conventional sandstone reservoir), the pore spaces are interconnected so that natural gas and crude oil can flow relatively easily from the reservoir rock to a wellbore. In reservoirs composed of tight formations, the pores are smaller and are poorly connected by very narrow capillaries which results in low permeability and these formations typically have a permeability on the order of 1 milliDarcy or less (<1 mD) which require stimulation by hydraulic fracturing to produce crude oil.

The most notable tight oil plays in North America include the Bakken shale, the Niobrara formation, the Barnett shale, the Eagle Ford shale, and the Miocene Monterey play of the San Joaquin Basin (California) and the Cardium play (Alberta, Canada). In many of these tight formations, the existence of large quantities of crude oil has been known for decades and efforts to commercially produce those resources have occurred sporadically with typically disappointing results. However, starting in the mid-first decade of the current century, advancements in well drilling (such as horizontal drilling) and stimulation technologies (such as hydraulic fracturing) (Chapter 4, Chapter 5) combined with favorable economics have turned tight oil resources into one of the most actively explored and produced crude oil resources and crude oil resources in North America (Chapter 3). The production method for Eagle Ford crude oil and Bakken crude oil is achieved by means of horizontal drilling followed by hydraulic fracturing of the tight formation.

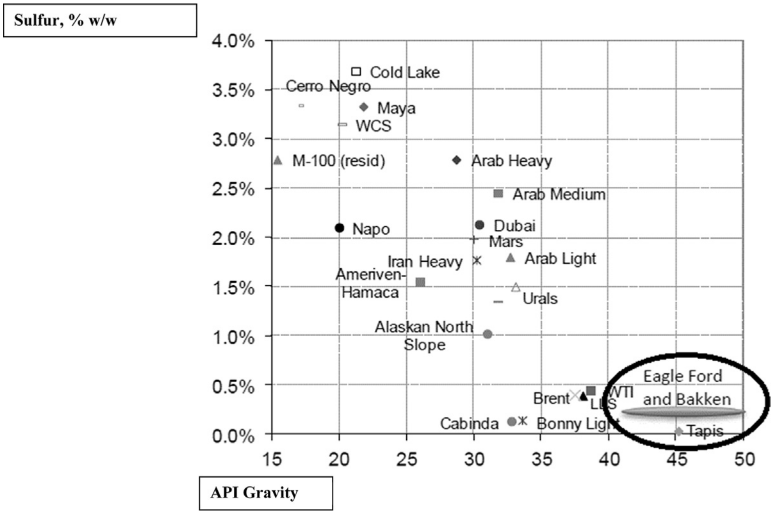


FIG. 10.1 API Gravity and sulfur content of various Crude Oils, Including Eagle Ford Crude Oil and Bakken Crude Oil.

The crude oil comes from the *Bakken formation*, a rock unit from the Late Devonian and early Mississippian age that occupies approximately 200,000 square miles (520,000 square kilometers) of the subsurface of the Williston Basin that underlies parts of Montana, North Dakota, Saskatchewan, and Manitoba (Fig. 10.2) (Nordquist, 1953; USGS, 2008). The oil is produced from the Bakken formation through horizontal wells in the natural fractures in the rock formation or through the use of horizontal drilling followed by hydraulic fracturing, which is the induced fracturing of the rock formation, accomplished through the high pressure injection of sand, water and chemicals (which can also include hydrochloric acid and ethylene glycol), in an attempt to release trapped oil and allow it to flow into the well (Chapter 5).

Other known tight formations (on a worldwide basis) include the R'Mah Formation (Syria), the Sargelu Formation (northern Persian Gulf region), the Athel Formation (Oman), the Bazhenov formation and Achimov Formation (West Siberia, Russia), the Coober Pedy formation (Australia), the Chicontepex formation (Mexico), and the Vaca Muerta field (Argentina) (US EIA, 2011, 2013). All are worthy of further investigation and possible development. However, tight oil formations are heterogeneous and vary considerably over relatively short distances. Thus, even in a single horizontal production well, the amount of oil recovered may vary and there may be variable recovery within a field or even variable recovery between adjacent wells. This makes evaluation of tight oil resources and decisions regarding the profitability of wells on a particular lease difficult. In addition, tight reservoirs which contain only crude oil (without natural gas as the pressurizing agent) may require a different economic treatment to make production and economic proposition (US EIA, 2011, 2013).

Thus while tight oil is found throughout the world, the United States, Canada, China, and Argentina are currently the only four countries in the world that are producing commercial volumes of either natural gas from shale formations (shale gas) or crude oil from tight

FIG. 10.2 Major basins with the potential for tight oil development. *Source: Adapted from US EIA, 2012. Energy Information Administration, United States Department of Energy, Washington, DC.*

formations (tight oil). Furthermore, the United States is by far the leading producer of both natural gas and crude oil from tight formations while Canada is the only other country to produce *both* natural gas and crude oil from tight formations.

The challenges associated with the production of tight oils are a function of the composition and the varied geological formations where they are found. These oils are low-density, but they are very waxy and reside in oil-wet formations which create some of the main difficulties associated with tight oil recovery. Such problems include scale formation, salt deposition, paraffin wax deposits, destabilized asphaltene constituents, and corrosion.

In summary, common characteristics of the tight oils (Table 10.1, Table 10.2, Table 10.3) can create unforeseen issues that require attention during refining although the sulfur content and other properties including distillate yields may compare favorably with similar properties for other light (low-density) crude oils.

This chapter will also present the methods that can be applied to the products of the refining of tight oil, viz: (i) naphtha, (ii) kerosene, (iii) gas oil, and the residuum.

TABLE 10.1 Comparison of properties of selected crude oils to illustrate the relative properties (API gravity sulfur content, and volatility) of Bakken and Eagle Ford crude oils.

	API	**Sulfur**	**Light ends**
Crude oil	**Gravity**	**% w/w**	**% v/v**[a]
Bakken	40–43	0.1	7.2
Eagle ford	48	0.1	8.3
West Texas intermediate	37–42	0.4	6.1
Louisiana light sweet	36–40	0.4	3.0
Brent (North Sea)	37–39	0.4	5.3
Arabian light	33	2.0	4.0
Arabian heavy	28	3.0	3.0

[a] *Light ends: low molecular weight organic constituents such as methane, ethane, propane, and butane which are included as components in the oil; in some crude assays, pentane and hexane may be included in the light ends fraction.*

TABLE 10.2 Common characteristics of tight oils.

Advantages
Gravity ranges 40–65° API – variations in composition
High yield of distillates
High yield of naphtha – useful for petrochemical feedstock
High paraffin content – useful for petrochemical feedstock
Low sulfur content – decrease in catalyst poisoning
Low nitrogen content – decrease in catalyst poisoning
Low content of heavy metals (Ni & V) – decrease in catalyst poisoning
Low yield of residuum – maximum production of distillates

Disadvantages
Batch to batch variability
The presence of hydrogen sulfide – toxic and corrosive
Unstable blends when mixed with some crude oils
High paraffin content – leads to wax deposition and incompatibility with other crudes
Level of alkaline metals may be high
Other contaminants (ba, Pb) may be present
Filterable solids – greater volume and smaller particle size – leading to fouling
Presence of production chemicals or contaminants – leading to fouling.
Low yield of residuum and (therefore) low yield of asphalt

2. Properties of tight oil

The crude oils found in reservoirs classed as tight reservoirs are typically light sweet crude oils (high API gravity) with a low sulfur content and a relatively high proportion of lower molecular weight volatile constituents (Table 10.1, Fig. 10.1). In fact, crude oils from tight formation are highly variable in their respective properties (Bryden et al., 2014). For example, density and other properties can show wide variation, even within

TABLE 10.3 Comparison of selected properties of crude oils from tight formations (eagle fiord, Bakken) with conventional light crude oils (Louisiana light sweet crude oil) and Brent crude oil.

	Eagle ford	Bakken	Louisiana light sweet	Brent (North Sea)
API	44–46	42–44	36–38	37–39
Sulfur, % w/w	0.2–0.3	0.05–0.10	0.35–0.45	0.35–0.45
N, ppm	200–400	300–500	900–1200	900–1100
TAN[a]	0.05–0.1	0.01–0.05	0.5–0.6	0.05–0.10
Light ends[b], % v/v	13%–14%	15–16	9–11	10–12
Naphtha, % v/v	22–24	25–27	19–21	19–21
Middle-distillates, % v/v	31%–33%	31–32	33–34	29–31
Vacuum gas oil, % v/v	24%–26%	22–24	28–29	28–30
Residuum, % v/v	4%–6%	3–5	7–9	9–11

[a] *TAN: total acid number.*

[b] *Light ends: low molecular weight organic constituents such as methane, ethane, propane, and butane which are included as components in the oil; in some crude assays, pentane and hexane may be included in the light ends fraction.*

the same field. However, as an illustration of all things not being equal, the low-density tight oils from the two different formations have different properties although sharing a common crude oil production technique.

American Petroleum Institute (API) gravity is a specific gravity scale developed by the oil industry to identify crude oils and other crude oil liquids based on the relative density. It is expressed in degrees (°API), and is an inverse measure of the relative density of a crude oil product and the density of water. Thus, the lower the API gravity, the heavier (higher density) the oil. Arbitrary numbers have been assigned to identify the various crude oils but these numbers should not be used to classify crude oils (Speight, 2014a, 2015a). For example, light crude oil has an API gravity higher than 30° while a medium crude oil falls in the API range 20 to 30° API and heavy crude oil is assigned an API gravity below 20° API. Sweet crude oils contain less than 0.5% w/w sulfur (sour crudes contain more than that). Crude oils from tight formations are typically light (low density) and sweet (low sulfur) with an API gravity on the order of 40 to 50° API.

Typical of the crude oil from tight formations (*tight oil, tight light oil, and tight shale oil* have been suggested as alternate terms, although the term *shale oil* is incorrect and adds confusion to the nomenclature) (Chapter 1) is the Bakken crude oil which is a light sweet highly volatile crude oil with an API gravity on the order of 40°–43° API and a sulfur content on the order of 0.2% w/w, or less (Table 10.1, Fig. 10.1). The relatively high quality of Bakken crude oil high quality is an advantage insofar as these properties make the oil easier to refine into commercial products but is also a disadvantage insofar as unless the oil is stabilized by removal of the light ends (low-boiling hydrocarbon gases), it is highly flammable when compared to many conventional crude oils. The *flash point* – the lowest temperature at which ignition can occur – is lower for Bakken crude oil than it is for many conventional crude oils, which should be (must be) interpreted as the Bakken crude oil is particularly flammable (in fact, it is highly flammable) and, moreover, when flammable gases (methane and the low-boiling hydrocarbon derivatives) are dissolved in oil, the oil should be stabilized (*degasified*) before transportation.

2.1 General properties

Unlike most conventional light crude oils, tight oils are light sweet oils, with a high paraffin content and low acidity. They also have minimal asphaltenic content and varying content of filterable solids, hydrogen sulfide (H_2S), and mercaptan derivatives. There are significant differences in the sulfur content and amount of the filterable solids. In addition, the streams from a tight oil production region can have significant variability, with colors ranging from pale amber to black.

Tight oils are, in general, light crude oils and the feed API derived from these oils are higher than API of feeds from conventional gas oils and typically have a lower amount of contaminants than conventional crude oils. However, the properties of tight oils are significantly different than typical crude oils and, as a result, a series of challenges exists that need to be solved to ensure uninterrupted transportation and refining of the tight oils to contend with and mitigate the potential disadvantages of the tight crude oils (Table 10.2).

On a comparative basis, tight oils typically have a higher API gravity than traditional crude oils, as well as much different properties. For example, Bakken crude oil and Eagle Ford crude oil have an API gravity on the order of 42–46° whereas Louisiana light sweet crude oil (a light sweet crude oil from the United States) and Brent crude oil (and international crude oil from the North Sea) have an API gravity on the order of 36–39°. In keeping with the higher API gravity, Bakken crude oil and Eagle Ford crude oil give a higher yield of light ends (low-boiling hydrocarbon gases) and naphtha than Louisiana light sweet crude oil or Brent (North Sea) crude oil as well as a lower yield of residuum (Table 10.3) (Olsen, 2015).

In addition, the crude oil assay reflects the yield pattern of distillates and is key information for determining the refinery products (Table 10.4). Thus, the tight formation crude oils

TABLE 10.4 Yields of distillate from eagle ford crude oil.

	Boiling range		Yield
Fraction	**IBP**[a]	**FBP**[b]	**% v/v**
C1–C4	<85	<85	1
Light naphtha	85	200	14
Heavy naphtha	200	350	23
Kerosene	350	450	12
Light gas oil	450	650	21
Vacuum gas oil	650	1050	24
Residuum	105+		5

[a] *IBP: initial boiling point.*
[b] *FBP: final boiling point.*

(such as Bakken crude oil, Eagle Ford crude oil, and Utica crude oil) typically have a lower boiling range with a higher API gravities, and have predominantly higher gas constituents, naphtha with less high-boiling vacuum gas oil vacuum residue materials. Furthermore the API gravity of crude oil can be used to approximate key properties, such as distillate yields, contaminants and paraffin concentration – there is a general trend of increasing lower-boiling constituents with increasing API (Speight, 2014a, 2015a). Consequently, Eagle Ford oil with an API on the order of 48° has (would be expected to have a higher yield of naphtha (boiling range: 50–200 °C (120–390 °F))) than Bakken crude oil with an API on the order of 40 to 43°. Contaminant levels also trend with gravity. For example, sulfur and nitrogen concentrations are generally lower for the light sweet crude oils produced from tight oil plays and higher for lower-gravity crude oils. However, higher-API gravity crudes typically have higher paraffin (wax) concentrations.

However, although tight oil is considered sweet (i.e., low sulfur content in the crude oil itself), hydrogen sulfide gas comes out of the ground with the crude oil. This gas is flammable (producing the noxious sulfur dioxide during combustion) and poisonous

$$H_2S + O_2 \rightarrow SO_2 + H_2O$$

Therefore, the presence of hydrogen sulfide must be monitored at the drilling site and during loading at the wellhead, transportation, and offloading of the crude oil at the refinery. Prior to transportation, amine-based scavengers should be added to the crude oil prior to transport to refineries. These scavengers react with the hydrogen sulfide to produce non-volatile products:

$$H_2S + RNH_2 \rightarrow RNH_3^+\ HS^-$$

However, mixing in the railcar due to movement, along with a change in temperature that raises the vapor pressure of the crude oil (an easily achievable event considering the volatility of the crude oil, Table 10.1, Table 10.3), can cause the release of hydrogen sulfide during offloading thereby creating a safety issues, especially when the crude oil is handled in warmer climates.

2.1.1 *Corrosivity*

Corrosivity due to the presence of naphthenic acids in crude oil is a particular concern for refineries, and had been raised as an issue in permitting the Keystone XL pipeline to transport Canadian oil sand derived crude oil. It is measured as the number of milligrams of potassium hydroxide (milligrams KOH per gram of crude oil, mg KOH/g/g) needed to neutralize the acids in one gram of oil, and reported as *total acid number* (TAN) (Speight, 2014b). As a rule-of-thumb, crude oils with a total acid number greater than 0.5 are considered potentially corrosive. Bakken crude oil and Eagle Ford crude oil each have a total acid number that is less than 0.1 mg potassium hydroxide (KOH) per gram of crude oil. In addition, some samples of Eagle Ford crude have been shown to contain olefin (>C=C<) and/or carbonyl (>C=O) compounds – both of which can act as fouling precursors (Speight, 2015b) that are not typically found in conventional crude oil.

2.1.2 *Flammability*

There is some risk with mixing any type of crude oil with air in the proper proportion which, in the presence of a source of ignition, can cause rapid combustion (flammable range) or, alternatively, an explosion (explosive range). The flammable range includes all concentrations of flammable vapor or gas in air, in which a flash will occur or a flame will travel if the mixture is ignited at or above a certain temperature (*flash point*). The *lower flammability limit* (lower flammable limit, LFL) is the minimum concentration of vapor or gas in air below which propagation of flame does not occur on contact with a source of ignition. The *upper flammability limit* (upper flammable limit, UFL) is the maximum proportion of vapor in air above which propagation of flame does not occur. The terms *lower explosive limit* (LEL) and *upper explosive limit* (UEL) are used interchangeably with LFL and UFL. Following from these definitions, liquids having a flash point at or above 100 °F (37.8 °C) are classed as *combustible* and liquids having a flash point below 100 °F (37.8 °C) are classed as *flammable*. However, crude oil may differ in terms of combustibility or flammability depending upon the proportion and properties of volatile and flammable constituents.

The flammability characteristics which include the flash point temperature (FPT), the auto ignition temperature (AIT), and the upper and lower flammability limits (UFL, LFL) are some of important safety specifications that must be considered in assessing the overall flammability hazard potential of hydrocarbon derivatives, defined as the degree of susceptibility to ignition or release of energy under varying environmental conditions. Experimental values of these properties are available from data tables that list the properties of hydrocarbon derivatives. Typically, the *flash point* is used as the determinant for assessing the flammability of hydrocarbon fuels under a variety of conditions.

The *flash point* of a hydrocarbon fuel is the lowest temperature at which the constituents of the fuel can vaporize to form an ignitable mixture in air. The flash point is not to be confused with the auto-ignition temperature (Speight, 2015a), which does not require an ignition source, or the fire point, the temperature at which the vapor continues to burn after being ignited. On the other hand, the auto-ignition temperature of a hydrocarbon fuel is the lowest temperature at which it will spontaneously ignite without an external source of ignition, such as a flame or spark while The fire point of a hydrocarbon fuel is the temperature at which it will continue to burn for at least 5 s after ignition by an open flame (Speight 2014a, 2015a).

A combustible gas-air mixture as illustrated by the lower boiling constituents of the Bakken crude oil, can be burned over a wide range of compositions when subjected either to elevated temperatures or exposed to a catalytic surface at ordinary temperatures (Zabetakis, 1965). For example, methane and other volatile hydrocarbon derivatives emanating from a crude oil can be readily oxidized on a heated surface and a flame will propagate from an ignition source at ambient temperatures and pressures.

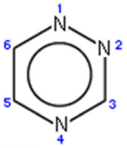
2.1.3 *Sulfur and hydrogen sulfide*

Challenges in handling and processing crude oils form tight formations include hydrogen sulfide entrained in the crude and amine-based hydrogen sulfide scavengers added in the pipeline or railcars prior to transportation. In addition, the amount of free sulfur in a crude oil is an indication of potential corrosivity from the formation of acidic sulfur compounds (such as the sulfur oxides, SO_x where x is 2 or 3, and the sulfur acids, H_2SO_3 and H_2SO_4). Sulfur oxides released into the air during combustion of refined crude oil products are also a major air pollutant. During the decomposition of organic matter that occurs with hydrocarbon derivatives in some geologic formations, sulfur may chemically combine with hydrogen to form hydrogen sulfide gas (H_2S), a highly corrosive, flammable, and toxic gas. Oil and gas reservoirs with high concentrations of hydrogen sulfide can be particularly problematic to produce. In addition, hydrogen sulfide causes sulfide-stress-corrosion cracking in the standard steel casing and valves used to construct oil wells, and thus require a switch to costly stainless steel (Speight, 2015b).

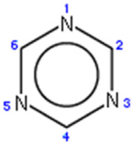
The sulfur content is measured as an overall percentage by weight (% w/w) of free sulfur and sulfur compounds in a crude oil (Speight, 2014a, 2015a). The total sulfur content in crude oils generally ranges from below 0.05%–5% w/w and crude oils with less than 0.5% free sulfur or other sulfur-containing compounds are typically (and arbitrarily) referred to as *sweet*, and above 0.5% sulfur as *sour*. Bakken crude oil and Eagle Ford crude oils are sweet, each with a low sulfur content (Table 10.1, Table 10.3) but hydrogen sulfide may occur at problematic levels.

Tight oils are typically low in sulfur (an advantage) but may, nonetheless, have high concentrations of hydrogen sulfide (a disadvantage). Triazine-based H2S scavengers are commonly used upstream for environmental, health and safety (EHS) compliance. The triazine derivatives are a class of nitrogen-containing heterocyclic compounds that are based on the molecular formula $C_3H_3N_3$:

1,2,3-triazine



1,2,4-triazine



1,3,5-triazine
or
s-triazine

However, the triazine contaminates the crude oil and can contribute to disadvantageous consequence, such as (i) emulsion stabilization, (ii) amine halide salt fouling, and under-deposit corrosion throughout the refinery. Modification of the acidity in the desalting unit can be effective in removing the triazine derivatives from the crude oil.

Unfortunately, these amines (the triazine derivatives) contribute to corrosion problems that arise from the conversion of the triazine derivatives to mono-ethanolamine ($HOCH_2CH_2NH_2$, MEA) in the atmospheric distillation unit. Once formed, the mono-ethanolamine reacts rapidly with chlorine from any residual brine associated with the crude oil to form chloride salts. These salts lose solubility in the hydrocarbon phase and become solids at the processing temperatures of the atmospheric distillation tower and form deposits on the trays or overhead system. The deposits are hygroscopic and, once water is absorbed, the deposits become very corrosive.

2.1.4 *Volatility*

Volatility refers to the evaporation characteristics or distillation characteristics of crude oil (and crude oil products) which includes the vapor pressure at 37.8 °C (100 °F) of crude oil products and crude oils with initial boiling point above 0 °C (32 °F) (ASTM D323). Vapor pressure is an important consideration for both crude oil producers and refiners in determining general handling and initial refinery treatment.

The liquids stream produced from the Bakken formation will include the crude oil, the low-boiling liquids, and gases that were not flared, along with the materials and by-products of the fracking process. These products are then mechanically separated into three streams: (i) produced salt water, often referred to as brine, (ii) gases, and (iii) crude oil liquids, which include condensates, natural gas liquids, and low-boiling constituents – this latter fraction is often referred to as light oil. Depending on the effectiveness and appropriate calibration of the separation equipment, which is controlled by the oil producers, varying quantities of gases remain dissolved and/or mixed in the liquids, and the whole is then transported from the separation equipment to the well-pad storage tanks, where emissions of volatile hydrocarbon derivatives have been detected as emanating from the oil.

The production of the crude oil also yields a significant amount of volatile gases (including propane and butane) and low-boiling liquids (such as pentane and natural gasoline – technically, the use of the term *natural gasoline* is incorrect since gasoline is a blended product from the refinery), which are often referred to collectively as (low-boiling or light) naphtha. By definition, natural gasoline (sometime also referred to as *gas condensate*) is a mixture of low-boiling liquid hydrocarbon derivatives isolate from crude oil and natural gas wells suitable for blending with low-boiling naphtha and/or refinery gasoline (Mokhatab et al., 2006; Speight, 2014a). Because of the presence of low-boiling hydrocarbon derivatives, low-boiling naphtha (*light naphtha*) can become extremely explosive, even at relatively low ambient temperatures. Some of these gases may be burned off (flared) at the field well-head, but others remain in the liquid products extracted from the well (Speight, 2014a).

2.1.5 Inorganic constituents

Initially, the composition of the inorganic constituents of crude oil can be an issue – select samples of Bakken crude have contained salt concentrations as high as 500 ppm, as well as non-extractable salts. Salt composition is higher in terms of the concentration of calcium and magnesium salts (70%–90% w/w) versus typical crude oils which are sodium based (70%–80% w/w). The impact of the shift to calcium and magnesium salts is the potential for hydrolysis in the atmospheric tower fired heater. Hydrolysis is the conversion or decomposition of a salt to the ion and hydrogen chloride – sodium salts do not hydrolyze readily while magnesium and calcium do hydrolyze. The result is a constant total salt concentration the expectation is higher chloride levels in the atmospheric tower overhead leading to the potential for higher corrosion (Speight, 2014c, 2015b).

In addition, scale deposits of calcite ($CaCO_3$), other carbonate minerals (minerals containing the carbonate ion, CO_3^{2-}), and silicate minerals (minerals classified on the basis of the structure of the silicate group, which contains different ratios of silicon and oxygen) must be controlled during production or plugging problems arise. A wide range of scale additives is available which can be highly effective when selected appropriately. Depending on the nature of the well and the operational conditions, a specific chemistry is recommended or blends of products are used to address scale deposition.

2.2 Incompatibility

Briefly, the term *incompatibility* refers to the formation of a *precipitate* (or *sediment*) or *separate phase* when two or more liquids are mixed. The term *instability* is often used in reference the formation of color, sediment, or gum in the liquid over a period of time and is usually due to chemical reactions, such as oxidation, and is chemical rather than physical. This term may be used to contrast the formation of a precipitate in the near term (almost immediately). The phenomenon of *instability* is often referred to as *incompatibility*, and more commonly known as *sludge formation*, and *sediment formation*, or *deposit formation*. In crude oil and its products, *instability* often manifests itself in various ways (Table 10.5) (Stavinoha and Henry, 1981; Power and Mathys, 1992; Speight, 2014a). Hence, there are different ways of defining each of these terms but the terms are often used interchangeably. Both phenomena have extremely important consequences for the production, transportation, and refining crude oils from tight formations.

The light tight crude oil from tight formation are predominantly paraffinic in character leading to the potential for incompatibility in the form of the deposition of the constitunets of paraffin wax (Speight, 2014a). When this occurs, the deposited wax adheres to the walls of railcars, crude oil tank walls, and piping. In the refinery, the wax constituents can foul the preheat sections of crude heat exchangers (before they are removed in the crude desalter) (Speight, 2015b). On the other hand, crude oils from tight formations are characterized by low content of asphaltene constituents, low-sulfur content and a significant molecular weight distribution of the paraffinic wax constituents. Paraffin carbon chains of C_{10} to C_{60} have been observed, with some tight oils containing carbon chains up to C_{72}. To control deposition and plugging in formations due to paraffins, the dispersants are commonly used. In upstream applications, these paraffin dispersants are applied as part of multifunctional additive packages where asphaltene stability and corrosion control are also addressed simultaneously.

TABLE 10.5 Examples of properties related to instability in crude oils and crude oil products.

Property	Comments
Asphaltene constituents	Influence oil-rock interactions
	Separates from oil when gases are dissolved
	Thermal alteration can cause phase separation
Heteroatom constituents	Provide polarity to oil
	Preferential reaction with oxygen
	Preferential thermal alteration
Aromatic constituents	May be incompatible with paraffinic medium
	Phase separation of paraffin constituents
Non-asphaltene constituents	Thermal alteration causes changes in polarity
	Phase separation of polar species
Wax constituents	Phase separation of high molecular weight paraffins
	Caused by changes in temperature or pressure
	Dependent upon solvent properties of medium

In the refinery processing tight crude oil, each heat exchanger unit upstream of the crude desalter should be equipped with online temperature sensors to monitor the temperatures at the inlet and outlet of the heat exchanger to detect any changes in the rate of heat transfer as they occur. In addition, filterable solids also contribute to fouling in the crude preheat exchangers and since a tight crude oil can contain more filterable solids than a conventional crude oil, filterable solids can be a major issue when refining crude oil from tight formations. In order to mitigate plugging of filters, the filters at the entrance of the refinery require assiduous and careful (automated) monitoring because of the need to capture the solid matter in the feedstocks. In addition, wetting agents may be added to the desalter to help capture excess solids in the water, rather than allowing the undesired solids to travel further downstream into the refinery and thereby causing problems with the various refinery punts, especially in the preheater units to the distillation tower and even within the distillation tower itself (Speight, 2015b).

An additional aspect of incompatibility occurs when crude oil is blended with other crude oils to generate a composite refinery feedstock. It has become common refinery practice that, in order to make optimal use of the available crude oils, to blend several crude oil, which includes blending tight oils with conventional and even with heavier crude oils to produce a more consistent (in terms of composition) feedstock to the distillation unit to facilitate an optimal operation. If tight oil refinery feedstocks are blended with heavier crude oil, the lower-boiling oil can create a bottleneck in the crude overhead and naphtha processing units and limit production in bottom-of-the-barrel processing units such as the delayed coker.

The stability of asphaltene constituents in crude oil has always played a role in blending asphaltene-containing crudes, the high paraffin content of tight oils greatly increases the potential impact of asphaltene precipitation upon blending, and its negative impact on the refinery process. There are several established and developing test methods that can evaluate an oil, or a blend, for asphaltene stability. Typically, when blending asphaltene-containing crude oils, the initial blending of the oils may seemingly produce a stable homogeneous mixture but over time (which varies from minutes to days depending upon the properties of the crude oils or other liquids in the blend), the asphaltene constituents start to associate in such a manner that such that they form a separate detectable phase in the fluid. Finally, after significant association (leading to agglomeration) has occurred and the asphaltene constituents have formed larger particles, phase separation occurs. These phase-separated asphaltene constituents contribute to fouling and can also stabilize desalter emulsions.

When crude oils are incompatible, increased asphaltene precipitation accelerates fouling in the heat exchanger train downstream of the crude desalter (Speight, 2015b) which may necessitate an unscheduled shutdown for cleaning. In addition, high naphtha content of tight oils also creates favorable conditions for separation and precipitation of the asphaltene constituents but it is not just missing the crude oils that can cause problems it is the relative amounts of each crude oil in the blend. For example, pentane – a precipitating medium for asphaltene constituents, when mixed in specific proportions does not cause separation and precipitation of the asphaltene constituents (Mitchell and Speight, 1973; Speight, 2014a, 2015b). Manual monitoring of heat exchanger fouling often fails to detect crude blends that are incompatible so it is beneficial to apply a series of test methods to determine the compatibility of the various crude oils in the refinery feedstock blend.

Another concern with tight oil refining is the potential for the phase separation of wax constituents. These waxes can contain very long-chain paraffins and iso-paraffins C_{35} and higher. The subsequent formation of waxy sludge can be problematic in transportation; in storage tanks, impacting storage capacity and tank drains; as well as increasing the potential for fouling in the cold train. In addition to asphaltene constituents and wax constituents, tight crude oils may introduce other contaminants that may cause fouling which can adversely affect heat transfer throughout the refinery. Chemical treatment programs can effectively address many of the issues related to processing both Eagle Ford and Bakken blends, although the best treatment program for one blend may be very different from the best for the other.

Oil from tight formations is characterized by low-asphaltene content, low-sulfur content and a significant molecular weight distribution of the paraffinic wax content (Speight, 2014a, 2015a). High molecular weight paraffins having carbon chains of C_{10} to C_{60} have been found, with some tight oils containing carbon chains up to C_{72}. To control deposition and plugging in formations due to paraffins, the dispersants are commonly used. In upstream applications, these paraffin dispersants are applied as part of multifunctional additive packages where asphaltene stability and corrosion control are also addressed simultaneously (Speight, 2014a, 2014b; 2014c, 2015a; 2015a).

Generally, the distillates containing high amounts of long-chain paraffins tend to exhibit poor cold flow properties because the paraffin constituents, which make these crude oils suitable for diesel production, are prone to wax production creating flocculation seen as high cloud points and as they crystallize with high pour points. The wax formation starts with a nucleation point for small crystals to collect (*cloud point*). As the crystal grows the larger crystals combine or agglomerate into larger collected masses until the fuel begins to gel (*pour point*). The thermodynamics are such that the heat of fusion can be measured by the differential temperature of the mixture. As a result, cold flow properties require improving via chemical additives, isomerization, or blending.

Crude oil blending operations and/or the product blending operations are the mainstays operations of many refineries, regardless of size or overall configuration. In the blending operations, refinery streams (crude oil or products) are blended in various proportions to produce the desired refinery feedstock mix or the desired finished refined products whose properties meet all applicable industry and government standards, at minimum cost. Production of each finished product requires multi-component blending because (i) refineries produce no single blend component in sufficient volume to meet demand for any of the primary blended products such as gasoline, jet fuel, and diesel fuel, (ii) many blend components have properties that satisfy some but not all of the relevant standards for the refined product into which they must be blended, and (iii) cost minimization dictates that refined products be blended to meet, rather than exceed, specifications to the extent possible. Typically, gasoline is a mixture of approximately 6–10 blend stocks and diesel fuel is a mixture of approximately 4–6 blend stocks (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017; Hsu and Robinson, 2017).

Gasoline blending is the most complex and highly automated blending operation. In modern refineries, automated systems meter and mix blend stocks and additives while on-line analyzers (supplemented by laboratory analyses of blend samples) continuously monitor the properties of the blend. Computer control and pre-bending mathematical models establish composition of the blends to produce the required (stable) product volumes and ensure that all blend specifications are met.

Wax deposition is particularly evident during recovery of crude oil from tight formations in addition to transportation, refining, and product (or crude oil) storage. The properties of the crude oils from tight formations are significantly different from the properties of typical conventional crude oils because of the high paraffin content. In addition, the varying content of filterable solids, hydrogen sulfide (H_2S), and mercaptan derivatives (RSH) also offer challenges during recovery, transportation, and storage. Solids content (and the potential for inorganic deposition) of samples from a single producing region can be highly variable and associated with the stage of fracturing and production from which the oil is produced.

The challenges associated with the production of crude oil from tight shale formation are a function of the wax content which leads to wax deposition. To control deposition and plugging in formations due to paraffins, dispersants are commonly used and, in upstream applications, the dispersants are applied as part of multifunctional additive packages where asphaltene stability and deposition control are also addressed simultaneously. Chemical and mechanical solutions are used to mitigate wax deposition and these deposit problems and preventive deposition control programs have been developed to manage the wax deposition occurring in storage tanks. Use of the appropriate chemical treatment to control wax buildup during production and during storage can accommodate and transfer larger quantities of waxy crude oil without significant plugging issues.

The high paraffin content of the light tight crude oils is a main contributor that leads to the issue of wax deposition during blending. Mixing oil from tight shale with an asphaltene-containing oil leads to destabilization of the asphaltene constituents, separation, and deposition (asphaltene deposition). In addition, several crude oils form tight formations have a high content of hydrogen sulfide (H_2S) that can lead to the need for hydrogen sulfide scavengers prior to distillation. The scavengers are often amine-based products − such as methyl triazine − that are converted into mono-ethanolamine ($HOCH_2CH_2NH_2$, MEA) in the atmospheric distillation unit and which contribute to problems in the unit. Once mono-ethanolamine forms, it rapidly reacts with chlorine [from any associated formation water (brine)] to form chloride salts which lose solubility in the hydrocarbon phase and become solids at the processing temperatures of the atmospheric unit and form deposits on the trays or overhead system. The deposits are hygroscopic, and, once water is absorbed, the deposits become very corrosive.

While the basic approach toward developing a tight oil play are expected to be similar from area to area, the application of specific strategies, especially with respect to well completion and stimulation techniques, will almost certainly differ from play to play, and often even within a given play. The differences depend on the geology (which can be very heterogeneous, even within a play) and reflect the evolution of technologies over time with increased experience and availability.

In general, a modern refinery must continue to adapt to increasing variability in crude oil quality. The onset of tight oil refining combined with blending of tight oils into the standard conventional crude oil refinery slate, and any form of standardized refinery operations is difficult, and has brought new issues for consideration into the refinery. Thus, processing difficult blends of crude oils, inclosing the light tight crude oils, can have a significant negative impact on overall refinery efficiency which affects product quality, unit reliability, on-stream time, and (above all) profitability.

Determining the means by which a new crude oil (specifically, a light tight crude oil) fits into a refinery operation requires a comprehensive understanding of the physical properties and unique characteristics of that crude and how it will interact with the rest of the typical crude slate (Speight, 2014a, 2015a; 2015b). Furthermore, the low yield of residuum (Table 10.3) is a disadvantage for refineries that configured for bottom-of-the-barrel upgrading and can limit the amount of tight oil that can be added to the blended cured oils that are the refinery feedstock. In order to balance the mix of products in the crude distillation tower to fit many refinery operations, blending tight oils with heavy asphaltic crude may be possible since the blend can result in a desirable distillation profile for the refinery but the blend may also exhibit a tendency for instability with the deposition of an insoluble (incompatible) phase (Chapter 17) (Speight, 2014a, 2015b).

3. Wellhead processing

Producing well sites are unmanned facilities which are visited only periodically by persons performing such functions as collecting crude oil or wastes, maintaining equipment and testing or otherwise operating wells. Since well site equipment, for the most part, is unattended, process and equipment reliability is crucial. However, there are situations in which the wellhead requires management and this is typically when the curd oil received preliminary process at the well head in the form of conditioning and/or stabilization. Thus, *wellhead processing* (also called *wellhead stabilization* and *wellhead conditioning*) is the processing of crude oil in proximity to the production well to remove impurities or stabilize the crude oil (by removing highly volatile constituents) prior to transport which has the potential to impact combustion-relevant crude oil properties.

It is recognized (and generally accepted) that no two wells are the same. Consequently, even though there are a limited number of basic types of equipment and configurations involved in crude oil conditioning, the specific configuration and operating conditions adopted for a particular well site depend upon the nature of the producing formation, the location and condition of the well, and ambient conditions at a particular point in time. Time is an important factor in well behavior for many tight oils because the depletion curve, which describes the change in crude oil production rate of a well over time, decreases over time.

The purpose of conditioning is to remove impurities from crude oil with the intent to eliminate compounds (typically non-hydrocarbon compounds) from the oil that lack fuel value or that unnecessarily elevate the hazard level of the crude oil, e.g., presence of toxic hydrogen sulfide. The principal purpose of stabilization, in contrast to conditioning, is to remove hydrocarbon compounds which possess fuel value, but which also possess higher vapor pressures (i.e., have lower boiling points) and to reduce the volatility of the crude oil. It should be noted, however, that stabilization also can remove remaining traces of higher vapor pressure impurities remaining in the oil. Even though the two processes have similar effects, i.e., removing components from crude oil, they are quite different in the effort and equipment required to perform the separation because, in a sense, water and inorganic gas impurities have inherent propensities to form separate phases from hydrocarbon derivatives in crude oil which aids separation, whereas lower-boiling (lower molecular weight) hydrocarbon derivatives which are the major contributor to crude oil volatility, have inherent affinity for the oil which impedes separation. The impact of this difference is that carefully designed fluid motion and step drops in pressure using gravity and available wellhead pressure, as well as possible chemical and heat addition, can be produced and introduced by equipment of relatively simple and reliable design with limited energy requirements to accomplish satisfactory conditioning.

Conditioning is the removal of water and solids form the crude oil equipment is a series of gravity-assisted, pressurized multiphase separators. The number, size, and design of these separators depend upon wellhead conditions, rate of production, relative amounts and phases of impurities, and the nature or composition of the crude oil. Different compositions of crude oil possess different affinities for impurities, such as water or sediment. Depending on the composition of the crude oil, for example, the crude oil and water might easily form two phases with little treatment or the two might form an emulsion that could require chemical additives, heat, quiet flow, centrifugation or other means to separate. After transit through separators, the conditioned crude oil as well as segregated wastewater and solids streams are retained on-site in tanks until collected and transported away from well site by truck or pipeline.

Depending on the quality of the produced water, the water may be recycled or treated and disposed of – often by deep-well injection. Any solids that were carried with the oil also require treatment and proper disposal. Minimally, conditioning that is performed at the well site yields a liquid product that can be safely and economically transported to a refinery or to another facility for further processing.

Stabilization is a process whereby higher vapor pressure components in the crude oil are removed and marketed separately from the stabilized crude oil. The gaseous products include hydrocarbon low molecular weight hydrocarbon derivatives (such as methane, ethane, propane, and butane) and inorganic gases that either made up a separate phase exiting the well or that were released from the crude oil during conditioning. The gaseous product has economic value, so it is generally collected in relatively low-pressure gathering lines which convey the gases to gas plants which, then, process the stream and ultimately sell it as natural gas and natural gas liquids or, in the absence of gathering lines, is flared at the well site.

On the other hand, stabilization which typically requires more complex processing and equipment, as well as more rigorous, energy-consuming vaporization and condensation of the crude oil. Additionally, while stabilization produces a lower vapor pressure crude oil, it also produces a vapor product that contains higher boiling constituents than those produced from its associated upstream conditioning system. Because of their tendency to condense in pipelines, their greater energy density in the vapor state and other reasons, natural gas pipeline operators have restricted how much of these constituents can be introduced into a natural gas pipeline. Consequently, the lower-boiling-components stream produced by stabilization requires (i) a process to remove components that are not permitted to be transported in natural gas pipelines from those that are permitted and (ii) a transportation system which is separate from both natural gas and stabilized crude oil.

Another approach to crude oil stabilization involves a multistage flash process. Similar to the conditioning processes, multistage flash units can be installed at well sites. However, these systems differ from conventional stabilization systems by possessing more stages that make more efficient use of pressure and heat management. Consequently, multistage flash units require more detailed fabrication as well as more careful monitoring likely have more restricted operating regimes than conventional conditioning equipment.

Fractionation by means of a distillation column is the conventional means of performing crude oil stabilization. In this process, conditioned crude oil is fed into a vertical column containing carefully fabricated structures that enhance vapor and liquid contact and promote mixing of vapor and liquid such that more volatile components in the oil transfer to the vapor phase while the less volatile condense in the liquid phase. Heating the liquid in a reboiler at the bottom of the column promotes movement of more volatile components in the oil to vaporize and move upward in the column, exiting at the top as a vapor. The complexity of the design and equipment makes the process more expensive and less reliable and requires more attention than simpler conditioning processes. The associated equipment includes items such as a furnace to heat the reboiler heating medium, a source of cooling medium for the crude oil cooler and a cooler for the vapor product, as well as ancillary pumps.

4. Transportation and handling

Tight oil is typically transported by means of pipeline, truck, barge, or rail car and the composition can impact operations and constrain margins. Pipelines are the traditional and, typically, the most economic method for moving conventional crude oils. In the case of tight oil, pipeline transportation can be impacted by slugs of wax that increase drag, reduce pipeline throughput, and require more frequent pigging operations. This will increase the number of pigging operations to clean out the pipeline have increased from twice a year to once a month.

By way of clarification, the term *pigging operations* refers to maintenance practice for pipelines using pipeline pigs, for cleaning or inspection of pipeline without stopping operation of the pipeline. Pipeline pigs are capsule shaped objects which travel through the pipeline, cleaning the inner walls of the pipeline by brushing action.

As a result of the potential deposition of wax in a pipeline that is used to transport tight crude oil, the use of a barge and/or a truck is often preferred over a pipeline due to challenges that are caused by wax precipitation. The transportation of tight oil demands the addition of paraffin dispersants and pour point depressants to keep the crude oil flowing. In addition, hydrgoen sulfide can cause fouling, and metal corrosion (Speight, 2015b) as well as posing serious health and safety concerns. In both barges and trucks, refiners have an opportunity to address issues related to the presence of hydrgoen sulfide and consequently improve margins by treating the gas with scavengers. However, the scavengers can contain tramp amines that can (or will) lead to corrosion in downstream refinery equipment. Because of these issues, the use of rail cars is often preferred as the most favorable mode of transportation for tight oil. However, rail cars have the same exposure to fouling and corrosion as pipelines, barges, and trucks. In addition, the management of the hydrogen sulfide and other sulfur compounds (such as mercaptan derivatives, RSH) is more critical since the railcars may travel through communities where the risk of exposure is at its greatest.

Another challenge encountered with crude oil from tight formations is the need for transportation – usually to a refinery – and the necessary transportation infrastructure (Andrews, 2014). Rapid distribution of the low-boiling sweet tight oils to the refineries is necessary to maintain consistent plant throughput. Some pipelines are in use, and additional pipelines need to be constructed to provide consistent supply to the refinery, remembering that the low-boiling sweet crude oil may be one of several crude oils blended to produce the refinery feedstock. During the interim, barges and railcars are being used, along with a significant expansion in trucking to bring the various these oils to the refineries. Thus, a more reliable infrastructure is needed to distribute this oil to multiple locations. Similar expansion in oil production is estimated for the Bakken crude oil and other identified (and perhaps as yet unidentified) crude oils from tight formations.

Thus, the dramatic increase in crude oil production from tight formations in the United States, coupled with the increase in crude oil transport by rail, has raised questions related to whether properties of these crude oils (such as the volatility of the unstabilized crude oil leading to flammability issues) – particularly Bakken crude oil from North Dakota – differ sufficiently from other crude oils to warrant any additional handling considerations. In fact, the United States Pipeline and Hazardous Materials Safety Administration (PHMSA) has already issued a Safety Alert to notify emergency responders, shippers, carriers, and the public that recent derailments crude oil-carrying railcars and the fires that result from such derailments indicate that the type of crude oil transported from the Bakken region of North Dakota may be more flammable than traditional light, medium, and heavy crude oils. The alert reminds emergency responders that light sweet crude oils, such as the crude oil being shipped from the Bakken region, pose significant fire risk if released from the package (tank car) in an accident. As a result, the Pipeline and Hazardous Materials Safety Administration has expanded the scope of lab testing to include other factors that affect proper characterization and classification of crude oil such as volatility, corrosivity, hydrogen sulfide content, and composition/concentration of the entrained gases (the low molecular weight hydrocarbon derivatives such as methane, ethane, propane, and butane) in the unstabilized crude oil.

However, it must be remembered that all crude oils are flammable, to a varying degree depending upon the composition, especially the presence of lower-boiling flammable hydrocarbon derivatives. The growing perception is that light sweet highly volatile crude oil, such as Bakken crude oil, is a root cause for catastrophic incidents and thus may be too hazardous to ship by rail. Furthermore, crude oils exhibit other potentially hazardous characteristics as well and equally hazardous and flammable liquids from other sources are routinely transported by rail, tanker truck, barge, and pipeline, though not without accident. A key question for state and federal legislators is whether or not the characteristics of Bakken crude oil make it particularly hazardous to ship by rail, or whether or not there other causes of transport incidents, such as (i) the lack of the necessary prescribed tank cars that should be used to transport such volatile crude oils, (ii) the lack of the correct maintenance practices, (iii) the lack of adequate safety standards, or unfortunately (iv) the occurrence of human error which is a collective grouping of the first three categories.

Crude oil shipments by rail have increased in recent years with the development of oil fields in North Dakota. With several derailments and releases of Bakken crude oil, regulators and others are concerned that it contains low molecular weight hydrocarbon constituents that exacerbate its volatility and thus its flammability. Absent new pipeline capacity, rail provides the primary takeaway capacity for Bakken producers. Unit train shipments of Bakken crude now supply refineries on both the East Coast and the West Coast.

However, the United States Gulf Coast region (Texas and Louisiana) makes up the most prolific region of domestic crude oil production, and the crude oils produced (such as West Texas intermediate crude oil, Eagle Ford crude oil, and Louisiana light sweet crude oil, among others) rival Bakken in the characteristics and, as a result, the alert posted by the United States Pipeline and Hazardous Materials Safety Administration has been called into scrutiny. The Gulf Coast does benefit from existing pipeline infrastructure but however, producers are relying on rail to access new markets, as evidenced by Eagle Ford crude oil moving from East Texas to St James, Louisiana by rail. A further policy question is whether Bakken crude oil significantly differs from other crude oils that the standard practices do not apply, and if this is the case, a series of policy steps should be put into place to mitigate the potential for accidents and to remedy safety concerns.

With some degree of justification, Bakken crude oil producers feel that they may have victimized as a result of the alert posted by the United States Pipeline and Hazardous Materials Safety Administration. True or not, serious efforts must be made and safety procedure put into place to mitigate the potential for such disastrous railcar derailments and the resulting fires (some of which have been explosive).

In addition, the paraffin content of the light sweet (low-boiling, low-sulfur) paraffin-rich crude oils is impacting all transportation systems. Deposits of paraffin wax have been found to coat the walls of railroad tank cars, barges and trucks. Bakken tight oil is typically transported in railcar, although pipeline expansion projects are in progress to accommodate the long-term need. These railcars require regular steaming and cleaning for reuse. Similar deposits are being encountered in trucks being used for tight oil transportation. The wax deposits also create problems in transferring the tight oils to refinery tankage. The wax deposits that occur in pipelines to the refinery or in the refinery regularly require *pigging* to maintain full throughput.

Pigging in the context of pipelines refers to the practice of using devices known as *pigs* to perform various maintenance (cleaning, dewaxing) operations and can be accomplished without stopping the flow of the product in the pipeline. Cleaning (dewaxing) by pigging is accomplished by inserting the pig into a *pig launcher* (*launching station*), which is an oversized section in the pipeline, then reducing to the normal pipeline diameter. The launcher/launching station is then closed and the pressure-driven flow of the product in the pipeline is used to push it along down the pipe until it reaches the receiving trap (the *pig catcher* or *receiving station*). There are various types of pigs − typically, the pig is cylindrical or spherical, pigs sweep the line by scraping the sides of the pipeline and pushing debris ahead.

Multiple chemical and mechanical solutions are used to mitigate the problems cause by wax and other deposits in pipelines. A combination of chemical-additive treatment solutions involving paraffin dispersants and flow drag-reducer technologies has proven to be effective in pipeline applications. Wax dispersants and wash solvents have been used to clean transportation tanks and refinery storage vessels. In the case of pipeline fouling management, a combination of these technologies, coupled with frequent pigging, are the main means to mitigate wax deposition. Preventive fouling control programs have been developed to manage the wax deposition occurring in storage tanks. By injecting the proper chemical treatment to control wax buildup in storage tanks, the production field and refinery can handle and transfer larger quantities of oil without significant plugging issues. One other problem encountered in storing and transporting tight oils is the concentrations of the light ends (volatile hydrocarbon gases) that accumulate in the vapor spaces, requiring increased safety and relief systems. Shipping Bakken crude via barges was challenged by the increased levels of volatile organic compounds (VOCs) and vapor-control systems ate necessary to ensure a safe environment.

Due to the paraffinic nature of tight oils and the absence of a substantial amount of high-boiling constituents that usually form the distillation residuum (Table 10.3), most refineries blend the light sweet crude with other crude oil feedstocks. Unfortunately, the light sweet crude oils have low aromatic content, so mixing with conventional crude oil often leads to asphaltene destabilization. If blended oils are transported, the deposits can consist of waxes and precipitated asphaltenes resulting in asphaltene deposition (incompatibility). Dispersants specifically designed for both hydrocarbon types can control deposit formation during transportation. Until safety issues in the transportation of the light sweet crude oil from tight formations are satisfied and the potential for accidents is diminished by the institution of a safe and reliable transportation infrastructure, significant issues relating to shipments of these crude oils and the potential for accidents remain distinct possibilities. In addition to this, refineries are already experiencing the impact of the variations in quality (composition) of light sweet crude oil from tight formations and the ensuing processing challenges.

Considering the volatility of crude oil from tight formations, such as Bakken crude oil, safety precautions are necessary prior to shipment. The most dangerous flammable liquids, based on their flash point and initial boiling point. For example, naphtha (a precursor to gasoline), vaporizes easily at a relatively low temperature to form a flammable mixture with air. Bakken crude oil, which contains naphtha constituents, is also highly flammable and precautions must be addressed before the crude oil is shipped. In addition, during transportation, stratification of the crude oil can occur in which the lower-boiling lower density constituents can move to the top of the liquid. These constituents are the most dangerous in terms of low flash point and high flammability and caution is advised when opening the containers to transfer the liquid to storage vessels, especially of the transportation containers are top loaders and unloaders.

5. Behavior in refinery processes

In a very general sense, crude oil refining can be traced back over 5000 years to the times when asphalt materials and oils were isolated from areas where natural seepage occurred. Any treatment of the asphalt (such as hardening in the air prior to use) or of the oil (such as allowing for more volatile components to escape prior to use in lamps) may be considered to be refining under the general definition of refining. However, crude oil refining as we know it is a very recent science and many innovations evolved during the 20th century.

Briefly, crude oil refining is the use of s series on integrated unit processes to separate of crude oil into fractions and the subsequent treating of these fractions to yield marketable products (Speight, 2014a). In fact, a refinery is essentially a group of manufacturing plants which vary in number with the variety of products produced (Fig. 10.3). Refinery processes must be selected and products manufactured to give a balanced operation in which crude oil is converted into a variety of products in amounts that are in accord with the demand for each. For example, the manufacture of products from the lower-boiling portion of crude oil automatically produces a certain amount of higher-boiling components. If the latter cannot be sold as, say, heavy fuel oil, these products will accumulate until refinery storage facilities are full. To prevent the occurrence of such a situation, the refinery must be flexible and be able to change operations as needed. This usually means more processes: thermal processes to change an excess of heavy fuel oil into more gasoline with coke as the residual product, or a vacuum distillation process to separate the heavy oil into lubricating oil stocks and asphalt.

The first major step in refining is distilling or separating crude oil into different hydrocarbon streams by boiling point (Fig. 10.3). Light crude oil will have a high share of low

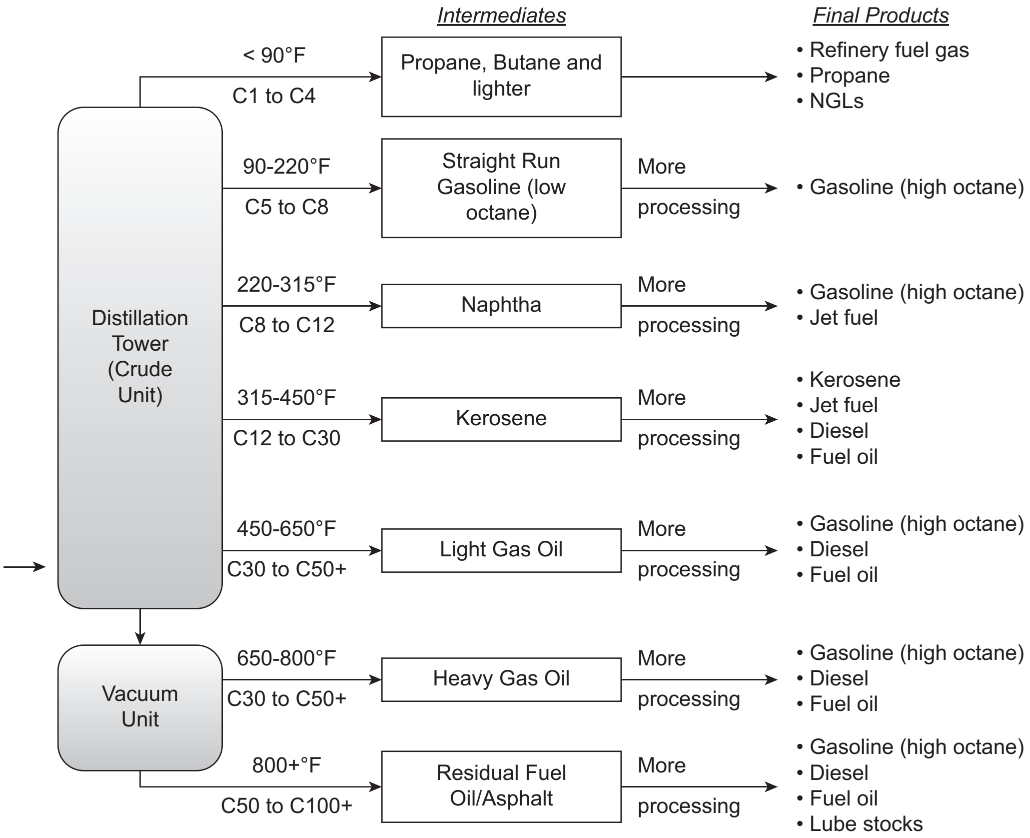


FIG. 10.3 Refinery schematic.

molecular weight constituents that boil at low temperatures, such as light (lower boiling) naphtha and heavy (higher boiling) naphtha, while heavy crude oils will have a smaller share of those light materials and a larger share of material that is viscous and boils at very high temperatures, like those present in atmospheric tower bottoms. As domestic refiners use more super light crude oils and less of other heavier crude types, they sometimes must alter the equipment that processes crude oil before it reaches the distillation unit, and may even alter the crude distillation unit. Regardless, the use of more super light crude oils would change what comes out of the crude distillation unit. Using proportionally more light crude oil results in higher yields (i.e., volume shares) of light streams like naphtha, and lower yields of higher-boiling streams.

Tight oil is currently more readily available for refiners in North America. However, tight oils present numerous challenges, which is why these crudes typically cost less than crude oils such as Brent (global crude oil benchmark) or West Texas Intermediate (US crude oil benchmark). Tight oils typically pose unique challenges because they: (i) are difficult to transport due to a lack of pipeline infrastructure, (ii) contain entrained hydrogen sulfide, H_2S, (iii) require the addition of amine-based ~ S scavengers in the pipeline, truck, or railcar prior to transport, (iv) are contaminated with paraffin waxes that cause fouling in piping, tank walls, and crude preheat exchangers, (v) contain large amounts of filterable solids, (vi) can have a wide range of API gravity, (vii) require crude blending to balance the atmospheric crude fractionator cut-point yields for best downstream utilization, (viii) may be incompatible with other types of crudes used for blending, (ix) require energy balancing across the crude preheat exchangers, and (x) may experience cold flow property deficiencies that require modifications to catalysts. In addition, the US has banned the export of crude oil, including tight oil. This exacerbates the mismatch between the abundant tight oil available to US refineries and the equipment designed to process medium to heavy crude oils.

Typically, the tight crude oils light, paraffinic and sweet and have a low a low amount of gas oil (feedstock to a fluid catalytic cracking unit) and while mot tight oils are generally easy to process, challenges arise when these crudes are the predominant feedstock in refineries designed for heavier crude oils. The lower vacuum gas oil (VGO) and vacuum residue yields directionally decreases coker, fluidized-bed catalytic cracker (FCC) and alkylation rates, decreasing their contribution to the gasoline pool (Olsen, 2015). Conversely, light naphtha, isomerate and reformate octane-barrels increase in the gasoline pool and play an increasing role in gasoline production and profitability.

The data from the crude assay (Table 10.3, Table 10.4) are an indicator of the yield pattern and are essential for determining the refinery products. The tight crude oils are typically lower density (higher API gravity) and have predominantly higher proportions of naphtha with less viscous vacuum gas oil and vacuum resid. Moreover, the API gravity of a crude oil can be used to relate to important key properties, such as product yields, contaminants, and paraffin concentration and there is a general trend of increasing lower boiling hydrocarbon derivatives with increasing API (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017; Hsu and Robinson, 2017). As an example, the Eagle Ford oil with an API of 55.6° produces a higher naphtha yield than Bakken oil with an API of 42.3°. Contaminant levels also trend with gravity. For example, sulfur and nitrogen concentrations are generally lower for the sweet, lower density crude oils produced from tight oil plays but the concentrations are typically higher for lower API gravity crude oils. However, higher-API gravity crudes typically have higher paraffin (wax) and naphtha concentrations.

In addition, tight oils, like other light sweet crude oils, have a much higher ratio of atmospheric distillates (650°F^-) to atmospheric residuum (650 °F^+) compared to conventional crude oils. For example, this distillation-to-residuum ratio for Bakken crude oil is on the order of 2:1 while typical conventional light oil have a ration closer to 1:1 (Bryden et al., 2014; Olsen, 2015). Thus, a refinery accepting a light tight oil as feedstocks would need to accommodate the higher proportion of atmospheric distillates which could cause on overload on ancillary equipment, such as the naphtha processing units. At the same time, the light tight oil provides insufficient feedstock (gas oil) for the catalytic cracking unit and feedstock (residuum) for the coking unit.

These trends are applicable within individual cuts. For example, naphtha and kerosene fractions form tight oil are more paraffinic in nature than the same fractions from many other light crude oils. On the positive side, the amount of contaminants in tight oils are usually lower than in conventional lights oils. The kerosene from a conventional light oil may have a lower content of paraffin derivatives which can results improved cold flow properties but, on the negative side, a lower cetane number.

Light oil is by no means new to the crude oil industry, but the recent expansion in the extraction of crude oil from the Bakken formation, the Eagle Ford formation, and from similar tight formations does represent a new and unexpected development for the crude oil industry. The initial scientific and technical reaction to these types of crude oils is that such crude oils will be easy to refine and produce valuable low-boiling fuel products. However, while this may be true to a point, it is not necessarily the complete story and several issues exist related to the production, transportation, and the development of unconventional tight reservoirs producing light tight oil leading to the storage, transportation, and refining of these light sweet crude oils that has presented the crude oil industry with several issues that have been, and are still being considered and resolved.

In fact, there are many areas of a refinery that can be impacted by the introduction of light sweet oils from tight formations, beginning at the tank farm. The presence of wax constituents, solids, and incompatibility as a result of blending can lead to unloading problems, wax sludge build-up and tank drain plugging. Increased solids, salts and other contaminants contribute to fouling in heat exchangers, furnaces, and atmospheric distillation columns (Speight, 2014a, 2015b).

Most refineries process are no longer limited to a single crude oil as the refinery feedstock and each crude oil can require different processing conditions in the major refinery units. Typically, a refinery is designed to process a feedstock with a particular composition and produce products with specified properties, with some flexibility based on the capabilities of equipment such as the reactors (and ancillary equipment such as pumps and heat exchangers) as well as the particular catalysts within the reactors. As a result, refiners try to match the crude oil composition to the configuration of the refinery, usually by blending several crude oils. However, over the past four decades, many refineries have made major investments to enable them to process heavier sour crude oils from sources such as Venezuela and Canada. These changes were made before the technological advancements that triggered the recent high interest in light sweet crude oils from tight formations. Moreover, because tight oil contains minor amounts of residuum and is low in sulfur content, there is often a mismatch between properties of the light sweet crude oil and the crude oil properties as required by the modified/upgraded refinery.

With the increase in supply of domestic unconventional oils, especially tight oils; for the first time in two decades, United States oil production has exceeded oil imports by the United States. Major Tight oil sources in the United States come from the Bakken, Eagle Ford and Permian Basin formations (Deepak et al., 2014) but current estimates of the total crude oil reserves in tight formations have been on the order of 50 billion barrels (50 × 10^9 bbls) of crude oil from tight formations in the United States (this number is continually being re-evaluated and by the time of publication of this book could be considerably different), indicates that tight oil is here to stay and will play an important role in current and future refinery activities and economics. Hence, fully understanding tight oil will be a crucial part of the current and future oil resource for refiners.

Common observations related to light tight crude oils are they produce high value (high API) low sulfur products but require changes to the operation to adjust to the differences in crude oil properties. As a consequence of these variations in the properties of the crude oils from tight formations, it is increasingly more important for refiners to be able to identify, interpret and respond quickly to changes in crude feed properties. Generally, these crude oils present numerous challenges, which is may be reflected in the price when compared to crude oils such as Brent crude oil (a global benchmark crude oil) or West Texas intermediate crude oil (a US benchmark crude oil benchmark). The challenges typically imposed by the light crude oils from tight formations include: (i) difficulty in transportation due to high volatility, (ii) the presence of hydrogen sulfide, which requires the addition of amine-based scavengers in the pipeline truck, or railcar prior to transportation, (iii) the presence of paraffin waxes that can cause fouling in piping, tank walls, and in crude preheat exchangers, (iv) the presence of relatively high amounts of filterable solids, (v) the requirement of blending with other crude oils to balance the input to the atmospheric distillation unit, (vi) the potential for incompatibility with other types of crude oils used in the blending operations, and (vii) there may be cold-flow property deficiencies because of the presence of wax constitunets that may require modifications to process catalysts. Other issues such as the requirement for energy balancing across the various preheat exchangers must also be taken into consideration.

The characteristics of light sweet crude oils from tight oil plays is a distinct contrast to the viscous, sour Canadian tar sands bitumen (Speight, 2013; Wier et al., 2016) and, in terms of refinery operations, the properties of crude oil from tight formations are highly variable (Bryden et al., 2014; Olsen, 2015) and present several challenges because they: (i) are difficult to transport due to a lack of pipeline infrastructure to handle such volatile crude oils, (ii) contain entrained hydrogen sulfide, (iii) require the addition of amine-based hydrogen sulfide scavengers during transportation, (iv) are contaminated with paraffin waxes that cause fouling in piping, tank walls, and crude preheat exchangers, (v) contain relatively high proportions of solids, (vi) can have a wide range of API gravity, (vii) require crude blending to balance the atmospheric tower cut-point yields for best downstream utilization, (viii) may be incompatible with other types of crude oils used in the blended refinery feedstock, (ix) may experience cold flow property because of the potential for wax separation.

These light crude oils have very different yield patterns for refined products, as well as contaminant levels, impacting refiners' processing units and product slates. Tight oil crudes typically have higher yields of light naphtha and heavy naphtha, presenting increasing challenges to the naphtha complex, typically consisting of naphtha hydrotreating (NHT), light naphtha isomerization and catalyst regeneration platforming units. More specifically, the light sweet crude oils from tight (low-permeability) formations have a composition that allows the yield of atmospheric distillate to approach 80% v/v of the crude oil while the yield of vacuum residue may be as low as 5% v/v (Furimsky, 2015). The waxy behavior of these crude oil is a result of a high content of n-paraffin derivatives and, thus, blending of tight oils and/or feedstocks derived from tight oils requires a pre-blending series of test methods (Speight, 2014a, 2015a) to determine the potential for incompatibility. In addition, safety precautions must be taken during all stages of handling and transportation of these crude oil because of a high content of methine-to-butane (C_1 to C_4) hydrocarbon derivatives.

Thus, although tight oil is considered sweet (low sulfur content in the crude oil itself), hydrogen sulfide gas comes out of the ground with the crude oil and because of the flammable and poisonous character of hydrogen sulfide, careful monitoring is required not only at the production site but at any point where the tight oil is handles prior to removal of the hydrgoen sulfide. Amine-based hydrgoen sulfide scavengers are added to the tight crude oil prior to transport to refineries. However, mixing during the transportation process as well as a change in temperature (such as a change in temperature from winter loading into the transportation system to a warmer temperature at the offloading destination) can cause the release of entrained hydrogen sulfide thereby creating a safety hazard.

Fouling by the separation of the constituents of paraffin wax (such as the separation of the C_{17+} paraffin constituents of the oil) can occur during transportation as well as in the refinery system can also occur. These constituents, once deposited can remain on the walls of railcars, crude oil tank walls, and pipeline walls. Wax deposition is also They are also known to foul the preheat sections of crude heat exchangers (before they are removed in the crude desalter). Paraffin wax constituents that adhere to pipe walls and vessel walls can trap amines (for example, the hydrogen sulfide scavengers) against the walls, which can create localized corrosion (Speight, 2015b; Speight and Radovanović, 2015).

Fouling caused by the presence of filterable solids occurs in the preheat exchangers − a tight crude oil can contain over seven times more filterable solids than a traditional crude. To mitigate filter plugging, the filters at the entrance of the refinery require automated monitoring because they need to capture large volumes of solids. In addition, wetting agents are added to the desalter to help capture excess solids in the water, rather than allowing the undesired solids to travel further downstream into the process.

Also, to best utilize existing downstream units, tight oils must be blended with heavier crudes, because a more-consistent feedstock to the atmospheric distillation unit to facilitate optimized operation and refinery efficiency. If tight crude oil is are not blended with one of more heavier crude oils, the lower boiling oil can create a bottleneck in the crude overhead and naphtha processing units, and limit production in bottom-of-the-barrel processing units such as the delayed coker. Also, blending a tight crude oil and a heavier crude oil can lead to incompatibility issues. Refineries are known to accept blends of two or more crude oils to achieve the right balance of feedstock qualities but this can lead to problems if the crude oils being mixed are incompatible. In such cases, there is a separation of the asphaltene constituents (Speight, 2015a) which accelerate fouling in heat exchangers of catalysts downstream of the desalting unit. Fouling can also necessitate an early shutdown for cleaning (Olsen, 2015; Speight and Radovanović, 2015; Speight, 2015b).

In addition, the properties of the tight oil-derived products are not always in keeping with the market demand. Properties such as cloud point, pour point, and cold filter plugging point are out of the range of the required product specifications because of the high paraffin content in the tight oil and the derived products. Additional processing, such as catalytic dewaxing or product blending with other product streams, may be required to meet the property specifications. Furthermore, tight oil often contains higher levels of calcium and iron than other crude oils which can lead to catalyst poisoning. In such cases, the functionality of catalysts much be changed to compensate for changes in feedstock properties and desired product qualities (Olsen, 2015).

Thus, many factors can affect the ability of refineries to process these crude oils and the effects are not only specific to the source of the light crude oil but also are very specific to each refinery and to individual process unit within a refinery. The effects may be manifested in the atmospheric distillation unit or in the downstream processing of the volatile constituents of the crude oil into finished products. Examples of such effects are (i) the atmospheric distillation unit does not have the necessary capacity for the more volatile constituents of the crude oil, (ii) the heater or heat exchanger has insufficient heater flexibility or limited ability to cool and condense higher volume of light ends, (iii) the saturated gas plant has insufficient capacity to process additional volume, and (iv) the downstream processing capacity of the refinery limits the ability of the refinery to convert the intermediate products into finished (saleable) products.

While these *tight oils* have revolutionized crude supplies in the United States, they also are presenting refiners with new challenges. These crudes produce hydrocracker feeds with significantly fewer contaminants than oil sands derived feeds or conventionally produced gas oils, but there are reports that they may be contributing to crude blending compatibility issues, furnace and heat exchanger fouling, yield selectivity changes, and product quality issues. Only through technology advances such as new-generation catalysts and process designs can refiners match the need to optimize existing and new facilities to take advantage of expanding production of the light sweet crude oils.

5.1 Desalting

Before separation of crude oil into its various constituents can proceed, there is the need to clean the crude oil, which may also occur at the wellhead as well as inside the refinery. This is often referred to as de-salting and de-watering in which the goal is to remove water and the constituents of the brine that accompany the crude oil from the reservoir to the wellhead during recovery operations. Field separation, which occurs at a field site near the recovery operation, is the first attempt to remove the gases, water, and dirt that accompany crude oil coming from the ground. The separator may be no more than a large vessel that gives a quieting zone for gravity separation into three phases: gases, crude oil, and water containing entrained dirt.

The desalting unit is the first line of defense for successful refinery crude unit corrosion and fouling control is optimal operation of the desalter (Dion, 2014). Most crude oils vary greatly in terms of quality and the processing challenges they represent. Additionally, crudes and their blends can be incompatible, precipitating asphaltene constituents and high molecular weight aliphatic compounds (wax constituents). This precipitation can increase the stability of emulsions and contribute to downstream fouling. Fluctuating crude quality and compatibility issues elevate the importance and challenge to effective desalter operation. Adopting an integrated approach to refinery operations when processing opportunity crudes can help anticipate and negate many of the negative impacts to downstream units, such as the waste water treatment plant, as well as provide an opportunity to improve overall plant reliability, such as with the use of low salting boiler amines to minimize crude unit overhead amine salt corrosion potential.

Tight oil is recovered from the reservoir mixed with a variety of substances: gases, water, and dirt (minerals) and, in that sense, is analogous to many opportunity crudes in regard to initial crude oil cleaning (Dion, 2014). Thus, refining actually commences with the production of fluids from the well or reservoir and is followed by pretreatment operations that are applied to the crude oil either at the refinery or prior to transportation. Pipeline operators, for instance, are insistent upon the quality of the fluids put into the pipelines; therefore, any crude oil to be shipped by pipeline or, for that matter, by any other form of transportation must meet rigid specifications in regard to water and salt content. In some instances, sulfur content, nitrogen content, and viscosity may also be specified.

Desalting is a water-washing operation performed at the production field and at the refinery site for additional crude oil cleanup. If the crude oil from the separators contains water and dirt, water washing can remove much of the water-soluble minerals and entrained solids. If these crude oil contaminants are not removed, they can cause operating problems during refinery processing, such as equipment plugging and corrosion as well as catalyst deactivation.

The usual practice is to blend crude oils of similar characteristics, although fluctuations in the properties of the individual crude oils may cause significant variations in the properties of the blend over a period of time. Blending several crude oils prior to refining can eliminate the frequent need to change the processing conditions that may be required to process each of the crude oils individually. However, simplification of the refining procedure is not always the end result. Incompatibility of different crude oils, which can occur if, for example, a paraffinic crude oil is blended with viscous asphaltic oil, can cause sediment formation in the unrefined feedstock or in the products, thereby complicating the refinery process (Mushrush and Speight, 1995).

Desalter performance has traditionally been measured by salt removal, oil dehydration and chloride control efficiency. However, the recent influx of oils from tight formations has introduced tremendous variability in the quality of the crude blends, prompting many refiners to rethink the role of the desalter. Refiners are now often running this equipment more as an extraction vessel, removing many more contaminants than just salt. While the individual desalter challenges may not be particularly new, the combination of issues is.

The high API gravity tends to improve desalting by creating a greater density difference between crude and water increasing the stokes settling velocity but there can be difficulties in the desalting unit due to the formation of emulsions and the high amount of filterable solids adds to the desalter load and reduces efficiency. On the other hand, in keeping with the high API gravity, there is an increase in the yield of naphtha and other distillate fractions compared to conventional crude oils. However, wax formation in the cold crude and distillate hydrotreater preheat exchangers causes fouling (Speight, 2015b) which reduces heat transfer and has increased pressure drop requiring cleaning at shortened intervals. Furthermore, the presence of hydrogen sulfide requires use of hydrogen sulfide-scavengers that leads to the formation of amine salts and corrosion.

However, compatibility problems can result from blending highly paraffinic crudes with asphaltenic crudes, which lead to asphaltene destabilization that can stabilize emulsions, as well as accelerate preheat and furnace fouling. Tight oils can cause wax precipitation, which can degrade desalter temperatures and plug cold train exchangers. Variability, due to raw salt as well as basic sediment and water (BS&W), can stabilize emulsions in the desalter, as well as impact corrosion control in the overhead system. Increased solids loading may exceed the design capability of the desalter, resulting in emulsion control issues, accelerated fouling of the preheat train and furnace, as well as more difficult phase separation downstream in the primary wastewater and slop oil handling systems.

Wetting agent adjunct chemistry can also be very helpful when processing tight oils. The fracking process used to extract tight oils increases the amount of entrained solids. Compared to those found in traditional crudes, these solids are smaller and the volume is typically higher as well. The increased solids loading can easily overwhelm the ability of the desalter to remove solids. Loadings as high as 300 pounds per thousand barrels in the raw crude have been documented when processing certain tight oils. The higher loadings can cause stabilized emulsions, which can lead to water carry-over in the oil and oily effluent brine as well. Entrained oil in the effluent brine can cause problems in the wastewater treatment plant. The solids are inorganic particles that are coated in oil. Wetting agents help strip the oil layer from the particles and make it easier for them to be removed from the desalter.

In addition to the desalting and corrosion challenges associated with processing tight oils, fouling of equipment beyond the desalter can be a major concern. The processing of lower boiling (lower-density) crude oils, with low asphaltenes, is not typically thought of as being particularly problematic. However, there are specific issues associated with these crudes that have been identified to cause issues in the refinery process. For example, when paraffinic tight oils are blended with asphaltenic crudes, the asphaltene constituents can destabilize and agglomerate, leading to emulsion stabilization, increased oil in the effluent, as well as preheat exchanger and furnace fouling. This is a lesser issue when refining tight crude oils because of the relative lack of asphaltene constituents. However, wax separation can be a major problem. Also, the cold train can experience wax precipitation, with the resultant loss of heat transfer causing low desalter temperatures in addition to increased pressure drop across the cold train heat exchangers. In addtion, the increased preheat and furnace fouling potential can be experienced with these crudes due to asphaltene precipitation, metal-catalyzed polymerization and/or solids deposition.

Thus, tight oil introduces a host of challenges in the desalting process, including formation of emulsions resulting from precipitated waxes, asphaltene constituents, and filterable solids. As the emulsion builds, salt removal and dehydration can be impacted, leading to downstream fouling and corrosion. Emulsions can also lead to oil in the effluent brine, creating challenges for the wastewater treatment plant. Thus, a critical understanding of the characteristics of the tight oils, as well as the blends being processed, is needed to properly address poor desalter performance, corrosion and fouling (Speight, 2014c, 2015b).

5.2 Refining options

To convert crude oil into desired products in an economically feasible and environmentally acceptable manner (Bryden et al., 2014). Refinery process for crude oil are generally divided into three categories: (i) separation processes, of which distillation is the prime example, (ii) conversion processes, of which coking and catalytic cracking are prime examples, and (iii) finishing processes, of which hydrotreating to remove sulfur is a prime example (Speight, 2014a, 2017).

The simplest refinery configuration is the *topping refinery* (*skimming refinery*) (Table 10.6, Fig. 10.4) which is designed to prepare feedstocks for petrochemical manufacture or for production of industrial fuels in remote oil-production areas. A version of the topping refinery may be installed as a wellhead refining unit. The topping refinery consists of tankage, a distillation unit, recovery facilities for gases and light hydrocarbon derivatives, and the necessary utility systems (steam, power, and water-treatment plants). Topping refineries produce large quantities of unfinished oils and are highly dependent on local markets,

TABLE 10.6 Comparison of various refinery types.

Refinery type	Processes	Alternate type name	Complexity	Comparative range[a]
Topping	Distillation	Skimming	Low	1
Hydroskimming	Distillation	Hydroskimming	Moderate	3
	Reforming			
	Hydrotreating			
Conversion	Distillation	Cracking	High	6
	Fluid catalytic cracking			
	Hydrocracking			
	Reforming			
	Alkylation (etc.)			
	Hydrotreating			
Deep conversion	Distillation	Coking	Very high	10
	Coking			
	Fluid catalytic cracking			
	Hydrocracking			
	Reforming			
	Alkylation (etc.)			
	Hydrotreating			

[a] *Indicates complexity on an arbitrary numerical scale of 1–10.*

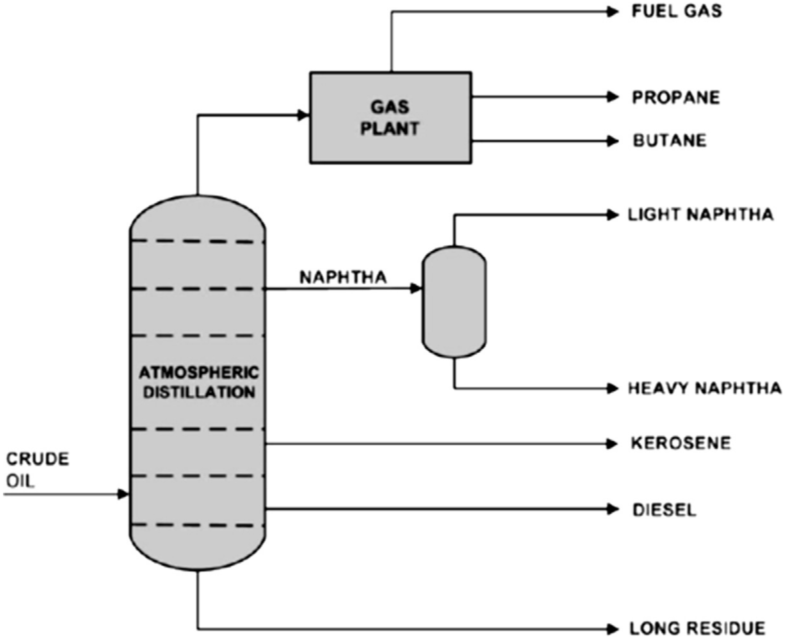


FIG. 10.4 A topping refinery.

but the addition of hydrotreating and reforming units to this basic configuration results in a more flexible *hydroskimming refinery* which can also produce desulfurized distillate fuels and high-octane gasoline. These refineries may produce up to half of their output as residual fuel oil, and they face increasing market loss as the demand for low-sulfur (even no-sulfur) high-sulfur fuel oil increases.

The most versatile refinery configuration is the *medium conversion refinery* (also called a cracking refinery) which incorporates all of the basic units found in both the topping and hydroskimming refineries, but it also features gas oil conversion plants such as catalytic cracking and hydrocracking units, olefin conversion plants such as alkylation or polymerization units but not always coking units (Table 10.6, Fig. 10.5). Modern conversion refineries may produce two-thirds of their output as unleaded gasoline, with the balance distributed between liquefied petroleum gas, jet fuel, diesel fuel, and a small quantity of coke. Many such refineries also incorporate solvent extraction processes for manufacturing lubricants and petrochemical units with which to recover propylene, benzene, toluene, and xylene isomers for further processing into polymers.

The *high conversion refinery* (*coking refinery*) is, as the name implies, a special class of conversion refinery which includes not only catalytic cracking and/or hydrocracking to convert gas oil fractions, but also a *coking unit* for reducing or eliminating the production of residual fuels and residua (Table 10.6, Fig. 10.6). The function of the coking unit is to convert the highest boiling and least valuable crude oil fraction (*residua*) by converting it into lower-boiling product streams that serve as additional feedstocks to other conversion processes (such as the catalytic cracking unit) and to upgrading processes (such as the catalytic reforming unit) that produce the more valuable light products. A high conversion

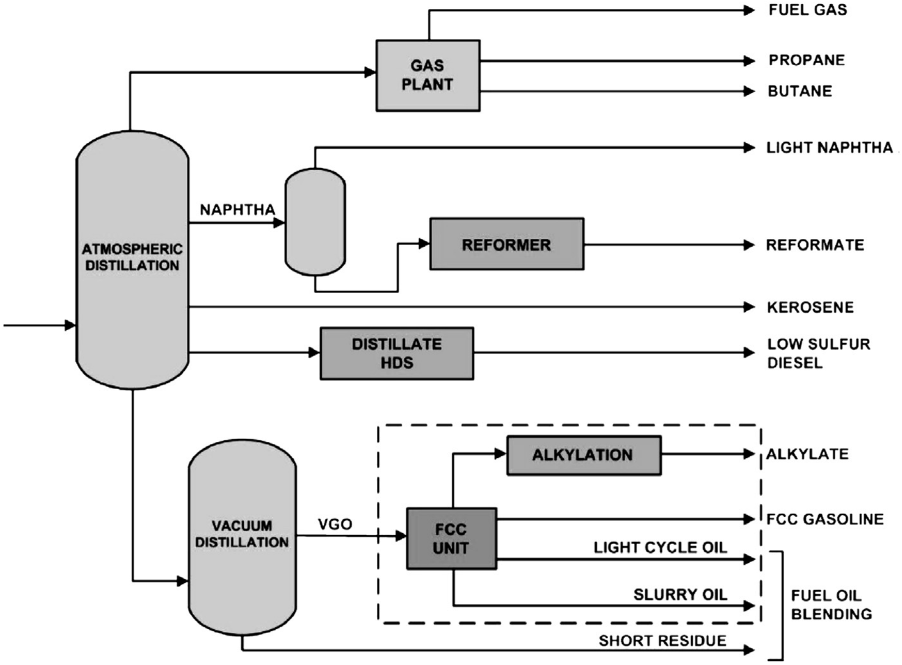


FIG. 10.5 A medium conversion (cracking) refinery.

refinery with sufficient coking capacity will convert all of the residua in the crude oil feedstocks slates and produce lower boiling products or, alternatively, to leave a portion of the residuum for asphalt production. Almost all of the refineries on the United States are either *medium conversion refineries* or *high conversion refineries*, as are the newer refineries in Asia, the Middle East, South America, and other areas experiencing rapid growth in demand for lower-boiling products. By contrast, most refining capacity in Europe and Japan is in *hydroskimming refineries* and *medium conversion refineries*.

Finally, the yields and quality of refined crude oil products produced by any given refinery depends on the mixture of crude oil used as feedstock and the configuration of the refinery facilities. Light/sweet crude oil is generally more expensive and has inherent great yields of higher value low boiling products such naphtha, gasoline, jet fuel, kerosene, and diesel fuel. Heavy sour crude oil is generally less expensive and produces greater yields of lower value higher boiling products that must be converted into lower boiling products. The configuration of refineries may vary from refinery to refinery. Some refineries may be more oriented toward the production of gasoline (large reforming and/or catalytic cracking) whereas the configuration of other refineries may be more oriented toward the production of middle distillates such as jet fuel, and gas oil.

The means by which a refinery operates in terms of producing the relevant products, depends not only on the nature of the crude oil feedstock but also on its configuration (i.e., the number of types of the processes that are employed to produce the desired product slate) and the refinery configuration is, therefore, influenced by the specific demands of a market.

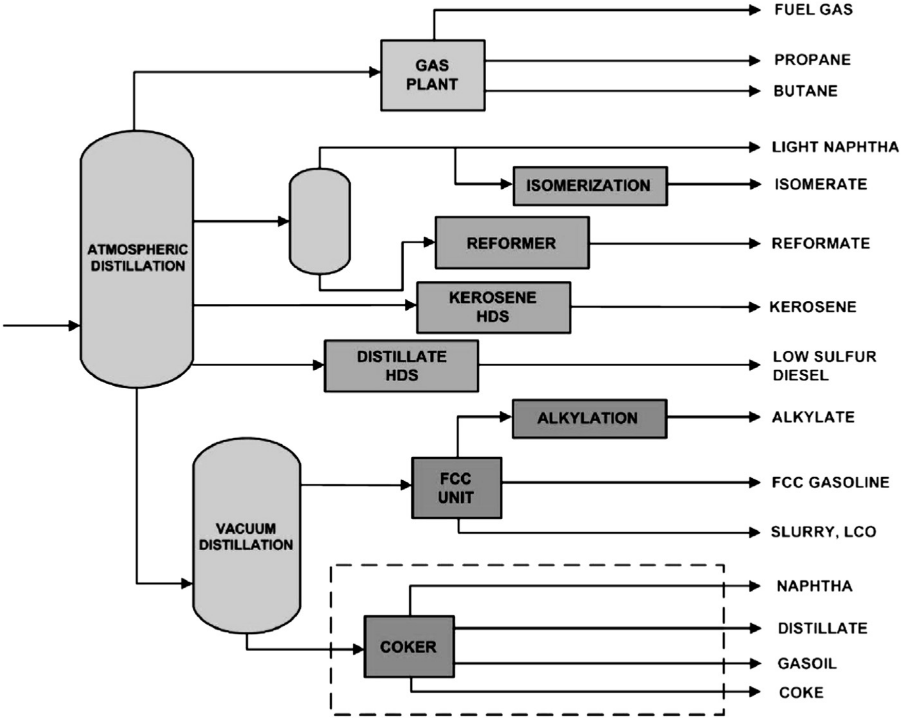


FIG. 10.6 A high conversion (coking) refinery.

Therefore, refineries need to be constantly adapted and upgraded to remain viable and responsive to ever changing patterns of crude supply and product market demands. As a result, refineries have been introducing increasingly complex and expensive processes to gain higher yields of lower boiling products from the higher boiling fractions and the residua.

The yields and quality of refined crude oil products produced by any given oil refinery depends on the mixture of crude oil used as feedstock and the configuration of the refinery facilities. Light/sweet crude oil is generally more expensive and has inherent great yields of higher value low boiling products such naphtha, gasoline, jet fuel, kerosene, and diesel fuel. Heavy sour crude oil is generally less expensive and produces greater yields of lower value higher boiling products that must be converted into lower boiling products (Speight, 2013, 2014a).

Since a refinery is a group of integrated manufacturing plants (Speight, 2014a, 2017) which are selected to give a balanced production of saleable products in amounts that are in accord with the demand for each, it is necessary to prevent the accumulation of non-saleable products, the refinery must be flexible and be able to change operations as needed. The complexity of crude oil is emphasized insofar as the actual amounts of the products vary significantly from one crude oil to another (Speight, 2014a). In addition, the configuration of refineries may vary from refinery to refinery. Some refineries may be more oriented toward the production of gasoline (large reforming and/or catalytic cracking) whereas the configuration of other refineries may be more oriented toward the production of middle distillates such as jet fuel, and gas oil.

Each refinery has a unique configuration, set of processing objectives, equipment limitations, and budget constraints. Therefore, there is no universal solution to maximize profitability. Solutions for refiners located in the Gulf Coast and Midwest regions that can access and sell products more readily may differ from refiners in other regions who incur higher product transportation costs.

5.3 Fouling during refining

One of the major causes of fouling during refining tight oils relates to the use of these oils as a refinery blend stock to produce the right blend for the utilization of existing downstream units. Having a more consistent feed to the crude unit allows for the opportunity to optimize operation. If light tight oil feeds are not blended, the lower-boiling oil can create an overflow (bottleneck) in the atmospheric distillation unit and also in the naphtha processing units. In addition, when the light tight oil is incompatible with another constituent of the blend (or with other constituents of the blend), accelerated fouling occurs in the crude unit heat exchanger train due to asphaltene separation and precipitation (Speight, 2015b).

There are typically two types of fouling in the hot train and furnaces. Coke and inorganic solids are the primary culprits. The coke can result from asphaltene precipitation or polymerization byproducts that fall out of the bulk fluid onto the tube surfaces and dehydrogenates. Metal catalyzed polymerization is somewhat rare in crude oil, but does occasionally occur due to sporadic spikes in the levels of reactive metals. Finally, high solids loading, common with these crudes, along with any carryover from the desalter can significantly contribute to fouling issues. Most refiners run years before fouling requires the furnace to be cleaned. Recently, some refiners have experienced as little as three months between turnarounds to clean the crude furnace.

In many crude oil, the separation of unreacted asphaltene constituents or reacted asphaltene constituents can cause solids deposition and fouling (Speight, 2015b). Refiners employ many performance management strategies to reduce or mitigate equipment fouling, including operational and mechanical adjustments as well as anti-fouling chemistries. Some of the common operational or mechanical approaches are reducing solids and salts by optimizing desalter performance, increasing fluid velocities to minimize deposition potential, and modifying furnace flame patterns by cleaning or changing burner tips to maximize performance and minimize impingement that can cause coking.

Using proper characterization methods to understand the root cause of the fouling can help determine the most appropriate management strategies. When starting to process problematic crude blends or increasing a problematic crude type in a blend, effective baseline monitoring is extremely important to understand the status of the current system, as well as to anticipate what limitations may develop. Thus, the unique challenges associated with processing tight oils can be overcome with a combination of baseline and ongoing monitoring, defining and implementing new operating envelopes, and utilizing multi-functional chemical treatment programs that provide refiners with the tools and the flexibility to address the specific process problems as they arise.

5.4 Other refining issues

In general, tight crude oils have low nitrogen and high paraffin content (Table 10.1) which can offer advantages or disadvantages to refiners. Heavy metals, such as nickel and vanadium, are generally low, but alkaline metals (calcium, sodium and magnesium) may be high. This is highly variable and, in addition, other contaminants such as barium and lead may be elevated. Filterable solids can be higher than conventional crude oils, with greater volume and smaller particle size.

Refining tight oil extracted through fracturing from fields such as Eagle Ford, Utica and Bakken has become prevalent in many areas of the United States. Although these oils are appealing as refinery feedstocks due to their availability and low cost, processing can be more difficult. The quality of the tight oils is highly variable. These oils can be high in solids with high melting point waxes. The light paraffinic nature of tight oils can lead to asphaltene destabilization when blended with heavier crudes. These compositional factors have resulted in cold preheat train fouling, desalter upsets, and fouling of hot preheat exchangers and furnaces. Problems in transportation and storage, finished-product quality, as well as refinery corrosion, have a high potential.

In addition to catalyst selection, an equally critical component to minimizing risks and challenges associated with processing unconventional feeds is solid technical service support (Bryden et al., 2014). Understanding feed impacts earlier allows opportunity to optimize the operating parameters and catalyst management strategies, enabling a more stable and profitable operation.

Hydroprocessing of naphtha from tight oils is necessary to increase octane number and that of middle distillates to attain cold flow properties of diesel fuel. Also, hydroprocessing of atmospheric residue from tight oils yields additional naphtha and middle distillate feedstocks for other refinery operations. Because of a great variability in properties, the prehydroprocessing of tight oil feedstocks feeds may be necessary. Hydroisomerization is the principal reaction during the hydroprocessing of atmospheric distillates feedstocks while hydrocracking and ring opening are the principal reactions when the atmospheric residuum from tight oil is hydroprocessed (Furimsky, 2015). In fact, one of the significant challenges for hydrocrackers processing significant amount of straight run material from tight oil crudes is a lower overall gas oil make. This lower gas oil yield provides less overall hydrocracker feed and has the potential to underutilize the unit capacity compared to processing conventional heavier crudes.

Refining the light tight crude oils is not an easy process and consideration must be given to desalter performance, corrosion, and fouling control. Furthermore, while tight oils have many physical properties in common, the characteristics that differentiate them from one another are, in many cases, the root cause of a variety of processing challenges. For example, the methods used to extract tight oil supplies often result in the oil containing more production chemicals and increased solids with smaller particle size than conventional crudes. When introduced to the refining process, tight oils can stabilize emulsions in the desalter, increase the potential for system corrosion and fouling, as well as negatively impact waste water treatment.

6. Mitigating refinery impact

Due to the variation in the content of filterable solids and the paraffin content, processing tight oils in refinery operations offers several challenges not the least of which are bottlenecks in the atmospheric distillation unit due to the higher amount of light ends in tight oil as well as solids deposition leading to corrosion (Table 10.7, Fig. 10.7) (Speight, 2014c; Olsen, 2015; US EIA, 2015). Problems can be found from the tank farm to the desalter, preheat exchangers and furnace, and increased corrosion in the atmospheric distillation unit. In the refinery tank farm, entrained solids can agglomerate and rapidly settle, adding to the sludge layer in the tank bottoms. Waxes crystalize and settle or coat the tank walls, thus reducing storage capacity. Waxes will stabilize emulsions and suspend solids in the storage tanks, leading to slugs of sludge entering the atmospheric distillation unit. Waxes will also coat the transfer piping, resulting in increased pressure drop and hydraulic restrictions. In addition, blending asphaltene-containing crude oil with paraffin-containing tight oils leads to asphaltene destabilization that contributes to stable emulsions and sludge formation through asphaltene deposition.

Solutions include using tank farm additives to control the formation of sludge layers, along with specially designed asphaltene dispersants and aggressive desalter treatments to ensure optimum operation (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Hsu and Robinson, 2017; Speight, 2017). Pretreatment, coupled with high-performance desalter programs, have provided the best overall desalter performance and desalted crude quality; multiple treatment options for both areas can ensure maximum performance. A crude-oil tank treatment program was initiated that broke waxy emulsions in tankage, enabling improved water resolution of the raw crude oil and minimizing sludge and solids entering the desalter. This program provided significant improvement of solids released into the desalter brine water compared to previous operations. Prior to initiating the pretreatment program, solids in the brine averaged 29 pounds of salt per thousand barrels of crude oil (29 PTB), and the emulsion band control was sporadic. After the tank pretreatment program started, the desalter emulsion band could be controlled with the emulsion breaker program, and solids removal to the brine water increased by a factor of 8 to an average of 218 pounds of salt per thousand barrels of crude oil (218 PTB).

Desalter operations may suffer from issues related to the tight oil properties. Solids loading can be highly variable, leading to large shifts in solids removal performance. Sludge layers from the tank farm may cause severe upsets, including growth of stable emulsion bands and intermittent increases of oil in the brine water. Agglomerated asphaltenes can enter from storage tanks or can flocculate in the desalter rag layer, leading to oil slugs in the effluent brine.

Preheat exchanger fouling has been observed in the cold train before the desalting units and in the hot train after the desalting operation. Cold train fouling results from the deposition of insoluble paraffinic hydrocarbon derivatives, coupled with agglomerated inorganic solids. Solutions to cold train exchanger fouling include the addition of wax dispersants and other oil management best practices to ensure consistent solids loading with minimum sludge processing. Crude oil management can include additives to stabilize asphaltenes and surfactants that resolve emulsions and improve water separation. These practices also include pro-active

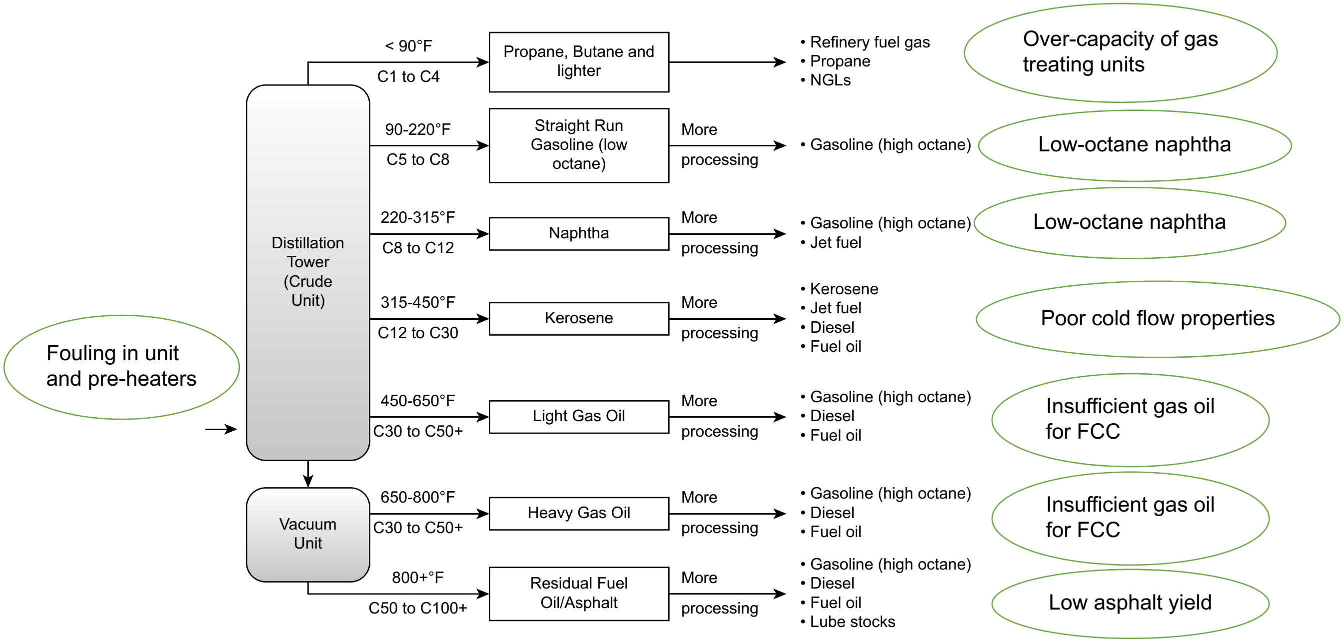


FIG. 10.7 Sites for potential issues during refining of crude oils from tight formations (compare with Figure 10.4).

TABLE 10.7 Examples of challenges and solutions in refining tight oil.

Process	Challenge	Solution
Transportation		
Pipelines	Presence of hydrogen sulfide	Hydrogen sulfide scavengers
	Wax deposition	Wax dispersants
	Throughput	Drag reducers
	Sludge formation	Compatibility testing
Barges/trucks/rail cars	Presence of hydrogen sulfide	Hydrogen sulfide scavengers
	Wax build-up	Disperse wax
	Blend compatibility	Monitor crude compatibility
Storage		
Crude oil tank farm	Wax build-up	Disperse wax
	Solids buildup	Disperse solids
	Hydrogen sulfide	Hydrogen sulfide scavengers
	Blending	Monitor and increase compatibility
Processing		
Cold preheat train	Fouling	Antifoulant treatment
Hot preheat train	Fouling	Antifoulant treatment
Desalter	Emulsion build-up	Destabilize emulsion
	Presence of amines	Amine removal
	Presence of other contaminants	Contaminant removal
Corrosion	Amine salt build-up	Remove in desalter
	Increased naphthenic acid corrosion	Mitigation strategy
Products		
Product quality	Pour point, cold flow	Testing, additives
	Water in distillates	Salt drying and coalescing
	Lubricity	Testing. Additives
	Hydrogen sulfide	Hydrogen sulfide scavengers
Shipping terminals		
Bend incompatibility	Additives	Compatibility tests
Intermediate cold flow	Additives	Pour point depressants, cold flow improvers

asphaltene stability testing to ensure that the crude blends to be processed retain an acceptable compatibility level (Speight, 2014a, 2015a).

Hot train fouling occurs from destabilized asphaltenes that agglomerate and form deposits. These materials entrain inorganics, such as iron sulfide and sediments from production formations, into the deposit matrix. Some deposits, including high molecular-weight paraffins, can form complexes with the asphaltene aggregates. Blending tight light sweet crude oils with asphaltene-containing crude oil crude oils results in rapid asphaltene agglomeration. Rapid hot train exchanger fouling will occur in units running crude oil blends with asphaltene concentrations on the order of 1% or less. This hydrogen-to-carbon ratio is consistent with deposits of asphaltene constituents. If the asphaltenes in the crude blend were not being rapidly destabilized, the asphaltene stability would have been well above 120. This data shows that mixing certain crude oils with tight oil can result in rapid asphaltene deposition. New technology can provide the capability to rapidly perform asphaltene stability measurements onsite with a high degree of accuracy.

Hot-train exchanger fouling can be controlled through antifoulant additives designed to control the agglomeration and deposition of asphaltenes and entrained inorganic solids. Another fouling control strategy is to do regular analysis of the stability of the asphaltenes in the crude oil blend under consideration for processing. This information can guide operations to minimize fouling problems.

Tight oils contain high concentrations of hydrogen sulfide that require treatment with scavengers due to safety purposes. Amine-based scavengers often decompose as the crude oil is preheated through the hot preheat train and furnace, forming amine fragments. Monoethanolamine (MEA), one of the most commonly used amines, readily forms an amine-chloride salt in the atmospheric tower which will deposit in the upper sections of the unit. Often, under-deposit corrosion is the major cause of failures in process systems because the atmospheric distillation tower under-salt corrosion rates can be 10 to 100 times faster than a general acidic attack. Mitigation strategies include controlling chloride to minimize the chloride traffic in the tower top and overhead, increasing the overhead operating temperature so that the salts move further downstream in the overhead system, and acidifying the desalter brine water to increase removal of amines into the water phase.

Also, when shale oil is treated with scavengers to curb the presence of hydrgoen sulfide, the resulting amines (sometime referred to as *tramp amines*) can affect unit performance and efficiency throughout the refining process. When present in the refinery feedstock (the crude blend), these amine derivatives can partition into the oil phase at the desalter. Once past the desalter, they can react with hydrogen chloride (HCl) in the atmospheric distillation unit and the overhead system which results in the deposition of corrosive salts.

The quality of the finished fuels from refining tight oils has changed significantly. As the tight oils have higher light-ends content, one benefit is increased production of naphtha for gasoline, and stable diesel and jet distillates which may be beneficial to the refinery but due to the properties (chemical nature) of these tight oil feedstocks, several challenges can be encountered. The streams are more paraffinic and, thus, they suffer from poor pour point and cloud point properties. In addition, tight oils are lower in sulfur content, so the need for lubricity additives is anticipated. Effective additives can be used to improve all distillate stream properties but to optimize any chemical treatment program, testing on specific product streams is required and suitable product selection should be customized.

Having a sufficiently advanced analysis capability is critical and, ideally, this analysis will be capable of rapidly discriminating between different types of crude, thereby providing information related to distinguishing characteristics (Speight, 2014a, 2015a). Such data can then serve as the source for any plan to deal with incoming feedstock. But more important, the analysis must also capture data related to crude properties in general. Often, the engineering and operations team at a refinery may not know exactly what will cause problems with heat exchangers, distillation columns, and other components of a crude processing unit.

Refineries operate in the real world and, consequently, there are some constraints on how they can be configured. However, the range of possible solutions can be expanded because there are two sides to this optimization puzzle. On the one hand, there is the refinery and its capabilities while, on the other hand, there is the feedstock. Any mismatch between the two will cause problems so, by carefully blending incoming feedstocks, it may be possible to create an input stream to the refinery that is a better match than any crude source may be on its own.

More important, the best crude oil blend would vary, depending upon refinery configuration and the desired fuel target to maximize during favorable market conditions. At one time, it might be gasoline. In another case, it might be either ultra-low sulfur diesel (ULSD) or jet aviation fuel, Jet A1. Lubricants and asphalts are another class of products that might be part of the decision matrix. Projects using an analyzer-driven blending system have shown that it is possible to determine quickly such important properties of crude oil as the true boiling point (TBP). Scheduling in such a blending scheme will be improved by having visibility into incoming crude characteristics as soon as possible. That implies that analysis should be done as soon as feasible in the supply chain.

One way to avoid going out of specifications as a result of feedstock, weather or other changes is to over-purify, leading to wasted energy and lower product yield. A better solution is to use advanced process control technology to automatically adjust distillation column parameters to optimal targets without violating constraints. Doing so will reduce product quality variation and off-specification production while minimizing energy consumption per unit of feed. It will also increase recovery of more valuable products and column throughput. In the context of the refinery where feedstocks are more variable, this will mean that blending operations will have more leeway because the blended feedstock can have a wider range of characteristics, yet the refinery will still be able to produce the required product blend.

This distillation process control also has to be dynamic because not only are the feedstocks to the refinery changing over time but the product demand is also changing. Thus, refinery process control should be adaptable in order to cope with changes in the feedstocks and the types of product. This must be followed by evaluation of the products to ensure that specifications are met.

7. Product evaluation

Upgrading tight oil to products involves processing (with some conversion when residuum is are present in the oil) into more salable, higher valued product. Improved characterization methods are necessary for process design, crude oil evaluation, and operational control. Definition of the boiling range and the hydrocarbon-type distribution in heavy distillates and in residua is increasingly important. Feedstock analysis to provide a quantitative boiling range distribution (that accounts for non-eluting components) as well as the distribution of hydrocarbon types in gas oil and higher boiling materials is important in evaluating feedstocks for further processing.

Even when tight oil is the refinery feedstock or the tight oil is contained in the refinery blend, the products are highly complex chemicals and considerable effort is required to characterize their chemical and physical properties with a high degree of precision and accuracy. Indeed, the analysis of petroleum products is necessary to determine the properties that can assist in resolving a process problem as well as the properties that indicate the function and performance of the product in service.

Thus, this section is a general follow-on from the following chapter (Chapter 10) in which four fractions of tight oil (naphtha, kerosene, gas oil, and resid) are used as possible examples of separate refinery feedstocks and were described in terms of analytical test methods and presents some of the methods that are generally applied to study the makeup of the feedstock in terms of chemical structures as well as methods that might be preferred for refining. There are, of course, many analytical methods the can be applied to the analysis of crude oil and crude oil products but they vary with sample condition and composition. More specifically, this chapter deals with the more common methods used to define chemical and physical properties of the sample. Furthermore, any of the methods described herein might also be applied to the analysis of sample for environmental purposes (Chapter 18).

7.1 Naphtha

Naphtha (*petroleum naphtha*) is a generic term applied to refined, partly refined or unrefined crude oil products and liquid products of natural gas which distill below 240 °C (465 °F) and is the volatile fraction of the crude oil, which is used as a solvent or as a precursor to gasoline. In fact, not less than 10% v/v of material should distil below 75 °C (167 °F); not less than 95% v/v of the material should distil below 240 °C (465 °F) under standard distillation conditions, although there are different grades of naphtha within this extensive boiling range that have different boiling ranges (Hori, 2000; Parkash, 2003; Pandey et al., 2004; Gary et al., 2007; Speight, 2014a, 2017; Hsu and Robinson, 2017) and the focus of this chapter is on the low-boiling fraction of naphtha (Boiling point 30−200 °C, 1−392 °F) that is approximately equivalent to the boiling point of gas condensate and the boiling point of natural gasoline.

More generally, naphtha is an intermediate hydrocarbon liquid stream derived from the crude oil and is usually desulfurized and then catalytically reformed to produce high-octane naphtha before blending into the streams that make up gasoline. Because of the variations in crude oil composition and quality as well as differences in refinery operations, it is difficult (if not impossible) to provide a definitive, single definition of the word naphtha since each refinery produces a site-specific naphtha − often with a unique boiling range (unique initial point and final boiling point) as well as other physical and compositional characteristics.

On a chemical basis, naphtha is difficult to define precisely because it can contain varying amounts of the constituents (paraffin derivatives, naphthene derivatives, aromatic derivatives, and olefin derivatives) in different proportions, in addition to the potential isomers of the paraffin derivatives that exist in the naphtha boiling range (the C_5 to C_8 or the C_5 to C_{10} boiling range) (Table 10.8, Table 10.9).

One test method (ASTM D5291) covers the determination of the aromatic hydrogen content and aromatic carbon content of hydrocarbon liquids using high-resolution nuclear magnetic resonance spectrometers. For pulse Fourier transform (FT) spectrometers, the detection limit is typically 0.1 mol % aromatic hydrogen atoms and 0.5 mol % aromatic carbon atoms. For continuous wave spectrometers, which are suitable for measuring aromatic hydrogen contents only, the detection limit is considerably higher and typically 0.5 mol% aromatic hydrogen atoms.

Generally, naphtha is comprised of shorter chain hydrocarbon derivatives (C_5—C_8), such as when gas condensate and natural gasoline are employed, can be aromatic (sweet smelling and carcinogenic), and can contain sulfuric compounds or other impurities. It has the lowest boiling point of all the crude oil-derived liquid, which gives it the highest vapor pressure. As a result, naphtha produces flammable vapors whenever it is not contained in a vapor-seal container, but those vapors will disperse quickly if well ventilated. Odor is particularly important since, unlike most other crude oil liquids, many of the manufactured products containing naphtha are used in confined spaces, in factory workshops, and in the home. As a result of the volatility, naphtha (especially naphtha containing gas condensate and natural gasoline) (i) is readily flammable, (ii) will evaporate quickly from most surfaces, and (iii) must be very carefully contained at all times. In addition, aromatic naphtha that contain a high percentage of aromatic constituents, can also be smoky, toxic, and carcinogenic. Some naphtha-based fuels have a reduced aromatic content, but many are naturally high or augmented in aromatic derivatives, especially if the blend stock (gas condensate or natural gasoline) contain aromatic derivative.

TABLE 10.8 General summary of product types and distillation range.

Product	Lower carbon limit	Upper carbon limit	Lower boiling point °C	Upper boiling point °C	Lower boiling point °F	Upper boiling point °F
Refinery gas	C_1	C_4	−161	−1	−259	31
Liquefied petroleum gas	C_3	C_4	−42	−1	−44	31
Naphtha	C_5	C_{17}	36	302	97	575
Gasoline	C_4	C_{12}	−1	216	31	421
Kerosene/diesel fuel	C_8	C_{18}	126	258	302	575
Aviation turbine fuel	C_8	C_{16}	126	287	302	548
Fuel oil	C_{12}	$>C_{20}$	216	421	>343	>649
Lubricating oil	$> C_{20}$		>343		>649	
Wax	C_{17}	$> C_{20}$	302	>343	575	>649
Asphalt	C_{20}		>343		>649	
Coke	$> C_{50}$[a]		>1000[a]		>1832[a]	

[a] *Carbon number and boiling point difficult to assess; inserted for illustrative purposes only.*

TABLE 10.9 Increase in the number of isomers with carbon number.

Carbon atoms	Number of isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
15	4347
20	366,319
25	36,797,588
30	4,111,846,763
40	62,491,178,805,831

In order to meet the demands of a variety of uses, certain basic naphtha grades are produced which are identified by boiling range. The complete range of naphtha solvents may be divided, for convenience, into four general categories: (i) special boiling point spirits having overall distillation range within the limits 30 to l65 °C (86—330 °F), (ii) pure aromatic compounds such as benzene, toluene, xylene isomers, or mixtures (BTX) thereof, (iii) white spirit, also known as mineral spirit and naphtha, usually boiling within 150—210 °C (302—410 °F), and (iv) high boiling crude oil fractions boiling within limits 160—325 °C (320—615 °F).

Since the end use dictates the required composition of naphtha, most grades are available in both high and low solvency categories and the various text methods can have major significance in some applications and lesser significance in others. Hence the application and significance of tests must be considered in the light of the proposed end use. To emphasize this point, naphtha contains varying amounts of its constituents viz., paraffin derivatives, naphthene derivatives, aromatic derivatives and olefin derivatives in different proportions in addition to potential isomers of paraffin that exist in naphtha boiling range. Naphtha resembles gasoline in terms of boiling range and carbon number, being a precursor to gasoline. Naphtha is used as automotive fuel, engine fuel, and jet-B (naphtha type). Broadly, naphtha is classified as *light naphtha* and *heavy naphtha*. Light naphtha is used as rubber solvent, lacquer diluent, while heavy naphtha finds its application as varnish solvent or naphtha in the dyeing and cleaning industries.

Volatility, solvent properties (dissolving power), purity and odor determine the suitability of naphtha for a particular use. The use of naphtha as an incendiary device in warfare, and as an illuminant dates back to AD 1200. Naphtha is characterized as lean (high paraffin content) or rich (low paraffin content). The rich naphtha with higher proportion of naphthene content is easier to process in the Platforming unit (Parkash, 2003; Gary et al., 2007; Speight, 2104; Hsu and Robinson, 2017; Speight, 2017).

If spilled or discharged in the environment, naphtha represents a threat of the toxicity of the constituents to land and/or to aquatic organisms. A significant spill may cause long-term adverse effects in the aquatic environment. The constituents of naphtha predominantly fall in the C_5-C_{16} carbon range: alkanes, cycloalkanes, aromatic derivatives and, if they are subject to a cracking process, alkenes as well. Naphtha may also contain a preponderance of aromatic constituents (up to 65%), others contain up to 40% alkenes, while all of the others are aliphatic in composition, up to 100%.

Water solubility ranges from very low for the longest-chain alkanes to high solubility for the simplest mono-aromatic constituents. Generally, the aromatic compounds are more soluble than the same-sized alkanes, iso-alkanes and cycloalkanes. This indicates that the components likely to remain in water are the one- and two-ring aromatic derivatives (C_6-C_{12}). The C_9-C_{16} alkanes, iso-alkanes and one- and two-ring cycloalkanes are likely to be attracted to sediments based on their low water solubility and moderate to high octanol-water partition coefficient (log K_{ow}) and organic carbon-water partition coefficient (log K_{oc}) values.

The main uses of crude oil naphtha fall into the general areas of (i) precursor to gasoline and other liquid fuels, (ii) solvents or diluents for paints, (iii) dry-cleaning solvents, (iv) solvents for cutback asphalt, (v) solvents in rubber industry, and (vi) solvents for industrial extraction processes. Turpentine, the older and more conventional solvent for paints has now been almost completely replaced by the cheaper and more abundant crude oil naphtha. Test methods are based on defining the suitability of naphtha for any of the aforementioned uses.

Finally, the nature of the uses found for naphtha demands compatibility with the many other materials employed in the formulation of the naphtha, including gas condensate and natural gasoline. Thus, the solvent properties of a given fraction must be carefully measured and controlled. For most purposes volatility is important, and, because of the wide use of naphtha in industrial and recovery plants, information on some other fundamental characteristics is required for plant design.

Condensate liquids are generally *water white* (colorless or near-colorless) or are light in color (brown, orange, or green), with an API gravity typically on the order of 40 and 60° API. The yields of these liquids can be as high as 300 stock tank barrels per million cubic feet (STB/MMscf). It has been suggested (McCain, 1990) that when yields are below approximately 20 stock tank barrels per million cubic feet, even though phase-behavior considerations may show retrograde behavior, the amount of liquid dropout in the reservoir can be insignificant.

There are many condensate sources, and each has its own unique gas condensate composition. In general, gas condensate has a specific gravity ranging from 0.5 to 0.8, and is composed of hydrocarbon derivatives such as propane, butane, pentane, hexane, and often higher molecular weight hydrocarbon derivatives up to decane. Natural gas compounds with more carbon atoms (e.g. pentane, or blends of butane, pentane and other hydrocarbon derivatives with additional carbon atoms) exist as liquids at ambient temperatures. Additionally, condensate may contain other impurities such as: (i) hydrogen sulfide, H_2S,

(ii) thiols, traditionally also called mercaptans and denoted as RSH, where R is an organic group such as methyl, ethyl, propyl, and the like, (iii) carbon dioxide, CO_2, (iv) straight-chain alkane derivatives having from 2 to 10 carbon atoms, denoted as C_2 to C_{12}, (v) cyclohexane and perhaps other naphthene derivatives, and (vi) aromatic derivatives such as benzene, toluene, xylene isomers, and ethylbenzene (Pedersen et al., 1989).

Condensate normally differs markedly from conventional crude oil insofar as (i) the color of crude oil typically varies from dark green to black, (ii) contains some naphtha, often incorrectly referred to as gasoline, (iii) is usually contains dark-colored, high molecular weight non-volatile components, and (iv) the API gravity, which is measure of its weight or density, is commonly less than 45°.

When a hydrocarbon reservoir is discovered it is important to know the type of fluids that are present as well as their main physicochemical characteristics, this is normally obtained by performing a pressure-volume-temperature analysis to a representative fluid sample of the reservoir. In most cases, having a pressure-volume-temperature analysis can take several months, which limits the number and type of reservoir studies that can be carried out during this period (Paredes et al., 2014). The only parameter that can be measured almost immediately after a well is completed, are conventional production measurements. In some cases, this production measurement can be obtained before completing the well by using special testing or measuring equipment such as a drill stem test (DST).

Fluids present in a crude oil reservoir are the result of a series of thermodynamic changes of pressure and temperature suffered by the original mixture of hydrocarbon derivatives over time and during its migration from the container rock to the trap. Reservoir pressure and temperature increase with depth and their relative relationship will influence the behavior of the low-boiling and high-boiling components that the fluid could contain. In general, the content of low-boiling constituents in a mixture of hydrocarbon derivatives increases with temperature and depth, which may result in reservoirs near the critical point; gas condensate reservoirs are included in this kind of fluids (Ovalle et al., 2007).

Reservoir fluid properties are used to characterize the condition of a fluid at a given state. A reliable estimation and description of the properties of hydrocarbon mixtures is fundamental in crude oil and natural engineering analysis and design. Fluid properties are not independent, just as pressure, temperature, and volume are not independent of each other. Equations of State provide the means for the estimation of the PVT relationship, and from them many other thermodynamic properties can be derived. Compositions are usually required for the calculation of the properties of each phase.

Correlation equations for gas condensates based on readily available field data have been developed. The correlations can be used to predict dewpoint pressures, decreases in surface condensate yields after reservoir pressure has decreased below dewpoint pressure, and decreases in reservoir-gas specific gravity at reservoir pressures below dewpoint pressure. A value of dewpoint pressure is essential data for any reservoir study. A reasonably accurate estimate of dewpoint pressure for a specific reservoir fluid is necessary in situations in which laboratory data are not available or before laboratory data are obtained. Laboratory measurements of dewpoint pressure and other gas properties of 615 gas condensates with worldwide origins were used to develop a dewpoint-pressure correlation based on initial producing gas/condensate ratio, initial stock-tank oil gravity, and specific gravity of the original reservoir gas.

This is the first proposed dewpoint-pressure correlation that does not require some laboratory-measured quantity.

Estimation of decreases in producing yields after the reservoir pressure drops below the dewpoint pressure is necessary for accurate prediction of condensate reserves. The reduction in surface yields can be as much as 75% during the primary production of a gas condensate. This reduction must be taken into account in the prediction of ultimate recovery of a condensate. A surface-yield correlation has been developed that is a function of a selected reservoir pressure, initial stock-tank oil gravity, specific gravity of the original reservoir gas, and reservoir temperature. The data set included laboratory studies of 190 gas-condensate samples. This is the first proposal offered in crude oil literature of a correlation to estimate the decreases in surface yield.

Density is customarily defined as the amount of mass contained in a unit volume of fluid. Density is the single-most important property of a fluid (Speight, 2014a, 2015a), once it is realized that most other properties can be obtained or related to density. Both specific volume and density — which are inversely proportionally related to each other indicate the distance between the molecules in a fluid are from each other. For liquids, density is high, which translates to a very high molecular concentration and short intermolecular distances. For gases, density is low, which translates to low molecular concentrations large intermolecular distances (Rayes et al., 1992; Piper et al., 1999).

Specific gravity is the ratio of fluid density to the density of a reference substance, both defined at the same pressure and temperature. These densities are usually defined at standard conditions (14.7 psia and 60 °F). For a condensate, oil or a liquid, the reference substance is water. By definition, the specific gravity of water is unity and, using the API scale, water has an API gravity of 10. Light crude oils have an API greater than or equal to 45° while the API gravities of gas condensates range between 50° and 70° API.

The formation volume factor of a natural gas **(B_g) relates the** volume of 1 lb-mol of gas at reservoir conditions to the volume of the same lb-mol of gas at standard conditions, as follows:

$$B_g = (\text{Volume of 1 unit of gas at reservoir conditions})/(\text{Volume of 1 unit of gas, SCF})$$

Those volumes are, evidently, the specific molar volumes of the gas at the given conditions. The formation volume factor of a condensate (B_o) relates the volume of 1 lb-mol of liquid at reservoir conditions to the volume of that liquid once it has gone through the surface separation facility:

$$B_o = (\text{Volume of 1 unit of liquid at reservoir conditions})/(\text{Volume of 1 unit of liquid after separation})$$

The oil formation volume factor can be also seen as the volume of reservoir fluid required to produce one barrel of oil in the stock tank.

Surface tension is a measure of the surface free energy of liquids, i.e., the extent of energy stored at the surface of liquids. Although it is also known as interfacial force or interfacial tension, the name *surface tension* is usually used in systems where the liquid is in contact with gas. Qualitatively, it is described as the force acting on the surface of a liquid that tends to minimize the area of its surface, resulting in liquids forming droplets with spherical shape, for instance. Quantitatively, since its dimension is of force over length (lbf/ft in English units), it is expressed as the force (in lbf) required to break a film of 1 ft of length. Equivalently, it may be restated as being the amount of surface energy (in lbf-ft) per square feet.

Fluid viscosity is a measure of its internal resistance to flow and, thus, viscosity is an indicator of flow properties of the condensate. The most commonly-used unit of viscosity is the centi-poise, which is related to other units as follows:

$$1\ c_p = 0.01\ \text{poise} = 0.000672\ \text{lbm/ft} - \text{s} = 0.001\ \text{Pa} - \text{s}$$

Natural gas viscosity (Chapter 7) is typically expected to increase both with pressure and temperature (Lee et al., 1966).

The following is a review of applicable test methods that can be used to measure some of the key parameters in the range of hydrocarbon derivative that occur in gas tight gas.

Because of the high standards set for naphtha and the high standards required (McCann, 1998), it is also essential to employ the same high-standard techniques to gas condensate and natural gasoline when taking samples for testing (ASTM D4057). This test method covers procedures and equipment for manually obtaining samples of liquid crude oil and crude oil products, crude oils, and intermediate products from the sample point into the primary container are described. The sampling of gas condensate and natural gasoline may fit into this test method, provided the potential high volatility of the gas condensate and natural gasoline is recognized by the investigator and the analyst. There are inherent limitations when performing any type of sampling, any one of which may affect the representative nature of the sample. As examples, a spot sample (Chapter 5) provides a sample from only one particular point in the tank, vessel compartment, or pipeline. In the case of running or all-level samples, the sample only represents the column of material from which it was taken.

However, based on the product, and testing to be performed, this test method (ASTM D4057) provides guidance on sampling equipment, container preparation, and manual sampling procedures for crude oil and crude oil products of a liquid, semi-liquid, or solid state, from the storage tanks, flowlines, pipelines, marine vessels, process vessels, drums, cans, tubes, bags, kettles, and open discharge streams into the primary sample container. However, mishandling of the sample or the slightest trace of contaminant in the sample can give rise to misleading results. Special care is necessary to ensure that containers are scrupulously clean and free from odor. Samples should be taken with the minimum of disturbance so as to avoid loss of volatile components; in the case of low-boiling naphtha may be necessary to chill the sample. And, while awaiting examination samples should be kept in a cool dark place so as to ensure that they do not lose volatile constituents or discolor and develop odors due to oxidation.

Another method for assessing the solvent properties of naphtha measures the performance of the fraction when used as a solvent under specified conditions such as, for example, by the Kauri Butanol test method (ASTM D1133). This test method is used to determine the Kauri-butanol value which is used as a measure of solvent power of hydrocarbon liquids − a high kauri-butanol values indicate relatively strong solvency. However, caution is advised in the use of this methods since the method is specifically designed for application to hydrocarbon liquids that have an initial boiling point over 40 °C (104 °F) and a dry point less than 300 °C

(570 °F) which may disqualify most gas condensate sample but be allowable only for higher-boiling natural gasoline samples.

Other methods that are applicable to hydrocarbon liquids typically involve determination of the surface tension from which the solubility parameter is calculated and then provides an indication of dissolving power and compatibility. A similar principal is applied to determine the amount of insoluble material in lubricating oil using *n*-pentane (ASTM D893; ASTM D4055) and can be applied to liquid fuels. The insoluble constituents measured can also assist in evaluating the performance characteristics of a liquid fuel in determining the cause of equipment failure and line blockage (Chapter 13) (Speight and Exall, 2014). One test method (ASTM D893) covers the determination of pentane and toluene insoluble constituents in used lubricating oils using pentane dilution and centrifugation as the method of separation. The other test method (ASTM D4055) uses pentane dilution followed by membrane filtration to remove insoluble constituents that have a size greater than 0.8 μm.

7.1.1 *Aniline point and mixed aniline point*

The aniline point for a hydrocarbon fraction is defined as the minimum temperature at which equal volumes of liquid hydrocarbon and aniline are miscible. Aniline ($C_6H_5NH_2$) is an aromatic compound with a structure of a benzene molecule where one atom of hydrogen is replaced by the amino (−NH2 group). The aniline point is important test method (ASTM D611) that can be used for the characterization of crude oil fractions and analysis of molecular type and in the analysis of mixtures of hydrocarbon derivatives. This test method includes sub-test methods, each of which is suitable for the conditions under which it is to be applied, none of which may be applicable to gas condensate samples, but the potential exists for application of a sub-test method possible (Method A) to natural gasoline. This test method also covers the determination of the mixed aniline point of crude oil products and hydrocarbon solvents having aniline points below the temperature at which aniline will crystallize from the aniline-sample mixture.

Test Method A (ASTM D611) is suitable for transparent samples with an initial boiling point above room temperature and where the aniline point is below the bubble point and above the solidification point of the aniline-sample mixture. Test Method B, a thin-film method, is suitable for samples too dark for testing by Test Method A. Test Methods C and D are for samples that may vaporize appreciably at the aniline point. Test Method D is particularly suitable where only small quantities of sample are available. Test Method E describes a procedure using an automatic apparatus suitable for the range covered by Test Methods A and B.

Within a hydrocarbon group, the aniline point increases with molecular weight or carbon number, but for the same carbon number the aniline point increases from aromatic hydrocarbon derivatives to paraffin hydrocarbon derivatives − generally, oils with higher aniline points have lower aromatic content. Aromatic derivatives have a relatively low aniline points in comparison with paraffin derivatives since aniline ($C_6H_5NH_2$) is an aromatic compound and has better miscibility with aromatic hydrocarbon derivatives. The aniline points of cycloparaffin derivatives (naphthene derivatives) and olefin derivaitves tend to fall between the two extremes of the aniline points of aromatic hydrocarbon derivatives the aniline points of paraffin hydrocarbon derivatives.

7.1.2 Benzene and aromatic derivatives

The accurate measurements of benzene and total aromatic derivatives in gasoline are regulated test parameters in modern solvents and liquid fuels (Speight, 2015), and since gas condensate and natural gasoline are used as gasoline blending stocks, the same applies to these two products of natural gas production. This test method covers the determination of benzene and toluene in low-boiling hydrocarbon liquids by gas chromatography. Benzene can be determined between the levels of 0.1 and 5 vol% and toluene can be determined between the levels of 2 and 20% v/v. For whatever reason, contain ethanol or methanol, since these components do not completely separate from the benzene peak. An Appendix, in the form of a modified test method provides an option for modifying the test method for analyzing samples containing ethanol. The modified method uses a different internal standard and a different set of gas chromatographic columns that gives better separation of ethanol or methanol containing fuels.

Another test method (ASTM D5580) that is used to determine benzene, toluene, ethylbenzene, xylene isomers, and higher-boiling aromatic derivative as well as the total concentration of aromatic derivative in the sample uses gas chromatography that has been developed to include liquid fuels that containing commonly-encountered alcohols and ethers. In the method, the aromatic hydrocarbon derivatives are separated without interferences from other hydrocarbon derivatives in the liquid sample. Non-aromatic hydrocarbon derivatives having a boiling point greater than *n*-dodecane (which may not be relevant when the relatively low-boiling gas condensate and natural gasoline are the samples under investigation) may cause interferences with the determination of the C_9 and higher molecular weight aromatic derivatives. For the C_8 aromatic derivatives, *p*-xylene and *m*-xylene co-elute while ethylbenzene and *o*-xylene are separated. Any C_9 and higher-boiling aromatic derivatives are determined as a single group. This test method covers the following concentration ranges, in liquid volume %, for the aromatic derivatives: (i) benzene, 0.1%–5% v/v, (ii) toluene, 1%–15% v/v, (iii) individual C_8 aromatic derivatives, 0.5%–10% v/v, (iv) total C_9 and higher boiling aromatic derivatives, 5%–30% v/v, and (v) total aromatic derivatives, 10%–80% v/v.

In addition gas chromatography and the instrumental methods cited above, the so-called hyphenated-analytical instrumental methods (ASTM D5769) that are used to determine benzene, toluene and total aromatic derivatives in liquid samples such as gas chromatography-mass spectrometry (GC/MS) gas chromatography-Fourier transform infrared spectroscopy and, (GC/FTIR) are also available for accurate measurement of benzene in any liquid sample (ASTM D5986) (DiSanzo and Giarrocco, 1988; De Bakker and Fredericks, 1995).

In the first test method (ASTM D5769), the determination of benzene, toluene, other specified individual aromatic compounds, and total aromatic derivatives in finished naphtha-type hydrocarbon liquids is covered. The method employs gas chromatography/mass spectrometry (GC/MS). The method can be applied to hydrocarbon liquids that contain the analytes in the following concentrations: (i) benzene, 0.1%–4% v/v, (ii) toluene, 1%–13%, (ii) and (iii) total (C_6–C_{12}) aromatic derivatives, 10%–42% v/v.

The determination of the total volume percent of saturates, olefin derivatives, and aromatic derivatives in crude oil fractions is important in characterizing the quality of crude oil fractions as gasoline blending components and as feeds to catalytic reforming processes.

This information is also important in characterizing crude oil fractions and products from catalytic reforming and from thermal and catalytic cracking as blending components for motor and aviation fuels. This information is also important as a measure of the quality of fuels, such as specified in another standard test method (ASTM D1655). However, this test method (ASTM D1655) describes the minimum property requirements for Jet A and Jet A-1 aviation turbine fuel and lists acceptable additives for use in civil operated engines and aircrafts. Thus, it may not be applicable to gas condensate or natural gasoline and the analyst should considered all of the possible properties of gas condensate or natural gasoline before applying this test method to the sample.

7.1.3 Composition

The number of potential hydrocarbon isomers in the naphtha boiling range (Table 10.8, Table 10.9) renders complete speciation of individual hydrocarbon derivatives impossible for the naphtha distillation range and methods are used that identify the hydrocarbon types as chemical groups rather than as individual constituents. However, it must be recognized that composition varies with depth in crude oil reservoirs (Speight, 2104) and component "segregation" due to gravitational forces is usually given as the physical explanation for the variation in composition. The result of gravitational segregation is that a gas condensate gets richer at greater depths, with increasing C_{7+} mole fraction (and dewpoint pressure) (Whitson and Belery, 1994). However, not all fields show compositional gradients with depth as predicted by the isothermal model. Some fields show practically no gradient over large depths while other oil fields have gradients larger than predicted by the isothermal model (Høier and Whitson., 1998). Variation in C_{7+} composition with depth will obviously affect the calculation of initial surface condensate in place, compared with a calculation based on a constant composition.

The accurate determination of the density, relative density (specific gravity), or API gravity of crude oil and its products is necessary for the conversion of measured volumes to volumes or masses, or both, at the standard reference temperatures of 15 °C or 60 °F during custody transfer. Thus, e data from the density (specific gravity) test method (ASTM D1298) provides a means of identification of a grade of naphtha but is not a guarantee of composition and can only be used to indicate evaluate product composition or quality when used in conjunction with the data from other test methods. Density data are used primarily to convert naphtha volume to a weight basis, a requirement in many of the industries concerned. For the necessary temperature corrections and also for volume corrections the appropriate sections of the crude oil measurement tables (ASTM D1250) are used.

The procedure (ASTM D1298) is most suitable for determining the density, relative density (specific gravity), or API gravity of low viscosity transparent liquids. In addition, the method can also be used for viscous liquids (not a relevant issue when the method is applied to gas condensate or natural gasoline) by allowing sufficient time for the hydrometer to reach temperature equilibrium, and for opaque liquids by employing a suitable meniscus correction. Additionally, for both transparent and opaque fluids the readings shall be corrected for the thermal glass expansion effect and alternative calibration temperature effects before correcting to the reference temperature.

The method (ASTM D1298) covers the laboratory determination using a glass hydrometer in conjunction with a series of calculations, of the density, relative density, or API gravity of hydrocarbon liquids that are typically handled as liquids, and having a Reid vapor pressure of 101.325 kPa (14.696 psi) or less. Values are determined at existing temperatures and corrected to 15 °C or 60 °F by means of a series of calculations and international standard tables.

The initial hydrometer readings obtained are uncorrected hydrometer readings and not density measurements. Readings are measured on a hydrometer at either the reference temperature or at another convenient temperature, and readings are corrected for the meniscus effect, the thermal glass expansion effect, alternative calibration temperature effects and to the reference temperature by means of the crude oil measurement tables. Values obtained at other than the reference temperature being hydrometer readings and not density measurements. Data determined as density, relative density, or API gravity can be converted to equivalent values in the other units or alternative reference temperatures by means of interconversion procedures (ASTM D1250).

The first level of compositional information is group-type totals as deduced by adsorption chromatography (ASTM D1319) to give volume percent saturates, olefin derivatives, and aromatic derivatives in materials that boil below 315 °C (600 °F). In this test method, a small amount of sample is introduced into a glass adsorption column packed with activated silica gel, of which a small layer contains a mixture of fluorescent dyes. When the sample has been adsorbed on the gel, alcohol is added to desorb the sample down the column and the hydrocarbon constituents are separated according to their affinities into three types (aromatic derivatives, olefin derivatives, and saturates). The fluorescent dyes also react selectively with the hydrocarbon types, and make the boundary zones visible under ultraviolet light. The volume percentage of each hydrocarbon type is calculated from the length of each zone in the column.

A standard test method (ASTM D2427) has been designed to determine the ethane (C_2) to pentane (C_5) hydrocarbon content in gasoline and low-boiling hydrocarbon liquids. The method is a mature method that utilizes packed columns and mechanical valves for the back-flush and fore-flush techniques needed to separate the volatile hydrocarbon derivatives from the rest of the naphtha sample. However, a sample containing significant concentrations of non-hydrocarbon additives (such as ethanol) may interfere with the existing method and there may be the need to develop an alternate procedure to determine the low-boiling hydrocarbon derivaitves.

An indication of composition may also be obtained from the determination of aniline point (ASTM D611), freezing point (ASTM D852; ASTM D1015), cloud point (ASTM D2500), and the solidification point or freezing point (ASTM D852; ASTM D1015). In the application of test method ASTM D852, the analyst should be aware that the method this test method is to be used for determining the purity of benzene. The closer the solidification point reaches that of pure benzene, the purer the sample. The freezing point measurement (ASTM D1015), when used in conjunction with the physical constants for the relevant hydrocarbon derivative (ASTM D1016), allows the determination of the purity of the test sample. The parameters of the test method do not allow general application of the method to bulk sample of gas condensate sample or natural gasoline sample. However, the parameters do allow purity checks (through the freezing point) for any individual sample separated from gas condensate or from natural gasoline. A knowledge of the purity of these hydrocarbon derivatives is often needed to help control their manufacture and to determine their suitability for use as reagent chemicals or for conversion to other chemical intermediates or finished products.

The alkalinity and acidity (ASTM D847; ASTM D1093; ASTM D1613; ASTM D2896) as well as olefin content should be low in all cases but there is no guarantee that this will be the case. Gas condensate or natural gasoline separated from crude oil wells may show vestiges of acidity or alkalinity or olefin content. In addition, gases produced from other sources (refinery process gas coal gas, biogas, landfill gas, and fuel gas) may show signs of acidity or alkalinity or olefin content. Application of the relevant tests using bromine number (ASTM D1159), bromine index (ASTM D2710), and flame ionization absorption (ASTM D1319) are necessary to insure low levels (at the maximum) of hydrogen sulfide as well as the sulfur compounds in general (ASTM D130; ASTM D849; ASTM D1266; ASTM D3120; ASTM D4045) and especially corrosive sulfur compounds such as are determined by the doctor test method (ASTM D4952).

Aromatic constituents can be present in gas condensate and natural gasoline and because the aromatic constituents influence a variety of properties including boiling range (ASTM D86), viscosity (ASTM D88; ASTM D445; ASTM D2161), stability (ASTM D525), and compatibility (ASTM D1133) with a variety of solutes the relevant test methods may need to be applied. Tests such as aniline point (ASTM D611) and Kauri-butanol number (ASTM D1133) are of a somewhat empirical nature and can serve a useful function as control tests. However, gas condensate composition and natural gasoline composition are is monitored mainly by gas chromatography and although most of the methods may have been developed for gasoline or naphtha (ASTM D2427; ASTM D6296), the applicability of the test methods to gas condensate composition and natural gasoline is in order.

A multidimensional gas chromatographic method (ASTM D5443) provides for the determination of paraffin derivatives, naphthene derivatives, and aromatic derivatives by carbon number in low olefin-type hydrocarbon streams having final boiling points lower than 200 °C (392 °F). The test method (ASTM D5443) that employs by multi-dimensional gas chromatography is available for determination of paraffin derivatives, naphthene derivatives, and aromatic hydrocarbon in crude oil distillates that boil up to 200 °C (390 °F) and can be used to measure hydrocarbon types by carbon number and, therefore, may be suitable for application of gas condensate and natural gasoline. This test method (ASTM D5443) is applicable to hydrocarbon refinery streams is useful for process control and quality assurance. The method is applicable to a variety of hydrocarbon mixtures including virgin, catalytically converted, thermally converted, alkylated and blended naphtha. The method covers the determination of paraffin derivatives, naphthene derivatives, and aromatic derivatives by carbon number in low olefin-containing hydrocarbon mixtures having final boiling points up to 200 °C (392 °F).

Hydrocarbon mixtures with boiling points greater than 200 °C and less than 270 °C (392–520 °F) are reported as a single group. Olefin derivatives, if present, should be hydrogenated and the resultant saturates are included in the paraffin and naphthene distribution. Aromatic derivatives boiling at C_9 and above are reported as a single aromatic group. However, this test method in contrast to other gas-chromatographic-based test methods, is not intended to determine individual components except for benzene and toluene that are the only C_6 and C_7 aromatic derivatives, respectively, and cyclopentane that is the only C_5 naphthene derivative. The lower limit of detection for a single hydrocarbon component or group is 0.05% w/w.

Other methods (ASTM D3257) for the determination of the amount of aromatic constituents, include various types of detectors and offer alternate routes to determining aromatic derivatives in naphtha. However, the method (ASTM D3257) covers the determination of ethylbenzene and total eight-carbon (C_8) and higher-boiling aromatic derivatives in the concentration range from 0.1% to 30% v/v in hydrocarbon liquids having a distillation range from 149 to 210 °C (300–410 °F) as determined by the standard test method (ASTM D86). The method is only applicable to the identification of any higher-boiling constituents present in natural gasoline – gas condensate frequently does not contain such high-boiling constituents.

Hydrocarbon composition, relevant to gas condensate and natural gasoline, is determined by mass spectrometry – a technique that has seen wide use for hydrocarbon-type analysis of naphtha and gasoline (ASTM D2789) as well as to the identification of hydrocarbon constituents in higher boiling naphtha fractions (ASTM D2425).

Another method (ASTM D2789) allows condensate and naphtha samples to be submitted for functional group hydrocarbon analysis by mass spectrometry. This test method covers the determination by mass spectrometry of the total paraffin derivatives, monocycloparaffin derivatives, dicycloparaffin derivatives (unlikely in gas condensate and natural gasoline), alkylbenzene derivatives, and other higher molecular weight cyclo-derivatives that are also unlikely in gas condensate and natural gasoline provided the sample has an olefin content of less than 3% v/v and a 95% v/v distillation point of less than 210 °C (410 °F) (ASTM D86). Olefin derivaitves can be determined application of alternate test methods (ASTM D1319). Generally, the method is suitable for samples of low-boiling hydrocarbon mixtures in which low-boiling hydrocarbon derivatives are to be determined in samples containing significant low volatility or polar components in the matrix. The method is also suitable to determine methane content of such mixtures and can be extended to include higher molecular weight hydrocarbon derivatives.

On the other hand, test method ASTM D2425 covers an analytical scheme using the mass spectrometer to determine the hydrocarbon types present in virgin middle distillates 204 °C–343 °C (400 °F–650 °F) boiling range, 5 %–95 % v/v. Samples with average carbon number value of paraffin derivatives between C_{12} and C_{16} and containing paraffin derivatives from C_{10} and C_{18} can be analyzed. Generally, the method is not suitable for samples of low-boiling hydrocarbon mixtures in which low-boiling hydrocarbon derivatives are to be determined in samples containing significant low volatility or in the mixture. Under the parameters described, the method would require considerable modification for application to gas condensate and natural gasoline unless each sample contained a substantial amount of a higher-boiling (middle distillate-type) residue.

One method (ASTM D6379) is available that can be used to determine the mono-aromatic and di-aromatic hydrocarbon contents in distillates boiling in the range from 50 to 300 °C (122–570 °F). This test method covers a high-performance liquid chromatographic test method for the determination of mono-aromatic and di-aromatic hydrocarbon contents in hydrocarbon liquids such as distillates boiling in the range from 50 to 300 °C (122–570 °F) and may be applicable (with some modification) to gas condensate and natural gasoline. The total aromatic content is calculated from the sum of the individual aromatic hydrocarbon-types. This test method is calibrated for hydrocarbon liquids containing from 10 to 25% w/w mono-aromatic hydrocarbon derivatives and from 0% to 7% w/x di-aromatic hydrocarbon derivatives. Constituents containing sulfur, nitrogen, and oxygen (which are not frequent constituents of gas condensate and natural gasoline) are possible interferents.

Another method (ASTM D2425) provides more compositional detail (in terms of molecular species) than chromatographic analysis and the hydrocarbon types are classified in terms of a Z-series in which Z (in the empirical formula C_nH_{2n+z}) is a measure of the hydrogen deficiency of the compound. This method requires that the sample be separated into saturate and aromatic fractions before mass spectrometric analysis (ASTM D2549) and the separation is applicable to some fractions not others. For example, the method is applicable to high-boiling naphtha but not to the low-boiling naphtha since it is impossible to evaporate the solvent used in the separation without also losing the lower boiling constituents of the naphtha under investigation.

The percentage of aromatic hydrogen atoms and aromatic carbon atoms can be determined by high-resolution nuclear magnetic resonance spectroscopy (ASTM D5292) that gives the mol percent of aromatic hydrogen or carbon atoms. Proton (hydrogen) magnetic resonance spectra are obtained on sample solutions in either chloroform or carbon tetrachloride using a continuous wave or pulse Fourier transform high-resolution magnetic resonance spectrometer. Carbon magnetic resonance spectra are obtained on the sample solution in chloroform-*d* using a pulse Fourier transform high-resolution magnetic resonance. This test method covers the determination of the aromatic hydrogen content (Procedures A and B) and aromatic carbon content (Procedure C) of hydrocarbon oils using high-resolution nuclear magnetic resonance (NMR) spectrometers. For pulse Fourier transform (FT) spectrometers, the detection limit is typically 0.1 mol % aromatic hydrogen atoms and 0.5 mol % aromatic carbon atoms. For continuous wave (CW) spectrometers, which are suitable for measuring aromatic hydrogen contents only, the detection limit is considerably higher and typically 0.5 mol % aromatic hydrogen atoms.

The determination of hydrocarbon components in naphtha is of great importance to the petrochemical industry and for process control of reforming processes, as well as for regulatory purposes. The data obtained by nuclear magnetic resonance (ASTM D5292) can be used to evaluate changes in aromatic contents in naphtha as well as kerosene, gas oil, mineral oil, and lubricating oil. However, results from this test are not equivalent to mass-percent or volume-percent aromatic derivatives determined by the chromatographic methods since the chromatographic methods determine the percent by weight or percent by volume of molecules that have one or more aromatic rings and alkyl substituents on the rings will contribute to the percentage of aromatic derivatives determined by chromatographic techniques.

Test method (ASTM D3701) is focused on the combustion quality of aviation turbine fuel has traditionally and may be only marginally suitable for application to gas condensate and natural gasoline. Typically, the test method has been applied to specifications along with such test methods that are relevant to the determination of the smoke point (ASTM D1322). Use of another test method (ASTM D4808) is more suitable for the determination of hydrogen in crude oil liquids.

As an example, test method ASTM D4808 covers the determination of the hydrogen content of crude oil products ranging from atmospheric distillates to vacuum residua using a continuous wave, low-resolution nuclear magnetic resonance spectrometer. One pof the sub-methods (Method A) is used for hydrocarbon liquids with the boiling range 15–260 °C (59–500 °F) and is, therefore, (if the determination of any lower boiling material can be accolated by another standard test method or by stabilization of the sample at 15 °C) is suitable for gas condensate and natural gasoline.

Although the focus of many tests is analysis of the hydrocarbon constituents of naphtha and other crude oil fractions, heteroatoms compounds that contain sulfur and nitrogen atoms cannot be ignored and methods for their determination are available. The combination of gas chromatography with element selective detection gives information related to the distribution of the element. In addition, many individual heteroatomic compounds can be determined. Thus, estimates of the purity of these products were determined in laboratories using a variety of procedures such as freezing point, flame ionization absorbance, ultraviolet absorbance, gas chromatography, and capillary gas chromatography, (ASTM D850; ASTM D852; ASTM D848; ASTM D849; ASTM D1015; ASTM D1016; ASTM D1078; ASTM D1319; ASTM D2008; ASTM D2360; ASTM D5134; ASTM D5917).

Gas chromatography (GC) has become a primary technique for determining hydrocarbon impurities in individual aromatic hydrocarbon derivatives and the composition of mixed aromatic hydrocarbon derivatives. Although a measure of purity by gas chromatography is often sufficient, gas chromatography is not capable of measuring absolute purity; not all possible impurities will pass through the gas chromatography column, and not all those that do will be measured by the detector. Despite some shortcomings, gas chromatography is a standard, widely used technique and is the basis of many current test methods for aromatic hydrocarbon derivatives (ASTM D2360, ASTM D3797, ASTM D4492, ASTM D5060, ASTM D5135, ASTM D5713, ASTM D5917, ASTM D6144).

Impurities other than hydrocarbon derivatives are of concern in the crude oil industry. For example, many catalytic processes are sensitive to sulfur contaminants. Consequently, there is also a series of methods to determine trace concentrations of sulfur-containing compounds (ASTM D4045, ASTM D4735). When classes of hydrocarbon derivatives, such as olefin derivatives, need to be measured, techniques such as bromine index are used (ASTM D1492; ASTM D5776). Chloride-containing impurities are determined by various test methods (ASTM D5194; ASTM D5808; ASTM D6069) that have sensitivity to 1 mg/kg, reflecting the needs of industry to determine very low levels of these contaminants.

Water is also a potential contaminant in gas condensate and natural gasoline that should be given consideration. Water content can be measured using the Karl Fischer method (ASTM E203; ASTM D1364; ASTM D1744; ASTM D4377; ASTM D4928; ASTM D6304), by distillation (ASTM D4006), or by centrifuging and excluded by relevant drying methods.

Tests should also be carried out for sediment if the gas condensate or natural gasoline has been subjected to events (such as oxidation) that could lead to sediment formation and instability of the naphtha and the resulting products. Test methods are available for the determination of sediment by extraction (ASTM D473) or by membrane filtration (ASTM D4807) and the determination of simultaneously sediment with water by centrifugation (ASTM D1796; ASTM D2709; ASTM D4007). Whether or not these test can be applied to gas condensate or natural gasoline depend upon the experimental protocols of each individual test method and, obviously, the need for sediment removal from the gas condensate or natural gasoline.

7.1.4 Correlative methods

Correlative methods have long been used as a way of dealing with the complexity of various crude oil fractions, including naphtha. Relatively easy to measure physical properties such as density (or specific gravity) (ASTM D3505; ASTM D4052) are also required.

TABLE 10.10 Refractive Index of Selected Hydrocarbon derivatives.

Compound	Refractive index n_D^{20}
n-Pentane	1.3578
n -hexane	1.3750
n -hexadecane	1.4340
Cyclopentane	1.4065
Cyclopentene	1.4224
Pentene-1	1.3714
1,3-Pentadiene	1.4309
Benzene	1.5011
cis-Decahydronaphthalene	1.4814
Methylnaphthalenes	1.6150

Viscosity (ASTM D88; ASTM D445; ASTM D2161), density (ASTM D287; ASTM D891; ASTM D1217; ASTM D1298; ASTM D1555; ASTM D1657; ASTM D4052; ASTM D5002) and refractive index (ASTM D1218) have been correlated to hydrocarbon composition (Table 10.10).

Using density as the example, density is a fundamental physical property that can be used in conjunction with other properties to characterize the quality of crude oil, and other hydrocarbon liquids. The density or relative density of crude oils is used for the conversion of measured volumes to volumes at the standard temperatures of 15 °C (or 60 °F) and for the conversion of crude mass measurements into volume units. The application of the density result obtained from this one of the test methods (ASTM D5002), for fiscal or custody transfer accounting calculations, can require measurements of the water and sediment contents obtained on similar specimens of the crude oil parcel. The method (ASTM D5002) covers the determination of the density or relative density of crude oils that can be handled in a normal fashion as liquids at test temperatures between 15 and 35 °C (59 and 95 °F) utilizing either manual or automated sample injection equipment. The method applies to crude oil (and, by inference, hydrocarbon liquids) with a high vapor pressure provided appropriate precautions are taken to prevent vapor loss during transfer of the sample to the density analyzer.

7.1.5 Density

Density (the mass of liquid per unit volume at 15 °C) and the related terms *specific gravity* (the ratio of the mass of a given volume of liquid at 15 °C to the mass of an equal volume of pure water at the same temperature), and *relative density* (same as *specific gravity*) are important properties of crude oil products as it is a part of product sales specifications, although it only plays a minor role in studies of product composition. Usually a hydrometer, pycnometer, or digital density meter is used for the determination in all these standards.

Density is an important parameter for naphtha and solvents and the determination of density (specific gravity) (ASTM D287; ASTM D891; ASTM D1217; ASTM D1298; ASTM D1555; ASTM D1657; ASTM D4052; ASTM D5002) provides a check on the uniformity of the naphtha and it permits calculation of the weight per gallon. The temperature at which the determination is carried out and for which the calculations are to be made should also be known and be in accordance with the volatility of the sample as determined by a standard test method (ASTM D86). Any such method must be subject to vapor pressure constraints and are used with appropriate precautions to prevent vapor loss during sample handling and density measurement. In addition, some test methods should not be applied if the samples are sufficiently colored and that the absence of air bubbles in the sample cell cannot be established with certainty. The presence of such bubbles can have serious consequences for the reliability of the test data.

7.1.6 Dew point pressure

The dewpoint pressure is the pressure where an incipient liquid phase condenses from a gas phase. Practically, the dewpoint marks the pressure where (i) reservoir gas phase composition changes and becomes leaner, and (ii) condensate accumulation starts in the reservoir. These two changes can have a profound effect on reservoir and well performance – or, they may have little impact.

The importance of the *actual dewpoint pressure* will vary from reservoir to reservoir, but in most situations accurate dewpoint determination is *not important*. First, in the context of compositional variation with pressure (and associated variation of condensate yield with pressure) accurate determination of the thermodynamic dewpoint pressure is *not* of particular importance. In fact, knowledge of the specific dewpoint at all as long as the variation of composition (C7+ content) with pressure is well defined "near" the thermodynamic dewpoint. Second, when the bottomhole flowing pressure (BHFP) drops below the dewpoint and two phases start flowing near the wellbore, gas relative permeability drops and well *productivity* drops.

However, as long as BHFP is "anywhere near" the dewpoint the well will have *excess deliverability* – i.e. we simply reduce the BHFP to produce more gas (even though the well *productivity* is lower). Only when the BHFP reaches a minimum value (dictated by some delivery-pressure constraint) will the well no longer be able to deliver the desired rate. At this point, well productivity *is* important. However, this occurs at a BH flowing pressure much lower than the dewpoint.

Another (less common) need for dewpoint pressure is when an underlying saturated oil zone *may exist* and a PVT model is used to predict the existence and location of the gas-oil contact (GOC). In this case, the PVT model dewpoint should be tuned precisely to an accurately measured dewpoint pressure.

7.1.7 Distillation

The primary method specified for determining boiling range of gasoline continues to be standard test method ASTM D86. The use of automated instrumentation has been incorporated into the method (ASTM D3710) which allows the method to be used for determining the boiling point properties of oxygenate-free hydrocarbon distillates. This test method (ASTM D3710) has the advantage that a smaller sample size is required and the method can be more easily automated but the data from the method are not directly equivalent to that obtained by distillation (ASTM D86). In addition, the data from this test method (ASTM D3710) are being used by some companies and vendors by applying correlations to predict test method (ASTM D86) distillation data for various refinery streams. Improvements in the GC simulated distillation procedures have been implemented in some laboratories and improvements include rapid gas chromatography techniques using very narrow bore capillary gas chromatography columns that will potentially reduce analysis time to a matter of minutes.

7.1.8 Evaporation rate

The vaporizing tendencies of crude oil products are the basis for the general characterization of liquid crude oil fuels, such as liquefied crude oil gas, natural gasoline, motor and aviation gasoline, naphtha, kerosene, gas oil, diesel fuel, and fuel oil. Standard test methods (ASTM D6; ASTM D2715) are available to determine the volatility of higher boiling products and can, with some cautious modifications, be adapted for lower boiling products.

Test method ASTM D6 is useful for the in characterizing certain hydrocarbon liquids by the determination of the loss in weight when heated under standard conditions using the correct safety and health protocols. Another method (ASTM D2715) that is often quoted as being suitable for weight-loss-on-heating studies (ASTM D2715) covers the determination of the rates of volatilization of lubricants in a thermal-vacuum environment at pressures and temperatures necessary to obtain a measurable rate of evaporation, or evidence of decomposition. The methods is unsuitable for application to gas condensate and natural gasoline.

For some purposes it is necessary to have information on the initial stage of vaporization and the potential hazards that such a property can cause. To supply this need, flash and fire, vapor pressure, and evaporation methods are available. The data from the early stages of the several distillation methods are also useful (Speight, 2015). For other uses it is important to know the tendency of a product to partially vaporize or to completely vaporize and, in some cases, to know if small quantities of high-boiling components are present. For such purposes, chief reliance is placed on the distillation methods.

Nevertheless, the evaporation rate is an important property of naphtha and although there is a significant relation between distillation range and evaporation rate, the relationship is not straightforward. A simple procedure for determining the evaporation rate involves use of at least a pair of weighed shallow containers, each containing a weighed amount of naphtha. The cover-free containers are placed in a temperature-controlled and humidity-controlled draft-free area. The containers are reweighed at intervals until the samples have completely evaporated or left a residue that does not evaporate further (ASTM D381; ASTM D1353). The evaporation rate can be derived either (i) by a plot of time versus weight using a solvent having a known evaporation rate for comparison or (ii) from the distillation profile (ASTM D86).

The above test method (ASTM D381) covers the determination of the existent gum content of aviation fuels, and the gum content of motor gasolines or other volatile distillates in their finished form, including those containing alcohol and ether type oxygenates and deposit control additives. Provisions are made for the determination of the heptane insoluble portion of the residue of non-aviation fuels. This test method would only be suitable for application to gas condensate and natural gasoline if suitable modifications were made to the test protocols as the necessary safety precautions were addressed. Similarly, another test method (ASTM D1353) covers the analytical measurement of residual matter in solvents that are intended to be 100 % volatile at 105 ± 5 °C (221 ± 9 °F). Volatile solvents are used in the manufacture of paint, varnish, lacquer, and other related products, and the presence of any residue may affect the product quality or efficiency of the process. This test method (again with suitable modifications and safety concerns addressed) may be modifiable for application to gas condensate and natural gasoline.

7.1.9 Flash point

The flash point is the lowest temperature at atmospheric pressure (760 mm Hg, 101.3 kPa) at which application of a test flame will cause the vapor of a sample to ignite under specified test conditions. The sample is deemed to have reached the flash point when a large flame appears and instantaneously propagates itself over the surface of the sample. The flash point data is used in shipping and safety regulations to define *flammable* and *combustible* materials. Flash point data can also indicate the possible presence of highly volatile and flammable constituents in a relatively non-volatile or non-flammable material. Sine the flash point of gas condensate and the flash point of natural gasoline are low, such as test method can also indicate the possible presence of even more highly volatile and flammable constituents in these two liquids.

Flash point for a hydrocarbon or a fuel is the minimum temperature at which vapor pressure of the hydrocarbon is sufficient to produce the vapor needed for spontaneous ignition of the hydrocarbon with the air with the presence of an external source, i.e., spark or flame. From this definition, it is clear that hydrocarbon derivatives with higher vapor pressures (lighter compounds) have lower flash points. Generally, flash point increases with an increase in boiling point. Flash point is an important parameter for safety considerations, especially during storage and transportation of volatile crude oil products (i.e., LPG, light naphtha, gasoline) in a high-temperature environment. The surrounding temperature around a storage tank should always be less than the flash point of the fuel to avoid possibility of ignition. Flash point is used as an indication of the fire and explosion potential of a crude oil product (ASTM D93). There is another method of measuring flash point known as *open cup* for those oils with flash point greater than 80 °C (ASTM D92). Flash point should not be mistaken with *fire point*, which is defined as the minimum temperature at which the hydrocarbon will continue to burn for at least 5 s after being ignited by a flame.

Thus, of the available test methods, the most common method of determining the flash point confines the vapor (closed cup) until the instant the flame is applied (ASTM D56; ASTM D93; ASTM D3828, 6450). An alternate method that does not confine the vapor open cup method (ASTM D92; ASTM D1310) gives slightly higher values of the flash point. For example, ASTM D56 describes the experimental protocols for the determination of the flash point, by tag manual and automated closed testers, of hydrocarbon liquids with a viscosity below 5.5 cSt at 40 °C (104 °F), or below 9.5 cSt at 25 °C (77 °F), and a flash point below 93 °C (200 °F). Gas condensate and natural gasoline typically fir into these property specifications. However, erroneously high flash points can be obtained when precautions are not taken to avoid the loss of volatile material. Samples should not be stored in plastic bottles, since the volatile material may diffuse through the walls of the container. The containers should not be opened unnecessarily. The samples should not be transferred between containers unless the sample temperature is at least 11 °C (20 °F) below the expected flash point.

Another test (ASTM E659) is available that can be used as a complement to the flash point test and involves determination of the auto-ignition temperature. The auto-ignition temperature is the minimum temperature at which hydrocarbon vapor when mixed with air can spontaneously ignite without the presence of any external source. Values of autoignition temperature are generally higher than flash point. Values of autoignition temperature for typical hydrocarbon liquids obtained from mineral sources are in the range of 150−320 °C (300−500 °F), for gasoline it is approximately 350 °C (660 °F), and for alcohol is approximately 500 °C (930 °F). With an increase in pressure the autoignition temperature decreases. This is particularly important from a safety point of view when hydrocarbon derivatives are compressed. However, the flash point should not be confused with auto-ignition temperature that measures spontaneous combustion with no external source of ignition.

This test method (ASTM E659) is dependent on the chemical and physical properties of the liquid under examination as well as the method and apparatus employed for its determination. The auto-ignition temperature by a given method does not necessarily represent the minimum temperature at which a given material will self-ignite in air. The volume of the vessel used is particularly important since lower autoignition temperatures will be achieved in larger vessels and vessel material can also be an important factor. The test method is not designed for evaluating materials which are capable of exothermic decomposition. For such materials, ignition is dependent upon the thermal and kinetic properties of the decomposition, the mass of the sample, and the heat transfer characteristics of the system. Also, the method can be used, with appropriate modifications, for chemicals that are gaseous at atmospheric temperature and pressure of which gas condensate and natural gasoline are example.

7.1.10 Hydrocarbon analysis

One test method, which produces a detailed analysis of crude oil naphtha through n-nonane by capillary gas chromatography, is applicable to olefin-free liquid hydrocarbon mixtures including raw naphthas (which include condensate and natural gasoline), reformates, and alkylates (ASTM D5134). This test method covers the determination of hydrocarbon components paraffin derivatives, naphthene derivatives, and monoaromatic derivatives (PNA) of crude oil naphthas. Components eluting after *n*-nonane (b.p. 150.8 °C. 303.4 °F) are determined as a single group. This method is applicable to olefin-free (<2 % v/v olefin derivatives) liquid hydrocarbon mixtures but the olefin content can be determined by other test methods (ASTM D1319). To be suitable for the test, the hydrocarbon mixture must be 98% w/w distilled at 250 °C (482 °F) or less as determined by an alternate test method (ASTM D3710).

Higher resolution gas chromatography capillary column techniques are in routine use in crude oil laboratories today to provide a detailed analysis of most of the individual hydrocarbon derivatives in gasoline, including many of the oxygenated blending components. Software is also available that allows one to summarize the data according to hydrocarbon type and predict other parameters such as vapor pressure and distillation from the results. High-resolution GC procedures for the detailed analysis of gasoline are being considered for adoption as standard ASTM standard test methods. Capillary GC techniques can be combined with mass spectrometry to enhance the identification of the individual components and hydrocarbon types (Teng and Williams, 1994).

7.1.11 Octane number

Octane number is a parameter defined to characterize antiknock characteristic of a fuel (gasoline) for spark ignition engines and a higher octane number for a liquid fuel (compared to other liquid fuels) indicates a better engine performance. The octane number is a measure of the ability of a liquid fuel to resist auto-ignition during compression and prior to ignition. The octane number of a fuel is measured based on two reference hydrocarbon derivatives of n-heptane with an assigned octane number of zero and isooctane (2,2,4-trimethylpentane) with assigned octane number of 100. A mixture of 70% v/v iso-octane and 30% v/v n-heptane has an octane number of 70. There are two methods of measuring octane number of a fuel in the laboratory. The methods are known as *motor octane number* (MON) and *research octane number* (RON).

The motor octane number is indicative of high-speed performance (900 rpm) and is measured under the conditions of heavy road use. The research octane number is indicative of normal road performance under low engine speed (600 rpm) city driving conditions. The third type of octane number is defined as *posted octane number* (PON), which is the arithmetic average of the MON and RON. Thus:

$$[\mathrm{PON} = (\mathrm{MON} + \mathrm{RON})/2]$$

Generally, iso-paraffin derivatives have higher octane number than do normal paraffin derivatives. Naphthene derivatives have relatively high octane number than the corresponding paraffin derivatives − aromatic derivatives also have very high octane numbers.

The octane number of a fuel can be predicted by using principal component regression of chromatographic data but the test methods based on spectroscopic techniques such as near-infrared (NIR), infrared (IR) spectroscopy, and nuclear magnetic resonance (NMR) are applied for the measurement and/or prediction of octane numbers and other parameters of gasoline and are preferred (Myers et al., 1975; Ichikawa et al., 1992; Welch et al., 1994; Andrade et al., 1997; Speight, 2104, 2015).

Application of any such test methods to gas condensate or natural gasoline may have a limited value if the gas condensate or natural gasoline is a very minor constituent of the gasoline blend. In such a case, the gas condensate or natural gasoline may only be a complementary constituent to make up the final blend for sales gasoline and the octane number would have little, if any, effect, on the octane number of the final blend.

7.1.12 Odor and color

The degree of purity of naphtha is an important aspect of naphtha properties and strict segregation of all distribution equipment is maintained in order to ensure strict and uniform specification for the product handled. Naphtha is refined to a low level of odor to meet the specifications for use. Purified naphtha is required to have a low level of odor to meet the specifications for use.

In general, the paraffinic hydrocarbon derivatives possess the mildest odor and the aromatic derivatives the strongest, the odor level (ASTM D268; ASTM D1296) being related to chemical character and volatility of the constituents. Odors due to the presence of sulfur compounds or unsaturated constituents are excluded by specification. And apart from certain high boiling aromatic fractions, that are usually excluded by volatility from the majority of the naphtha fractions, which may be pale yellow in color, naphtha is usually colorless (water white).

Usually, gas condensate and natural gasoline have little, if any, color (in such cases, the liquid is described as being) but gas condensate and natural gasoline containing higher amounts of aromatic constituents may be pale yellow. Measurement of color (ASTM D156; ASTM D848; ASTM D1209; ASTM D1555; ASTM D5386) provides a rapid method of checking the degree of freedom from contamination. Observation of the test for residue on evaporation (ASTM D381; ASTM D1353) provides a further guard against adventitious contamination.

Assuming that sample volatility does not have an adverse effect on the outcome of the test method, on the test method, a near-clear liquid can be tested for color by a method (ASTM D5386) that is applicable to the color measurement of clear, liquid samples, free of haze and the method is applicable to non-fluorescent liquids with light absorption characteristics similar to those of the color standard solutions.

7.1.13 Sulfur content

Sulfur-containing components exist in some gas condensate and natural gasoline samples. Individual sulfur components can be speciated (ASTM D5623) and the method uses a gas chromatographic capillary column coupled with either a sulfur chemiluminescence detector or atomic emission detector (AED). The total sulfur content is an important test parameter in hydrocarbon liquid that are designated as liquid fuels or are used as blending stock for sales gasoline (ASTM D2622; ASTM D4045; ASTM D5453).

7.1.14 Vapor pressure

The vapor pressure of gasoline is a critical physical test parameter for hydrocarbon liquids (ASTM D323; ASTM D5191). The former test method (ASTM D323) describes procedures for the determination of vapor pressure volatile hydrocarbon liquids such as gasoline, volatile crude oil, and other volatile crude oil products as well as other crude oil-related liquids that have a vapor pressure of less than 26 psi (Procedure A). However, one of the sub-procedures (Procedure C) can be applied to hydrocarbon liquids with a vapor pressure of greater than 26 psi. Gas condensate and natural gasoline can fit into either of these procedures. Because the external atmospheric pressure is counteracted by the atmospheric pressure initially present in the vapor chamber, the Reid vapor pressure is an absolute pressure at 37.8 °C (100 °F) in kilopascals (pounds-force per square inch). The Reid vapor pressure differs from the true vapor pressure of the sample due to some small sample vaporization and the presence of water vapor and air in the confined space. However, this test method (ASTM D323) is not applicable to liquefied crude oil gases or fuels containing oxygenated compounds other than methyl *t*-butyl ether (MTBE) and other test methods are recommended.

The latter test method (ASTM D5191) describes the use of automated vapor pressure instruments to determine the total vapor pressure exerted in vacuum by air-containing, volatile, liquid crude oil products, including automotive spark-ignition fuels with or without oxygenates. This test method is suitable for testing samples with boiling points above 0 °C (32 °F) that exert a vapor pressure between 7 kPa and 130 kPa (1.0 psi and 18.6 psi) at 37.8 °C (100 °F) at a vapor-to-liquid ratio of 4:1 — these parameters are typically applicable to gas condensate and natural gasoline.

7.1.15 Viscosity

Oil viscosity is important in the proper modeling of "condensate blockage" — i.e. the two-phase gas/oil flow effect on gas relative permeability in the region around the wellbore. Oil viscosity is usually low for reservoir condensates, ranging from 0.1 to 1 cp in the near-wellbore region. Measurement of condensate viscosities is not made in routine laboratory tests, and it may be difficult to obtain measurements for lean condensates (where volumes of condensate are small).

The oil viscosity model can be tuned to measured viscosities of a separator condensate sample at reservoir temperature and pressures in the range of 1500—6000 psi. More appropriate condensate viscosity measurements can be designed (at greater expense), but having oil viscosity data from a separator oil sample to tune the viscosity correlation should ensure reasonably accurate oil viscosity predictions of the condensate actually flowing in the near-wellbore region when bottomhole flowing pressures drop below the dewpoint.

Gas viscosity for most systems will vary from 0.02 to 0.03 cp for all pressure conditions. For near-critical gas condensates and high-pressure gases the viscosity may initially be 0.05 cp, but in most of the near-wellbore region experiencing significant pressure losses the viscosity will be in the lower range of 0.02—0.03 cp. Consequently, the absolute value of viscosity does not vary greatly for a given gas, or from gas to gas system. Viscosity correlations are fairly reliable at predicting accurate gas viscosities, within 5%—10% in most cases.

7.1.16 Volatility

Naphtha fractions (including gas condensate and natural gasoline) grades are often referred to by a boiling range, which is the defined temperature range in which the fraction distils. The ranges are determined by standard methods (ASTM D86), it being especially necessary to use a recognized method since the initial and final boiling points which ensure conformity with volatility requirements and absence of *heavy ends* are affected by the testing procedure. A simple test for the evaporation properties of naphtha (including gas condensate and natural gasoline with any suitable *ad hoc* modifications to the test method) is available (ASTM D381). The need for vacuum distillation (ASTM D1160) as a product specification in the boiling range of naphtha is not necessary. Gas condensate and natural gasoline very rarely (if at all) have such a high boiling point.

Thus, one of the most important physical parameters of gas condensate and natural gasoline is the boiling range distribution (ASTM D86; ASTM D1078; ASTM D2268; ASTM D2887; ASTM D2892). The significance of the distillation test is the indication of volatility that dictates the evaporation rate that is an important property for gas condensate and natural gasoline used in coatings and similar application where the premise is that the gas condensate and natural gasoline evaporates over time. In the basic test method (ASTM D86) a 100-mL sample is distilled (manually or automatically) under prescribed conditions prescribed. Temperatures and volumes of the gas condensate or the natural gasoline are recorded at regular intervals from which the boiling profile is derived.

The determination of the boiling range distribution of distillates such as gas condensate and natural gasoline by gas chromatography (ASTM D3710) not only helps identify the constituents but also facilitates on-line controls at the refinery. This test method is designed to measure the entire boiling range of gas condensate and natural gasoline with either high or low Reid vapor pressure (ASTM D323). In the method, the sample is injected into a gas chromatographic column that separates hydrocarbon derivatives in boiling point order. The column temperature is raised at a reproducible rate and the area under the chromatogram is recorded throughout the run. Calibration is performed using a known mixture of hydrocarbon derivatives covering the expected boiling of the sample.

Another method is described as a method for determining the carbon number distribution (ASTM D2887) and the data derived by this test method are essentially equivalent to that obtained by true boiling point (TBP) distillation (ASTM D2892). The sample is introduced into a gas chromatographic column that separates hydrocarbon derivatives in boiling point order. The column temperature is raised at a reproducible rate and the area under the chromatogram is recorded throughout the run. Boiling temperatures are assigned to the time axis from a calibration curve, obtained under the same conditions by running a known mixture of hydrocarbon derivatives covering the boiling range expected in the sample. From these data, the boiling range distribution may be obtained. However, this test method is limited to samples having a boiling range greater than 55 °C (100 °F), and having a vapor pressure (ASTM D323; ASTM D4953; ASTM D5191; ASTM D5482; ASTM D6377; ASTM D6378) sufficiently low to permit sampling at ambient temperature without contamination.

However, test method ASTM D2887 describes the determination of the boiling range is applicable to hydrocarbon liquids (and crude oil-fractions) that have a final boiling point of 538 °C (1000 °F) or lower at atmospheric pressure as measured by this test method. This test method is limited to samples having a *boiling range* greater than 55.5 °C (100 °F), and having a vapor pressure sufficiently low to permit sampling at ambient temperature. The method may not be applicable to certain sample of gas condensate and natural gasoline without some form of modification.

On the other hand, test method ASTM D2892 describes the procedure for the distillation of stabilized hydrocarbon liquids (such as crude oil) to a final cut temperature of 400 °C (750 °F) atmospheric equivalent temperature (AET). The method also provides details of the procedures for the production of a liquefied gas, distillate fractions, and residuum of standardized quality on which analytical data can be obtained, and the determination of yields of the above fractions by both mass and volume.

7.2 Kerosene

Kerosene (*kerosine*), also called paraffin or paraffin oil, is a flammable pale-yellow or colorless oily liquid with a characteristic odor intermediate in volatility between gasoline and gas/diesel oil and distills between 125 °C (257 °F) and 260 °C (500 °F) (Table 10.8; Fig. 10.8) (Parkash, 2003; Pandey et al., 2004; Gary et al., 2007; Speight, 2104; Hsu and Robinson, 2017; Speight, 2017).

Kerosene was first manufactured in the 1850s from coal tar, hence the name *coal oil* as often applied to kerosene, but crude oil became the major source after 1859. From that time, the kerosene fraction is and has remained, a distillation fraction of crude oil. However, the quantity and quality vary with the type of crude oil, and although some crude oils yield excellent kerosene quite simply, others produce kerosene that requires substantial refining.

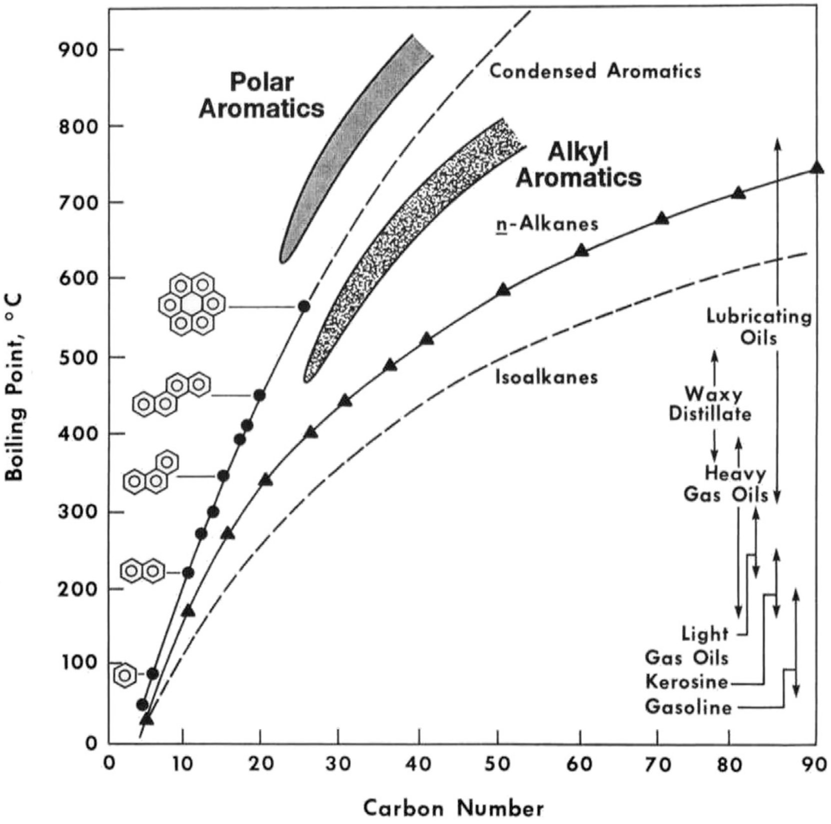


FIG. 10.8 Boiling point and carbon number for various hydrocarbons and petroleum products.

Kerosene is less volatile than gasoline (boiling range: approximately 140 °C/285 °F to 320 °C/610 °F), and is obtained by fractional distillation of crude oil (Parkash, 2003; Pandey et al., 2004; Gary et al., 2007; Speight, 2104; Hsu and Robinson, 2017; Speight, 2017). To decrease smoke generation, paraffinic stocks are used normally in the manufacture of kerosene for lighting and heating. For the same reason, aromatic stocks and cracked components are avoided. Some crude oils, especially the paraffinic crude oils, contain kerosene fractions of very high quality, but other crude oils, such as those having an asphalt base, must be thoroughly refined to remove aromatic derivatives and sulfur compounds before a satisfactory kerosene fraction can be obtained. Cracking the less volatile constituents of crude oil is now a major process for kerosene production.

Chemically, kerosene is a mixture of hydrocarbon derivatives and the constituents include *n*-dodecane (n-$C_{12}H_{26}$), alkyl benzenes, and naphthalene and its derivatives (ASTM D1840). The chemical composition depends on its source and has a high number (>100,000) of isomers that are possible (Table 10.9). The actual number of compounds in kerosene is much lower, and there are claims to less than 100 constituents but that, again, is source dependent and process dependent.

Kerosene is composed chiefly of hydrocarbon derivatives containing 12 or more carbon atoms per molecule. Although the kerosene constituents are predominantly saturated materials, there is evidence for the presence of substituted tetrahydronaphthalenes. Dicycloparaffin derivatives also occur in substantial amounts in kerosene. Other hydrocarbon derivatives with both aromatic and cycloparaffin rings in the same molecule, such as substituted indane, also occur in kerosene. The predominant structure of the dinuclear aromatic derivatives appears to be that in which the aromatic rings are condensed, such as naphthalene whereas the *isolated* two-ring compounds, such as biphenyl, are only present in traces, if at all (ASTM D1840).

Low proportions of aromatic and unsaturated hydrocarbon derivatives are desirable to maintain the lowest possible level of smoke during burning. Although some aromatic derivatives may occur within the boiling range assigned to kerosene, excessive amounts can be remove by extraction; that kerosene is not usually prepared from cracked products almost certainly excludes the presence of unsaturated hydrocarbon derivatives.

The essential properties of kerosene are flash point (ASTM D56; ASTM D93; ASTM D3828), distillation range (ASTM DD 86; ASTM D1160; ASTM D2887; ASTM D6352), burning characteristics (ASTM D187), sulfur content (ASTM D129; ASTM D2622; ASTM D3120; ASTM D3246; ASTM D4294; ASTM D5453; ASTM D5623), color (ASTM D156; ASTM D1209; ASTM D1500; ASTM D2392; ASTM D6045), and cloud point (ASTM D2500; ASTM D5772; ASTM D5771; ASTM D5773). In the case of the flash point (ASTM D56), the minimum flash temperature is generally placed above the prevailing ambient temperature; the fire point (ASTM D92) determines the fire hazard associated with its handling and use.

7.2.1 Acidity

Acidic constituents can be present in kerosene aviation turbine fuels due to acid treatment during production. These trace acid quantities are undesirable because of the possibility of metal corrosion and impairment of the burning characteristics and other properties of the kerosene.

One test method (ASTM D1093) is used solely for the qualitative determination of the acidity of hydrocarbon liquids and their distillation residues. The results are qualitative. Basicity determination can also be done by a small change in the procedure (see below). In the test method, a sample is shaken with water and the aqueous layer is tested for acidity using methyl orange indicator (red color). Basicity can be determined using phenolphthalein indicator (pink color) instead of the methyl orange indicator.

Another test method (ASTM D3242) covers the determination of the acidity in an aviation turbine fuel in the range 0.000–0.100 mg potassium hydroxide per gm but the test is not suitable for determining significant acid contamination. In the test, a sample is dissolved in a solvent mixture (toluene plus isopropyl alcohol, and a small amount of water) and under a stream of nitrogen is titrated with standard alcoholic *KOH* to the color change from orange in acid to green in base via added indicator p-naphthol benzein solution.

7.2.2 Burning characteristics

The ability of kerosene to burn steadily and cleanly over an extended period (ASTM D187) is an important property and gives some indication of the purity or composition of the product. The quality of a kerosene as a burning oil is related to its burning characteristics and is dependent on such factors as its composition, volatility, viscosity, calorific value, sulfur content, and freedom from corrosive substances or contaminants. This test method covers the qualitative determination of the burning properties of kerosene to be used for illuminating purposes. In the test, a kerosene sample is burned for 16 h in a specified lamp under specified conditions. The average rate of burning, the change in the shape of the flame, and the density and color of the chimney deposit are reported.

However, the effect of hydrocarbon type composition is greater with wick-fed yellow flame burners than with wick-fed blue flame burners. With the former, kerosene which are mainly paraffinic burn well in lamps with a poor draught, while under the same conditions kerosene containing high proportions of aromatic derivatives and naphthene derivatives burn with a reddish or even smoky flame.

The smoke point test (ASTM D1319; ASTM D1322) enables this property to be measured. In this test the oil is burned in a standard wick-fed lamp in which flame height can be varied against a background of a graduated scale. The maximum flame height in millimeters at which the oil burns without smoking under the standard conditions is termed the smoke point. Even if full advantage is not taken to utilize maximum non-smoking flame height, the property of high smoke point ensures that in the event of sudden draught causing extension in flame height, there will be less tendency for smoking to occur in such circumstances. The smoke point test is also used in the assessment of the burning characteristics of certain aviation turbine fuels.

The 24-h burning test (ASTM D187) involves noting the average oil consumption, change in flame dimensions, and final appearance of wick and chimney are noted. In this method the oil is burned for 24 h in the standard lamp with a flame initially adjusted to specified dimensions. At the conclusion of the test, the oil consumption and the amount of char formed on the wick are determined and the char value calculated as milligrams per kilogram of oil consumed. A qualitative assessment of the appearance of the glass chimney is also made.

The considerable effect on char-forming tendency of even traces of high boiling contaminants is demonstrated by the fact that the addition of 0.01% of a viscous lubricating oil to a kerosene of a char value of 10 mg/kg (0′001%), can result in doubling that char value.

7.2.3 Calorific value

The calorific value (heat of combustion) (ASTM D240; ASTM D1405; ASTM D2890; ASTM D3338; ASTM D4529; ASTM D4809) is a direct measure of fuel energy content and is determined as the quantity of heat liberated by the combustion of a unit quantity of fuel with oxygen in a standard bomb calorimeter. A high calorific value is obviously desirable in oil used for heating purposes. Calorific value does not, however, vary greatly in the range of paraffin-type kerosene (ASTM D240).

When an experimental determination of heat of combustion is not available and cannot be made conveniently, an estimate might be considered satisfactory (ASTM D3338). In this test method, the net heat of combustion is calculated from the density, sulfur, and hydrogen content but this calculation is justifiable only when the fuel belongs to a well-defined class for which a relationship between these quantities has been derived from accurate experimental measurements on representative samples. Thus, the hydrogen content (ASTM D1018; ASTM D1217; ASTM D1298; ASTM D3701; ASTM D4052; ASTM D4808; ASTM D5291), density (ASTM D129; ASTM D1250; ASTM D1266; ASTM D2622; ASTM D3120), and sulfur content (ASTM D2622; ASTM D3120; ASTM D3246; ASTM D4294; ASTM D5453; ASTM D5623) of the sample are determined by experimental test methods and the net heat of combustion is calculated using the values obtained by these test methods based on reported correlations.

Another equation that can be used to calculate the heat of combustion is based on the specific gravity of the kerosene:

$$Q = 12,400 - 2,100d^2$$

Q is the heat of combustion and d is the specific gravity. However, the accuracy of any method used to calculate such a property is not guaranteed and can only be used as a guide or approximation to the measured value

An alternative criterion of energy content is the *aniline gravity product* (AGP) that is related to calorific value (ASTM D1405). The *aniline gravity product* is the product of the API gravity (ASTM D287; ASTM D1298) and the aniline point of the fuel (ASTM D611). The aniline point is the lowest temperature at which the fuel is miscible with an equal volume of aniline and is inversely proportional to the aromatic content. The relationship between the aniline gravity product and calorific value is given in method. In another method (ASTM D3338), the heat of combustion is calculated from the fuel density, the 10%, 50%, and 90% distillation temperatures, and the aromatic content. However, neither method is legally acceptable and other methods (ASTM D240; ASTM D1655; ASTM D4809) are preferred.

7.2.4 Composition

Because of the estimated (or real) number of isomers in this carbon number range (Table 10.9), complete speciation of individual hydrocarbon derivatives is not possible for middle distillates. Compositional analysis of middle distillates is obtained in terms of hydrocarbon group type totals. These groups are most often defined by a chromatographic separation.

Thus, the first level of compositional information is group-type totals as deduced by adsorption chromatography form the distribution of saturates, olefin derivatives, and aromatic derivatives in materials that boil below 315 °C (600 °F) (ASTM D1319). Adsorption methods (ASTM D2007) can also be sued to determine hydrocarbon types in kerosene but, with all adsorption methods, allowances must be made for the loss of volatile constituents during the work up procedure. Thus, column chromatography would be best done using a stabilized (volatile removed to a pre-determined temperature) feedstock.

Burning oil kerosene contains three main types of hydrocarbon derivatives-paraffinic, naphthenic, and aromatic, with a preponderance of the paraffinic type. This is in contrast to *power kerosene*, or *tractor vaporizing oil* that has a comparatively high content of aromatic derivatives and naphthene derivatives favorable for high octane rating. It may also contain slight amounts of sulfur in the form of a variety of organic compounds.

Compositional analysis of kerosene distillates can also be obtained in terms of mass spectral Z-series (ASTM D2425; ASTM D2789; ASTM D3239; ASTM D6379). Mass spectrometry has been a powerful technique for hydrocarbon-type analysis of middle distillates and can provide more compositional detail than chromatographic analysis. Hydrocarbon types are classified in terms of a Z-series. Z in the empirical formula C_nH2_{n+z} is a measure of the hydrogen deficiency of the compound (ASTM D2425). This method requires that the sample be separated into saturate and aromatic fractions before mass spectrometric analysis. This separation is standardized (ASTM D2549) and is applicable to kerosene.

The percentage of aromatic hydrogen atoms and aromatic carbon atoms can be determined by high-resolution nuclear magnetic resonance spectroscopy (ASTM D5292) but the results from this test are not equivalent to mass- or volume-percent aromatic derivatives determined by the chromatographic methods. The chromatographic methods determine the percent by weight (or the percent by volume) of molecules that have one or more aromatic rings. Any alkyl substituents on the rings (Fig. 10.9) contribute to the percentage of aromatic derivatives determined by chromatographic techniques but the presence of an aromatic ring (no matter what the length of the alkyl side chain) dictates that the compound by isolated as an aromatic thereby leading to erroneous estimates of the carbon atoms in aromatic derivatives.

Because the aromatic hydrocarbon content of aviation turbine fuels affects their combustion characteristics and smoke forming tendencies, the amounts of aromatic derivatives (ASTM D1319) are limited. Aromatic constituents also increase the intensity of the combustion flame, which can have an adverse effect the in-service life the combustion chamber.

The content of the aromatic derivatives in kerosene can also be determined by a test method (ASTM D5186) in which a small aliquot of the sample is injected on to a packed silica adsorption column and eluted using supercritical carbon dioxide as the mobile phase. Mononuclear aromatic derivatives and polynuclear aromatic derivatives in the sample are separated from non-aromatic derivatives and detected using a flame ionization detector. The chromatographic areas corresponding to the mono-, polynuclear, and non-aromatic components are determined and the mass percent content of each of these groups is

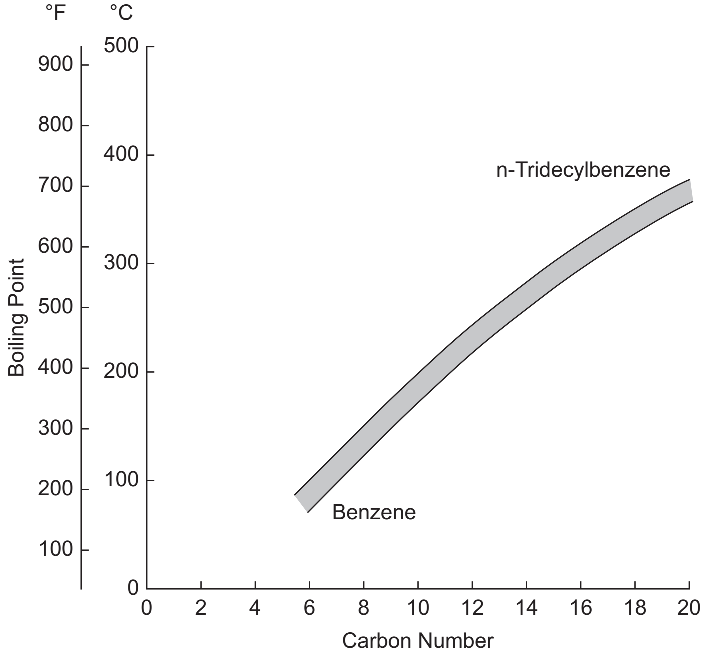


FIG. 10.9 Effect of size of the alkyl chain on the boiling point of benzene.

calculated by area normalization. The results obtained by this method are at least statistically more precise than those obtained by other test methods (ASTM D1319; ASTM D2425).

In yet another test method for the determination of aniline point and mixed aniline point (ASTM D611), the proportions of the various hydrocarbon constituents of kerosene can be determined. This test is most often used to estimate the aromatic content of kerosene. Aromatic compounds exhibit the lowest aniline points and paraffin compounds have the highest aniline points with cycloparaffin derivatives (naphthene derivatives) and olefin derivatives having aniline points between the two extremes. In any homologous series the aniline point increases with increasing molecular weight.

There are five sub-methods in the test (ASTM D611) for the determination of the aniline point: (i) Method A is used for transparent samples with an initial boiling point above room temperature and where the aniline point is below the bubble point and above the solidification point of the aniline-sample mixture, (ii) Method B, a thin film method, is suitable for samples too dark for testing by Method A, (iii) Methods C and D are employed when there is the potential for sample vaporization at the aniline point, (iv) Method D is particularly suitable where only small quantities of sample are available, and (v) Method E uses an automatic apparatus suitable for the range covered by methods A and B.

Olefin derivatives in kerosene also influence the burning characteristics and can be determined by the bromine number (ASTM D1159; ASTM D2710). The bromine number is the grams of bromine that will react with 100 gm of the sample under the test conditions. The magnitude of bromine number is an indication of the quantity of bromine-reactive constituents and is not an identification of constituents. It is used as a measure of aliphatic unsaturation in crude oil samples, and as percentage of olefin derivatives in crude oil distillates boiling up to approximately 315 °C (600 °F). In the test, a known weight of the sample dissolved in a specified solvent maintained at 0−5 °C (32−41 °F) is titrated with standard bromide-bromate solution. Determination of the end point is method dependent.

Gas chromatography (ASTM D2427; ASTM D5443; ASTM D5580) remains the most reliable method for the determination of hydrocarbon types, including olefin derivatives (ASTM D6296), in kerosene and similar boiling fractions. In particular, methods in which a combination of gas chromatography and Fourier transform infrared spectroscopy (GC-FTIR) (ASTM D5986) and gas chromatography and mass spectrometry (GC−MS) (ASTM D5769) are finding increased use. Indeed, Fourier transform infrared spectroscopy has been used to predict properties such as density, freezing point, flash point, aromatics content, initial boiling point, final boiling point and viscosity.

The significance of the total sulfur content of kerosene varies greatly with the type of oil and the use to which it is put. Sulfur content is of great importance when the oil to be burned produces sulfur oxides that contaminate the surroundings. Only slight amounts of sulfur compounds remain in kerosene after refining. Refining treatment includes among its objects the removal of such undesirable products as hydrogen sulfide, mercaptan sulfur, and *free* or corrosive sulfur. Hydrogen sulfide and mercaptans cause objectionable odors and both are corrosive. Their presence can be detected by the Doctor Test (ASTM D4952). The Doctor test (which is pertinent for crude oil product specifications, ASTM D235) ensures that the concentration of these compounds is insufficient to cause such problems in normal use. In the test, the sample is shaken with sodium plumbite solution, a small quantity of sulfur is added, and the mixture shaken again. The presence of mercaptans or hydrogen sulfide or both is indicated by discoloration of the sulfur floating at the oil-water interface or by discoloration of either of the phases.

Free, or corrosive, sulfur in appreciable amount could result in corrosive action on the metallic components of an appliance. Corrosive action is of particular significance in the case of pressure burner vaporizing tubes that operate at high temperatures. The usual test applied in this connection is the corrosion (copper strip) test (ASTM D130; ASTM D849).

The copper strip test methods are used to determine the corrosiveness to copper of gasoline, diesel fuel, lubricating oil, or other hydrocarbon derivatives. Most sulfur compounds in crude oil are removed during refining. However, some residual sulfur compounds can have a corroding action on various metals. This effect is dependent on the types of sulfur compounds present. The copper strip corrosion test measures the relative degree of corrosivity of a crude oil product.

One method (ASTM D130) uses a polished copper strip is immersed in a given quantity of sample and heated at a temperature for a time period characteristic of the material being tested. At the end of this period the copper strip is removed, washed and compared with the copper strip corrosion standards. This is a pass/fail test. In another method (ASTM D849) a polished copper strip is immersed in 200 mL of specimen in a flask with a condenser and placed in boiling water for 30 min. At the end of this period, the copper strip is removed and compared with the ASTM copper strip corrosion standards. This is also a pass-fail test.

It is important that the total sulfur content of burning oil should be low (ASTM D1266). All the sulfur compounds present in an oil are converted to oxides of sulfur during burning.

Gas chromatography with either sulfur chemiluminescence detection or atomic emission detection has been used for sulfur selective detection. Selective sulfur and nitrogen gas chromatographic detectors, exemplified by the flame photometric detector (FPD) and the nitrogen-phosphorus detector (NPD), have been available for many years. However, these detectors have limited selectivity for the element over carbon, exhibit non-uniform response, and have other problems that limit their usefulness.

Nitrogen compounds in middle distillates can be selectively detected by chemiluminescence. Individual nitrogen compounds can be detected down to 100 ppb nitrogen.

Correlative methods have long been used as a way of dealing with the complexity of crude oil fractions. Relatively easy to measure physical properties such as density, viscosity, and refractive index (ASTM D1218) have been correlated to hydrocarbon structure (Table 10.10) with the potential; to relate refractive index data to the nature of the constituents of a crude oil product. In recent years an entirely new class of correlative methods has been developed. These use near-infrared (NIR) or mid-infrared spectra together with sophisticated chemometric techniques to predict a wide variety of properties. Properties such as composition (saturates, aromatic derivatives), freezing point, density, viscosity, aromatic derivatives, and heat of combustion have been successfully predicted. However, it is important to recognize that these methods are correlations and should not be used to estimate properties that are outside of the calibration set.

The *color* of kerosene is of little significance, but a product darker than usual may have resulted from a change in composition due to contamination or aging, and in fact a color darker than specified (ASTM D156) may be considered by some users as unsatisfactory. Finally, the cloud point of kerosene (ASTM D2500) gives an indication of the temperature at which the wick may become coated with wax particles, thus lowering the burning qualities of the oil.

Alternatively, the wax appearance point may also be estimated form the cloud point (ASTM D2500) determined as a means of estimating the composition of kerosene in terms of the wax (*n*-paraffin derivatives) content. The wax appearance point is the temperature at which wax crystals begin to precipitate from a fuel and is estimated for the cloud point. In this test (ASTM D2500; ASTM D5771; ASTM D5772; ASTM D5773), a sample is cooled under prescribed conditions with stirring and the temperature at which wax first appears is the wax appearance point.

7.2.5 Density

Density (specific gravity) is an important property of crude oil products and is often part of product specifications (Table 10.11). Materials are usually bought and sold on that basis or if on volume basis then converted to mass basis via density measurements. This property is almost synonymously termed as density (mass of liquid per unit volume), specific gravity the ratio of the mass of a given volume of liquid to the mass of an equal volume of pure water at the same temperature, and relative density (same as specific gravity). Usually a hydrometer, pycnometer or a digital density meter is used in these standards (ASTM, 2013).

Specific gravity has no relation to burning quality but is a useful aid in checking consistency of production of a particular grade. The specific gravity of kerosene can be determined very conveniently by the hydrometer method (ASTM D1298).

7.2.6 Flash point

The flashpoint test is a guide to the fire hazard associated with the use of kerosene and can be determined by several test methods and the results are not always strictly comparable. Generally, the flash point of kerosene is specified as being in excess of 38 °C (100 °F), due to production as well as safety considerations.

The minimum flash point is usually defined by the Pensky-Martens method (ASTM D93). The TAG method (ASTM D56) is used for both the minimum and maximum limits, while certain military specifications also give minimum limits by the Pensky-Martens method (ASTM D93).

TABLE 10.11 Specific gravity and API gravity of crude oil and selected products.

Material	Specific gravity 60°/60 °F	API gravity, deg
Crude oils	0.65–1.06	87–2
Casinghead liquid	0.62–0.70	97–70
Gasoline	0.70–0.77	70–52
Kerosene	0.77–0.82	52–40
Lubricating oil	0.88–0.98	29–13
Residua and cracked residua	0.88–1.06	29–2

7.2.7 *Freezing point*

The freezing point of kerosene is not of the same importance as the freezing point of aviation fuel but deserves mention because of its influence on kerosene use. There are two ASTM test methods available for determination of the freezing point.

In the first test method (ASTM D2386), a measured fuel sample is placed in a jacketed sample tube, also holding a thermometer and a stirrer. The tube is placed in a vacuum flask containing the cooling medium. Various coolants used are acetone, methyl alcohol, ethyl alcohol, or iso-propyl alcohol, solid carbon dioxide, or liquid nitrogen. As the sample cools, it is continuously stirred. The temperature at which the hydrocarbon crystals appear is recorded. The jacketed sample is removed from the coolant and allowed to warm, stirring it continuously. The temperature at which the crystals completely disappear is recorded.

In the second method (ASTM D5972), an automated phase transition method is used in the temperature range -80 to 20 °C (-112 °F to 68 °F). In this test, a specimen is cooled at a rate of 15 ± 5 °C/min while continuously being illuminated by a light source. The specimen is continuously monitored by an array of optical detectors for the first formation of solid hydrocarbon crystals. After that the specimen is warmed at the rate of 10 ± 0.5 °C per minute until all crystals return to the liquid phase, and that temperature is also recorded.

The *pour point* should not be confused with the *freezing point*. The *pour point* that is an index of the lowest temperature at which the crude oil will flow under specified conditions. The maximum and minimum pour point temperatures provide a temperature window where crude oil, depending on its thermal history, might appear in the liquid as well as the solid state. The pour point data can be used to supplement other measurements of cold flow behavior and the data are particularly useful for the screening of the effect of wax interaction modifiers on the flow behavior of crude oil.

In the original (and still widely used) test for pour point (ASTM D97), a sample is cooled at a specified rate and examined at intervals of 3 °C (5.4 °F) for flow characteristics. The lowest temperature at which the movement of the oil is observed is recorded as the pour point.

A later test method (ASTM D5853) covers two procedures for the determination of the pour point of crude oils down to -36 °C. One method provides a measure of the maximum (upper) pour point temperature. The second method measures the minimum (lower) pour point temperature. In the methods, the test specimen is cooled (after preliminary heating) at a specified rate and examined at intervals of 3 °C (5.4 °F) for flow characteristics. Again, the lowest temperature at which movement of the test specimen is observed is recorded as the pour point.

In any determination of the pour point, crude oil that contains wax produces an irregular flow behavior when the wax begins to separate. Such crude oil possesses viscosity relationships that are difficult to predict in pipeline operation. In addition, some waxy crude oil is sensitive to heat treatment that can also affect the viscosity characteristics. This complex behavior limits the value of viscosity and pour point tests on waxy crude oil.

7.2.8 *Smoke point*

While a low smoke point is undesirable in that it may not give a satisfactory range of smokeless performance, a high smoke point alone is no guarantee that a kerosene has generally satisfactory burning characteristics. The smoke point test adequately reflects the essential feature of hydrocarbon type composition in relation to burning characteristics, as already indicated, and consequently no analysis for composition is necessary in the normal evaluation of burning oils.

Kerosene can vary widely in its burning quality as measured by carbon deposition, smoke formation and flame radiation. This is a function of hydrocarbon composition - paraffin derivatives have excellent burning properties in contrast to those of the aromatic derivatives (particularly the polynuclear aromatic hydrocarbon derivatives). As a control measure the smoke point test (ASTM D1322) gives the maximum smokeless flame height in millimeters at which the fuel will burn in a wick-fed lamp under prescribed conditions. The combustion performance of wide-cut fuels correlates well with smoke point when a fuel volatility factor is included, since carbon formation tends to increase with boiling point. A minimum smoke volatility index (SVI) value is specified and is defined as:

$$\text{SVI} = \text{Smoke Point} + 0.42\ (\text{percent distilled below } 204\,^{\circ}\text{C: } 400\,^{\circ}\text{F})$$

However, the smoke point test is not always a reliable criterion of combustion performance and should be used in conjunction with other properties. Various alternative laboratory test methods have previously been specified such as the lamp burning test (ASTM D187) and a limit on the polynuclear aromatic content (ASTM D1840). The test apparatus is a smoke point lamp modified to include a photoelectric cell for flame radiation measurement and a thermocouple to measure temperature rise across the flame.

7.2.9 Viscosity

The kinematic viscosity of many crude oil fuels is important for their proper use, for example, flow of fuels through pipelines, injection nozzles and orifices, and the determination of the temperature range for proper operation of the fuel in burners.

The quantity of oil flowing up a wick is related to the height of the top of the wick above the level of oil in the container and the viscosity and surface tension of the oil. Viscosity (ASTM D445) is more significant in this respect than surface tension, since it varies more in magnitude than the latter with different kerosene and with change of temperature.

7.2.10 Volatility

An abnormally high final boiling point and percentage residue of a kerosene may indicate contamination with higher boiling constituents, although the presence of trace quantities of very heavy oils sufficient to cause high char values might not necessarily be revealed by these features. Thus, the boiling range of kerosene is an important aspect of kerosene properties.

The boiling range (ASTM D86) is of less importance for kerosene than for gasoline, but it is an indication of the viscosity of the product, for which there is no requirement for kerosene. The nature of the distillation range is of significance with regard to burning characteristics. The initial boiling point and the 10% point chiefly affect the flash point and ease of ignition, while the mid-boiling point is more relevant to the viscosity.

Another test method (ASTM D6352) that can be used for product specification testing is applicable to crude oil distillate fractions with an initial boiling point less than 700 °C (less than 1290 °F) at atmospheric pressure. This test method extends the scope of other test methods (ASTM D86; ASTM D1160; ASTM D2887) to boiling range determination by gas chromatography. In the method, a non-polar open tubular capillary gas chromatographic column is used to elute the hydrocarbon components of the sample in order of increasing boiling point. A sample aliquot diluted with a viscosity reducing solvent is introduced into the chromatographic system. The column oven temperature is raised at a specified linear rate to effect separation of the hydrocarbon components. The detector signal is recorded as area slices for consecutive retention time intervals during the analysis. Retention times of known normal paraffin hydrocarbon derivatives spanning the scope of the test method are used for normalizing the retention times of the unknown mixture area slices.

One of the most important physical parameters defining these products is their boiling range distribution that can be determined using a low-efficiency, one theoretical plate distillation procedure (ASTM D86). This has been adequate for product specification purposes; however, engineering studies require true boiling point (TBP) data (ASTM D2887; ASTM D2892).

The vapor pressure of crude oil products at various vapor-liquid ratios is an important physical property for shipping and storage. Although determining the volatility of kerosene is usually accomplished through a boiling range distribution (ASTM D86) although other methods such as determining the Reid vapor pressure (ASTM D323) can also be used along with several other methods (ASTM D5482; ASTM D6378).

7.2.11 Water and sediment

Kerosene, because of its higher density and viscosity, tends to retain fine particulate matter and water droplets in suspension for a much longer time than gasoline. Free water in kerosene can be detected by the use of a dean and Stark adaptor (ASTM D4006), by the Karl Fischer titration method (ASTM D1744; ASTM D6304), by the distillation method (ASTM D95), or by a series of alternate tests (ASTM D4176; ASTM D4860). The standard water reaction test method (ASTM D1094) can also be used.

In addition to water, sediment can also occur and will cause fouling of the fuel handling facilities and the fuel system. An accumulation of sediment in storage tanks and on filter screens can obstruct the flow of kerosene during use and a test method is available to determine the water and sediment in fuels (ASTM D2709). In the test method, a sample of kerosene is centrifuged at a rcf of 800 for 10 min at 21–32 °C in a centrifuge tube readable to 0.005 mL and measurable to 0.01 mL. After centrifugation, the volume of water and sediment that has settled into the tip of the centrifuge tube is read to the nearest 0.005 mL.

7.2.12 Gas Oil

Gas oil is a crude oil fraction produced in conventional (atmospheric or vacuum) distillation operations as a dark-colored viscous, residual material remaining as the result of refinery distillation of crude oil either alone or as a blend with light components and that is used for steam generation and various industrial processes. The term is sometimes used to refer to the light, amber colored middle distillates that are distinguished from the residual fraction by being characterized as distillate fuel oil (ASTM D396).

The manufacture of gas oil at one time largely involved using what was left after removing desired products from crude oil. The quality and performance requirements for gas oil differs widely although general quality limitations for various fuel grades are used to serve as guides in the manufacture and use of the oils. These quality definitions typically involve requirements such as the vapor pressure (ASTM D323) and metals content (ASTM D5184; ASTM D4951; ASTM D5185; ASTM D5708; ASTM D5863).

Gas oil has a range of applications and the choice of a standard procedure to be used for assessing the use (typically as a feedstock for a catalytic cracking unit) must, of necessity, depend both upon the desired product slate.

7.2.13 Acidity

The presence of inorganic acids in gas oil, resulting from refinery treatment, is unlikely. If required, the acidity is determined through the *acid number* that is the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample, required to titrate a sample in the solvent from its initial meter reading to a meter reading corresponding to a freshly prepared non-aqueous basic buffer solution or a well-defined inflection point as specified in the test method. Test methods include and indicator-indicator titration (ASTM D974).

One the test method (ASTM D974) resolves constituents into groups having weak-acid and strong-acid ionization properties. However, a gas oil is typically dark-colored and cannot be analyzed by this test method due to obscurity of the color-indicator end point an should be analyzed by another test method (ASTM D664). The test method may be used to indicate relative changes that occur in an oil during use under oxidizing conditions regardless of the color or other properties of the resulting oil. In the practice of the method, the sample is dissolved in a mixture of toluene and *iso*-propyl alcohol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide using a glass indicating electrode and a calomel reference electrode and the end points are taken at well-defined inflections in the resulting curve.

7.2.14 Ash

Ash is the organic-free (or carbonaceous-free) residue that remains after combustion of a fuel oil at a specified, high temperature (ASTM D482). Small amounts of non-burnable material are found in fuel oil in the form of soluble metallic soaps and solids and these materials are designated as ash, although ash-forming constituents is a more correct term. In the test for the quantitative determination of ash-forming constituents (ASTM D482), a small sample of fuel oil is burned in a weighed container until all of the combustible matter has been consumed indicated by the residue and container attaining a constant weight. The amount of unburnable residue is the ash yield, and is reported as percent by weight of the sample.

7.2.15 Calorific value

Since the function of gas oil, when used as a fuel oil, is to produce heat the calorific or heating value (ASTM D240) is one of the important properties and a knowledge of this is necessary in obtaining information regarding the combustion efficiency and performance of all types of oil burning equipment.

The determination is made in a bomb calorimeter under specified conditions, the oxygen in the bomb being saturated with water vapor prior to the ignition of the fuel so that the water formed during combustion is condensed. The calorific value so determined will include the latent heat of water at the test temperature and is known as the Gross Calorific Value at constant volume. The corresponding Net Calorific Value at constant pressure is obtained by deducting the latent heat of water formed during the burning of the hydrogen present in the fuel to produce water. The calorific value is usually expressed in British Thermal Units per pound (Btu/lb) or in calories per gram (c∼/g). In Europe the net calorific value is more often called for in calculations on burner efficiency since the water formed during combustion passes out as water vapor with the flue gases and hence its latent heat of condensation is not realized as useful heat. In the UK the gross calorific value is normally used for this purpose.

An alternate method of calculation of the calorific value, when an experimental determination is not available or cannot be made conveniently, involves an estimate of this property (ASTM D3338) from the net heat of combustion is calculated from the density, sulfur, and hydrogen content but this calculation is justifiable only when the fuel belongs to a well-defined class for which a relationship between these quantities has been derived from accurate experimental measurements on representative samples.

7.2.16 Carbon residue

The carbon residue of a crude oil product gives an indication of the propensity for that product to form a carbonaceous residue under thermal conditions. The carbonaceous residue is correctly referred to as the *carbon residue* but is also often referred to as *coke* or *thermal coke*.

Assessing the carbon forming tendencies of a gas oil is carried out using a carbon residue test. The test methods are (i) the Conradson carbon residue (ASTM D189), the Ramsbottom carbon residue (ASTM D524), and the microcarbon carbon residue (ASTM D4530). The data give an indication of the amount of coke that will be formed during thermal processes.

7.2.17 Composition

The chemical composition of gas oil is extremely complex and an extremely high number of compounds can be present through the hydrocarbon types, the range of isomeric hydrocarbon derivatives (Table 10.9), and the various types and isomers of heteroatom constituents. Therefore, It is not practical to perform individual compound analyses but it is often helpful to define the compounds present under broad classifications, such as aromatic derivatives, paraffin derivatives, naphthene derivatives and olefin derivatives.

Thus, the first level of compositional information is group-type totals as deduced by adsorption chromatography (ASTM D1319; ASTM D2007) or by emulsion chromatography (ASTM D2549) to give volume percent saturates, olefin derivatives, and aromatic derivatives in materials that boil below 315 °C (600 °F). In addition, and depending upon the characteristics of the fuel oil, gas chromatography can also be used for the quantitative determination of olefin derivatives (ASTM D6296). Following from the chromatographic separation, compositional analysis of the fractions by a mass spectral Z-series on which Z in the empirical formula $CnH2n + z$ is a measure of the hydrogen deficiency of the compound is also warranted (ASTM D2425; ASTM D2786; ASTM D3239; ASTM D6379).

The percentage of aromatic hydrogen atoms and aromatic carbon atoms can be determined (ASTM D5292). Results from this test are not equivalent to mass- or volume-percent aromatic derivatives determined by the chromatographic methods. The chromatographic methods determine the mass- or volume-percentage of molecules that have one or more aromatic rings. Any alkyl substituents on the rings contribute to the percentage of aromatic derivatives determined by chromatographic techniques.

Correlative methods have long been used as a way of dealing with the complexity of crude oil fractions. Such methods include the use of viscosity-temperature charts (ASTM D341), calculation of the viscosity index (ASTM D2270), calculation of the viscosity gravity constant (ASTM D2501), calculation of the true vapor pressure (ASTM D2889), and estimation of the heat of combustion (ASTM D3338).

Organic sulfur compounds (e.g. mercaptans, sulfides, polysulfides, thiophenes) are present in crude oil products to a greater or lesser extent depending upon the crude oil origin and the refinery treatment. The sulfur content of fuel oil (ASTM D396) can be determined by a variety of methods (ASTM D129; ASTM D1552; ASTM D2622; ASTM D4294) with mercaptan sulfur in cracked stocks being particularly necessary for evaluation (ASTM D3227).

Corrosion of heating equipment can occur if the sulfur oxides formed on combustion of fuel oil are allowed to condense in the presence of moisture on the cooler parts of the flue system. Corrosion of metal parts of the fuel system may also reflect the presence of corrosive sulfur components in the fuel. The corrosive tendencies of the fuel may be detected by the copper strip test (ASTM D130; ASTM D849), the effect of these sulfur compounds being indicated by discoloration of the copper strip.

Nitrogen can be determined by elemental analysis (ASTM D3228; ASTM D5291; ASTM D5762). Nitrogen compounds in middle distillates can be selectively detected by chemiluminescence (ASTM D4629). Individual nitrogen compounds can be detected down to 100 ppb nitrogen.

7.2.18 Density

The density (specific gravity) of gas oil is an index of the weight of a measured volume of the product (ASTM D287; ASTM D1250; ASTM D1298; ASTM D1480; ASTM D1481; ASTM D4052).

The density is the mass (weight *in vacuo*) of a unit volume of fuel oil at any given temperature (ASTM D1298). On the other hand, the specific gravity of a fuel oil is the ratio of the weight of a given volume of the material at a temperature of 15.6 °C (60 °F) to the weight of an equal volume of distilled water at the same temperature, both weights being corrected for the buoyancy of air.

The API gravity (ASTM D1298) is an arbitrary number that is related to the Baumé gravity and the specific gravity (Speight, 2014a):

$$\text{API} = 141.5/(\text{Specific Gravity @ } 60/60\ {}^\circ\text{F})/131.5$$

7.2.19 Metallic constituents

Metals in fuel oil can seriously affect the use and outcome of fuel oil systems. Even trace amounts of metals can be deleterious to fuel oil use. Hence, it is important to have test methods that can determine metals, both at trace levels and at major concentrations. Metallic constituents in fuel oil can be determined by several methods including atomic absorption spectrophotometry (ASTM D5863; ASTM D5863), X-ray fluorescence spectrometry (ASTM D4927), wave length-dispersive X-ray fluorescence spectrometry (ASTM D6443), and inductively coupled plasma emission spectrometry (ICPAES) (ASTM D5708).

Inductively coupled argon plasma emission spectrophotometry (ASTM D5708) has an advantage over atomic absorption spectrophotometry (ASTM D4628; ASTM D5863) because it can provide more complete elemental composition data than the atomic absorption method. Flame emission spectroscopy is often used successfully in conjunction with atomic absorption spectrophotometry (ASTM D3605). X-ray fluorescence spectrophotometry (ASTM D4927; ASTM D6443) is also sometimes used but matrix effects can be a problem.

The method to be used for the determination of metallic constituents in crude oil is often a matter of individual preference.

7.2.20 Pour point

The *pour point* (ASTM D97) is the lowest temperature at which the fuel oil will flow under specified conditions. The maximum and minimum pour point temperatures provide a temperature window where a crude oil product, depending on its thermal history, might appear in the liquid as well as the solid state. The pour point data can be used to supplement other measurements of cold flow behavior and the data are particularly useful for the screening of the effect of wax interaction modifiers on the flow behavior of crude oil. The *pour point* should not be confused with the *freezing point* that is an index of the lowest temperature at which the crude oil will flow under specified conditions. Test methods (ASTM D2386; ASTM D5972) for the freezing point are not usually applicable to fuel oil but are more applicable to diesel fuel and aviation fuel.

In any determination of the pour point, crude oil that contains wax produces an irregular flow behavior when the wax begins to separate. Such crude oil possesses viscosity relationships that are difficult to predict in fuel line operation. In addition, some waxy crude oil is sensitive to heat treatment that can also affect the viscosity characteristics. This complex behavior limits the value of viscosity and pour point tests on waxy crude oil.

7.2.21 Stability

Fuel oil must be capable of storage for many months without significant change and should not break down to form gum or insoluble sediments or darken in color (ASTM D156; ASTM D381; ASTM D1209; ASTM D1500; ASTM D1544). In other words, fuel oil must be stable. The extent of fuel oil oxidation is determined by measurement of the hydroperoxide number (ASTM D6447) and the peroxide number (ASTM D3703). Deterioration of fuel oil results in the formation of the peroxides as well as other oxygen-containing compounds and these numbers are indications of the quantity of oxidizing constituents present in the sample as determined by measurement of the compounds that will oxidize potassium iodide.

In addition, thermal treatment may cause the formation of asphaltene-type (heptane-insoluble) material in the gas oil. The asphaltene fraction (ASTM D893; ASTM D2007; ASTM D3279; ASTM D4124; ASTM D6560) is the highest molecular weight and most complex fraction in crude oil. The asphaltene content is and indicator of the amount of carbonaceous residue that can be expected during thermal use or further processing (ASTM D189; ASTM D524; ASTM D4530) (Parkash, 2003; Pandey et al., 2004; Gary et al., 2007; Speight, 2014a, 2017; Hsu and Robinson, 2017).

In any of the methods for the determination of the asphaltene content (ASTM D893; ASTM D2007; ASTM D3279; ASTM D4124; ASTM D6560), the crude oil or product (such as asphalt) is mixed with a large excess (usually in excess of 30 vol hydrocarbon per volume of sample) low-boiling hydrocarbon such as *n*-pentane or *n*-heptane. For an extremely viscous sample, a solvent such as toluene may be used prior to the addition of the low-boiling hydrocarbon but an additional amount of the hydrocarbon (usually >30 vol hydrocarbon per volume of solvent) must be added to compensate for the presence of the solvent. After a specified time, the insoluble material (the asphaltene fraction) is separated (by filtration) and dried. The yield is reported as percentage by weight of the original sample.

It must be recognized that, in any of these tests, different hydrocarbon derivatives (such as *n*-pentane or *n*-heptane) will give different yields of the asphaltene fraction and if the presence of the solvent is not compensated by use of additional hydrocarbon the yield will be erroneous. In addition, if the hydrocarbon is not present in a large excess, the yields of the asphaltenes fraction will vary and will be erroneous (Speight, 2014a, 2015).

7.2.22 Viscosity

The viscosity of a fluid is a measure of its resistance to flow and is expressed as Saybolt Universal seconds (SUS), Saybolt Furol seconds (SFS), or centistokes (cSt, kinematic viscosity). Viscosity is one of the more important heating oil characteristics since it is indicative of the rate at which the oil will flow in fuel systems and the ease with which it can be atomized in a given type of burner.

For the determination of the viscosity of crude oil products various procedures, e.g. Saybolt (ASTM D88) and Engler, are available and have been in use for many years, all being of an empirical nature, measuring the time taken in seconds for a given volume of fuel to flow through an orifice of specified dimensions.

The use of these empirical procedures is being superseded by the more precise kinematic viscosity method (ASTM D445) in which a fixed volume of fuel flows through the capillary of a calibrated glass capillary viscometer under an accurately reproducible head and at a closely controlled temperature. The result is obtained from the product of the time taken for the fuel to flow between two etched marks on the capillary tube and the calibration factor of the viscometer and is reported in centistokes. Since the viscosity decreases with increasing temperature the temperature of test must also be reported if the viscosity value is to have any significance. For distillate fuel oils the usual test temperature is 38 °C (100 °F).

The *viscosity index* (ASTM D2270) is a widely used measure of the variation in kinematic viscosity due to changes in the temperature of crude oil and crude oil products between 40 °C and 100 °C (104 °F and 212 °F). For samples of similar kinematic viscosity, the higher the viscosity index the smaller is the effect of temperature on its kinematic viscosity. The accuracy of the calculated viscosity index is dependent only on the accuracy of the original viscosity determination.

7.2.23 Water and sediment

Considerable importance is attached to the presence of water or sediment in fuel oil because they lead to difficulties in use such as corrosion of equipment and blockages in fuel lines. The sediment consists of finely divided solids that may be drilling mud or sand or scale picked up during the transport of the oil, or may consist of chlorides derived from evaporation of brine droplets in the oil. The solids may be dispersed in the oil or carried in water droplets. Sediment in crude oil can lead to serious plugging of the equipment, corrosion due to chloride decomposition, and a lowering of residual fuel quality. In any form, water and sediment are highly undesirable in fuel oil and the relevant tests involving distillation (ASTM D95; ASTM D4006), centrifuging (ASTM D4007), extraction (ASTM D473), and the Karl Fischer titration (ASTM D4377; ASTM D4928) are regarded as important in examinations of quality.

The Karl Fischer test method (ASTM D1364; ASTM D6304) covers the direct determination of water in crude oil products. In the test, the sample injection in the titration vessel can be performed on a volumetric or gravimetric basis. Viscous samples can be analyzed using a water vaporizer accessory that heats the sample in the evaporation chamber, and the vaporized water is carried into the Karl Fischer titration cell by a dry inert carrier gas.

Water and sediment can be determined simultaneously (ASTM D4007) by the centrifuge method. Known volumes of the fuel oil and solvent are placed in a centrifuge tube and heated to 60 °C (140 °F). After centrifugation, the volume of the sediment-and water layer at the bottom of the tube is read. For fuel oil that contains wax, a temperature of 71 °C (160 °F) or higher may be required to completely melt the wax crystals so that they are not measured as sediment.

Sediment is also determined by an extraction method (ASTM D473) or by membrane filtration (ASTM D4807). In the former method (ASTM D473), an oil sample contained in a refractory thimble is extracted with hot toluene until the residue reaches a constant mass. In the latter test, the sample is dissolved in hot toluene and filtered under vacuum through a 0.45 μm porosity membrane filter. The filter with residue is washed, dried, and weighed.

7.3 Resid

The high-boiling material from tight oil — the resid — represents the highest boiling product in the tight oil. By way of recall, a *resid* (*residuum*, *pl. residua*) is the residue obtained from crude oil after nondestructive distillation has removed all the volatile materials. The temperature of the distillation is usually maintained below 350 °C (660 °F) since the rate of thermal decomposition of crude oil constituents is minimal below this temperature but the rate of thermal decomposition of crude oil constituents is substantial above 350 °C (660 °F). A residuum that has held above this temperature so that thermal decomposition has occurred is known as a *cracked resid*.

Resids are typically, dark-colored, sometimes black, viscous materials and are obtained by distillation of a crude oil under atmospheric pressure (atmospheric residuum) or under reduced pressure (vacuum residuum). They may be liquid at room temperature (generally atmospheric residua) or almost solid (generally vacuum residua) depending upon the nature of the crude oil (Parkash, 2003; Gary et al., 2007; Speight, 2014a; Speight, 2017). When a residuum is obtained from a crude oil and thermal decomposition has commenced, it is more usual to refer to this product as *pitch* (Speight, 2014a) The differences between a parent crude oil and the residua are due to the relative amounts of various constituents present, which are removed or remain by virtue of their relative volatility.

The chemical composition of a residuum is complex (Speight, 2014a, 2015a). Physical methods of fractionation usually indicate high proportions of asphaltene constituents and resin constituents, even in amounts up to 50% (or higher) of the residuum. In addition, the presence of ash-forming metallic constituents, including such organometallic compounds as those of vanadium and nickel, is also a distinguishing feature of residua and the heavier oils. Furthermore, the deeper the *cut* into the crude oil, the greater is the concentration of sulfur and metals in the residuum and the greater the deterioration in physical properties (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017; Hsu and Robinson, 2006).

7.3.1 Production and properties

Residua are the starting materials for asphalt manufacture and therefore the properties of the asphalt depend on the properties of the residuum from which the asphalt is manufactured. And residua properties can vary, depending upon the cut point of the residuum (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017, 2015a; Hsu and Robinson, 2017).

At one time, the residua produced in a refinery were considered to be the garbage of a refinery, had little value and little use, other than as a (passable in some cases but not in every case) road oil. In fact, the development of delayed coking (once the so-called the refinery garbage can) was with the purpose of converting residua to liquids (valuable products) and coke (fuel).

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The significance of a particular test is not always apparent by reading the procedure, and sometimes can only be gained through working familiarity with the test. The following tests are commonly used to characterize resids.

7.3.2 Acid number

The acid number is a measure of the acidity of a product and is used as a guide in the quality control of the properties of the resid. A resid typically contains a small amount of organic acids and saponifiable material that is largely determined by the percentage of naphthene (cycloparaffin) acids of higher molecular weight that are originally present in the crude oil. Acidic constituents may also be present as additives or as degradation products formed during service, such as oxidation products (ASTM D5770). The relative amount of these materials can be determined by titrating with bases. The acid number is used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degradation in service. Any condemning limits must be empirically established.

In a manner akin to the *acid number*, the *base number* (often referred to as the *neutralization number*) is a measure of the basic constituents in the oil under the conditions of the test. The base number is used as a guide in the quality control of oil formulation and is also used as a measure of oil degradation in service. The *neutralization number* is expressed as the *base number* is a measure of this amount of basic substance in the oil always under the conditions of the test. The neutralization number is used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degradation in service; however, any condemning limits must be empirically established.

The *saponification number* expresses the amount of base that will react with 1 gm of the sample when heated in a specific manner. Since compounds certain elements are sometimes added to asphalt and also consume alkali and acids, the results obtained indicate the effect of these extraneous materials in addition to the saponifiable material present. In the test method (ASTM D94), a known weight of the sample is dissolved in methyl ethyl ketone or a mixture of suitable solvents and the mixture is heated with a known amount of standard alcoholic potassium hydroxide for between 30 and 90 min at 80 °C (176 °F). The excess alkali is titrated with standard hydrochloric acid and the saponification number calculated.

7.3.3 Asphaltene content

The asphaltene fraction (ASTM D2007; ASTM D3279; ASTM D4124; ASTM D6560) is the highest molecular weight and most complex fraction in crude oil. The asphaltene content gives an indication of the amount of coke that can be expected during processing (Speight, 1999; Speight, 2001, 2014a, 2017).

In any of the methods for the determination of the asphaltene content, the resid is mixed with a large excess (usually >30 vol hydrocarbon per volume of sample) low-boiling hydrocarbon such as *n*-pentane or *n*-heptane. For an extremely viscous sample, a solvent such as toluene may be used prior to the addition of the low-boiling hydrocarbon but an additional amount of the hydrocarbon (usually >30 vol hydrocarbon per volume of solvent) must be added to compensate for the presence of the solvent. After a specified time, the insoluble material (the asphaltene fraction) is separated (by filtration) and dried. The yield is reported as percentage (% w/w) of the original sample.

It must be recognized that, in any of these tests, different hydrocarbon derivatives (such as *n*-pentane or *n*-heptane) will give different yields of the asphaltene fraction and if the presence of the solvent is not compensated by use of additional hydrocarbon the yield will be erroneous. In addition, if the hydrocarbon is not present in a large excess, the yields of the asphaltenes fraction will vary and will be erroneous (Speight, 1999).

The *precipitation number* is often equated to the asphaltene content but there are several issues that remain obvious in its rejection for this purpose. For example, the method to determine the precipitation number (ASTM D91) advocates the use of naphtha for use with black oil or lubricating oil and the amount of insoluble material (as a % v/v of the sample) is the precipitating number. In the test, 10 mL of sample is mixed with 90 mL of ASTM precipitation naphtha (that may or may not have a constant chemical composition) in a graduated centrifuge cone and centrifuged for 10 min at 600–700 rpm. The volume of material on the bottom of the centrifuge cone is noted until repeat centrifugation gives a value within 0.1 mL (the precipitation number). Obviously, this can be substantially different from the asphaltenes content.

In another test method (ASTM D4055), pentane insoluble materials above 0.8 μm in size can be determined. In the test method, a sample of oil is mixed with pentane in a volumetric flask, and the oil solution is filtered through a 0.8-μm membrane filter. Te flask, funnel, and the filter are washed with pentane to completely transfer the particulates onto the filter that is then dried and weighed to give the yield of pentane insoluble materials.

Another test method (ASTM D893) that was originally designed for the determination of pentane and toluene insoluble materials in used lubricating oils can also be applied to a resid. However the method may need modification by first adding a solvent (such as toluene) to the asphalt before adding pentane (or heptane) (Speight, 2104, 2105). The pentane insoluble constituents can include oil-insoluble materials.

There are two test methods used. Procedure A covers the determination of insoluble constituents without the use of coagulant in the pentane and provides an indication of the materials that can be readily separated from the resid-solvent mixture by centrifugation. Procedure B covers the determination of insoluble constituents in resid containing additives (that may have been added to the tight oil during recovery operations) and employs a coagulant. In addition to the materials separated by using Procedure A, this coagulation procedure separates some finely divided materials that may be suspended in the resid. The results obtained by Procedures A and B should not be compared since they usually give different values. The same procedure should be applied when comparing results obtained periodically on an oil in use, or when comparing results determined in different laboratories.

In Procedure A, a sample is mixed with pentane and centrifuged. The resid solution is decanted, and the precipitate washed twice with pentane, dried and weighed. For toluene insoluble constituents a separate sample of the resid is mixed with pentane and centrifuged. The precipitate is washed twice with pentane, once with toluene-alcohol solution, and once with toluene. The insoluble material is then dried and weighed. In Procedure B, Procedure A is followed except that instead of pentane, a pentane-coagulant solution is used.

7.3.4 Carbon disulfide insoluble constituents

The resid is a hydrocarbonaceous material that is made of constituents (containing carbon, hydrogen, nitrogen, oxygen, and sulfur) that are completely soluble in carbon disulfide. The component of highest carbon content is the fraction termed *carboids* and consists of species that are insoluble in carbon disulfide or in pyridine. The fraction that has been called *carbenes* contains molecular species that are soluble in carbon disulfide and soluble in pyridine but which are insoluble in toluene (Speight, 2014a, 2015a).

The carbene and carboids fractions are generated by thermal degradation or by oxidative degradation and are not considered to be naturally occurring constituents of the resid. The test method for determining the toluene insoluble constituents of tar and pitch (ASTM D4072; ASTM D4312) can be used to determine the amount of carbenes and carboids (both are ill-defined constituents) in a resid (Parkash, 2003; Gary et al., 2007; Speight, 2014a, 2017; Hsu and Robinson, 2006).

7.3.5 Carbon residue

The *carbon residue* of a resid serves as an indication of the propensity of the sample to form carbonaceous deposits (thermal coke) under the influence of heat. The produced is also often used to provide thermal data that give an indication of the composition of the resid (Speight, 2014a, 2015a).

Tests for Conradson carbon residue (ASTM D189), the Ramsbottom carbon residue (ASTM D524), the microcarbon carbon residue (ASTM D4530), and asphaltene content (ASTM D2007; ASTM D3279; ASTM D4124; ASTM D6560) are sometimes included in inspection data on crude oil. The data give an indication of the amount of coke that will be formed during thermal processes as well as an indication of the amount of high boiling constituents in crude oil. In the Conradson carbon residue test (ASTM D189), a weighed quantity of sample is placed in a crucible and subjected to destructive distillation for a fixed period of severe heating. At the end of the specified heating period, the test crucible containing the carbonaceous residue is cooled in a desiccator and weighed and the residue (the Conradson carbon residue or Con Carbon) is reported as a percentage (% w/w) of the original sample.

In the Ramsbottom carbon residue test (ASTM D524), the sample is weighed into a glass bulb that has a capillary opening and is placed into a furnace (at 550 °C, 1020 °F). The volatile matter is distilled from the bulb and the non-volatile matter that remains in the bulb cracks to form thermal coke. After a specified heating period, the bulb is removed from the bath, cooled in a desiccator, and weighed to report the residue (Ramsbottom carbon residue) as a percentage (% w/w) of the original sample.

In the microcarbon residue test (ASTM D4530), a weighed quantity of the sample placed in a glass vial is heated to 500 °C (930 °F) under an inert (nitrogen) atmosphere in a controlled manner for a specific time and the carbonaceous residue [*carbon residue (micro)*] is reported as a percent (% w/w) of the original sample.

7.3.6 Density

For clarification, it is necessary to understand the basic definitions that are used: (i) *density* is the mass of liquid per unit volume at 15.6 °C (60 °F), (ii) *relative density* is the ratio of the mass of a given volume of liquid at 15.6 °C (60 °F) to the mass of an equal volume of pure water at the same temperature, (iii) *specific gravity* is the same as the relative density and the terms are used interchangeably.

Density (ASTM D1298) is an important property of crude oil products since crude oil and especially crude oil products are usually bought and sold on that basis or if on volume basis then converted to mass basis via density measurements. This property is almost synonymously termed as density, relative density, gravity, and specific gravity, all terms related to each other. Usually a hydrometer, pycnometer or more modem digital density meter is used for the determination of density or specific gravity.

In the most commonly used method (ASTM D1298), the sample is brought to the prescribed temperature and transferred to a cylinder at approximately the same temperature. The appropriate hydrometer is lowered into the sample and allowed to settle and, after temperature equilibrium has been reached, the hydrometer scale is read and the temperature of the sample is noted.

The accurate determination of the API gravity of crude oil and its products (ASTM D287) is necessary for the conversion of measured volumes to volumes at the standard temperature of 60 °F (15.6 °C). Gravity is a factor governing the quality of crude oils. However, the gravity of a crude oil product is an uncertain indication of its quality. Correlated with other properties, gravity can be used to give approximate hydrocarbon composition and heat of combustion. This is usually accomplished through use of the API gravity that is derived from the specific gravity:

$$\text{API gravity, deg} = (141.5/\text{sp gr } 60/60\ ^\circ\text{F}) - 131.5$$

and is also a critical measure for reflecting the quality of crude oil.

API gravity or density or relative density, can be determined using one of two hydrometer methods (ASTM D287; ASTM D1298). The use of a digital analyzer (ASTM D5002) is finding increasing popularity for the measurement of density and specific gravity.

For solid and semisolid resid fractions, a pycnometer is generally used and a hydrometer is applicable to liquid resid (ASTM D3142).

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CHAPTER

11

Origin and properties of oil shale

1. Introduction

By way of introduction, shale oil is produced from a special class of kerogen-containing rocks (sometime referred to as bituminous rocks but this term is more appropriate for application to tar sand formations – oil sand formations in Canada) bituminous rocks that has achieved some importance is the resource called *oil shale* which is an argillaceous, laminated sediment of generally high organic content that can be thermally decomposed to yield appreciable amounts of oil, commonly referred to as *shale oil*. Oil shale does not yield shale oil without the application of high temperatures and the ensuing thermal decomposition that is necessary to decompose the organic material (*kerogen*) in the shale. The kerogen produces a liquid product (shale oil) by thermal decomposition at high temperature (>500 °C, >930 °F). Shale oil also contains heteroatom species (nitrogen-, oxygen, and sulfur-containing organic compounds). The refined (hydrotreated) shale oil (Chapter 16), in which the heteroatom content has been reduced to acceptable levels, may also be referred to as *synthetic crude oil* that is sent to a refinery for further processing into various products. The raw oil shale can even be used directly as a fuel akin to a low-quality coal. Indeed, oil shale deposits have been exploited as such for several centuries and shale oil has been produced from oil shale since the 19th Century (Chapter 11).

Interest in producing an oil product from oil shale in order to produce a competitively priced synthetic fuel has been intensified since the oil embargo of the 1970s. The commercial interest, once very high in the decades of the 1970s and 1980s, diminished considerably substantially in 1990s due to the stable and low price of crude oil. The interest in oil shale for clean liquid fuel source is being revitalized in the 21st century, mainly triggered by the ever-increasing price of crude oil as well as the shortage of crude oil in the global market. However, it should be noted that oil shales have been used as liquid and/or solid fuels in certain areas for a long period of time and its research also has quite a long history. Mixed with a variety of sediments over a lengthy geological time period, shale forms a tough, dense rock ranging in color from light tan to black. Based on its apparent colors, shales are often called *black shale* or *brown shale* – the color is dependent upon the amount of organic material in the shale and the darker the shale the higher the organic content.

Oil shale is widely distributed throughout the world with known deposits in every continent. In this regard, oil shale is quite different from crude oil which is more concentrated in

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certain regions of the world. Oil Shale has been used in the past as a source of liquid fuel throughout the world including (alphabetically) Australia, Brazil, China, France, Scotland, Russia, South Africa, Sweden, and the United States. However, the oil shale industry has experienced several up-and-down trends, due to various reasons that include political, socio-economic, market, and environmental causes.

Even though no written history explicitly justifies or explains it, it is believed that oil shale has been used directly as solid fuels in various regions of the world, especially in the areas where rich shales were readily available from ground surfaces. An oil shale deposit at Autun, France, was exploited commercially as early as 1839. As early as the 1850s, shale oil was being touted as a replacement for the wood that America depended on for its energy. Logically, the oil shale industry in the United States was an important part of the economy of the United States prior to the discovery of crude oil in 1859. As Colonel Drake brought in his first oil well in Titusville, Pennsylvania, shale oil and its commercial production were gradually forgotten and virtually disappeared with the availability of vast supplies of inexpensive liquid fuel, i.e., crude oil. Similarly, Scotland had an operating shale industry from 1850 to 1864, when the low price of imported crude oil forced it to cease its operation. In Russia, oil shale from Estonia once supplied fuel gas for Leningrad.

In 1912, the President of the United States, by Executive Order, established the Naval Petroleum and Oil Shale Reserves. The Office of Fossil Energy of the US Department of Energy has been overseeing the strategic interests of the United States in oil shale since that time. Interest in oil shale revived briefly in the 1920s in the United States, as domestic reserves of crude oil were found to decline. But, discoveries of large quantities of oil deposits in Texas again set aside the hopes of an embryonic oil shale industry. A serious interest in oil shale commercialization and development revived yet another time, in the 1970s and 1980s, since the Arabian oil embargo gave a scare to the world energy supply and affected the world economy. In 1974, Unocal developed the Union B retort process and later in 1976 planned a commercial scale plant at Parachute Creek to be built when investment is believed to be economic. Many other companies initiated their own versions of oil shale development and they included Exxon, Shell, Dow Chemical, Sohio, TOSCO ARCO, AMOCO, Paraho, and others. Unocal began construction of Long Ridge 50,000 bbl./day plant based on their Union B retorting technology in 1981. AMOCO completed in-situ retorting demonstration of 1900 and 24,400 barrels of shale oil in 1980 and 1981, respectively.

In 1980, Exxon purchased ARCO Colony interest and began Colony II construction in 1981 aiming at 47,000 bbl/day production based on the TOSCO-II process. However, as the energy scenario changed, Exxon announced closure of Colony II in 1982 because of the low demand and high cost. Shell had continued their in-situ experiments at Red Pinnacle until 1983 when the Congress of the United States abolished the Synthetic Liquid Fuels Program after an $8 billion ($8,000, 000, 000) investment over a 40 year period.

Unocal operated the last large-scale experimental mining and retorting facility in western United States from 1980 until its shutdown of Long Ridge project in 1991. During this time, Unocal produced a total of 4.5 million barrels of shale oil from oil shale averaging 34 gallons of shale oil per ton of rock over the life of the project. Since the Unocal shutdown in 1992, there has been no oil shale production in the United States. In the 1980s and 1990s, the stable crude price again served as a principal reason for diminishing interest in the field of oil shale.

Shell continued some efforts involving in-situ heating technology at Mahogany property in Colorado. A notable experiment on in-situ heating was done in 1997. While the oil shale activities in the US have been all but halted, some significant efforts have been continued in Brazil and Estonia.

Once again, there is a sign of renewed interest in oil shale because of the volatility (pun not intended) and instability of crude oil prices including those for natural gas and crude oil products were experienced in most developed regions of the world at the onset of the new century. Examples of energy-related crises include, gasoline price surges in various regions of the United States in 2000 and 2001, California black-outs in 2001, high gasoline price due to short supply of crude oil in 2004, very high crude oil price in 2005 and 2006, and sharp increases in residential energy costs in 2000 and 2001 as well as in 2005 and 2006. However, the recent high interest in tight oil has cost oil shale some of its popularity and it remains to be seen if the desire for energy self-sufficiency or independence will again swing the balance in favor of the development of the oil shale formations in the western United States.

In summary, Market forces based on the supplies and demand will greatly affect the commercial development of oil shale. Besides competing with conventional crude oil and natural gas, shale oil will have to compete favorably with coal-derived fuels for similar markets. Nevertheless, oil-importing countries should be on guard — the liquid fuels derived from coal will be methanol, other products of indirect liquefaction, Fischer-Tropsch hydrocarbon derivatives, or oxygenated derivatives.

2. History of oil shale use

The use of oil shale can be traced back to ancient times and has a long history. In fact, humans have used oil shale as a fuel since prehistoric times, since it generally burns without any processing. It was also used for decorative purposes and construction. In Iron Age Britain (c.800 BCE to AD 100), oil shale was used to polish and form oil shale into ornaments. Oil shale was also used as a decorative material during the Greek period (c.800 to 400 BCE), the Roman period (c.700 BCE to AD 400), the Umayyad period (c.660 to AD 750), and the Abbasid period (c.750 to AD 1250) to decorate mosaics and floors of the palaces, churches and mosques. The use of oil shale was recorded in Austria in 1350. By the seventeenth century, oil shale was being exploited in several countries. As early as 1637, alum shale was roasted over wood fires to extract potassium aluminum sulfate, a salt used in tanning leather and for fixing colors in fabrics.

The first shale oil patent, British Crown Patent No. 330, was issued in 1694 to Martin Eele, Thomas Hancock and William Portlock, who (quote) after much paines and expences hath certainely found out a way to extract and make great quantityes of pitch, tarr and oyle out of a sort of rock (end quote). Oil shale utilization on an industrial scale did not, however, follow immediately. It was in 1838 was the first industrial oil shale plant put into service at Autun, France. Soon, plants in Scotland (1850), Australia (1865) and Brazil (1881) followed. In addition to oil shale as a source of refined shale oil products, it was soon discovered that torbanite, an especially organic-rich type of oil shale, was useful for increasing the luminosity of illuminating gas flames. This provided an important market for the early Scottish oil shale industry and later, as the Scottish torbanite deposits were depleted, for the early Australian, shale industry.

The modern use of oil shale to produce oil dates to Scotland in the 1850s. In 1847 Dr James Young prepared lighting oil, lubricating oil and wax from coal. Then he moved his operations to Edinburgh where oil shale deposits were found. In 1850 he patented the process of cracking the oil into its constituent parts. By the 1870s, Australian torbanite was being exported not only to Great Britain, but also to the United States, Italy, France and Holland. The invention of the Welsbach gas mantle and the advent of low-cost, high-quality kerosene from crude oil in the United States brought this period to an end. As the need for liquid transportation fuels increased, the Australian oil shale operations consolidated. Elsewhere, oil shale plants followed in New Zealand (1900), Switzerland (1915), Sweden (1921), Estonia (now USSR, 1921), Spain (1922), China (1929) and South Africa (1935).

The high point of this stage of oil shale development was reached during, or just after, World War II. However, the oil shale industry in Estonia and neighboring Leningrad Province still flourishes, most of the mined shale being burned directly in electric power generating plants with the remaining 10% or so retorted to provide chemical feedstock and smaller quantities of refined products. In 1926, Japan began the commercial production of shale oil from the large Chinese oil shale deposits at Fushun in Manchuria. Improved retorts were installed at this complex in 1941 to provide important supplies of liquid fuels for the Japanese forces during World War II. At Maoming, near Canton in southern China, a second oil shale project was developed. Shale oil production in the China peaked in 1975 and has since declined as emphasis has shifted to newly-discovered crude oil supplies.

Estonia first used oil shale as a low-grade fuel in 1838 after attempts to distill oil from the material failed. However it was not exploited until fuel shortages during World War I. Mining began in 1918 and has continued since, with the size of operation increasing with demand. After World War II, Estonian-produced oil shale gas was used in Leningrad and the cities in North Estonia as a substitute for natural gas. Two large oil shale-fired power stations were opened, a 1400 MW plant in 1965 and a 1600 MW plant in 1973. Oil shale production peaked in 1980 at 31.35 million tonnes (1 tonne = 2240 lbs). However, in 1981 the fourth reactor of the Sosnovy Bor nuclear power station opened in the nearby in Leningrad Oblast of Russia, reducing demand for Estonian shale. Production gradually decreased until 1995, since when production has increased again albeit only slightly. In 1999 the country used 11 million tonnes of shale in energy production of crude oil with plans to decrease the share of primary energy production from 62% to 47–50% in 2010.

Australia mined 4 million tonnes of oil shale between 1862 and 1952, when government support of mining ceased. More recently, from the 1970s on, oil companies have been exploring possible reserves. Since 1995 Southern Pacific Petroleum N.L. and Central Pacific Minerals N.L. (SPP/CPM) (at one time joined by the Canadian company Suncor) has been studying the Stuart Deposit near Gladstone, Queensland, which has a potential to produce 2.6 billion barrels of oil. From June 2001 through to March 2003, 703,000 barrels of oil, 62,860 barrels of low-density fuel oil, and 88,040 barrels of ultra-low sulfur naphtha were produced from the Gladstone area. Once heavily processed, the oil produced will be suitable for production of low-emission petrol. Southern Pacific Petroleum was placed in receivership in 2003, and by July 2004, Queensland Energy Resources announced an end to the Stuart Shale Oil Project in Australia.

Brazil has produced oil from oil shales since 1935. Small demonstration oil-production plants were built in the 1970s and 1980s, with small-scale production continuing at the time of writing. China has been mining oil shale to a limited degree since the 1920s near Fushun, but the low price of crude oil has kept production levels down. Russia has been mining its reserves on a small-scale basis since the 1930s.

Because of the abundance and geographic concentration of the known resource, oil shale has been recognized in the United States as a potentially valuable energy resource since as early as 1859, the same year Colonel Drake completed his first oil well in Titusville, Pennsylvania. Early products de-rived from shale oil included kerosene and lamp oil, paraffin, fuel oil, lubricating oil and grease, naphtha, illuminating gas, and ammonium sulfate fertilizer.

Oil distilled from shale was first burnt for horticultural purposes in the 19th Century, but it was not until the 1900s that larger investigations were made and the Office of Naval Petroleum and Oil Shale Reserves was established in 1912. The reserves were seen as a possible emergency source of fuel for the military, particularly the United States Navy, which had, at the beginning of the 20th century, converted its ships from coal to fuel oil, and the economy of the United States was transformed by gasoline-fueled automobiles and diesel fueled trucks and trains, concerns have been raised related to assuring adequate supplies of liquid fuels at affordable prices to meet the growing needs of the nation and its consumers.

The abundance of oil shale resources in the United States were initially eyed as a major source for these fuels. Numerous commercial entities sought to develop oil shale resources. The Mineral Leasing Act of 1920 made crude oil and oil shale resources on Federal lands available for development under the terms of federal mineral leases. Soon, however, discoveries of more economically producible and refinable liquid crude oil in commercial quantities caused interest in oil shale to decline.

Interest resumed after World War II, when military fuel demand and domestic fuel rationing and rising fuel prices made the economic and strategic importance of the oil shale resource more apparent (DOE, 2004a, 2004b; 2004c). After the war, the booming post-war economy drove demand for fuels ever higher. Public and private research and development efforts were commenced, including the 1946 United States Bureau of Mines Anvil Point, Colorado oil shale demonstration project. Significant investments were made to define and develop the resource and to develop commercially viable technologies and processes to mine, produce, retort, and upgrade oil shale into viable refinery feedstocks and by-products. Once again, however, major crude oil discoveries in the lower-48 United States, off-shore, and in Alaska, as well as other parts of the world reduced the foreseeable need for shale oil and interest and associated activities again diminished. Lower-48 United States crude oil reserves peaked in 1959 and lower-48 production peaked in 1970.

By 1970, oil discoveries were slowing, demand was rising, and crude oil imports, largely from Middle Eastern states, were rising to meet demand. Global oil prices, while still relatively low, were also rising reflecting the changing market conditions. On-going oil shale research and testing projects were re-energized and new projects were envisioned by numerous energy companies seeking alternative fuel feedstocks. These efforts were significantly amplified by the impacts of the 1973 Arab Oil Embargo which demonstrated the vulnerability of the United States to crude oil import supply disruptions, and were underscored by a new supply disruption associated with the 1979 National Revolution in Iran and the attack on the Embassy of the United States.

By 1982, however, technology advances and new discoveries of offshore oil resources in the North Sea and elsewhere provided new and diverse sources for United States oil imports, and dampened global energy prices. Global political shifts promised to open previously restricted provinces to oil and gas exploration, and led economists and other experts to predict a long future of relatively low and stable oil prices. Despite significant investments by United States energy companies, numerous variations and advances in mining, restoration, retorting, and in-situ processes, the costs of oil shale production relative to foreseeable oil prices, made continuation of most commercial efforts impractical.

In summary, the near-term future of oil shale is uncertain. Very clearly, this future will be influenced by international crude oil prices and supplies. Indeed, the rise of interest in oil shale during the late 1970s was due largely to the high prices and tight supply of crude oil. With the decline of crude prices and growth of a crude oil surplus, interest in oil shale and other synfuels waned. How long this will continue is difficult to predict. At present, commercial oil shale development is hard to foresee, unless impetus is provided by political or security concerns. Several projects failed for technical and design reasons. Federal research and development, leasing, and other activities were significantly curtailed, and most commercial projects were abandoned. The collapse of world oil prices in 1984 seemed to seal the fate of oil shale as a contributory part of the energy strategy of the United States.

However, the current lull in development activity offers a golden opportunity for scientific research to attack the many chemical, physical and material problems that were uncovered or brought into sharper focus during the late period of activity.

3. Origin

A shale formation is typically composed of clay minerals and quartz grain, and is typically gray. Addition of variable amounts of minor constituents alters the color of the rock. Black shale results from the presence of greater than one percent carbonaceous material and indicates a reducing environment. Red, brown and green colors are indicative of ferric oxide (Fe_2O_3, hematite − red), iron hydroxide (goethite − brown and limonite − yellow), or micaceous minerals (chlorite, biotite and illite − green) (Blatt and Tracy, 1996).

Clay minerals (represented predominantly by kaolinite, montmorillonite, and illite) are the major constituent of shales and other mudrocks. Clay minerals of Late Tertiary mudstones are expandable smectite minerals whereas in older rocks especially in mid-Paleozoic to early-Paleozoic shales, illite minerals predominate. The transformation of smectite to illite produces silica, sodium, calcium, magnesium, iron and water.

In the process (compaction) in the rock cycle which forms shale, the fine particles that compose shale can remain suspended in water long after the larger particles of sand have deposited. Shale formations are typically deposited in very slow moving water and are often found in lakes and lagoons, in river deltas, on flood plains, and offshore from beach sands. They can also be deposited in sedimentary basins and on the continental shelf in relatively deep, quiet water at which time organic material may be co-deposited thereby giving rise to an organic component that eventually becomes kerogen.

Black shale formations are dark, as a result of being especially rich in unoxidized carbon (organic material) and were commonly deposited in an anoxic (reducing environment) such as in stagnant water columns. Some black shale formations contain abundant heavy metals such as molybdenum, uranium, vanadium, and zinc. The enriched values are of controversial origin, having been alternatively attributed to input from hydrothermal fluids during or after sedimentation or to slow accumulation from sea water over long periods of sedimentation (Vine and Tourtelot, 1970).

Oil shale represents a large and mostly untapped resource that could assist in the future demand for hydrocarbon fuels. Like tar sand (*oil sand* in Canada) and coal, oil shale is considered unconventional because oil cannot be produced directly from the resource by sinking a well and pumping. Oil has to be produced thermally from the shale. The organic material contained in the shale is called *kerogen*, a solid material intimately bound within the mineral matrix (Baughman, 1978; Allred, 1982; Scouten, 1990; Lee, 1991; Speight, 2013, 2014, 2019b).

Oil shale is distributed widely throughout the world with known deposits in every continent. Oil shale ranging from Cambrian to Tertiary in age occurs in many parts of the world (Table 11.1). Deposits range from small occurrences of little or no economic value to those of enormous size that occupy thousands of square miles and contain many billions of barrels of potentially extractable shale oil. However, crude oil and crude oil-based products are cheaper to produce than shale oil and shale oil-derived products because of the additional costs of mining and extracting the energy from oil shale. Because of these higher costs, only a few deposits of oil shale are currently being exploited in China, Brazil, and Estonia. However, with the continuing decline of crude oil supplies, accompanied by increasing costs of crude oil-based products, oil shale presents opportunities for supplying some of the fossil energy needs of the world in the future (Culbertson and Pitman, 1973; Bartis et al., 2005; Andrews, 2006).

Oil shale is not generally regarded as true shale by geologists nor does it contain appreciable quantities of free oil (Scouten, 1990; Speight, 2019b). The fracture resistance of all oil shales varies with the organic content of the individual lamina and fractures preferentially initiate and propagate along the leaner horizontal laminas of the depositional bed.

TABLE 11.1 Estimate of Oil Shale Reserves (Tonnes × 10^6).

Region	Shale reserves	Kerogen reserves	Kerogen in place
Africa	12,373	500	5,900
Asia	20,570	1,100	–
Australia	32,400	1,700	37,000
Europe	54,180	600	12,000
Middle East	35,360	4,600	24,000
North America	3,340,000	80,000	140,000
South America	–	400	10,000

Notes.
1 tonne = 2204 lbs.
To convert tonnes to barrels, multiply by 7 indicating approximately 620 billion barrels (620 × 10^9 bbls) of known recoverable kerogen, which has been estimated to be capable of producing 2600 billion barrels (2600 × 10^9 bbls or 2.6 × 10^{12} bbls) of shale oil. This compares with 1200 billion barrels of known worldwide petroleum reserves *(Source: BP Statistical Review of World Energy, 2006).*
Source: World Energy Council, WEC Survey of Energy Resources.

Oil shale was deposited in a wide variety of environments including freshwater to saline ponds and lakes, epicontinental marine basins, and related subtidal shelves as well as shallow ponds or lakes associated with coal-forming peat in limnic and coastal swamp depositional environments. Most oil shale contains organic matter derived from varied types of marine and lacustrine algae, with some debris of land plants, depending upon the depositional environment and sediment sources but, most important, oil shale deposits differ by, for example, genesis, composition, calorific value and oil yield. There is currently no comprehensive overview of oil shale resources and their distribution around the world, so it is not possible to reach detailed conclusions that apply to oil shales as a whole. For example, while the organic matter content of oil shales can be as high as 50% in some very high grade deposits such as the kukersite deposits in Estonian which, in most cases it varies between 5% and 25%. Because of that the heating value of oil shale is highly variable, but in most cases is substantially less than 3000 kcal/kg. Compared to other traditional solid fuels, the heating value of oil shale is limited. In the best cases, it is comparable to that of brown coal or average forest residues, but less than half of that of average bituminous coal. This give rise to a variety of different oil shale types which are grouped, using the mode of deposition as the discriminatory criterion, into the three primary divisions of terrestrial, lacustrine and marine oil shales (Table 11.2). The type and abundance of liptinite is then used to subdivide these three groups into cannel coal, torbanite, lamosite (further subdivided into Rundle-type lamosite and Green River-type lamosite), marinite, tasmanite and kukersite (Hutton, 1987, 1991). Thus, it is not surprising, therefore, that oil shale exhibit a wide range in organic and mineral composition (Scouten, 1990; Mason, 2006; Ots, 2007; Wang et al., 2009).

TABLE 11.2 Various names for organic-rich sediments.

Organic-rich sedimentary rocks		
Humic coal		
Tar sand oil sand)		
Oil shale		
	Terrestrial oil shale	
		Cannel coal
	Lacustrine oil shale	
		Lamosite
		Torbanite
	Marine oil shale	
		Kukersite
		Tasmanite
		Mannite

Organic matter in oil shale is a complex mixture and is derived from the carbon-containing remains of algae, spores, pollen, plant cuticle and corky fragments of herbaceous and woody plants, plant resins, pant waxes, and other cellular remains of lacustrine, marine, and land plants (Scouten, 1990; Dyni, 2003, 2006). These materials are composed chiefly of carbon, hydrogen, oxygen, nitrogen, and sulfur. Generally, the organic matter is unstructured and is best described as amorphous (*bituminite*) – the origin of which has not been conclusively identified but is theorized to be a mixture of degraded algal or bacterial remains. Other carbon-containing materials such as phosphate and carbonate minerals may also be present which, although of organic origin, are excluded from the definition of organic matter in oil shale and are considered to be part of the mineral matrix of the oil shale.

Oil shale has often been called *high-mineral coal* but nothing can be further from reality. Maturation pathways for coal and kerogen are different and, in fact, the precursors of the organic matter in oil shale and coal also differ (Tissot and Welte, 1978; Durand, 1980; Scouten, 1990; Hunt, 1996; Speight, 2013b). Furthermore, the origin of some of the organic matter in oil shale is obscure because of the lack of recognizable biologic structures that would help identify the precursor organisms, unlike the recognizable biological structures in coal (Speight, 2013b). Such materials may be of (i) bacterial origin, or (ii) the product of bacterial degradation of algae, or (iii) other organic matter, or (iv) all of the above.

In terms of the origin of oil shale, there are distinct differences between the origin of oil shale and the origin of crude oil. In the creation of crude oil, the source rock (sediments containing organic detritus) are buried by natural geological processes and, over geologic time, th organic material is converted to gases and liquids that can migrate through cracks and pores in the rocks until it reaches the surface or is trapped by a tight overhead formation. The result is a natural gas and/or a crude oil reservoir. – both types of reservoir can exist as independent reservoirs or as a reservoir containing both natural gas and crude oil (Speight, 2014, 2019a).

The oil shale rocks containing organic carbon rich sediments, were deposited with inorganic matter, when the rocks were formed by microscopic organisms and algae sinking to the bottom of relatively stagnant bodies of water, along with very fine mineral particles. These types of deposits are still in the process of forming in deep waters in the Gulf of Mexico and other water bodies which have a poorly mixed, low oxygen (anaerobic), and low temperature environments, where decomposition is slowed and the recycle of carbon into the active carbon cycle is prevented. Carbon in these source rocks can only be naturally released by: a) weathering, where tectonic forces push the rocks to the land surface, where rainfall, organisms or direct oxidation can return the carbon to active circulation over billions of years (slow carbon cycle); b) thermal conversion to gaseous or liquid hydrocarbon derivatives (natural gas or crude oil) by heat and pressure from deep burial, through subduction into the earth (millions of years); c) biogenesis, or biological conversion to natural gas through slow in-situ biological activity after burial.

The kerogen in oil shales is an organic material, whose properties will vary depending on where the original organic material was deposited, how the resulting oil shales formed and what geologic temperatures, pressures and other conditions they were exposed to over geologic time. The type of kerogen, and the relative composition of the kerogen in terms of hydrogen, carbon and oxygen content, will impact the type of crude oil which can be produced from it, either naturally or through processing the oil shale (Table 11.3).

TABLE 11.3 General description of the different types of kerogen based on source material.

Kerogen type	Source material, composition, natural hydrocarbons formed	General environment of deposition
I	Mainly algae – rich in hydrogen, low in oxygen	Lacustrine (lake) setting
II	Mainly plankton, some contribution from algae – rich in hydrogen, low in carbon	Marine setting
III	Mainly higher plants – lower hydrogen, higher oxygen; gas prone	Terrestrial setting
IV	May be matured I, II, and III; high carbon, hydrogen poor	Varied settings

The processes that convert the organic precursors to conventional crude oil (and natural gas) are referred to as (i) diagenesis, (ii) catagenesis, and (iii) metagenesis (Peters and Cassa, 1994; Speight, 2014).

Diagenesis refers to all chemical, biological, and physical changes to the organic matter during and after deposition of sediments but prior to reaching burial temperatures greater than approximately 60–80 °C (140–176 °F). The quantity and quality of organic matter preserved and modified during diagenesis in a sediment ultimately determine the potential of the rock to produced oil and/or gas.

Catagenesis occurs at temperatures between 50 and 150 °C (122–300 °F) where chemical bonds are broken and crude oil is generated in what is usually called an *oil window*. Further temperature increases and secondary "cracking" of the oil will produce wet gas and condensates. The process can be divided into the *oil zone*, which corresponds to the *oil window*, where liquid oil generation is accompanied by gas formation, and the more mature *wet gas zone*, where lower-boiling hydrocarbon derivatives are generated through cracking and their proportion increases rapidly (Peters and Cassa, 1994). *Wet gas* (<98% v/v methane) contains methane and significant amounts of ethane, propane, and higher-boiling hydrocarbon derivatives. The *gas window* corresponds to the interval from the top of the wet gas zone to the base of the dry gas zone.

Metagenesis the process in which further heating to 150–200 °C (300–390 °F) which converts any remaining kerogen into a solid carbon residue and dry methane which may also contain carbon dioxide (CO_2), nitrogen (N_2) and hydrogen sulphide (H_2S). This also corresponds to the *dry gas zone* where dry gas is generated which consists of 98% v/v. Dry gas is also found as deposits of bacteriogenic (microbial) gas generated during diagenesis of organic matter by methanogenic bacteria under anoxic conditions – i.e. conditions where there are depleted levels of oxygen.

The generation of natural gas and crude oil through natural processes takes a considerable length of time, and even in rocks at temperatures hot enough for conversion to occur, only a small percentage of the kerogen will be converted, and it will still be difficult to generate enough permeability (through fracturing) for the products to flow into a trap or well. Artificially enhancing the maturation process of the kerogen, either in-situ or ex-situ after mining, can accelerate and enhance the natural process and generate higher yields of distillable oil from a given volume of oil shale. However, artificial enhancement of the maturation process by increasing the temperature can also change the chemistry of the process after which the data interpretation must be questionable and extremely speculative.

As in nature, processing the kerogen to get liquid, gaseous and solid fuels is accomplished mainly by heating the oil shale. The quality and quantity of produced fuels depend not only on the shale properties, but also on the retorting (sometimes referred to as destructive distillation or pyrolysis) process used. Each shale in a given process, will produce different products and volumes, depending on the type of kerogen it contains, its composition and degree of natural maturation which has already occurred. Numerous retorting processes have been developed, categorized into general types based on the method of exposing the raw shale to retorting temperatures.

Another term that is worthy of consideration at this point is *thermal maturity* refers to the extent of temperature-drive and time-drive reactions that convert sedimentary organic matter (source rock) to oil, wet gas, and finally to dry gas and an ill-defined product known as pyrobitumen (a type of solid, amorphous organic matter that is insoluble in organic solvents). Thermally *immature* source rocks may have been affected by diagenesis but without a pronounced effect of temperature and are source rocks in which microbial gas is produced. Thermally *mature* organic matter was in the *oil window* and has been affected by thermal processes covering the temperature range that generates crude oi at temperatures on the order of 60−150 °C (140−300 °F). Thermally *postmature* organic matter is in the wet and dry gas zones (gas window) and has been heated to such high temperatures (approximately 150−200 °C, 300 to 390 °F) that it has been reduced to a hydrogen-poor residue capable of generating only small amounts of hydrocarbon gases. It is generally accepted (Peters and Cassa, 1994) that crude oil is unstable at higher temperatures and progressively decomposes to gases and *pyrobitumen*, a thermally-altered, solidified bitumen.

Sedimentary rocks that are, or may become, or have been able to generate crude oil are *source rocks* and an *effective source rock* is generating or has generated and expelled crude oil. This definition excludes the requirement that the accumulations should be commercially significant because (i) the terms *significant* and *commercial* are difficult to quantify and change depending on economic factors, and (ii) oil-source rock relationships are never proven because some level of uncertainty always exists depending on the available data. Nonetheless, effective source rocks satisfy three geochemical requirements that are more easily defined by (i) the quantity, or amount of organic matter, (ii) the quality, or type of organic matter, and (iii) the thermal maturity, or extent of burial heating.

A *potential source rock* contains adequate quantities of organic matter to generate crude oil, but only becomes an effective source rock when it generates bacterial gas or oil at low temperatures or it reaches the proper level of thermal maturity to generate crude oil. An *active source rock* is generating and expelling crude oil at the critical moment, most commonly because it is within the oil window (Peters and Cassa, 1994).

Active source rocks include rocks or sediments that are generating natural gas and crude oil without thermal maturation. For example, a peat bog might produce microbially generated gas (*marsh gas* consisting mostly of bacteriogenic methane) without significant heating due to shallow burial By this definition, trapped methane and nearby unconsolidated swamp muds from which it was derived represent a crude oil system. On the other hand, an *inactive source rock* has stopped generating crude oil, although it still shows crude oil potential. For example, an inactive source rock might be uplifted to a position where temperatures are insufficient to allow further generation of crude oil. A *spent oil source rock* has reached the postmature stage of maturity and is incapable of further oil generation, but may still be capable of generating wet and dry gas.

Oil shale was deposited in a wide variety of environments including freshwater to saline ponds and lakes, epicontinental marine basins and related subtidal shelves. They were also deposited in shallow ponds or lakes associated with coal-forming peat in limnic and coastal swamp depositional environments. It is not surprising, therefore, that oil shale exhibit a wide range in organic and mineral composition. Most oil shale contains organic matter derived from varied types of marine and lacustrine algae, with some debris of land plants, depending upon the depositional environment and sediment sources.

Oil shale does not undergo that natural maturation process but produces the material that has come to be known as kerogen (Scouten, 1990). In fact, there are indications that kerogen, being different from crude oil, may be a by-product of the maturation process. The kerogen residue that remains in oil shale is formed during maturation and is then rejected from the organic matrix because of its insolubility and relative unreactivity under the maturation conditions (Speight, 2014). Furthermore, the fact that kerogen, under the conditions imposed upon it in the laboratory by high-temperature pyrolysis, forms hydrocarbon products does not guarantee that the kerogen of oil shale is a precursor to crude oil.

Oil shale ranging from Cambrian to Tertiary in age occurs in many parts of the world (Chapter 12). Deposits range from small occurrences of little or no economic value to those of enormous size that occupy thousands of square miles and contain many billions of barrels of potentially extractable shale oil. Total world resources of oil shale are conservatively estimated at 2.6 trillion barrels (2.6×10^{12} bbls) of potential shale oil (Table 11.1). The continuing decline of crude oil supplies, accompanied by increasing costs of crude oil-based products, presents opportunities for supplying some of the fossil energy needs of the world from oil shale in the years ahead.

Furthermore, oil shale does not undergo the maturation process that is often conveniently represented for crude oil and/or coal but produces the material that has come to be known as *kerogen* (Scouten, 1990). In fact, there are indications that kerogen may be a by-product of the maturation process. The kerogen residue that remains in oil shale is formed during maturation and is then rejected from the organic matrix because of its insolubility and relative unreactivity under the maturation conditions (Speight, 2014). Furthermore, the fact that kerogen, under the high-temperature pyrolysis conditions imposed upon it in the laboratory, forms hydrocarbon distillates (albeit with relatively high amounts of nitrogen) does not guarantee that the kerogen of oil shale is a precursor to crude oil.

The thermal maturity of oil shale refers to the degree to which the organic matter has been altered by geothermal heating. If oil shale is heated to a high enough temperature – the actual historical temperature to which the shale has been heated is not known with any degree of accuracy and is typically speculative – as may be the case if the oil shale were deeply buried, the organic matter *may* thermally decompose to form liquids and gas. Under such circumstances, there is much unfounded speculation (other than high-temperature laboratory experiments) that oil shale sediments can be the source rocks for natural gas and crude oil.

The degree of thermal maturity of an oil shale formation can be determined in the laboratory by several methods. One technique is to observe the changes in color of the organic matter in samples collected from varied depths in a borehole. Assuming that the organic matter is subjected to geothermal heating as a function of depth, the colors of certain types of organic matter change from lighter to darker colors which can be noted by a petrographer and measured using photometric techniques.

Geothermal maturity of organic matter in oil shale is also determined by the reflectance of vitrinite (a common constituent of coal derived from vascular land plants), if present in the rock. Vitrinite reflectance is commonly used as an aid in crude oil exploration to determine the degree of geothermal alteration of petroleum source rocks in a sedimentary basin. A scale of vitrinite reflectance has been developed that indicates when the organic matter in a sedimentary rock has reached temperatures high enough to generate oil and gas. However, this method can pose a problem with respect to oil shale, because the reflectance of vitrinite may be depressed by the presence of lipid-rich organic matter. Vitrinite may be difficult to recognize in oil shale because it resembles other organic material of algal origin and may not have the same reflectance response as vitrinite, thereby leading to erroneous conclusions. For this reason, it may be necessary to measure vitrinite reflectance from laterally equivalent vitrinite-bearing rocks that lack the algal material.

In areas where the rocks have been subjected to complex folding and faulting or have been intruded by igneous rocks, the geothermal maturity of the oil shale should be evaluated for proper determination of the economic potential of the deposit.

Furthermore, as stated above, the fact that the high-temperature thermal decomposition of kerogen (in the laboratory) gives crude oil-like material is no guarantee that kerogen is or ever was a precursor to crude oil. The implied role of kerogen in crude oil formation is essentially that − implied but without conclusive experimental foundation. However, caution is advised in choosing the correct definition of kerogen since there is the distinct possibility that kerogen, far from being a precursor to crude oil, is one of the by-products of the crude oil generation and maturation processes and may not be a direct precursor to crude oil.

Crude oil precursors and crude oil itself is indeed subject to elevated temperatures (the *geothermal gradient*) in the subterranean formations due to the *geothermal gradient*. Although the geothermal gradient varies from place to place, it is generally on the order of 25−30 °C/km (15 °F/1000 ft or 120 °C/1000 ft, i.e. 0.015 °C per foot of depth or 0.012 °C per foot of depth). This leaves serious question related to whether or not the material has been subjected to temperatures in excess of 250 °C (>480 °F).

Such experimental work is interesting insofar as it shows similar molecular moieties in kerogen and crude oil (thereby confirming similar origins for kerogen and crude oil). However, the absence of geologic time in the laboratory is not a reason to increase the temperature and it must be remembered that application of high temperatures (>250 °C, <480 °F) to a reaction not only increases the rate of reaction (thereby making up for the lack of geologic time) but can also change the *nature* and the *chemistry* of a reaction. In such a case, the geochemistry is altered. Furthermore, introduction of a pseudo-activation energy in which the activation energy of the kerogen conversion reactions are reduced leave much to be desired because of the assumption required to develop this pseudo-activation energy equation(s). In fact, not only will the oil window (the oil-producing phase) vary from kerogen-type to kerogen-type it is not valid to use a fixed set of kinetic parameters within each of these groups.

It is claimed that the degree of thermal maturity of an oil shale can be determined in the laboratory by any one of several methods. One method is to observe the changes in color of the organic matter in samples collected from varied depths − assuming that the organic matter is subjected to geothermal heating (the temperature being a function of depth), the color of the organic matter might be expected to change from a lighter color (at relatively shallow depths) to a darker color (at relatively shallow depths). Then another unknown − the issue of shifting of the sedimentary strata − comes into play.

Suffice it to state that the role played by kerogen in the crude oil maturation process is not fully understood (Tissot and Welte, 1978; Durand, 1980; Hunt, 1996; Scouten, 1990; Speight, 2014). What obviously needs to be addressed more fully in terms of kerogen participation in crude oil generation is the potential to produce crude oil constituents from kerogen by low-temperature processes rather than by processes that involve the use of temperatures in excess of 250 °C (>480 °F) (Burnham and McConaghy, 2006; Speight, 2014).

If such geochemical studies are to be pursued, a thorough investigation is needed to determine the potential for such high temperatures being present during the main phase, or even various phases, of crude oil generation on order to give stronger indications that kerogen is a precursor to crude oil (Speight, 2014). Much of the work performed on oil shale has referenced the ol shale from the Green River formation in the western United States. Thus, unless otherwise stated, the shale referenced in the following text is the Green river shale.

The oil shale deposits found in the Green River Formation in the states of Colorado, Wyoming, and Utah are the largest in terms of the size of deposit and most studied in the United States. It has been estimated that these formations are capable of yield as much as 2 trillion (2,000, 000, 000,000) barrels of shale oil − recall that oil shale does not contain oil but contain kerogen which can be thermally decomposed to an oil product. Due to the vast resources and the high oil content of shales, this region has long been the most attractive to oil shale industries. The Devonian-Mississippian Eastern black shale deposits are widely distributed between Appalachian and Rocky Mountains. Even though these oil shale formations also represent a vast resource of fossil fuel, they are generally lower in grade (oil content per unit mass of shale rock) than Green River Formation oil shale (Lee, 1991).

4. Oil shale types

Mixed with a variety of sediments over a lengthy geological time period, shale forms a tough, dense rock ranging in color from light tan to black. Based on its apparent colors, shale may be referred to as *black shale* or *brown shale*. Oil shale has also been given various names in different regions (Table 11.2) (Smith and Jensen, 2007). For example, the Ute Indians, on observing outcroppings burst into flames after being hit by lightning, referred to it as *the rock that burns*.

Thus it is not surprising that definitions of the types of oil shale can be varied and confusing. It is necessary to qualify the source of the definition and the type of shale that fits within that particular definition. For example, one definition is based on the mineral content of which three categories can recognized namely: (i) carbonate-rich oil shales, which contain a high proportion of carbonate minerals (such as calcite and dolomite) and which usually have the organic-rich layers sandwiched between carbonate-rich layers − these shales are hard formations that are resistant to weathering and are difficult to process using mining (ex-situ), (ii) siliceous oil shales which are usually dark brown or black shales and are deficient in carbonate minerals but plentiful in siliceous minerals (such as quartz, feldspar, clay, chert and opal) – these shales are not as hard and weather-resistant as the carbonate shales and may be better suited for extraction via mining (ex-situ) methods, and (iii) cannel oil shales, which are typically usually dark brown or black shales and consist of organic matter that completely encloses other mineral grains – these shales are suitable for extraction via mining (ex-situ).

However, minerals content aside, it is more common to define oil shale on the basis of origin and formation of the shale as well as the character of the organic content of the shale. More specifically, the nomenclature is related to whether or not the shale is of (i) *terrestrial* origin, (ii) *marine* origin, or (iii) *lacustrine* origin (Hutton, 1987, 1991). This classification reflects differences in the composition of the organic matter and of the distillable products that can be produced from the shale. This classification also reflects the relationship between the organic matter found in sediment and the environment in which the organic precursors were deposited.

4.1 Terrestrial oil shale

Terrestrial oil shales include those composed of lipid-rich organic matter such as resin spores, waxy cuticles, and corky tissue of roots, and stems of vascular terrestrial plants commonly found in coal-forming swamps and bogs. Lacustrine oil shales include lipid-rich organic matter derived from algae that lived in freshwater, brackish, or saline lakes. Marine oil shales are composed of lipid-rich organic matter derived from marine algae, acritarchs (unicellular organisms of questionable origin), and marine dinoflagellates. The precursors to terrestrial oil shale (sometimes referred to as *cannel coal*) were deposited in stagnant, oxygen-depleted waters on land (such as coal-forming swamps and bogs).

Cannel coal is brown to black oil shale composed of resins, spores, waxes, and cutinaceous and corky materials derived from terrestrial vascular plants together with varied amounts of vitrinite and inertinite. Cannel coals originate in oxygen-deficient ponds or shallow lakes in peat-forming swamps and bogs. This type of shale is usually rich in oil-generating lipid-rich organic matter derived from plant resins, pollen, spores, plant waxes and the corky tissues of vascular plants. The individual deposits usually are small in size, but they can be of a very high grade.

The latter also holds for lacustrine oil shales. This group of oil shales was deposited in freshwater, brackish or saline lakes. The size of the organic-rich deposits can be small, or they can occur over tens of thousands of square miles as is the case for the Green River Formation in Colorado, Utah and Wyoming. The main oil-generating organic compounds found in these deposits are derived from algae and/or bacteria. In addition, variable amounts of higher plant remains can be present as well.

4.2 Lacustrine oil shale

Lacustrine oil shales (lake-bottom-deposited shales) include lipid-rich organic matter derived from algae that lived in freshwater, brackish, or saline lakes.

The lacustrine oil shales of the Green River formation which were discussed above are among the most extensively studied of sediments. However, their strongly basic depositional environment is certainly unusual, if not unique. Therefore, it is useful to discuss the characteristics of the organic material in other lacustrine shales.

Lacustrine sequences from the Permian oil shales of Autun (France) and the Devonian bituminous flagstones of Caithness (Scotland) exhibited several series of biomarkers were prominent in extracts from these shales: hopanes, steranes and carotenoids. Algal remains were abundant in both shales. Blue-green algae, similar to those that contributed largely to the Green River oil shale kerogen, were found in the Devonian shale, for which a stratified lake environment similar to Green River has been proposed (Donovan and Scott, 1980).

In contrast, *Botryococcus* remains were found in the Permian Autun shale and are presumed to be the major source of organic matter, except for one sample. No *Botryococcus* remains were found in this sample and the oil produced by its retorting was nearly devoid of the straight-chain alkanes and 1-alkenes which are prominent in oils from *Botryococcus-derived* shales. Evidently, some as yet unidentified algae contributed to the organic matter in this stratum. Biodegradation cannot be ruled *out* but seems unlikely due to the lack of prominent iso- and ante-iso-alkanes. Straight-chain alkanes and 1-alkenes were also prominent in gas chromatograms of the retorted oils from the Devonian shale. However, in this case a pronounced hump, which usually indicates polycyclic derivatives, was also prominent. Both extracts and oil from the Devonian shale were found to be rich in steranes and tricyclic compounds. Di - and triterpenoids have been suggested as precursors for the di- and tricyclic compounds found in many oil shales. Rock-eval pyrolysis results indicate that these shales have high hydrogen indices; the kerogen are all type I or type II, with one of the Devonian samples being clearly type I.

Lamosite is pale, gray-brown and dark gray to black oil shale in which the chief organic constituent is lamalginite derived from lacustrine planktonic algae. Other minor components include vitrinite, inertinite, telalginite, and bitumen. The Green River oil-shale deposits in western United States and a number of the Tertiary lacustrine deposits in eastern Queensland, Australia, are lamosites. Other major lacustrine oil shale deposits include the Triassic shales of the Stanleyville Basin in Zaire and the Albert shales of New Brunswick, Canada (Mississippian).

Torbanite, named after Torbane Hill in Scotland, is a black oil shale whose organic matter is composed mainly of telalginite found in fresh-water to brackish-water lakes. Torbanite that originated from a morphologically recognizable colonial alga of terrestrial and fresh-water origin. The deposits are lenticular and associated with Permian coals and are commonly small, but can be extremely high grade.

By way of further definition, telalginite is a structured organic matter (alginite) in sapropel that is composed of large discretely occurring colonial or thick-walled unicellular algae which fluoresce brightly in shades of yellow under blue/ultraviolet light (Dyni, 2006). Lamalginite is a similar structured organic material (alginate) in sapropel that is composed of thin-walled colonial or unicellular algae that occurs as distinct laminae, cryptically interbedded with mineral matter. It displays few or no recognizable biologic structures. Lamalginite also fluoresces brightly in shades of yellow under blue/ultraviolet light (Dyni, 2006). Finally, sapropel is a term used in marine geology to describe dark-colored sediments that are rich in organic matter.

4.3 Marine oil shale

Marine oil shales (marine-bottom-deposited shales) are composed of lipid-rich organic matter derived from marine algae, acritarchs (unicellular organisms of questionable origin), and marine dinoflagellates.

Marine oil shales are usually associated with one of two settings (Fig. 11.1). The anoxic silled basin shown (Fig. 11.1A) can occur in the shallow water of a continental shelf. High phytoplankton growth rates near the surface will give a high deposition rate. The sill shields the trough from the circulation of oxygen-laden water. Under these conditions, the decomposition of organic sedimentary matter will rapidly deplete oxygen within the confines of the basin, thereby providing the strongly anoxic (reducing, low-Eh) environment that is needed for efficient preservation.

The anoxic zone in an upwelling area (Fig. 11.1B) arises from circulation of an open-ocean current over cold, oxygen -depleted bottom layer. Mixing of nutrient -rich current, such as the Gulf Stream, into the carbon dioxide-rich and light-rich eutrophic zone gives an environment capable of sustaining very high organic production. Such environments occur today along the west coasts of Africa and the Americas, where good fishing is found along with the potential for organic-rich sediments (Debyser and Deroo, 1969).

Information related to the nature of organic matter in marine environments has resulted from studies of recent deposits and the contemporary oceans (Bader et al., 1960; Bordovskiy, 1965). Only a small part of primary production in the oceans reaches the bottom. Of an estimated annual production of 9×10^{19} tons of dry matter, it has also been estimated that approximately 2% reaches the floor in shallows and only approximately 0.02% in the open sea. The major part of marine primary production is consumed by predators; most of the rest by microbes. The principal marine microbial scavengers are bacteria that live free in the water or are attached to organic particles. In ocean water, organics occur in solution, in

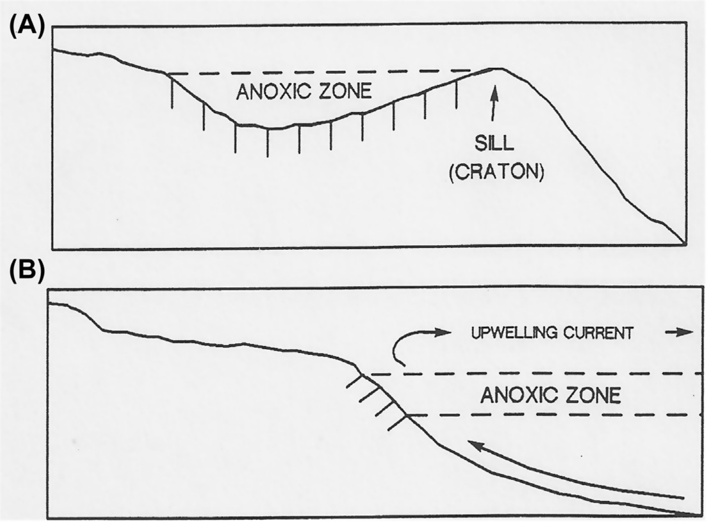

FIGURE 11.1 Schematic of an anoxic-silled basin (Scouten, 1990).

colloidal suspension, and as particulate matter comprising bodies and body fragments of living and dead organisms. Except in regions of a seaweed or plankton "bloom," the dissolved organics usually predominate. As a result, marine bacteria are most abundant only in the very upper part of the water column and in the organic detritus at the very bottom. Even in the oceans, the adsorption of organics onto inorganic detritus, such as the silica parts of diatoms, plays an important part in sedimentation.

After the organic sediment reaches the bottom, reworking begins. Bottom-dwelling (benthic) organisms feed on both the sediment and the dissolved organics and, in turn, are fed on by predators (e.g., crustaceans). In this sphere, the benthic bacteria are largely responsible for the decomposition of organics and the synthesis of new organics through enzymatic transformations. Approximately 60%–70% of the sedimentary organic carbon is typically liberated as carbon dioxide during this reworking, while most of the rest is converted into new compounds, resulting in an extremely complex mixture.

The various organic compound classes in oil shales include carbohydrates, lignins, humates and humic acids, lipid-derived waxes and the saturated and polyene acids in algal lipids which can serve as precursors of these waxes, and biological pigments and their derivatives (e. g., carotenoids, porphyrins). Only the latter three were judged to have sufficient inertness to be major contributors to oil shale kerogen (Cane, 1976).

Proteins, carbohydrates, and humates in marine sediments occur in marine sediments. Protein-derived materials included both original and altered proteins and their decomposition products (amines, amino. acids, amino-complexes). Carbohydrates are rapidly hydrolyzed and generally not important in oil shales. Humates can be important, even in marine shales, when deposited near shore, though obviously humic material has been found in marine sediments that were deposited far from land. It is possible that some humic material may be derived from proteins and/or carbohydrates, perhaps when these materials are adsorbed on inorganic particulates (e. g., clays and volcanic ash) in a moderately oxidizing environment.

Lipids are produced by phytoplankton and also synthesized from carbohydrates by microbial activity (Bordovskiy, 1965). With respect to oil shales, the polyene fatty acids are especially interesting. It is well known that adverse conditions can lead to very high lipid production by algae. At low temperature and with limited oxygen, for example, *ChIarella* may produce lipids to >75% of their body weight. Much of these lipids are unsaturated. As expected, due to some decarboxylation and other chemical reactions such as polymerization, polyene acids in lipid fats disappear on heating, while saturated acids remained unaltered. The role or unsaturated lipid acids in the products left by *Batryococcus braunii* blooms in the Coorong of southern Australia involves polymerization of the unsaturated lipid residue to produce *coorongite*, a resilient, insoluble material that resembles kerogen in many respects. Iso- and ante-iso-fatty acids have been found in some oil shales, but these are probably secondary products. In fact, bacteria are active in transforming n -alkanoic acids into the branched iso- and ante-iso-acids. Other bacterially induced transformations include the hydrogenation of oleic and linoleic acids, decarboxylation and polymerization of alkanoic acids, as well as lipid hydrolysis.

Carotenoid pigments have been found in many oil shales and in crude oil and coal. Studies of the carotenoids isolated from DSDP (Deep Sea Drilling Project) cores from the Quaternary sediments in the Cariaco Trench shows that the chemistry of these materials is largely reductive and traceable over 50,000–350.000 years (Watts and Maxwell, 1977; Watts et al., 1977).

This work gives useful insight into the diagenetic transformations of carotenoids which lead to the observance of partially and perhydrogenated carotenoids in marine oil shale.

The black marine shales formed in shallow seas have been extensively studied, as they occur in many places. These shales were deposited on broad, nearly flat sea bottoms, and therefore usually occur in thin deposits (10–50 m thick), but may extend over thousands of square miles. The Irati shale (Permian) in Brazil extends over more than 1000 miles from north to south. The Jurassic marine shales of Western Europe, Silurian shales of North Africa, and the Cambrian shales of northern Siberia and northern Europe are other examples of this kind of marine oil shale (Tissot and Welte, 1978).

Several quantitatively important petrographic components of the organic matter in oil shale-telalginite, lamalginite, and bituminite-are adapted from coal petrography. Telalginite is organic matter derived from large colonial or thick-walled unicellular algae, typified by genera such as Botryococcus. Lamalginite includes thin-walled colonial or unicellular algae that occurs as laminae with little or no recognizable biologic structures. Telalginite and lamalginite fluoresce brightly in shades of yellow under blue/ultraviolet light. On the other hand, bituminite, on the other hand, is largely amorphous, lacks recognizable biologic structures, and weakly fluoresces under blue light. It commonly occurs as an organic ground mass with fine-grained mineral matter. The material has not been fully characterized with respect to its composition or origin, but it is commonly an important component of marine oil shales. Coaly materials including vitrinite and inertinite are rare to abundant components of oil shale; both are derived from humic matter of land plants and have moderate and high reflectance, respectively, under the microscope.

Marinite is a gray to dark gray to black oil shale of marine origin in which the chief organic components are lamalginite and bituminite derived chiefly from marine phytoplankton. Marinite may also contain small amounts of bitumen, telalginite, and vitrinite. Marinites are deposited typically in an epeiric sea (a sea extending inland from a continental margin) such as on broad shallow marine shelves or inland seas where wave action is restricted and currents are minimal. The Devonian–Mississippian oil shales of eastern United States are typical Marinites. Such deposits are generally widespread covering hundreds to thousands of square kilometers, but they are relatively thin, often less than 300 feet.

Tasmanite, named from oil-shale deposits in Tasmania, is a brown to black oil shale. The organic matter consists of telalginite derived chiefly from unicellular algae of marine origin and lesser amounts of vitrinite, lamalginite, and inertinite. Tasmanite that is constituted from what is believed to be algae of unknown affinity. The deposits are stratified and of marine origin.

Kukersite, which takes its name from Kukruse Manor near the town of Kohtla-Järve, Estonia, is a light brown marine oil shale. Its principal organic component is telalginite derived from green algae. Kukersite is the main type of oil shale in Estonia and western Russia and the kukersite layers in Estonia occur between limestone layers. (Chapter 2). The organic matter of *kukersite* is considered to be entirely of marine origin, and consists almost entirely of accumulations of discrete bodies, telalginite derived from a colonial microorganism termed *Gloeocapsomorpha prisca.* As compared with other rocks containing telalginite, kukersite have low atomic H/C (1.48) and high atomic O/C (0.14) ratios and generally plots as Type II kerogen on the van Krevelen diagram (Cook and Sherwood, 1991). The other type of oil shale in Estonia is alum shale (dictyonema argillite) which is poorer in organic matter but has been mined because of metals content.

Some oil shales (black shales) contain appreciable amount of metals. The precipitation of metallic compounds (especially sulfide minerals) is enhanced by reducing conditions − alum shale is a good example of such oil shale. Uranium, vanadium, antimony, molybdenum, silver, gold, nickel, cadmium, selenium, and zinc are common metals in black shale formations.

5. Composition and properties

Oil shale is typically a fine-grained sedimentary rock containing relatively large amounts of organic matter (*kerogen*) from which significant amounts of shale oil and combustible gas can be extracted by thermal deposition with ensuing distillation from the reaction zone. However, oil shale does not contain any oil − this must be produced by a process in which the kerogen is thermally decomposed (cracked) to produce the liquid product (shale oil). Thus any estimates of shale oil reserves can only be based on speculative estimates from application of the Fischer assay test method to (often) non-representative samples taken from an oil shale deposit and the assay data (in terms of oil yield in gallons per ton) must not to be taken as *proven reserves*.

It is a fact the term *oil shale* describes an organic-rich rock from which little carbonaceous material can be removed by extraction (with common crude oil-based solvents) but which produces variable quantities of distillate (*shale oil*) when raised to temperatures in excess of 350 °C (660 °F) by the decomposition of the organic matter in the shale, commonly known as kerogen (Chapter 13). Thus, oil shale is assessed by the ability of the mineral to produce shale oil in terms of gallons per ton (g/t) by means of a test method (Fischer Assay) in which the oil shale is heated to 500 °C (930 °F).

In terms of mineral and elemental content, oil shale differs from coal in several distinct ways. Oil shales typically contain much larger amounts of inert mineral matter (60%−90% w/w) than coals, which have been defined as containing less than 40% mineral matter. The organic matter of oil shale (kerogen), which is the source of liquid and gaseous hydrocarbons, typically has a higher hydrogen and lower oxygen content than that of lignite and bituminous coal. In general, the precursors of the organic matter in oil shale and coal also differ. Much of the organic matter in oil shale is of algal origin, but may also include remains of vascular land plants that more commonly compose much of the organic matter in coal (Scouten, 1990; Lee, 1991; Speight, 2013). The origin of some of the organic matter in oil shale is obscure because of the lack of recognizable biologic structures that would help identify the precursor organisms. Such materials may be of bacterial origin or the product of bacterial degradation of algae or other organic matter.

The mineral component of oil shale is variable − some oil shales are composed of carbonate minerals including calcite ($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$), and siderite ($FeCO_3$), with lesser amounts of aluminosilicate minerals. For other oil shales, the reverse is true − silicate minerals including quartz, feldspar, and clay minerals are dominant and carbonate minerals are a minor component. Many oil-shale deposits contain small, but ubiquitous, amounts of sulfide minerals including pyrite (FeS_2) and marcasite (FeS_2 − the same formula as pyrite but a different crystal form to pyrite), indicating that the sediments probably accumulated in dysaerobic to anoxic waters that prevented the destruction of the organic matter by burrowing organisms and oxidation.

In the United States there are two principal oil shale types, the shale from the Green River Formation in Colorado, Utah, and Wyoming, and the Devonian-Mississippian black shale of the East and Midwest (Table 11.4) (Baughman, 1978). The Green River shale is considerably richer, occurs in thicker seams, and has received the most attention for synthetic fuel. The mineral matter (shale) consists of fine-grained silicate and carbonate minerals. The ratio of kerogen-to-shale for commercial grades of oil shale is typically in the range 0.75:5 to 1.5:5 – as a comparison, for coal the organic matter-to-mineral matter ratio in coal is usually greater than 4.75:5 (Speight, 2013).

The common property of these two types of oil shale is the presence of the ill-defined kerogen. The chemical composition of the kerogen has been the subject of many studies (Scouten, 1990) but whether or not the data are indicative of the true nature of the kerogen is extremely speculative. Based on solubility/insolubility in various solvents (Koel et al., 2001) it is, however, a reasonable premise (remembering that regional and local variations in the flora that were the precursors to kerogen) led to differences in kerogen composition and properties kerogen from different shale samples – similar to the varying in quality, composition, and properties of crude oil from different reservoirs (Speight, 2014).

The other component of oi shale is the organic component, referred to as kerogen which is insoluble in common organic solvents (but which also contains a soluble fraction referred to as bitumen) which is speculated to have originated during the formation of crude oil from the sedimentary organic matter. While this may be true, the follow-on deduction that kerogen is a precursors to crude oil has not been conclusively proven and the theory that the first phase in the transformation of organic matter to crude oil is mere speculation (Speight, 2014). Kerogen that has not thermally matured beyond the diagenesis (low-temperature) stage is typically due to the relatively shallow depth of burial. The Green River oil shale of Colorado has matured to the stage that heterocyclic constituents have formed and predominate, with up to 10% normal-paraffins and isoparaffins that boil in the range that includes natural naphtha

TABLE 11.4 Composition (% w/w) of the Organic Matter in the Mahogany Zone and New Albany Shale (Baughman, 1978).

Component	Green river	New albany
%W/w	Mahogany zone	
Carbon	80.5	82.0
Hydrogen	10.3	7.4
Nitrogen	2.4	2.3
Sulfur	1.0	2.0
Oxygen	5.8	6.3
Total	100.0	100.0
H/C atomic ratio	1.54	1.08

and gasoline constituents. The relatively high hydrogen/carbon ratio (1.6) is a significant factor in terms of yielding high quality fuels. However, the relatively high nitrogen content (1%–3% w/w) is a major issue in terms of producing stable fuels (unrefined crude oil typically contains less than 0.5% nitrogen), as well as producing environmentally-detrimental nitrogen oxides during combustion.

The original organic matter is believed to be derived from the varied types of marine and lacustrine algae, with some debris of land plants, is largely dependent on the depositional environment and sediment sources. Bacterial processes were probably important during the deposition and early diagenesis of most oil shale deposits – these processes could produce significant quantities of biogenic methane, carbon dioxide, hydrogen sulfide, and ammonia. These gases in turn could react with dissolved ions in the sediment waters to form authigenic minerals (minerals generated where they were found or observed) such as calcite ($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$), pyrite (FeS_2), and even such rare authigenic minerals as buddingtonite (ammonium feldspar – $NH_4 \cdot Al.Si_3O_8.0.5H_2O$).

The organic matter in oil shale is composed chiefly of carbon, hydrogen, and oxygen with lesser amounts of sulfur and nitrogen. Because of the high molecular weight (best estimates are on the order of several thousand) and molecular complexity, oil shale kerogen is almost totally insoluble in crude oil-based solvents and conventional organic solvents (such as carbon disulfide) Tissot and Welte (1978); Durand (1980); Scouten (1990); Hunt (1996); Speight (2014). A portion of the organic matter in oil shale is soluble and is (incorrectly and confusingly) termed *bitumen*. The bitumen, which is soluble, is dispersed throughout the kerogen network, although even in finely crushed shale much of the bitumen may be inaccessible to the solvent. As a result, only a small fraction of the hydrocarbonaceous material in oil shale can be removed by conventional solvent-extraction techniques.

Briefly, the term *bitumen* is more correct when applied to the organic content of tar sand (oil sand) deposits, although the name also applied in Europe and other areas to road asphalt (Speight, 2014, 2019b). Using this name in reference to the soluble portion of the organic constituents of oil shale is more for convenience that scientific correctness. Small amounts of bitumen that are soluble in organic solvents are present in some oil shale. Because of its insolubility, the organic matter must be retorted at temperatures on the order of 500 °C (930 °F) to decompose it into shale oil and gas. After thermal decomposition of the organic matter, some carbon (in the form of a carbonaceous deposit) remains with the shale residue after retorting but can be burned to obtain additional energy.

The organic matter of *kukersite* is considered to be entirely of marine origin, and consists almost entirely of accumulations of discrete bodies, telalginite derived from a colonial microorganism termed *G. prisca.* As compared with other rocks containing telalginite, kukersite has a low atomic hydrogen-to-carbon ratio ($H/C = (1.48$) and high atomic oxygen-to-carbon ratio ($O/C = 0.14$) ratios and generally falls into the as Type II kerogen on the van Krevelen diagram (Fig. 11.2) (Cook and Sherwood, 1991).

The four general types of kerogens in thermally immature coal and sedimentary rock are defined by the van Krevelen diagram based on the original atomic hydrgoen-to-carbon (H/C) (Peters and Cassa, 1994):

(i) Oil-prone kerogen – Type I kerogen – that is dominated by liptinite macerals; high atomic hydrgoen-to-carbon ratio ($H/C \geq 1.5$) and low oxygen-to-carbon ratio ($O/C \leq 0.1$).

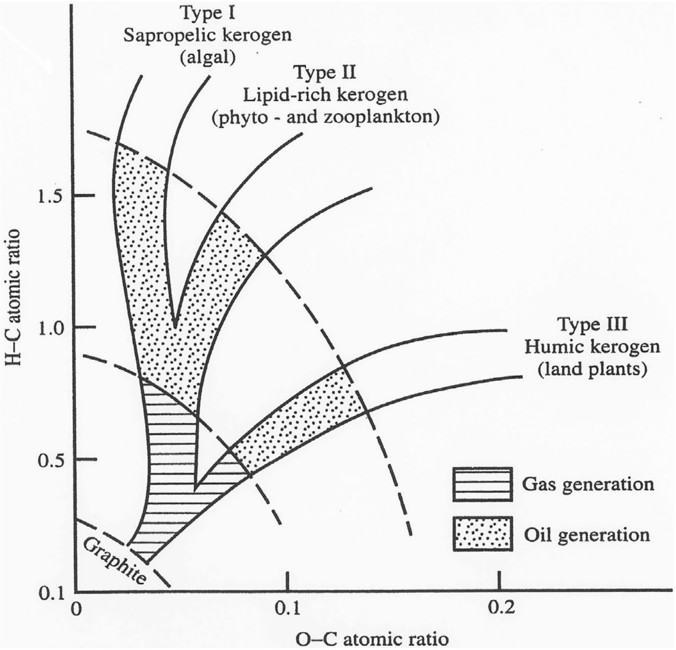

FIGURE 11.2 The Van Krevelen Diagram showing the Different Types of Kerogen.

(ii) oil-prone kerogen — Type II kerogen — shows a moderate atomic hydrogen-to-carbon ratio (H/C 1.2–1.5) and low oxygen-to-carbon atomic ratio (O/C) compared with types III and IV; some kerogens of this type also contain abundant organic sulfur (8–14% w/w sulfur; atomic $S/C \geq 0.04$) and are designated as type IIS;

(iii) Gas-prone kerogen — Type III kerogen — shows a low atomic hydrgoen-to-carbon ratio H/C (<1.0) and a high oxygen-to-carbon ratio ($O/C \leq 0.3$); the term *gas-prone* is misleading because Type III kerogen typically yields less gas than Type I kerogen or Type II kerogen.

(iv) Dead carbon — Type IV kerogen —show a low atomic hydrogen-to-carbon ratio (H/C ~0.5 to 0.6) and a variable oxygen-to-carbon ratio ($O/C \leq 0.3$).

Intermediate compositions between Types I, II, III, and IV are common on the van Krevelene diagram. For example, a Type III kerogen might be composed dominantly of gas-prone vitrinite macerals or it could be a mixture of Type II kerogen and Type IV kerogen and thus have significant oil-prone character. Furthermore, kerogen types can vary within any depositional setting. For example, a lacustrine source rock might contain Type I, II, III, and IV kerogen depending on location within the basin and the depositional setting for the organic matter. Other common misconceptions are that Type I kerogen originated from lacustrine source rocks, such as the Mahogany Ledge unit in the Green River Formation, and that all Type II kerogen is from marine source rocks, such as the Toarcian shale formation in the Paris Basin. Major components of this kerogen are phenolic moieties with linear alkyl side-chains. In spite of the predominance of phenolic moieties kukersite appears as a highly aliphatic Type II-Type I kerogen due to the presence of associated long, linear alkyl chains (Derenne et al., 1989). The formation of kukersite kerogen is believed to have occurred via the selective preservation pathway and the phenolic moieties correspond to important basic structures of the resistant macromolecular material (Derenne et al., 1994). Different extraction methods give a bitumen yield from kukersite on the order of 1%–3% w/w.

The yield of oil and gas under slow retorting conditions is not the same as under Fischer assay. Gas compositions reported for slow, modest pressure retorting indicate that energy content of the gas could be as much as 70% greater than for Fischer assay (Burnham and Singleton, 1983). This increase has at least three sources of uncertainty: (i) possible leaks in their gas collection system at the slowest heating rate at elevated pressure, (ii) difficulty in recovering low-boiling hydrocarbon derivatives dissolved in the oil at elevated pressure, and (iii) the likelihood that oil cracking at higher geological pressures in the liquid phase are less than in the self-purging reactor, which requires volatilization for expulsion. Nevertheless, it is likely that the gas yields will be higher for methane due to oil coking reactions, which was the main reason for the 70% increase, so it is likely that slow retorting would generate gases with good heat content (Burnham, 2003).

Finally, the gross heating value of oil shales on a dry-weight basis ranges from approximately 500 to 4000 kilocalories per kilogram (kcal/kg) of rock. The high-grade kukersite oil shale of Estonia, which fuels several electric power plants, has a heating value of approximately 2000 to 2200 kcal/kg. By comparison, the heating value of lignite ranges from 3500 to 4600 kcal/kg on a dry-mineral-free basis (Speight, 2013).

5.1 Mineral components

Oil shale has often been termed as (incorrectly and for various illogical reasons) high-mineral coal but nothing could be further from the truth than this misleading terminology. Coal and oil shale are fraught with considerable differences (Speight, Speight, 2013, 2019b) and such terminology should be frowned upon. Furthermore, the precursors of the organic matter in oil shale and coal also differ. Much of the organic matter in oil shale is of algal origin, but may also include remains of vascular land plants that more commonly compose much of the organic matter in coal (Scouten, 1990; Dyni, 2003, 2006; Speight, 2013). In addition, the lack of recognizable biologic structures in oil shale that would help identify the precursor organisms in oil shale makes it difficult to identify the origin of the organic matter.

In terms of mineral and elemental content, oil shale differs from coal in several distinct ways. Oil shale typically contains much larger amounts of inert mineral matter (60–90% w/w) (Table 11.5) (Scouten, 1990; Lee, 1991) than coal, which has been defined as containing less than 40% mineral matter (Speight, 2013). The organic matter of oil shale, which is the source of liquid and gaseous hydrocarbon derivatives, typically has a higher hydrogen and lower oxygen content than that of lignite and bituminous coal.

The mineral component of some oil shale deposits is composed of carbonates including calcite($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$), siderite ($FeCO_3$), nahcolite ($NaHCO_3$), dawsonite [$NaAl(OH)_2CO_3$], with lesser amounts of aluminosilicates – such as alum

TABLE 11.5 Examples of the types of mineral that occur in oil shale.

Minerals	**Chemical formula**
Calcite	$CaCO_3$
Dolomite	$CaCO_3 \cdot MgCO_3$
Analcite	$NaAlSi_2O_6.H_2O$
Shortite	$Na_2Ca_2(CO_3)_3$
Trona	$Na_2CO_3.NaHCO_3.2H_2O$
Pyrite	FeS_2
Potassium feldspar	$KAlSi_3O_8$
Gaylussite	$CaNa_2(CO_3)_2.5H_2O$
Illite	$K_{0\cdot6}(H_3O)_{0\cdot4}Al_{1\cdot3}Mg_{0\cdot3}Fe^{2+}{}_{0.1}Si_{3\cdot5}O_{10}(OH)_2 \cdot (H_2O)$ [Empirical formula]
Plagioclase	$NaAlSi_3O_8$—$CaAl_2Si_2O_8$
Nahcolite	$NaHCO_3$
Dawsonite	$NaAl(OH)_2CO_3$
Gibbsite	γ-$Al(OH)_3$
Ankerite	$Ca(Mg, Mn, Fe)(CO_3)_2$
Siderite	$FeCO_3$
Albite	$NaAlSi_3O_8$
Quartz	SiO_2

[$KAl(SO_4)_2.12H_2O$] — and sulfur, ammonium sulfate, vanadium, zinc, copper, and uranium, which add by-product value (Beard et al., 1974). For other deposits, the reverse is true — silicates including quartz (SiO_2), feldspar [$xAl(Al.Si)_3O_8$, where x can be sodium (Na), and/or calcium (Ca), and/or potassium (K)], and clay minerals are dominant and carbonates are a minor component. Many oil-shale deposits contain small, but ubiquitous, amounts of sulfides including pyrite (FeS_2) and marcasite (FeS_2, but which physically and crystallographically distinct from pyrite), indicating that the sediments probably accumulated in dysaerobic (a depositional environment with 0.1—1.0 mL of dissolved oxygen per liter of water) to anoxic waters that prevented the destruction of the organic matter by burrowing organisms and oxidation.

Formation of an oil shale requires simultaneous sources of both fine-grained minerals and organics, under conditions where the organics can be preserved. In addition to these clastic, detrital components, biogenic and authigenic minerals are also present in most shales. Detrital minerals typically include quartz, feldspar and clays (often including illite, montmorillonite and kaolinite), and sometimes volcanic ash.

Biogenic minerals (product made by or of life forms) include amorphous silica and calcium carbonate, usually in very minor amounts. Authigenic minerals (minerals form by in situ inorganic precipitation on the seafloor and within the sediment column) typically include pyrite and other metal sulfides, carbonates (calcite, dolomite, siderite), chert and phosphates. Authigenic silica from clay diagenesis is also an important mineral in many shales, serving to cement together the larger detrital particles. The saline minerals trona (Na_2CO_3), nahcolite ($NaHCO_3$), dawsonite [$NaAlCO_3(OH)_2$], and halite (NaCl) are often important in oil shales (as for example, in the Green River shales) that are formed in stratified lacustrine environments.

However, mineral assemblages vary from shale to shale, from top to bottom within a given oil shale deposit; even from sample to sample within a given stratum which complicates mineralogy studies. As a result, comprehensive mineralogy studies of oil shales are few and most studies have focused on the occurrence or genesis of one particular mineral or mineral type, while other studies have concentrated on minerals of economic interest.

Green River oil shale contains abundant carbonate minerals including dolomite, nahcolite, and dawsonite. The latter two minerals have potential by-product value for assay their soda ash and alumina content, respectively. The effect of heat on dawsonite is of special interest because the recovery of aluminum will probably follow the recovery of oil from these shales by retorting. Dawsonite decomposes at 370 °C (700 °F) according to the equation (Huggins and Green, 1973):

$$NaAl(OH)_2CO_3 \rightarrow H_2O + CO_2 + NaAlO_2$$

An alternative route for the decomposition at 290–330 °C (555–625 °F) is (Huggins and Green, 1973):

$$2NaAl(OH)_2CO_3 \rightarrow Na_2CO_3 + Al_2O_3 + 2H_2O + CO_2$$

The oil shale deposits of the eastern United States are low in carbonate content but contain notable quantities of metals, including uranium, vanadium, molybdenum, and others which could add significant by-product value to these deposits.

There is the potential for low emissions due to the inherent presence of carbonate minerals. Calcium carbonate present in oil shale ash binds sulfur dioxide and it is not necessary to add limestone for desulfurization:

$$CaCO_3 \rightarrow CaO + CO_2$$
$$2CaO + SO_2 + O_2 \rightarrow CaSO_4$$

Illite (a layered alumino-silicate, $[K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2,(H_2O)]$ is ever-present in Green River oil shale – it is generally associated with other clay minerals but frequently occurs as the only clay mineral found in the oil shale (Tank, 1972). Smectite (a group of clay minerals that includes montmorillonite, which tends to swell when exposed to water) is present in all three members of the Green River Formation, but its presence frequently shows an inverse relationship to both analcime (a white, gray, or colorless tectosilicate mineral which consists of hydrated sodium aluminum silicate, $NaAlSi_2O_6.H_2O$) and loughlinite (a silicate of magnesium, $Na_2Mg_3Si_6O_{16}.8(H_2O)$. Chlorite (a group of mostly monoclinic but also triclinic or orthorhombic micaceous phyllosilicate minerals) occurs only in the silty and sandy beds of the Tipton Shale Member. The distribution of random mixed-layer structures and amorphous material is irregular. Several independent lines of evidence favor an in situ origin for many of the clay minerals. Apparently the geochemical conditions favoring the accumulation of the oil shale also favored in situ generation of illite.

Finally, precious metals and uranium are contained in good amounts in oil shale of the Eastern United States. It may not be in the near future to recover these mineral resources, since a commercially favorable recovery process has not yet been developed. However, there are many patents on recovery of alumina from Dawsonite-bearing beds [$NaAl(CO_3)(OH)_2$] by leaching, precipitation, and calcination.

5.2 Grade

The grade of oil shale has been determined by many different methods with the results expressed in a variety of units (Scouten, 1990; Dyni, 2003, 2006). For example, the heating value is useful for determining the quality of an oil shale that is burned directly in a power plant to produce electricity. Although the heating value of a given oil shale is a useful and fundamental property of the rock, it does not provide information on the amounts of shale oil or combustible gas that would be yielded by retorting (destructive distillation).

Alternatively, the grade of oil shale can be determined by measuring the yield of distillable oil produced from a shale sample in a laboratory retort (Scouten, 1990). This is perhaps the most common type of analysis that has been, and still is, used to evaluate an oil-shale resource – however the end result of the evaluation depends upon the source of the sample and whether or not the sample is representative of the deposit.

Evaluation of an oil-shale resource is especially difficult because of the wide variety of analytical units that are reported. The grade of a deposit is variously expressed in US or Imperial gallons of shale oil per short ton of the shale, liters of shale oil per metric ton (l/t) of rock, barrels, short or metric tons of shale oil, kilocalories per kilogram (kcal/kg) of oil shale, or gigajoules (GJ) per unit weight of oil shale. To bring some uniformity into this assessment, oil-shale resources in this report are given in both metric tons of shale oil and in equivalent barrels (US barrels) of shale oil, and the grade of oil shale, where known, is expressed in liters of shale oil per metric ton (l/t) of rock. If the size of the resource is expressed only in volumetric units (barrels, liters, cubic meters, and so on), the density of the shale oil must be known or estimated to convert these values to metric tons. Most oil shales produce shale oil that ranges in density from about 0.85 to 0.97 by the modified Fischer assay method. In cases where the density of the shale oil is unknown, a value of 0.910 is assumed for estimating resources.

The method commonly used in the United States is the *modified Fischer assay* test method (ASTM D3904). The standard Fischer assay test method (ASTM D3904), now withdrawn but still used in many laboratories) consists of heating a 100-g sample crushed to -8 mesh (2.38-mm) screen in a small aluminum retort to 500 °C (930 °F) at a rate of 12 °C (21.6 °F) per minute and held at that temperature for 40 min. The distilled vapors of oil, gas, and water are passed through a condenser cooled with ice water into a graduated centrifuge tube. The oil and water are then separated by centrifuging. The quantities reported are the weight percentages of shale oil (and its specific gravity), water, shale residue, and (by difference) gas plus losses. Some laboratories have further modified the Fischer assay method to better evaluate different types of oil shale and different methods of oil-shale processing.

The Fischer assay is a simple and representative quantity that can be obtained quite easily for all kinds of oil shale by following the standardized retorting procedure under nitrogen atmosphere. However, the Fischer assay is not a standard analytical procedure. Rather, the Fischer assay is a performance test and because it is an assay − a performance test − insofar as the data obtained are dependent upon the test procedure. Variances in the test procedures, permitted in the formerly widely accepted united States Bureau of Mines Fischer assay method, do cause significant differences i n the data obtained.

Also, in the test method, the actual oil content in the oil shale both theoretically and nominally exceeds the Fischer assay and, depending upon the treatment processes as well as the type of oil shale, the oil yield from oil shale often exceeds the Fischer assay value by as much as 50%. Examples of such extraction processes include (i) retorting in hydrogen-rich environment, (ii) retorting in carbon dioxide sweep gas environment, and (iii) supercritical fluid extraction of oil shale. The procedure for Fischer Assay of oil shale is modified from a Fischer assay procedure for carbonization of coal at low temperature (Stanfield and Frost, 1949; Goodfellow et al., 1968).

However, the Fischer assay test method does not recover all of the organic matter originally contained in the shale, and leaves char associated with ash in the rock matrix as well as larger molecular weight hydrocarbonaceous derivaitves blocking the pores. Nevertheless, the method is used as a very convenient measure of recoverable thermally-produced oil and provides a common basis for comparison among various oil shale types. If this value is higher than 26 US gallons (100 L) per ton, the shale is typically considered a rich shale but if the oil yield is less than 8 US gallons (30 L) per ton, the shale is considered to be a lean shale.

Also, the Fischer assay method does not measure the total energy content of an oil shale sample because the gases, which include methane, ethane, propane, butane, hydrogen, hydrogen sulfide, and carbon dioxide can have significant energy content, but are not individually specified and are determined by difference as “gas and loss” rather than directly. Some liquid hydrocarbon derivatives are also lost as mist. Thus, the yields of these important parts of the product slate can only be inferred (Scouten, 1990; Allix et al., 2011).

Furthermore, the yield of oil depends not only on retorting temperature but on heating rate as well. A high yield of oil is generally obtained by rapid heating to an optimum temperature. The Fischer assay is not useful for evaluating oil yield under such conditions. This has led to the development of alternative thermal assay methods (of which the Rock-Eval method is notable) (Scouten, 1990). Also, some retort methods, especially those that heat at a different rate or for different times, or that crush the rock more finely, may produce more oil than that produced by the Fischer assay method. Therefore, the method can only be used as a reference point and, at best, the data from the Fischer assay test method can only be employed to approximate the energy potential of an oil shale deposit.

Other retorting methods, such as the Tosco II process, are known to yield in excess of 100% of the yield reported by Fischer assay. In fact, some methods of retorting can increase oil yields of some oil shales by as much as three to four times the yield obtained by the Fischer assay method (Scouten, 1990; Dyni, 2003, 2006).

Another method for characterizing organic richness of oil shale is a pyrolysis test developed by the Institut Français du Pétrole for analyzing source rocks (Allix et al., 2011). The Rock-Eval test heats a 50-mg to 100-mg sample through several temperature stages to determine the amounts of hydrocarbon and carbon dioxide generated. The results can be interpreted for kerogen type and potential for oil and gas generation. The method is faster than the Fischer assay and requires less sample material Kalkreuth and Macauley, 1987).

5.3 Physical properties

The physical properties of oil shale are based on the fact that oil shale is an organic-rich fine-grained sedimentary rock that contains kerogen (a solid organic material) from which liquid hydrocarbon derivatives can be produced. The inorganic component of oil shales differs little from that of conventional shales. There is a framework of detrital grains of quartz (SiO_2), feldspar (tectosilicate mineral, $KAlSi_3O_8 - NaAlSi_3O_8 - CaAl_2Si_2O_8$), and mica (any mineral of a group hydrous potassium, aluminum, silicate minerals). Substantial amounts of clay are present, both detrital floccules and authigenic crystals. Various carbonate minerals are present, both calcitic skeletal fragments and authigenic calcite ($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$), ankerite [a mineral of the group of rhombohedral carbonates with formula: $Ca(Fe.Mg.Mn)(CO_3)_2$], and siderite ($FeCO_3$). Authigenic pyrite (FeS_2) is especially characteristic of oil shales because of its anaerobic origin. The presence of this sulfur causes one of the major problems of oil shale refining.

Not surprisingly, the properties of oil shale are not consistent and do vary from country to country (Table 11.6) which will be reflected in differences in the physical properties. In addition, though many shale formations are similar in their formation process, the origin of some of the organic matter in oil shale is obscure because of the lack of recognizable biologic structures that would help identify the precursor organisms. Such materials may be of bacterial origin or the product of bacterial degradation of algae or other organic matter (Dyni, 2006). Also, the product (shale oil) of the thermal treatment of oil shale, should not be confused with tight oil, which is oil produced from tight formations (such as shale, sandstone, and carbonate formation) without thermal decomposition.

Furthermore, oil shale differs from bitumen-impregnated rocks (tar sand formation, also called oil sand formations but which do not contain oil) and crude oil reservoir rocks), humic coal, and carbonaceous shale. The general composition of oil shales constitutes inorganic matrix, bitumen (soluble organic material that is dissimilar to tar sand bitumen) and kerogen. While the bitumen portion of oil shales is soluble in carbon disulfide (CS_2), the kerogen portion is insoluble in carbon disulfide and may contain iron, vanadium, nickel, and molybdenum (Cane, 1976; Scouten, 1990). In commercial grades of oil shale the ratio of organic matter to mineral matter lies approximately between 0.75:5 and 1.5:5 and the organic matter in oil shale has an atomic ratio of hydrogen to carbon (H/C) on the order of 1.2−1.8 times lower than for crude oil.

Moreover, many different kinds of carbonate and silicate minerals occur in oil shale formations. Trona beds [$Na_5(CO_3)(HCO_3)_3$] in Wyoming are a major source of soda ash (sodium carbonate, Na_2CO_3), while nahcolite ($NaHCO_3$) is a potential byproduct of oil shale mining from Utah and Colorado. Precious metals and Uranium are contained in good amounts in shale formation of the eastern United States. It may not be in the near future to recover these mineral resources, since a commercially favorable recovery process has not yet been developed. However, it should be noted that there are many patents on recovery of alumina from Dawsonite-bearing beds, such as leaching, precipitation, and calcination. The chemical formula for dawsonite is $NaAl(CO_3)(OH)_2$ (Lee, 1991).

The gross heating value of oil shales on a dry-weight basis ranges from about 500 to 4000 kilocalories per kilogram (kcal/kg) of th mineral. The high-grade kukersite oil shale of Estonia, which fuels several electric power plants, has a heating value on the order of 2000

TABLE 11.6 Properties of oil shale from different countries.

Country	Location	Type	Age	Organic carbon, % w/w)	Oil yield, % w/w
Australia	New South Wales	Torbanite	Permian	40	31
	Tasmania	Tasmanite	Permian	81	75
Brazil	Irati formation, Irati	Marinite	Permian		7.4
	Paraíba valley	Lacustrine shales	Permian	13–16.5	6.8–11.5
Canada	Nova Scotia	Torbanite; lamosite	Permian	8–26	3.6–19
China	Fushun	Cannel coal; lacustrine shales	Eocene	7.9	3
Estonia	Estonia deposit	Kukersite	Ordovician	77	22
France	Autun, St. Hilarie	torbanite[13]	Permian	8–22	5–10
	Creveney, Severac		Toarcian	5–10	4–5
South Africa	Ermelo	Torbanite	Permian	44–52	18–35
Spain	Puertollano	Lacustrine shale	Permian	26	18
Sweden	Kvarntorp	Marinite	Lower Paleozoic]	19	6
United Kingdom	Scotland	Torbanite	Carboniferous	12	8
United States	Alaska		Jurassic	25–55	0.4–0.5
	Green river formation	Lamosite	Early to mid-Eocene	11–16	9–13
	Mississippi	Marinite	Devonian		

to 2200 kcal/kg. By comparison, the heating value of lignite (the lowest rank coal) ranges from 3500 to 4600 kcal/kg on a dry, mineral-free basis.

5.3.1 *Permeability*

Permeability is the ability, or measurement of a ability of a rock formation, to transmit fluids, typically measured in Darcies or millidarcies. Permeability is part of the proportionality constant in Darcy's law which relates the flow rate of the fluid and the fluid viscosity to a pressure gradient applied to the porous media.

Permeability is part of the proportionality constant in Darcy's law which relates the flow rate of the fluid and the fluid viscosity to a pressure gradient applied to the porous media. Darcy's Law is based on the conservation of momentum that describes the flow of a fluid through a porous medium. A simple relationship relates the instantaneous discharge rate (local volumetric flow rate) through a porous medium to the local hydraulic gradient (change in hydraulic head over a distance, i.e., $\Delta h/L$, dh/dL, or ∇h) and the hydraulic conductivity (k) at that point.

$$Q = -kA\frac{h_a - h_b}{L}$$

Dividing the both sides by the area, A, yields:

$$q = -k\nabla h$$

In this equation, q is the Darcy flux that is the discharge rate per unit area, expressed in terms of [length/time]. Even though the final unit of the Darcy flux is the same as that of the velocity, a clear conceptual difference between the two must be realized. Based on the analogy between the Darcy's law and Poiseuille's law, the hydraulic conductivity term can be factored out in terms of intrinsic permeability and the fluid properties as:

$$k = (k')\cdot(\rho g / \mu)$$

k' is the intrinsic permeability which has the dimension of [length^2]. While the term $[\rho g/\mu]$ describes the penetrating fluid properties, the intrinsic permeability (k') summarizes the properties of the porous medium. The usual unit for permeability is the *Darcy*, or more commonly the *milli-Darcy* or *md* (1 Darcy = 10^{-12} m^2).

The permeability of raw oil shale is essentially zero, because the pores are filled with a non-displaceable organic material. In general, oil shale constitutes a highly impervious system. Thus, one of the major challenges of any *in-situ* retorting project is in the creation of a suitable degree of permeability in the formation. This is why an appropriate rubbelization technique is essential in the success of an in situ pyrolysis project.

Of practical interest is the dependency of porosity or permeability on temperature and organic contents. Upon heating to 510 °C (950 °F), an obvious increase in oil shale porosity is noticed. These porosities, which vary from 3% to 6% v/v of the initial bulk oil shale volume, represented essentially the volumes occupied by the organic matter before the retorting treatment. Therefore, the oil shale porosity increases as the extent of pyrolysis reaction proceeds.

In oil shale that produces a low yield of oil by the Fischer assay method (lean oil shale), structural breakdown of the cores is insignificant and the porosities are those of intact porous structures. However, in the high Fischer assay oil shales, i.e., rich oil shales, this is not the case because structural breakdown and mechanical disintegration due to retorting treatment become extensive and the mineral matrices no longer remain intact. Thermal decomposition of the mineral carbonates, such as magnesium carbonate ($MgCO_3$) and calcium carbonate ($CaCO_3$), actively occurring around 380—900 °C (715—1650 °F) also results in an increase in porosity.

The increase in porosity from low to high Fischer assay oil shales varies from 2.82% to 50% (Table 11.7) (Chilingarian and Yen, 1978). These increased porosities constitute essentially the combined spaces represented by the loss of the organic matter and the decomposition of the mineral carbonates. Crackling of particles is also due to the devolatilization of organic matter

TABLE 11.7 Porosity and permeability of raw and treated oil shale (Chilingarian and Yen, 1978).

	Porosity			Permeability	
Fischer Assay	Raw	Heated to 815 °C	Plane	Raw	Heated to 815 °C
1.0[a]	9.0[b]	11.9	A[c]		0.36[d]
			B		0.56
6.5	5.5	12.5	A		0.21
			B		0.65
13.5	0.5	16.4	A		4.53
			B		8.02
20.0	<0.03	25.0	A		
			B		
40.0	<0.03	50.0	A		
			B		

[a] *Fischer Assay in gal/ton.*
[b] *Numbers in percentages of the initial bulk volume. Porosity was taken as an isotropic property, i.e., property that is independent of measurement direction.*
[c] *Plane A is perpendicular to the bedding plane; plane B is parallel to the bedding plane.*
[d] *Units in milidarcy.*

that increases the internal vapor pressure of large non-permeable pores to an extent the mechanical strength of the particle can no longer contain. Liberation of carbon dioxide from mineral carbonate decomposition also contributes to the pressure build-up in the oil shale pores.

Gas permeability is low in both planes of the mineral matrices from the three low Fischer assay oil shale heated to 815 °C (1,140 °F). In some types of oil shale, structural breakdown of the mineral matrices under a stress-free environment may be extensive which can preclude measurements of the permeability in high Fischer assay oil shale (Lee, 1991). Dolomite ($CaCO_3 \cdot MgCO_3$) decomposition via half-calcination and full-calcination reactions is very active at temperatures higher than 380 °C (715 °F), at which temperature magnesium carbonate ($MgCO_3$) starts to decompose readily, releasing carbon dioxide. Once the temperature is raised beyond 890 °C, decomposition of calcite ($CaCO_3$) via calcination reaction becomes quite active and thermodynamically favored.

$$MgCO_3 \rightarrow MgO + CO_2$$
$$CaCO_3 \rightarrow MgO + CO_2$$

In the case of oil shale from formations (especially Devonian oil shales) in the eastern United States, the decomposition of kerogen produces lower-boiling hydrocarbon derivatives than the hydrocarbon derivatives form for other shales (Lee, 1991). This often results in a substantial increase in volatile pressure in the solid matrix, which leads to cracking and mechanical disintegration of solid structure. This is also the reason why the oil yield from Eastern oil shale pyrolysis via a procedure similar to Fischer Assay is not necessarily an accurate measure for the organic content of the shale.

5.3.2 *Porosity*

The porosity (void fraction) is a measure of the void spaces in a material such as a reservoir rock, and is a fraction of the volume of void space over the total volume, between and is expressed as a fractional number between 0 and 1, or as a percentage between 0 and 100. However, the porosity of porous material can be defined in a number of different ways, depending on what specific pores are looked at and how the void volumes are measured. They include: (i) inter-particle porosity, (ii) intra-particle porosity, (iii) internal porosity, (iv) porosity by liquid penetration, (v) porosity by saturation, (vi) porosity by liquid absorption, (vii) the superficial porosity, (viii) the total open porosity, (ix) the bed porosity, which is the bed void fraction, and (x) the packing porosity.

The porosity of the mineral matrix of oil shale cannot be determined by the methods used in determining porosity of crude oil reservoir rocks, because the organic matter in the shale exists in a form of solid and is essentially insoluble. However, inorganic particles contain some micropore structure, approximately 2.36%–2.66% v/v and although the mineral particles have an appreciable surface area, 4.24–4.73 m^2/g for oil shale capable of producing 29 to 75 gallons per ton in the Fischer assay, the measurement of porosity may be limited to the characteristics of the external surface rather than to the actual pore structure.

Except for the two low-yield oil shale samples, naturally occurring porosities in the raw oil shales are almost negligible and they do not afford access to gases (Table 11.7). Porosity may exist to some degree in the oil shale formation where fractures, faults, or other structural defects occurred. It is also believed that a good portion of pores is either blind or very inaccessible. Cracking and fractures, or other structural defects often create new pores and also break up some of the blind pores – closed or blind pores are normally not accessible by mercury porosimetry even at high pressures. Due to the severity of mercury poisoning, the instrument based on pressurized mercury penetration through pores is no longer used.

In the process of the production of shale oil from oil shale, both chemical and physical properties of oil shale play important roles. The low porosity, low permeability and high mechanical strength of oil shale rock matrix make the extraction process less efficient by making the mass transport of reactants and products much harder as well as the process efficiency (Scouten, 1990).

Furthermore, the changes in properties as a function of temperature and pressure present implications of the evolution of these properties for in situ exploitation and basin modeling. While the mechanical properties at room temperature are well known, the existing data suggest a positive correlation between oil shale grade (organic matter content) and Poisson ratio, whereas tensile and compressive strength as well as modulus of elasticity show negative correlations.

Briefly, the Poisson ratio is a measure of the Poisson effect, the phenomenon in which a material tends to expand in directions perpendicular to the direction of compression. Conversely, if the material is stretched rather than compressed, it usually tends to contract in the directions transverse to the direction of stretching. In certain rare cases, a material may actually shrink in the transverse direction when compressed (or expand when stretched) which will yield a negative value of the Poisson ratio.

These properties are strongly affected by temperature – an increase in temperature results in loss of strength and decrease in Young's modulus (Scouten, 1990). Strength follows a logarithmic decrease with increasing temperature, depending on grade. Creep is much enhanced by elevated temperature. Extrapolation of laboratory data to nature suggests that tensile fracturing may occur more easily during crude oil generation, and creep is more prominent in oil shales than in other rocks at this depth in the crust (Eseme et al., 2007).

5.3.3 Compressive strength

Raw oil shale has a high compressive strength both perpendicular and parallel to the bedding plane (Lee, 1991). After heating, the inorganic matrices of low Fischer assay oil shales retain high compressive strength in both perpendicular and parallel planes. This indicates that a high degree of inorganic cementation exists between the mineral particles comprising each lamina and between adjacent laminae. With an increase in organic matter of oil shale the compressive strength of the respective organic-free mineral matrices decreases, and it becomes very low in those rich oil shale (Lee, 1991).

Also worthy of note is the existence of the structural transition point. Gradual expansion (volume swelling) of oil shale under a stress-free environment was noted immediately upon application of heat. At approximately 380 °C (715 °F), the samples are seen to undergo drastic changes in compressive strength. The greater loss of compressive strength at the yield point and the low recovery on reheating for the richer oil shales are both attributed to extensive effects, known as plastic deformation. The degree of plastic deformation is proportional to the amount of organic matter in oil shale. The discontinuities in the pressure plot at temperatures below the yield point presumably arise from the evolution of pore water from the oil shale matrix. The well-defined transition point at 380 °C (715 °F), therefore, represents a pronounced change in the compressive strength of richer oil shale. It is interesting to note that near this temperature most coals also exhibit similar plastic properties. Similarity in plastic properties between oil shale and coal may be attributed to their macromolecular structures of organic matters.

5.4 Thermal properties

Thermal properties are those properties that are directly (or even indirectly) related to the transport, absorption, or release of heat (thermal energy). Properties such as thermal conductivity, thermal diffusivity, enthalpy, density, and heat capacity fall into this classification. For materials that undergo thermal decomposition or phase transformation (this is the case with oil shales in general), it is necessary to characterize their thermal behavior by thermoanalytical methods such as thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (Lee, 1991; Hill, 2005).

5.4.1 Thermal conductivity

Oil-shale retorting is thermal process and, thus, the thermal conductivity of oil shale is an important property (Tisot, 1967; Prats and O'Brien, 1975). A detailed knowledge of the thermal conductivity is necessary before the temperature distribution in oil shale rocks is necessary. The thermal conductivity of oil shale can vary with temperature and kerogen content and the composition of the mineral matrix compositions and, therefore, it is unreasonable to expect two oil shale samples of equal grade but different mineral composition would exhibit identical thermal and electrical conductivity.

Generally, measurements of thermal conductivity of oil shale show that blocks of oil shale are anisotropic related to the bedding plane and thermal conductivity as a function of temperature, oil shale assay and direction of heat flow, parallel to the bedding plane (parallel to the surface of the Earth for a flat oil shale bed), was slightly higher than the thermal conductivity perpendicular to the bedding plane (Lee, 1991). As layers of material were laid to form the oil shale bed over a long period of geological years, the resulting continuous strata have slightly higher resistance to heat flow perpendicular to the strata than parallel to the strata (Table 11.8).

The thermal conductivity of retorted and burnt shale is lower than those of the raw shales from which they are obtained (Table 11.8). This is attributable to the fact that the mineral matter is a better conductor of heat than the organic matter and, on the other hand, the organic matter is still a far better conductor than the voids created by its removal. While the first of the above hypotheses is well justified when one takes into account the contribution of the lattice conductivity to the overall value, the effect of the amorphous carbon formed from the decomposition of the organic matter could also be of importance in explaining the difference in thermal conductivity values for retorted shales and the corresponding burnt samples. The role of voids in determining the magnitude of the effective thermal conductivity is likely to be significant only for samples with high organic contents.

The thermal conductivity of oil shale is, to some extent, dependent on the temperature. However, extreme caution needs to be exercised in the interpretation of results at temperatures close to the decomposition temperature of the shale organic matter. This is due to the fact that the kerogen decomposition reaction (or, pyrolysis reaction) is endothermic in nature

TABLE 11.8 Comparison between thermal conductivity values for green river oil shale.

Temperature range (°C)	Fischer assay, gal/ton	Plane#	Thermal conductivity (J/m-sec- °C)
38–593	7.2–47.9	–	0.69–1.56 (raw shales)
			0.26-1.38 (retorted shales)
			0.16-1.21 (burnt shales)
25–420	7.7–57.5	A	0.92-1.92
		Average	1.00-1.82 (burnt shales)
38–205	10.3–45.3	A	0.30–0.47
		B	0.22–0.28
20–380	5.5–62.3	A	1.00-1.42 (raw shales)
		B	0.25-1.75 (raw shales)

Note: # A - parallel to the bedding plane.
B - perpendicular to the bedding plane.
Average - average of both directions.

and as such the temperature transients can be confounded between the true rate of heat conduction and the rate of heat of reaction.

5.4.2 *Thermal decomposition*

Compared to coal, oil shale kerogen is relatively hydrogen-rich and can, therefore, be subjected to thermal conversion leading to higher yields of distillable oil and gas. This is in keeping with volatile products from fossil fuels being related to the hydrogen content of the fossil fuel and whether or not the oil shale is pyrolyzed in the present of oil shale ash (Scouten, 1990; Lee, 1991; Oja et al., 2007; Van Puyvelde, 2007; Speight, 2013, 2014, 2019b).

High-yield oil shale sustains combustion hence the name older Native American name *the rock that burns* but in the absence of air (oxygen) three carbonaceous end products result when oil shale is thermally decomposed. Distillable oil is produced as are non-combustible gases and a carbonaceous (high-carbon) deposit remains on the rock on (the surface or in the pores) as char − a coke-like residue similar. The relative proportions of oil, gas, and char vary with the pyrolysis temperature and to some extent with the organic content of the raw shale. All three products are contaminated with nonhydrocarbon compounds and the amounts of the contaminants also vary with the pyrolysis temperature (Bozak and Garcia, 1976; Scouten, 1990).

The thermal decomposition of oil shale is very much dependent upon the kerogen content and the nature of the kerogen (Maaten et al., 2016). Also, the composition and properties of the offgas from kerogen pyrolysis vary considerably with the parameters of the pyrolysis process. Gas from the Fischer retort typically has a heating value comparable to that of natural gas (approximately 1030 Btu per cubic foot for methane), but does very considerable with the composition of the natural gas. Such high-quality gas could be used as plant fuel in the oil shale facility, or it could be pipelined to other areas for commercial or industrial applications. In contrast, gas from a commercial directly-heated retort is highly diluted with carbon dioxide (from combustion and from the decomposition of carbonate minerals) and nitrogen and may have only approximately 10% of the heating value of natural gas. Such gas could be useful within the oil shale facility but could not be transported economically over any significant distance, nor could they be upgraded to higher heating values at reasonable cost. Surplus retort gas could become valuable byproducts if it was burned for power generation.

Nevertheless, the thermal decomposition process can be represented as consisting of three main processes: (i) water evaporation at lower temperatures (<200 °C, <390 °F), (ii) pyrolysis of kerogen at temperatures in the range 200−600 °C, 390 to 1,110 °F), and (iii) decomposition of carbonate minerals at temperatures above 700 °C (1,290 °F) (Bai et al., 2014; Liu et al., 2014). Typically the pyrolysis process is studied in an inert atmosphere, for example such as nitrogen, thereby avoiding the oxidation of the sample. The majority of the kinetic rate models for the thermal decomposition consider kerogen decomposition in the pyrolysis process as a first order reaction (Rajeshwar, 1981; Jaber and Probert, 2000; Williams and Ahmad, 2000; Bai et al., 2014).

At temperatures on the order of 500 to 520 °C (930−970 °F), oil shale produces shale oil while the mineral matter of the oil shale is not decomposed. The yield and quality of the products depend on a number of factors, whose impact has been identified and quantified for some of the deposits, notably the US Green River deposits and the Estonian Deposits

(Miknis, 1990; Brendow, 2003, 2009). A major factor is that oil shale ranges widely in organic content and oil yield. Commercial grades of oil shale, as determined by the yield of shale oil range from approximately 25 to 50 gallons per ton of rock (typically using the Fischer Assay method).

The correlation of the shale oil yield with the chemical and physical properties of oil shale and/or kerogen have been based on many different kinds of measurements, ranging from simple, qualitative tests that can be performed in the field to more complicated measurements in the laboratory.

One simple aspect of the thermal decomposition of oil shale kerogen is the relationships of the organic hydrogen content and the nitrogen content, and the yield of distillate oil as determined by the Fischer assay test. Stoichiometry suggests that kerogen with a higher organic hydrogen-to-carbon atomic ratio can yield more oil per weight of carbon than kerogen that is relatively hydrogen-poor (Scouten, 1990). However, the hydrogen-to-carbon atomic ratio is not the only important factor. South African kerogen with an atomic hydrogen-to-carbon ratio of 1.35 has a lower oil yield than Brazilian kerogen with an atomic hydrogen-to-carbon ratio of 1.57. In general, the oil shale containing kerogen that is converted efficiently to oil contains relatively low levels of nitrogen (Scouten, 1990).

During retorting, kerogen decomposes into three organic fractions: (i) shale oil, (ii) gas, and (iii) carbonaceous residue. Oil shale decomposition begins at relatively low retort temperatures (300 °C, 572 °F) but proceeds more rapidly and more completely at higher temperatures (Scouten, 1990). The highest rate of kerogen decomposition occurs at retort temperatures of 480−520 °C (895−970 °F). In general, the yield of shale oil yield decreases, the yield of gas yield increases, and the aromaticity of the oil increases with increasing decomposition temperature (Dinneen, 1976; Scouten, 1990). Furthermore, variation of [product distribution with time in the reaction zone can cause a change in product distribution (Fig. 11.3) (Hubbard and Robinson, 1950).

However, there is an upper limit on optimal retorting temperature as the mineral content of the shale may decompose if the temperature is too high. For example, the predominant mineral component of Estonian kukersite shales is calcium carbonate, a compound that dissociates at high temperatures (600−750 °C, 1112−1382 °F for dolomite, and 600−900 °C, 1112−1652 °F for calcite). Thus carbon must be anticipated as a product of and oil shale decomposition process, which will dilute the off-gases (adding to emissions issues) produced from the retorting process. The gases and vapors leaving the retort are cooled to condense the reaction products, including oils and water.

Kinetically, the active devolatilization of oil shale begins at approximately 350−400 °C (660−750 °F), with the peak rate of oil evolution at approximately 425 °C (800 °F), and with devolatilization essentially complete in the range of 470−500 °C (890−930 °F) (Hubbard and Robinson, 1950; Shih and Sohn, 1980). At temperatures near 500 °C (930 °F), the mineral matter, consisting mainly of calcium/magnesium and calcium carbonates, begins to decompose yielding carbon dioxide as the principal product. The properties of crude shale oil are dependent on the retorting temperature, but more importantly on the temperature-time history because of the secondary reactions accompanying the evolution of the liquid and gaseous products. The produced shale oil is dark brown, odoriferous, and tending to waxy oil.

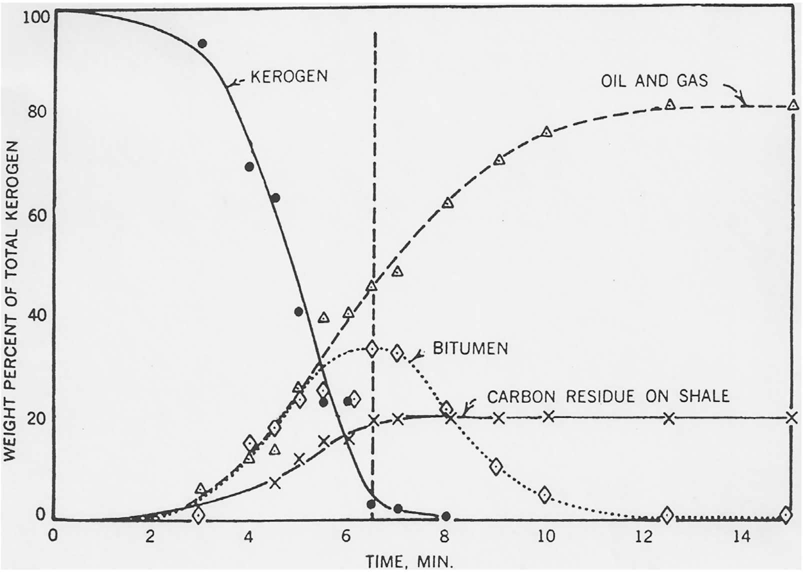

FIGURE 11.3 Variation of product yield with time (Hubbard and Robinson, 1950).

Kinetic studies (Scouten, 1990) indicate that below 500 °C (930 °F) the kerogen (organic matter) decomposes into an extractable product (*bitumen*) with subsequent decomposition into oil, gas, and carbon residue. The actual kinetic picture is influenced by the longer time required to heat the organic material, which is dispersed throughout the mineral matrix, and to the increased resistance to the outward diffusion of the products by the matrix which does not decompose. From the practical standpoint of oil shale retorting, the rate of oil production is the important aspect of kerogen decomposition.

The processes for producing oil from oil shale involve heating (retorting) the shale to convert the organic kerogen to a raw shale oil (Janka and Dennison, 1979; Rattien and Eaton, 1976; Burnham and McConaghy, 2006). Conversion of kerogen to oil without the agency of heat has not yet been proven commercially, although there are schemes for accomplishing such a task but, in spite of claims to the contrary, these have not moved into the viable commercial or even demonstration stage.

However, since there are issues to consider when using the Fischer assay to determine the potential yields of oil from shale, there are other issues to consider relating to the rate of heating (Dyni, 1989; Allix et al., 2011). The reactions that convert kerogen to oil and gas are understood generally, but not in precise molecular detail and can only be represented by simple equations. The amount and composition of generated hydrocarbon derivatives depend on the heating conditions: the rate of temperature increase, the duration of exposure to heat and the composition of gases present as the kerogen breaks down.

Generally, surface-based retorts heat the shale rapidly. The time scale for retorting is directly related to the particle size of the shale, which is why the rock is crushed before being heated in surface retorts. Pyrolysis of particles on the millimeter scale can be accomplished in minutes at 500 °C (930 °F) while pyrolysis of particles tens of centimeters in size takes much longer.

In situ processes heat the shale more slowly. However, slow heating has advantages – the quality of the oil increases substantially. Coking and cracking reactions in the subsurface tend to leave the higher molecular weight (higher boiling) less desirable components in the ground. As a result, compared with surface processing, an in situ process can produce lower boiling products with fewer contaminants.

From the standpoint of shale oil as a substitute for crude oil products, its composition is of great importance. Oils of paraffin types are similar to paraffin crude oil. However, the composition of the kukersite shale oil of Estonia is more complicated and very specific – it contains abundant oxygen compounds, particularly phenols, which can be extracted from oil. The oil cannot serve directly as raw oil for high-quality engine fuel, but is well used as heating fuel. It has some specific properties as lower viscosity and pour point, and relatively low sulfur content, making it suitable for other uses such as marine fuel.

Contrary to other oil shales, obtaining high oil yields of distillable oil from kukersite needs specific conditions of processing. It can be explained by the fact that on thermal processing of kukersite, its elevated moisture percentage and the predominance of calcium carbonate in its mineral part result in high values of specific heat consumption in the process (Yefimov and Purre, 1993). Also shale is rich in organic matter and must pass the temperatures of thermobitumen formation and coking at a relatively high speed to avoid caking and secondary pyrolysis of oil.

One of the characteristics of kukersite causing considerable difficulties in its commercial scale processing is the conversion to a bitumen-like on slow heating – the transition to the plastic state within the temperature range 350–400 °C 660 to 750 °F). The maximum yield of thermobitumen is produced at 390–395 °C (735–745 °F) and it constitutes makes up to 55%–57% w/w of the organic products. At these temperatures carbon content of solid residue (remaining after extraction with mixture of ethanol-benzene) is of the minimum value. However, as the heating continues to 510–520 °C (950–970 °F) the carbon content of the residue increases two-to-three fold. As a result most of the carbonaceous residue in semicoke is of secondary origin formed at the pyrolysis of unstable components like oxygen-containing compounds (Yefimov and Purre, 1993).

The thermal characterization of Australian oil shale involved separation of the unique components of oil shale, the kerogen (organic component) and the clay minerals (inorganic components), using chemical and physical techniques (Berkovich et al., 2000). The heat capacity and enthalpy changes for the kerogen and clay minerals were measured using non-isothermal modulated differential scanning calorimetry from 25 to 500 °C (77–930 °F). Heat capacity data was obtained over a temperature range spanning several hundred degrees in a single experiment. Heat capacity was also estimated by incorporating thermogravimetric data during regions where thermal reactions involving mass loss occurred. Enthalpy data for dehydration and pyrolysis of kerogen were also determined (Scouten, 1990; Berkovich et al., 2000).

The mineralogy of Green River Formation is radically changed when the raw oil shale is subjected to the extreme temperatures of processing (Milton, 1977; Smith et al., 1978; Essington et al., 1987). Mineral reactions from high temperature oil shale retorting can be summarized by two general steps, (i) decomposition of raw minerals and (ii) crystallization from the melt) Complete decomposition of carbonate minerals and silicate minerals forms a pyrometamorphic melt containing the principle ions: Ca^{2+}, Na^{+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Si^{4+}, Al^{3+}, and O^{2+} (Park et al., 1979; Mason, 2006). Trace elements are abundant in the Green River

Formation and are undoubtedly present in the melt, but low abundances is believed to make their contribution to the crystallization of new minerals negligible, although some partitioning has been recorded (Shendrikar and Faudel, 1978).

Silicate mineral products of high temperature oil shale processing fall into several general types; olivine group, melilite group, ortho- and clinopvroxenes, amphibole, feldspar group, quartz, and clay minerals. Amorphous silica (glass) is also common product in oil shale that has been processed at high temperatures then cooled rapidly. Although variation within the mineral groups can be in part due to minor differences in the composition of the raw oil shale, the final mineral suite appears to vary very little when examining material from different processes and localities (Mason, 2006). However, some oil-shale deposits contain minerals and metals that add byproduct dawsonite [$NaAl(OH)_2CO_3$], sulfur, ammonium sulfate, vanadium, zinc, copper, and uranium.

One aspect not normally presented in an oil shale text is that kerogen-rich oil shales tend to become plastic and agglomerate during retorting. This agglomeration can lead to uneven gas and solid flows, or even plugging in extreme cases, in retorts where solids flow is gravity-driven. Because there is always a positive mechanical force available to move the shale up through the retort, anything more than local agglomeration within the bed is avoided. Also, conditions can be selected so that retorting takes place near the top of the bed where interparticle pressures are low, hence the tendency to agglomerate is lowest. Thus, agglomeration is not generally a problem, even with very rich shales, but does deserve consideration when planning a retorting process.

5.5 Combustion

Oil shale can be utilized by several techniques such as direct burning or oil/gas extraction (Al Asfar et al., 2012). The direct burning involves generation of heat by direct combustion of oil shale. Circulated fluidized bed combustion is one of the new technologies used to enhance the efficiency and reduce the emission of environmentally harmful gas emissions (Hammad et al., 2006). This technique is applied in many countries and the results are encouraging. During oil shale combustion, oil shale undergoes the ignition, devolatilization, and solid char particles combustion stages. Ignition is considered as the process initiating the combustion phenomenon. It is very important due to its influence on flame stability, pollutant formation and emission, and flame extinction. Devolatilization process involves the emission of the volatile gaseous matters, which are ignited and undergoes a homogenous combustion after heated up to a certain temperature. Solid char particles combustion, that is ignited as a result of volatile combustion, followed by a heterogeneous reaction, involves the direct attack of oxygen on the solid particles (Jaber and Probert, 1999).

Combustion of oil shale produces significant amounts of pollutants such as sulfur dioxide and nitrogen oxides that cause acid rain and photochemical smog. Large quantities of ash area also formed as a result of burning oil shale. The concentration of the sulfur dioxide increases with bed temperature when first reaching its maximum value at 750 °C (1,360 °F). Above this temperature, the concentration of sulfur dioxide in the gases decreases with increased bed temperature and also drastically decreases with increasing circulating ratio while it increases with increase of secondary air ratio as well as with increased particle size.

Nitric oxide (NO) and nitrogen dioxide (NO_2) concentrations increase with increasing bed temperature up to a temperature on the order of when first reaching the maximum at 850 °C (1,560 °F), and this temperature above the emission of these gases they decrease with increased bed temperature. Also, the emissions of nitric oxide and nitrogen dioxide decease with the secondary air ratio (Jaber and Probert, 1999).

Finally, there are two main categories of oil shale processing (Chapter 14, Chapter 15) which are differentiated by the processes by which the oil shale is accessed, with some shallower deposits accessed by mining (surface strip mining or underground mining) but with the majority of the resource requiring the use of in-situ processing methods if they are too deep and hazardous to mine. Mine based processes have been the most common methods used to date, on oil shales which locally outcrop at surface or near surface, and have been used for hundreds of years. More recently a great deal of effort has been devoted by some major oil and gas producers, to assess various in-situ retorting methods which can be applied to shale oil and oil shale formations after initial depletion of any naturally matured natural gas or crude oil. Ex-situ process (Chapter 14) are preferred for shallow oil shale resources, while in-situ processes (Chapter 15) tend to be favored for deeper deposits.

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CHAPTER

12

Oil shale resources

1. Introduction

Oil shale (i.e. a kerogen-containing shale that produced oil when heated to a high temperature) comprises a truly enormous, and largely untapped fossil fuel resource. As readily accessible crude oil sources dwindle, utilization of the oil shale resource to meet world needs for energy and chemical feedstocks will become both necessary and economically attractive. World-wide oil shale deposits have been estimated to contain in excess of 30 trillion barrels (30×10^{12} bbls) of producible shale oil, but only a small fraction of this amount is easily recoverable using current technology. Thus, the utilization of oil shale to replace crude oil will mean finding economically efficient and environmentally acceptable methods for recovering the energy-rich organic material locked inside the rock matrix of the oil shale and for upgrading the recovered shale oil.

The definition of oil shale is strictly an economic definition insofar as oil shale is a compact, laminated rock of sedimentary origin, yielding in excess of 33% w/w mineral ash and containing organic matter that yields oil when distilled, but not appreciably when extracted with the ordinary solvents for crude oil. Thus, the term *oil shale* is used in this book to denote an organic-rich (kerogen-containing) rock that contains no free oil. In addtion, shale oil is the oil produced from an oil shale by heating.

Three other terms will used extensively, hence their definitions are important. Bitumen (separate from, not to be confused with, the bitumen in tar sand formations) is the organic material which can be extracted from oil shale by organic solvents, such as benzene, toluene, tetrahydrofuran (THF) and chloroform (CHCl3) or mixtures (generally azeotropes) of solvents, such as benzene-methanol (60:40). Kerogen, which comprises the major part of the organic material, is not soluble in such solvents.

These are operational definitions and the relative proportions of bitumen and kerogen depend on the choice of solvent and extraction conditions. Another definition refers to the organic concentrate that is produced by beneficiation or chemical demineralization of an oil shale and is referred to as *kerogen concentrate*. Strictly speaking, this term should refer only to that part of the organic concentrate that is insoluble in organic solvents. However, in common usage, kerogen concentrate refers to the total organic material (kerogen plus bitumen) obtained by removing the mineral (inorganic) constituents of the oil shale. The common usage will be followed in this book, unless stated otherwise.

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Thus, the term *oil shale* (as used in this book) is sedimentary marlstone rock (a rock that consists of a mixture of clay materials and calcium carbonate) that is embedded with rich concentrations of an organic material known (referred to as kerogen). Oil shale is a complex and intimate mixtures of organic and inorganic materials and vary widely in their compositions and properties. Some, such as the oil shale of the Green River formation are not even true shale in the geological sense. Nevertheless, the oil shale of the United States contains approximately 15% organic material, by weight. By heating oil shale to high temperatures, kerogen can be released and converted to a liquid that, once upgraded, can be refined into a variety of liquid fuels, gases, and high value chemical and mineral byproducts.

Thus, oil shale represents a large and mostly untapped source of hydrocarbon fuels. Like oil sands, it is an unconventional or alternate fuel source and it does not contain oil. Oil is produced by thermal decomposition of the kerogen, which is intimately bound within the shale matrix and is nor readily extractable. Many estimates have been published for oil shale reserves (in fact resources), but the rank of countries vary with time and authors but, nevertheless, the United States is listed as number one and Brazil listed most frequently as number two. In the United States, the oil shale formations are concentrated in the Green River Formation in the states of Colorado, Wyoming and Utah, account for nearly three-quarters of this potential.

In fact, estimating shale oil reserves is complicated by several factors. First, the amount of kerogen contained in oil shale deposits varies considerably. Second, some nations report as reserves the total amount of kerogen in place, including all kerogen regardless of technical or economic constraints; these estimates do not consider the amount of kerogen that may be extracted from identified and assayed oil shale rock using available technology and under given economic conditions. By most definitions, *reserves* refers only to the amount of resource which is technically exploitable and economically feasible under current economic conditions. The term *resources*, on the other hand, may refer to all deposits containing kerogen. Third, shale oil extraction technologies (although not in general use in North America) are still developing, so the amount of recoverable kerogen can only be estimated.

There is a wide variety of extraction methods, which yield significantly different quantities of useful oil. As a result, the estimated amounts of resources and reserves display wide variance. The kerogen content of oil shale formations differs widely, and the economic feasibility of its extraction is highly dependent on international and local costs of oil. Several methods are used to determine the quantity and quality of the products extracted from shale oil. At their best, these methods give an approximate value to its energy potential. One standard method is the Fischer assay (Chapter 1, Chapter 11), which yields an oil yield. This method has been modified, standardized, and adapted but the method does not, however, indicate the exact amount oil that could be extracted from a sample of oil shale. As a result, some processing methods yield considerably more useful of the shale oil product than the Fischer Assay would indicate (Heistand, 1976). In summary, any estimates of shale oil reserves can only be based on speculative estimates from application of the Fischer assay test method to (often) non-representative samples taken from an oil shale deposit and the assay data (in terms of oil yield in gallons per ton) must not to be taken as *proven reserves* as long as they are subject to speculation. It is safe to state, however, that the world resources of oil shale and reserves of potentially producible shale oil are enormous!

On a global scale, oil shale formations are found on all continents and such deposits contain a solid hydrocarbonaceous material (*kerogen*) (Chapter 1, Chapter 13) that can be converted to crude shale oil by thermal decomposition (Chapter 14, Chapter 15). The deposits in Colorado, Utah, and Wyoming contain both a solid hydrocarbonaceous organic material (kerogen) that can be converted to crude shale oil by heating, and sodium minerals that can be used in air pollution control, in glassmaking, and to produce aluminum. Deposits of somewhat different chemical composition and geology are found elsewhere. Those in other countries (Scotland, Spain, Australia) have been the sites of very small-scale industries in the past. Other countries (Brazil, Russia, and the People's Republic of China) either have such industries or are at various stages of resource development. However, in spite of the published numbers and (at best, speculative) projections, it is difficult to gather realistic production data (given either in shale oil or oil shale in weight or in volume). In many cases, there are significant discrepancies between percentages in reserve and in production because of the assumptions of the *estimates* of the total resource and recoverable reserves. Because of the varied assumptions, caution is advised when assembling data that are purported to represent the amount of the oil shale resource. Thus, this aspect of oil shale technology requires serious review.

In regard to local (United States) deposits of oil shale, the deposits that occur in the western United States have a different chemical composition and geological history to the deposits of the western United States. In addition, oil shale deposits that are found elsewhere – in countries such as Australia, Brazil, Estonia, People's Republic of China, Russia, Scotland, and Spain – also offer chemical and geological differences to the deposits found the United States. Nevertheless, these countries have been the sites of small-scale oil shale industries in the past and the various levels of government and private industry have recognized the potential for oil shale as a source of liquid fuels and still continue attempts to establish an oil shale industry, or are giving the idea serious consideration (Brendow, 2003, 2009).

Oil shale formations occur in many parts of the world and range from Cambrian to Tertiary age, may occur as minor accumulations of little or no economic value or giant deposits that occupy thousands of square kilometers and reach thicknesses of 2000 feet or more. Oil shale formations were deposited in a variety of depositional environments, including fresh-water to highly saline lakes, epicontinental marine basins and subtidal shelves, and in limnic and coastal swamps, commonly in association with deposits of coal. In this regard, oil shale is quite different from crude oil, which is more concentrated in certain regions of the world. Depending upon the data source and the year of reporting, the statistical values vary. In fact, before progressing to *resources* and *reserves* for various countries, it is necessary to first understand that *in-place resources* and *proved reserves* (*proven reserves*) have markedly different meanings (Speight, 2007, 2008, 2011, 2013).

The former (*in-place resources*) relates to *potential reserves* while only the latter (*proved reserves* or *proven reserves*) indicates the existence of fossil fuel resources that can be exploited. For example, a deposit of oil shale having economic potential is typically one that is at or near to the surface to be developed by open-pit or conventional underground mining or by in-situ methods (Scouten, 1990; Dyni, 2003, 2006). Although some Colorado oil shale reaches the surface at places such as the Colony deposit, many deposits typically start at approximately 1000 feet beneath the surface and extend downward for as much as another 2000 feet.

Within the oil shale column are rocks that vary considerably in kerogen content, with some portions of the section having a higher kerogen content (richer oil shale) and other portions of the deposit having a lower kerogen content (leaner oil shale). The entire column has been estimated to be able to produce on the order of one million barrels of oil equivalent per acre (BOE/acre) over its productive life – but that is only an estimate and is based upon many factors, some of which are out of the control of the developer due to chemical and geological factors and/or may be subject to politics more than to an accurate assessment of the resources (Speight, 2011).

Equating oil shale with other types of hydrocarbon fossil fuel and hydrocarbon-producing fossil fuels often indicates (to some observers) that comparable means of exploiting oil shale can be used. However, oil shale is not directly comparable to either crude oil or coal or even tar sand bitumen, though it may appear to share some characteristics of each (Speight, 2008). Each ton of oil shale – a carbonate rock, generally mudstone or siltstone (Chapter 1) – contains significant quantities of a solid organic sedimentary (conveniently referred to as *kerogen*) with a trace of extractable organic material (conveniently but incorrectly referred to as *bitumen*), and gas. Some oil shale is rich in carbonate (marl or marlstone – a calcium carbonate – rich or lime-rich mud or mudstone which contains variable amounts of clay and silt), whereas other deposits are relatively rich in clay minerals (Scouten, 1990; Dyni, 2006). All of which serves to make oil shale resource estimation (especially the potential for producing shale oil) that much more difficult.

Indeed, the reliability of resource data, as indicated in the foregoing paragraphs, can range from excellent to poor. Data for some deposits that have been explored extensively by core drilling, such as the Green River oil shale in Colorado, the kukersite deposit in Estonia, and some of the Tertiary deposits in eastern Queensland, Australia, are especially good in comparison to others. Many other resource data are open to question, speculation, and (at best) inspired guesswork.

Thus, a word of caution is advised. The numbers presented from geological studies of the deposits in the various countries are a mixed bag. Evaluation of world oil-shale resources is especially difficult – even more difficult than an estimation of crude oil resources or coal resources (Speight, 2011, 2013 – because of the wide variety of analytical units that are reported. Furthermore, some resources are presented as reserves of *in situ shale oil* – at best only a potential and highly speculative number – while others are presented as percent by weight of in-place organic matter – again, an estimated number but still better than the former number since none of the formations contain shale oil. And, the yield of shale oil from a formation is speculative and subject to the behavior of the kerogen under thermal conditions. In addtion, there are sufficient difference in the properties of the shale oil (Tables 12.1 and 12.2) that can make refining the raw oil a significant task (Chapter 16).

2. Total resources

The terms oil shale (for the rock or formation) and shale oil (for the retorted product) has been well understood for more than one hundred years (WEC, 2016). These two terms have been consistently applied to the fine-grained, organic-rich rock that only yields its petroleum product on heating either at the surface or at depth.

TABLE 12.1 Properties of shale oil from various sources.

Location	Specific gravity (API)	Elemental analysis % w/w					Composition of<350 °C % w/w		
		C	H	O	N	S	Saturates	Olefins	Aromatic
Colorado, USA	0.943 (18.6)	84.90	11.50	0.80	2.19	0.61	27	44	29
Kukersite, Estonia	1.010 (9.0)	82.85	9.20	6.79	0.30	0.86	22	25	53
Rundle, Australia	0.64 (0.91)	79.50	11.50	7.60	0.99	0.41	48	2	50
Irati, Brazil	0.92 (22.5)	84.30	12.00	1.96	1.06	0.68	23	41	36
Maoming, China	0.903 (24.0)	84.82	11.40	2.20	1.10	0.48	55	20	25
Fushun, China	0.912 (26.0)	85.39	12.09	0.71	1.27	0.54	38	37	25

TABLE 12.2 Properties of shale oil from different formations in China.

Producing area	Fushun	Maoming	Huadian	Yaojie
Properties				
Specific gravity	0.9033	0.9122	0.8789	0.93
Freezing point, °C	33	30	26	26
Wax content, % w/w	20.2	13.2	5.9	10
Resid, % w/w	0.85	1.54	0.9	5
Distillation range, °C				
Initial boiling point	216	214	173	211
10% @	264	259	221	258
20% @	293	283	250	284
30% @	318	306	278	311
40% @	343	330	301	334
50% @	362	3540	331	366
Elemental composition, % w/w				
Carbon	85.39	84.82	85.17	84.84
Hydrogen	12.1	11.4	12.2	11.1
Sulfur	0.54	0.48	0.42	0.7
Nitrogen	1.27	1.1	0.75	0.97
Oxygen	0.71	2.2	1.43	2.4

The most commonly used classification of oil shale divides it into three groups based on how it was formed: (i) terrestrial oil shale, (ii) lacustrine oil shale, and (iii) marine oil shale (Chapter 11). Most known oil shales are deposited at the bottom of bodies of water and therefore, belong to the first two groups. In addition to the kukersite found in Estonia, tasmanite and marinite are also marine type oil shales. Oil shale can also be divided into three groups according to its composition: (i) carbonate rich shale where minerals such as calcite and dolomite are dominant, (ii) marleous shale, which contains both carbonate and clay minerals, and (iii) clayey shales, which mainly consist of terrigenous clay materials. The Estonian kukersite is one of the carbonate rich shales, whereas the Green River oil shale from the United States is marleous. The oil shale formations in Brazil, the Fushun oil shale formation in China, and the Stuart oil shale formation in Australia consists of clayey shale.

The potential resources of oil shale in the world are enormous but a precise evaluation of world oil shale resources, like crude oil resources, is made difficult because of the numerous ways by which the resources are assessed (Speight, 2011; WEC, 2016). While many oil shale deposits have been explored only to a minor extent, some deposits have been fairly well delineated by drilling and analyses (Scouten, 1990; Dyni, 2003, 2006). These include the Green River oil shale in western United States, the Tertiary deposits in Queensland, Australia, the deposits in Sweden and in Estonia, the El-Lajjun deposit in Jordan, as well as some of the deposits in Brazil, France, Germany, and Russia. The remaining deposits are poorly delineated and further competent investigation and analysis are needed to adequately determine their resource potential.

The largest known deposit is the Green River formation in the western United States which is a geologic entity underlying some 34,000 square miles of terrain in northwestern Colorado, southwestern Wyoming, and northeastern Utah. The formation has been divided into several distinct geologic basins. The Green River, Great Divide, and Washakie basins occur primarily in Wyoming. Together with the Sand Wash basin in northern Colorado, these basins underlie approximately 14,000 square miles. Approximately 35 million years ago they were occupied by a single large and long-lasting freshwater lake.

The formation has been estimated to contain a total estimated in-place resource that *may* have the potential to produce approximately 5 trillion barrels (5×10^{12} bbls) of shale oil. In Colorado alone, the total in-place resource is supposed to be on the order of 1.5 trillion barrels (1.5×10^{12} bbls) of oil. The Devonian black shales of the eastern United States are estimated to have the potential to produce 189 billion barrels (189×10^{9} bbls) of oil.

A 2016 estimate places the total world resources of oil shale equivalent to yield of 6.05 trillion barrels (6.05×1012 bbls) of shale oil, with the largest resource deposits in the United States accounting more than 80% of the world total resource (WEC, 2016). For comparison, at the same time the world's proven conventional crude oil reserves are estimated to be 1.6976 trillion barrels (1.6976×10^{12} bbls). The largest deposits in the world occur in the United States in the Green River Formation, which covers portions of Colorado, Utah, and Wyoming and approximately 70% of this resource lies on land owned or managed by the federal government of the United States. Deposits in the United States constitute more than 80% of world resources; other significant resource holders being China, Russia, and Brazil.

The actual data for the oil shale resources of the world could be much higher (or even much lower) since the oil shale resources of some countries are not reported and many known deposits have not been fully investigated. On the other hand, several deposits, such as those of the Heath and Phosphoria Formations and portions of the Swedish alum oil shale, have been degraded by geothermal heating. Therefore, the resources reported for such deposits are probably too high and somewhat misleading. The amount of shale oil that can be recovered from an oil shale deposit (recoverable resources) depends upon many factors, not the least of which are (i) the character of the deposit and (ii) the method used for assessment.

To determine the former (i.e., character of the deposit) requires careful drilling and geochemical investigation. The method used for the latter (i.e., assessment of the potential to produce shale oil) is always open to question. Gravimetric, volumetric, and heating values have all been used to determine the oil shale grade, which is usually expressed in gallons per ton (or liters per tonne) if the grade of oil shale is given in volumetric measure (gallons per ton), tonne), the specific gravity (density) of the oil must be known to convert gallons to a weight percent estimate (Scouten, 1990; Dyni, 2003, 2005; 2006; Speight, 2008). A deposit worthy of commercial investigation might be expected to produce at least ten gallon per ton of shale oil.

The obvious need is for new and improved methods for the economic recovery of shale oil and any added-value products but the deciding factor for oil shale development has always been governed by the price of crude oil. The fluctuating price of crude oil (usually fluctuating to the high side of the price range) and the geopolitics of recent decades have prompted governments around the world to re-examine national energy supplies and to consider national security issues (Speight, 2011). All seem to have reached the same conclusions: energy security can only be accomplished by developing the indigenous natural resources (such as oil shale).

At present, oil shale is commercially exploited in several countries: Brazil, China, Estonia, and Australia. Brazil has a long history of oil shale development and it is known that oil shale in Brazil has long been exploited since the late nineteenth century. In China, 80 new retorts (Fushun retorts) are employed to produce shale oil (Qian et al., 2003). There are also claims that China has the fourth largest oil shale deposits in the world after the United States, Brazil, and Russia.

Oil shale reserves refers to oil shale resources that are economically recoverable under current economic conditions and technological abilities. Oil shale deposits range from small presently economically unrecoverable to large potentially recoverable resources. Defining oil shale reserves is difficult, as the chemical composition of different oil shales, as well as the kerogen content and extraction technologies, vary significantly. The economic feasibility of shale oil production and extraction is highly dependent on the price of conventional oil; if the price of crude oil per barrel is less than the production price per barrel of shale oil, it is uneconomic.

As source rocks for most conventional crude oil reservoirs, oil shale deposits are found in all world oil provinces, although most of them are too deep to be exploited economically. There are more than 600 known oil shale deposits around the world. Although resources of oil shale occur in many countries, only 33 countries possess known deposits of possible economic value. Many deposits need more exploration to determine their potential as reserves. Well-explored deposits, which could ultimately be classified as reserves, include the Green River deposits in the western United States, the Tertiary deposits in Queensland (Australia), deposits in Sweden, Estonia, the El-Lajjun deposit in Jordan, and deposits in

France, Germany, Brazil, China, and Russia. It is expected that these deposits would yield at least 0.25 bbl of shale oil per metric ton of shale, using the Fiscvher assay data.

3. Occurrence and history by country

Oil shale represents a large and mostly untapped source of hydrocarbon fuels. Like tar sands (*oil sands* in Canada), it is an unconventional and/or alternate fuel source and it does not contain oil. Oil is produced by thermal decomposition of kerogen, which is intimately bound within the mineral matrix of the shale and, as such, is not readily extractable.

Many estimates have been published for oil shale reserves (in fact resources), but the rank of countries vary with time and authors, except that US is always on number one over 60 %. Brazil is the most frequent number two. The United States has vast known oil shale resources that could translate into as much as 2.2 trillion barrels (2.2×10^{12} bbls) of *oil-in-place*. In fact, the largest known oil shale deposits in the world are in the Green River Formation, which covers portions of Colorado, Utah, and Wyoming. Estimates of the oil resource within the Green River formation vary from 1.5 to 1.8 trillion barrels ($1.5–1.8 \times 10^{12}$ bbls) (Scouten, 1990; Dyni, 2005, 2006). However, not all resources in place are recoverable but, for policy planning purposes, it is enough to know that any amount in this range is very high. For example, the half-way point in the estimate (800–900 billion barrels, ($800–900 \times 10^{9}$ bbls) is more than triple the proven oil reserves of Saudi Arabia. With present demand for crude oil products in the United States at approximately 17–20 million barrels per day, oil shale (by only meeting a quarter of that demand) would last for more than 400 years.

Oil shale occurs in nearly 100 major deposits in 27 countries worldwide (Duncan and Swanson, 1965; Culbertson and Pitman, 1973; Culbertson et al., 1980; Bauert, 1994). It is generally shallower (<3000 feet) than the deeper and warmer geologic zones required to form oil. On a worldwide basis, the oil shale resource base is believed to contain approximately 2.6 trillion barrels (2.6×10^{12} bbls) of which the vast majority (eastern plus western shale) – approximately 2.2 trillion barrels (2.2×10^{12} bbls) – is located within the United States.

3.1 Australia

Australia has significant potential unconventional oil resources contained in oil shale deposits in several basins (Fig. 12.1), which Australia range from small and noneconomic to deposits large enough for commercial development. The demonstrated oil-shale resources of Australia total 58 billion tons (58×10^{9} tons), from which approximately 24 billion barrels (24×10^{9} bbls) of shale oil is recoverable (Crisp et al., 1987; Cook and Sherwood, 1989; Australian Government, 2010).

Production from oil shale deposits in southeastern Australia began in the 1860s, coming to an end in 1952 when government funding ceased. Between 1865 and 1952 some 4 million tonnes (4.4×10^{6} US tons) of oil shale were processed. Much of the early production of oil shale in Australia was from the torbanite deposits of New South Wales. During the early years of mining, torbanite was used for gas enrichment in Australia and overseas, but paraffin, kerosene, and wood preserving and lubricating oils were also produced. Of 30 deposits in New South Wales, 16 were commercially exploited (Crisp et al., 1987).

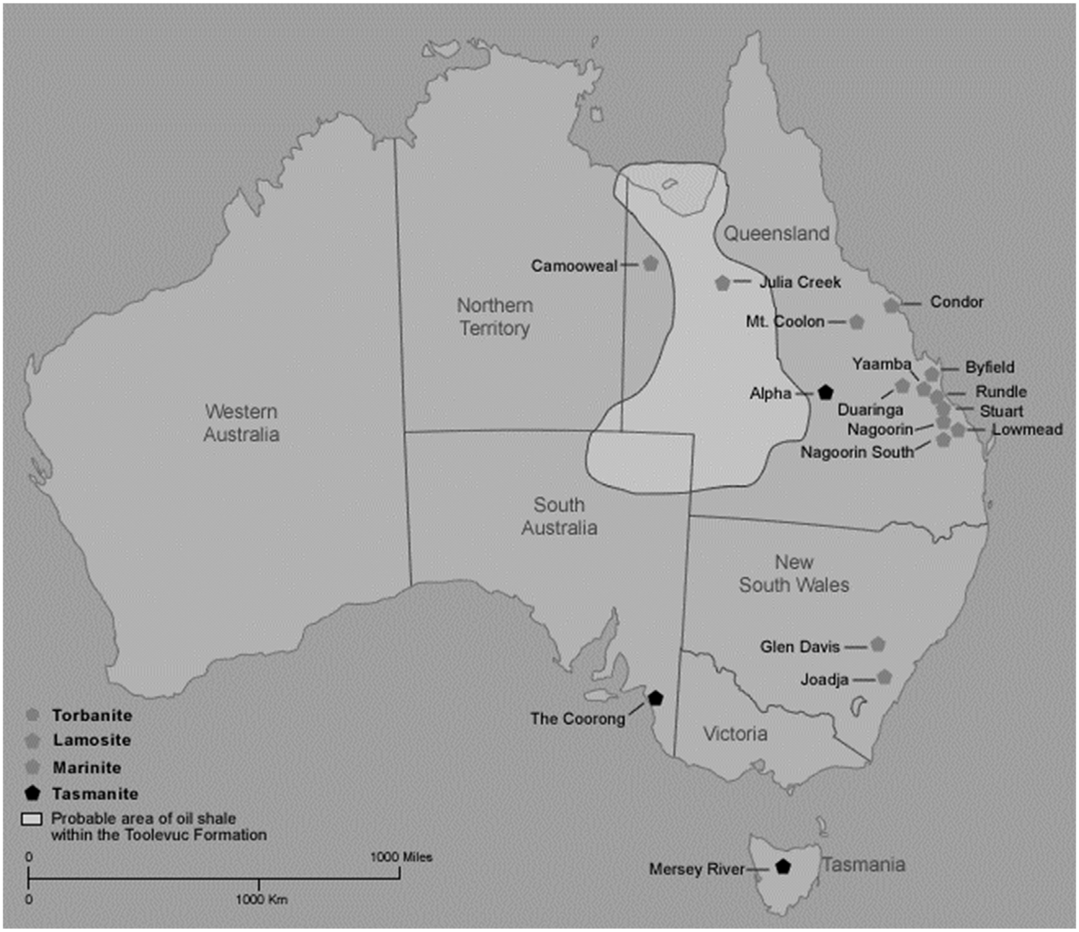

FIGURE 12.1 Australian oil shale deposits.

Two small deposits of torbanite have been investigated in Queensland. These include the small but high-grade Alpha deposit, which constitutes a potential in-situ resource of 19 million US barrels (19 × 10^6 US bbls) (Noon, 1984, p. 4) and a smaller deposit at Carnarvon Creek. Several companies attempted to develop the marine Tasmanite deposits of Permian age in Tasmania during the early 1900s. Between 1910 and 1932, a total of 1100 m^3 (approximately 7600 barrels) of shale oil was produced from several intermittent operations. Further developments are unlikely unless new resources are found (Crisp et al., 1987).

Oil shale in the marine Toolebuc Formation of Early Cretaceous age underlies approximately 18,000 square miles (approximately 12, 000, 000 acres) in parts of the Eromanga and Carpenteria Basins in Queensland and adjacent States. The oil-shale zone ranges up to 25 feet in thickness but yields on average only approximately 10 gallons per ton. However, the Toolebuc Formation is estimated to contain the potential for approximately 1.7 trillion barrels (1.7 × 10^{12} bbls) of in-situ shale oil that could be produced by open pit mining of the shale (Ozimic and Saxby, 1983; Sherwood and Cook, 1983). The atomic hydrogen to carbon (H/C) ratio of the organic matter is approximately 1.1 ± 0.2 with high aromaticity (>50%). However, only approximately 25% of the organic matter converts to oil by conventional retorting (Ozimic and Saxby, 1983) which substantially reduces to potential yield of shale oil.

As a result of the increase in the price of crude oil related to the oil crisis of 1973 and 1974, exploration for oil shale in Australia was greatly accelerated during the late 1970s and early 1980s. However, by 1986, the prices of crude oil dropped dramatically, and interest in the exploitation of oil shale diminished (Crisp et al., 1987).

During the late 1970s and early 1980s a modern exploration program was undertaken by two Australian companies, Southern Pacific Petroleum NL and Central Pacific Minerals NL (SPP/CPM). The aim was to find high-quality oil shale deposits amenable to open-pit mining operations in areas near infrastructure and deep-water ports. The program was successful in finding a number of silica-based oil shale deposits of commercial significance along the coast of Queensland. Ten deposits clustered in an area north of Brisbane were investigated and found to have an oil shale resource in excess of 20 billion barrels (20×10^9 bbls) (based on a cutoff grade of 50 L/t at 0% moisture), which could support production of more than 1 million barrels per day of shale oil.

Since 1995, Southern Pacific Petroleum NL and Central Pacific Minerals NL (continuing their interest and at one time joined by the Canadian oil sand company Suncor Energy Inc.) have been studying the Stuart Deposit near Gladstone, Queensland, which has an estimated potential to produce 2.6 billion barrels (2.6×10^9 bbls) of oil. From June 2001 until to March 2003, 703,000 barrels of oil, 62,860 barrels of light fuel oil, and 88,040 barrels of ultra-low sulfur naphtha were produced from the Gladstone area. After processing, the shale oil could be converted to a low-emissions gasoline. In Suncor had had the role of operator of the Stuart project and in April 2001, Southern Pacific Petroleum and Central Pacific Minerals purchased interest owned by Suncor.

Having committed itself to ensuring that the Stuart oil shale project had a sustainable development, Southern Pacific Petroleum put various schemes into operation to achieve its stated environmental goals. One in particular launched in 1998 was a reforestation carbon dioxide sink. Approximately 250,000 trees were planted on deforested lands in Central Queensland. In September 2000, the first carbon trade in Queensland was announced between Southern Pacific Petroleum and the state government and was based on the reforestation trials.

The Stuart project (found to have a total *in situ* shale oil resource of 2.6 billion barrels (2.6×10^9 bbls) and a capacity to produce more than 200,000 b/d) incorporated the Alberta-Taciuk Processor (ATP) retort technology into the project (Schmidt, 2003), which involved a revolving kiln (originally developed for Alberta tar sand projects. The project had three stages: (i) the demonstration plant, which produced a 42° API gravity shale oil containing 0.4% w/w/sulfur and 1.0% w/w nitrogen, was constructed between 1997 and 1999 and produced over 500 000 barrels of oil product. The plant was designed to process 6000 tonnes (6600 US tons) per day of run-of-mine (wet shale) to produce 4500 barrels per day of shale oil products; (ii) the process was to be scaled up by a factor of 4 to a commercial-sized module processing 23,500 tonnes (27,600 US tons) per day to produce 15,500 barrels per day of shale oil − it was envisaged that multiple commercial Taciuk processors units would come on stream during 2010–3 giving the plant the ability of the plant processing up to 380,000 tonnes (41,900 US tons) per day and producing up to 200,000 barrels per day shale for a period in excess of 30 years; and finally (3) the third stage was conceived as processing 125,000 tonnes (138,000 US tons) per day of oil shale to give 65,000 barrels per day of shale oil products, bringing total Stuart production to approximately 85,000 barrels per day. Overall, shale oil production ran for 87 days of operation from and peaked at 3700 barrels per day.

However, the project ended when Southern Pacific Petroleum was placed in receivership in 2003. In February 2004 Queensland Energy Resources Ltd. (QER) acquired the oil shale assets of Southern Pacific Petroleum and ran final plant trials at the demonstration facility. However, no production ensued and the Environmental Protection Agency regulated operations until the plant was closed in mid-2004. The facility is now on *care and maintenance* in an operable condition. Queensland Energy Resources continues to assess the possibilities for the future commercial operation of the Stuart project. The company (QER) spent the 2005 to 2007 period testing indigenous Australian oil shale at a pilot plant in Colorado and demonstrated successfully that, by using the Paraho process, it could operate an oil shale-to-shale oil and liquid products business in Queensland.

In August 2008 the Queensland Government announced that it had issued a 20-year moratorium on the development the McFarlane oil shale resource by Queensland Energy Resources. The McFarlane deposit, located some 10 miles south of Proserpine in central Queensland, is considered a strategically important resource with the potential to supply in excess of 1.6 billion barrels (1.6×10^9 bbls) of oil. Following more than a quarter of a century of extraction of test material, Queensland Energy Resources announced during third quarter 2009 that it had reached agreement with the Queensland Government to back fill and rehabilitate the McFarlane box cut.

Also in 2008, it was announced by Queensland Energy Resources that the company had decided against the use of the Taciuk processor because of potential problems in scale-up of the technology to commercial size. Queensland Energy Resources decided in favor of the Paraho II technology to develop oil shale deposits along the east coast of Queensland. The company also noted that the oil shale deposits, collectively known as the McFarlane oil shale, have the potential to produce 1.6 billion barrels (1.6×10^9 bbls) of shale oil over the next 40 years.

During 2009, Queensland Energy Resources undertook refurbishment of the site and dismantled the Taciuk retort. In May 2010 the company (QER) announced that construction of a demonstration plant would begin at Yarwun, north of Gladstone. Using Paraho II technology (Chapter 4), the plant when complete is expected to process 2.5 tonnes (2.8 US tons) of shale per hour and produce between 37 and 40 barrels per day of synthetic crude oil.

In September 2011, Queensland Energy Resources Ltd (QER) produced its first crude oil from its demonstration Paraho II vertical shaft kiln processing plant at the Stuart deposit near Gladstone, central Queensland. Further news is awaited with eager anticipation.

3.2 Brazil

The Brazilian oil shale resource base is one of the largest in the world and nine deposits of oil shale ranging from Devonian to Tertiary age have been reported in different parts of Brazil (Padula, 1969). Of these, two deposits have received the most interest: (i) the lacustrine oil shale of Tertiary age in the Paraíba Valley in the State of São Paulo northeast of the city of São Paulo; and (ii) the marinite oil shale of the Permian Iratí Formation, which outcrops extensively in southern Brazil, contains estimated reserves of more than 700 million barrels of oil (700×10^6 bbls) and 880 billion cubic feet (880×10^9 ft^3) of natural gas.

The Paraíba Valley deposits contain an estimated reserve of oil shale with the potential to produce 840 million barrels (840×10^6 bbls) of shale oil and the total resource is estimated at 2 billion barrels (2×10^9 bbls). The deposit (approximately 145 feet thick) includes several types of oil shale: (i) brown to dark brown fossiliferous laminated paper shale, (ii) semi-papery oil shale of the same color, and (iii) dark olive, sparsely fossiliferous, low-grade oil shale that fractures semi-conchoidally (Dyni, 2006).

The Iratí oil shale is dark gray, brown, and black, very fine grained, and laminated. Clay minerals compose 60–70% of the shale and organic matter makes up much of the remainder, with minor contributions of detrital quartz, feldspar, pyrite, and other minerals. Carbonate minerals are sparse. The Iratí oil shale is not notably enriched in metals, unlike marine oil shales such as the Devonian oil shales of eastern United States.

Brazil started production of shale oil in 1881 and is the second rank after the United States for resources (well distributed) and after Estonia for production. In 1935 shale oil was produced at a small plant in Sìo Mateus do Sul in the State of Paran and in 1950, following government support, a plant capable of producing 10,000 barrels per day shale oil was proposed for Tremem b, Sìo Paulo. Brazil developed the largest surface oil shale pyrolysis reactor in the world – the Petrosix 11-m vertical shaft gas combustion retort.

In 1935 shale oil was produced at a small plant in São Mateus do Sul in the State of Paraná and in 1950, following government support, a plant capable of producing 10 000 b/d shale oil was proposed for Tremembé, São Paulo. The oil shale resource base is substantial and was first exploited in the late nineteenth century in the State of Bahia (Dyni, 2006). Further demonstration plants were built in the 1970s and 1980s and shale oil production has continued since that time.

After the development of the Petrosix process for shale oil production, operations were concentrated on the reservoir of Sìo Mateus do Sul and brought a pilot plant (8 inch internal diameter retort) into operation in 1982. A 6-feet internal diameter retort demonstration plant followed in 1984 and is used for the optimization of the Petrosix technology. A 2200 tons per day, 18-feet (internal diameter) prototype retort (the Irati Profile Plant), originally brought on line in 1972, began operating on a limited commercial scale in 1981 and a further commercial plant – a 36-feet internal diameter retort was brought into service in December 1991.

Surface facilities at Sao Mateus do Sul, in the state of Parana, are capable of processing 7800 US tons of shale per day to produce fuel oil, naphtha, liquefied petroleum gas (LPG), shale gas, sulfur and asphalt additives. As near as can be determined, the Petrosix retorting process (Petrosix) where the shale undergoes pyrolysis yields a nominal daily output of approximately 3870 barrels of shale oil along with fuel gas and sulfur.

There are reports that the intention of Petrobras is to maintain the technological expertise and development of its indigenous capacity but without expansion.

3.3 Canada

Oil shale occurs throughout Canada and 19 oil shale deposits identified. However, the majority of the potentially-producible oil shale resources remain poorly defined – the most explored deposits are those in the provinces of Nova Scotia and New Brunswick (Macauley, 1981; Hyde, 1984; Ball and Macauley, 1988; Kalkreuth and Macauley, 1987).

The Devonian-Lower Mississippian oil shale deposits in the eastern United States extend north into Ontario and Quebec and have a high volume of organic-rich shale (Matthews et al., 1980; Matthews, 1983). A similar setting also occurs in the Ordovician in Canada, but the total volume of organic-rich shale is lower. Flooding of the continental margin also occurred in Arctic Canada in the Devonian and Ordovician, and organic-rich shales of these ages are present in the Northwest Territories. In eastern Canada, a series of rift basins developed in Nova Scotia, New Brunswick, and Newfoundland in the Carboniferous era. In several of these basins, intervals of organic-rich lacustrine shales developed, but the total volume of the oil shale had not been fully defined and the potential of the oil shale to produce shale oil may be limited (Hyde, 1984).

The oil-shale deposits range from Ordovician to Cretaceous age and include deposits of lacustrine and marine origin; as many as 19 deposits have been identified (Macauley, 1981; Davies and Nassichuk, 1988). During the 1980s, a number of the deposits were explored by core drilling (Macauley, 1981, 1984a; 1984b; Macauley et al., 1985; Smith and Naylor, 1990).

Outcrops of Lower Carboniferous lacustrine oil shale (Grinnell Peninsula, Devon Island, Canadian Arctic Archipelago) are as much as 300 feet thick and yield up to 100 gallons per ton of shale. However, for most Canadian deposits, the resources of in-situ shale oil remain poorly known (Dyni, 2006).

Of the areas in Nova Scotia known to contain oil shale, development has been attempted at two deposits – Stellarton and Antigonish. Mining took place at Stellarton from 1852 to 1859 as well as during 1929 and 1930 and at Antigonish in 1865. The Stellarton Basin is estimated to hold some 825 million tonnes (909×10^6 US tons) of oil shale, with a hypothetical *in situ* oil content of approximately 168 million barrels. The Antigonish Basin has the second largest oil shale resource in Nova Scotia, with an estimated 738 million tonnes (813×10^6 US tons) of shale capable of producing a speculative 76 million barrels of shale oil.

Investigations into retorting and co-combustion (with coal for power generation) of Albert Mines oil shale (New Brunswick) have been conducted, including some experimental processing in 1988 at the Petrobras plant in Brazil. Interest has been shown in the New Brunswick deposits for the potential they might offer to reduce sulfur emissions by co-combustion of carbonate-rich shale residue with high-sulfur coal in power stations.

In mid-2006, Altius, a Canadian company based in Newfoundland, was awarded a license to explore for oil shale in the Albert Mines prospect. During 2008, 2009 a drilling program was undertaken within a license area of 240 acres. It is believed that the oil shale resource is likely to be significant but detailed evaluation is necessary before any reasonable estimates can be made.

Development of the Alberta oilfields and the Athabasca (Alberta) tar sand deposits and Lloydminster (Alberta-Saskatchewan border) has taken precedence (Speight, 2007, 2009) and the need to develop the oil shale deposits has only continued on a low level of effort.

3.4 China

The oil shale deposits oil in China are widely distributed and the formations vary in geological age – ranging from Carboniferous, Permian (Paleozoic), Triassic, Jurassic of Mesozoic to the leading Tertiary of Neozoic (Hou, 1984; Han et al., 2006; Liu et al., 2017).

The oil shale deposits in China range widely in age, from the Late Paleozoic to the Cenozoic, while the Carboniferous-Permian, Jurassic, Cretaceous and Paleogene were the most important periods as regards oil shale accumulation. Controlled by three geodynamic systems of the Paleo-Asian Ocean, the Tethys—Paleo-Pacific Ocean and the Indian-Pacific Ocean, the age of oil shale deposits becomes progressively younger from the northwest to the southeast. The Upper Paleozoic oil shale includes the Lower Permian oil shale mainly distributed in the Yaomoshan, Shuimogou and Lucaogou basins in the northern area of Bogda Mountain in the southern Junggar Basin of western China, as well as a small number of Upper Carboniferous oil shale deposits in the Jining and Liupanshan basins in the northwestern region of the country.

Mesozoic oil shale deposits originate from the Jurassic and Cretaceous periods. Oil shale of Middle Jurassic age is distributed in the Qiangtang, Qaidam and Hetao basins in western China. The Lower Cretaceous oil shale is concentrated in some small basins in northeastern China, such as Dayangshu, Laoheishan, Luozigou, Yangshugou, Chaoyang and Fuxin. The Upper Cretaceous oil shale is mainly accumulated in large basins like Songliao.

The youngest oil shale deposits are of Eocene and Oligocene age and are found in the Fushun, Huadian, Yilan, Shulan and Huangxian basins in eastern China, with some secondary deposits in the Maoming and Beibu Gulf basins in southern China, as well as small occurrences in the western Lunpola Basin in northern Tibet. The Paleocene oil shale is found only in the Xiangxian Basin, and the Miocene oil shale of Neogene is only distributed in the Maoming Basin.

Oil shale resources in China are abundant, with deposits mainly found in the continental environment and, secondarily, in marine-continental facies. The color of oil shale is black to grayish black, black to gray brown or gray to dark gray. In general, the darker the color, the higher the quality of oil shale. The most common minerals in oil shale are clay minerals, quartz and feldspars. The concentration of organic carbon in Chinese oil shale is high, between 7.48 and 38.02% w/w. By organic genetic type, oil shale can be divided into sapropelic, humosapropelic and saprohumic oil shale. Oil shale used for industrial purposes has a medium to high oil yield and high ash content. Oil shale resources in China are mainly concentrated in 20 provinces and autonomous regions, 50 basins and 83 petroliferous shale areas. Total oil shale resources are estimated at approximately 978 billion tons, i.e. approximately 61 billion tons (61×10^9 tons, approximately 40×10^9 bbls) of potentially-producible shale oil, mainly distributed throughout eastern and central China and the Qinghai-Tibet Region in western China. Oil shale in China was deposited mainly in extensional and intra-plate basins during the Mesozoic and the Cenozoic. The size of the basins diminishes from older to younger deposits. Oil shale resources that yield shale oil more than 5% w/w account for approximately 72% of the total resources in the country (Liu et al., 2017). The two main resources of oil shale occur in Fushun (Liaoning Province) and Maoming (Guangdong Province) (Baker and Hook, 1979; Shi, 1988; Liu et al., 2017).

From 2003 to 2006, China evaluated its oil shale resources for the first time ever. The working area for evaluation was divided into five regions: eastern, central, southern and western China and the Qinghai-Tibet Region in western China. In practice, the system of evaluation and basic terminology of national oil shale resources were established, with due consideration of geological, economic and feasibility factors, as well as three-dimensional resources classification concepts in line with international standards were adopted. The resource evaluation methods used were mainly the traditional volumetric method and geological analogy, and the boundary evaluation parameters were oil yield more than 3.5%, buried depth less than 3000 feet and thickness of signal-layer oil shale more than 2 feet. With the improvement of oil shale exploration after 2006, the size of the oil shale resources in China has changed greatly, especially in Northeast China. The Geological Survey Institute of Jilin Province conducted a detailed survey on oil shale in the southeastern uplift of the Songliao Basin from 2006 to 2010, and discovered four large-scale oil shale deposits in the region: Fuyu-Changchunling, Qianguo-Nong'an, Sanjingzi-Dalinzi and Shenjingzi.

The data originate from the Geological Archives of Jilin Province. The Tuha Oil Field of PetroChina Company Limited discovered a new, Bagemaode oil shale-bearing area in Bayinnaoer City of the Inner Mongolia Autonomous Region in 2007. The Daqing Oil Field of PetroChina Company Limited carried out a thorough investigation of the Linkou Basin in Heilongjiang Province in 2006, and found that oil shale resources had increased. From 2006 to 2008, Royal Dutch Shell performed a series of hole drillings in the Huadian, Meihe and other basins. As a result, the resource prediction accuracy in these oil shale-bearing areas increased significantly. Combined with the new exploration progress, the evaluation results showed that the oil shale resources in China are abundant and are widely distributed across the country.

The oil shale resources of China are concentrated in 50 basins in 20 provinces and autonomous regions. There are 83 petroliferous shale areas in total throughout the country. The oil shale resources of China rich but only part of the resources has been explored, although in recent years exploration has been quite extensive and a number of new oil shale deposits have been discovered. The amount of discovered oil shale resources has increased a lot, but the overall extent of exploration is still very low. Only 14% of oil shale resources have been investigated.

Oil shale is mainly distributed in eastern and central China, and the Qinghai-Tibet Region in western China. With approximately 602 billion tons (602×10^9 tons), oil shale resources in eastern China are the most abundant, comprising 62% of the total Chinese oil shale resources. The resources in central, western and southern China and the Qinghai-Tibet Region form approximately $161{,}120 \times 10^9$ tons, $75{,}120 \times 10^9$ tons, 19120×10^9 tons, and 120 billion tons (161, 75, 19 and 120×10^9 tons), making up 17%, 8%, 2%, and 12% of the total oil shale resources of China, respectively. According to the plate characteristics and the classification of sedimentary basins, the oil shale-bearing basins in China can be divided into four types: extensional basins, flexural basins, intra-plate basins and strike-slip basins.

The Mesozoic-Cenozoic oil shale-bearing basins in eastern and southern China have the tectonic attributes of extensional basins. Typical representatives are the Songliao, Bohaiwan, Maoming, Qinxian, Jurong and Beibuwan basins. Estimated at approximately 632 billion (632×10^9) tons, oil shale resources in extensional basins are the most abundant, making 65% of the total oil shale resources in China. Of the 632 billion (632×10^9) tons, the amount of oil shale resources discovered in extensional basins is approximately 125 billion (125×10^9) tons, or approximately 6 billion tons (6×10^9 tons = approximately 40 billion barrels (43×10^9 bbls) of potentially-producible (potentially-producible) shale oil.

The intra-plate oil shale-bearing basins are mainly distributed in central China, and from the north to the south, the largest are Ordos, Sichun and Chuxiong. Oil shale resources in basins of this type are estimated at approximately 161 billion tons (161×10^9 tons), or 16.5% of total oil shale resources, i.e. approximately 9.8 billion tons (9.8×10^9 tons) of potentially-producible shale oil. Of these estimated 161 billion tons, the amount of discovered oil shale resources accounts for ca 1.9 billion tons, i.e. approximately 0.1 billion tons of potentially-producible shale oil (Liu et al., 2017). The flexural oil shale-bearing basins are mostly spread in western China, typical examples are Junggar and Qiangtang. Oil shale resources in basins of this type are estimated at approximately 99 billion tons, or 10% of total oil shale resources, or approximately 10 billion tons of potentially-producible shale oil. Of these 99 billion tons (99×10^9 tons), the amount of discovered oil shale resources is approximately 0.6 billion tons (600×10^6 tons), or 0.04 billion tons (40×10^6 tons = approximately 280×10^6 bbls) of potentially producible shale oil.

The strike-slip oil shale-bearing basins are concentrated in the Qinghai-Tibet plate in western China, and the eastern Tancheng-Lujiang Fault Zone and its two branches. The current findings are the Lunpola Basin in western China, the Beibu Gulf and Lanping-simao basins in southern China, and the Jiaolai, Yilan-yitong, Fushun, Huadian and Meihe basins in eastern China. Compared to the above basin types, the size of this type of basins is smaller, and oil shale resources are estimated at approximately 85 billion tons (85×10^9 tons), or 9% of total oil shale resources, or approximately 9 billion tons (9×10^9 tons − approximately 63×10^9 bbls) of potentially-producible shale oil (Liu et al., 2017).

In the Fushun area (Jijuntun Formation), extensive layers lacustrine oil shale (49–190 ft thick, 15–58 m thick) are mined along with coal, both from Eocene lacustrine deposits. The oil yield of the shale ranges from approximately 5 to 16% w/w of the shale, and the mined shale averages 19 to 25 gallons per ton shale oil. In the vicinity of the mine, oil-shale resources are estimated at 260 million tonnes (), of which 235 million tonnes (90%) are considered mineable. The total resource of oil shale at Fushun is estimated at 3.6 billion tonnes (3.6×10^9 US tons) (Dyni, 2006; Fanf et al., 2008).

The oil shale in the Jijuntun Formation can be divided into two parts of differing composition: (i) the lower 49 feet (15 m) of light-brown oil shale of low-grade and (ii) the upper 330 feet (100 m) of brown to dark-brown, finely laminated oil shale. The oil content of the low-grade oil shale is less than 4.7% w/w and the richer upper grade is greater than 4.7% w/w. However, depending on the exact location of the deposit, the maximum oil content can be as high as 16% w/w. It has been reported that the average oil production is on the order of 78–89 L of oil per tonne of oil shale (assuming a 0.9 specific gravity).

The Maoming oil shale deposit (Youganwo Formation) has total reserves on the order of 5 billion tons (5×10^9 tons) oil shale, of which 860 million tons are in the Jintang mine. The Fischer assay yield of shale oil is 4–12% w/w of the oil shale. The Eocene Maoming oil shale occurs as a laterally uniform stratigraphic section and the sediments included lignite, a vitrinite lens from the overlying claystone, and four intervals from the massive oil shale deposit.

The shale oil resources can be determined and solutions for the reasonable development and use of oil shale provided based on oil yield evaluation. Oil shale resources with an oil yield by weight between 3.5 and 5% are estimated at 390 billion tons, i.e. 17 billion tons (119×10^9 bbls) of potentially-producible shale oil, or 40 and 27% of national oil shale and shale oil resources, respectively. Oil shale resources with an oil yield by weight between 5 and 10% are estimated at 461 billion tons, i.e. 30 billion tons (210×10^9 bbls) of potentially-producible shale oil, or respectively 47 and 50% of national oil shale and shale oil resources. Oil shale resources with an oil yield by weight higher than 10% are estimated at 126 billion tons, i.e. 14 billion tons (98×10^9 bbls) of potentially-producible shale oil, or 2 and 23% of national oil shale and shale oil resources, respectively. Potentially-producible shale oil resources with an oil yield by weight higher than 5% account for 73% of total shale oil resources in the country. These results demonstrate that oil shale in China is of medium to high grade.

In strata from the Late Paleozoic to the Mesozoic to the Cenozoic, the oil shale grade increases and, hence, oil yield increases, but the size of deposits decreases. This study found that oil shale in most of the current Late Paleozoic and Mesozoic basins has a low oil yield (typically 4–5% w/w), while in a few basins the oil yield of oil shale is high (more than 8%). Oil shale in most of the Cenozoic oil shale-bearing basins has a medium oil yield (6–8% on average), but in a few basins the oil shale oil yield is high (more than 8%) (Liu et al., 2017).

Among the few Late Paleozoic oil shale-bearing basins, the oil yield of oil shale in the Jining Basin is the highest (16.5%), but the area of the basin is very small. The oil yield of Yaomoshan oil shale in the large Junggar Basin is medium, and the oil yield of Liupanshan oil shale is very low. There have been found numerous Mesozoic oil shale-bearing basins in China, such as Songliao, Minhe, Yangshugou, Heishan, Chuxiong, Fuxin, Jianchang and Hetao, in which the oil yield of oil shale is very low. However, in some basins such as Laoheishan, Qiangtang and Qaidam, the oil yield of oil shale is high, being particularly high in the Laoheishan Basin (15%). Among the Cenozoic oil shale-bearing basins, the oil yield of oil shale in the Huangxin, Lunpola, Linkou and Huadian basins is very high, being the highest in the Huadian Basin (24.8%). In the other Mesozoic basins, such as Yilan, Maoming, Qinxian, Napeng, Bohaiwan, Fushun and Shulan, the oil shale oil yield is medium, averaging generally between 6 and 8% w/w.

The minerals of oil shale mainly originate from sedimentary terrigenous clastics and sediments formed by biochemical action. The most common minerals in continental oil shale in China are clay minerals, quartz, feldspars, calcite, siderite and pyrite, of which quartz and feldspars account for 47.6% w/w on average, and clay and carbonate minerals respectively 46.1 and 14.1%. Of the clay minerals, kaolinite shows a relatively high content, followed by illite and illite/smectite mixed-layer minerals, while Dalianhe oil shale surpasses Maoming, Yaojie and Dongsheng oil shales in kaolinite content (57% w/w). Montmorillonite is the most abundant clay mineral in Huadian oil shale.

At the same time, the Junggar Basin oil shale is devoid of clay minerals, but instead, dolomite is present in remarkable amounts. By contrast, there is a good linear relationship between the contents of clay minerals and organic matter of oil shale, that is, the higher the content of clay minerals, the higher the abundance of organic matter. The total organic content is poorly correlated with the content of terrigenous detrital minerals but correlates well with that of clay minerals. The respective correlation coefficients indicate that clay minerals play a decisive role in organic matter enrichment.

Oil shale retorting was carried out in Fushun, Manchuria in 1929 with the construction of the first of three plants. After World War II, Refinery No. 1 had 200 retorts, each with a daily throughput of 100–200 tonnes of oil shale. It continued to operate and was joined by the Refinery No. 2 starting up in 1954. In Refinery No. 3 shale oil was hydrotreated for producing light liquid fuels. Shale oil was also open-pit mined in Maoming, Guangdong Province and 64 retorts were put into operation there in the 1960s.

A second plant began production in 1954 and a third facility began producing shale oil at Maoming in 1963. At the beginning of the 1960s, 266 retorts were operating in Fushun Refineries Nos. 1 and 2. However, by the early 1990s the availability of much cheaper crude oil had led to the Maoming operation and Fushun Refineries No. 1 and 2 being shut down. It has been estimated that production of the Chinese oil shale industry in the mid-1970s was expanded to 55,000 to 80,000 barrels per day of shale oil. A new facility – the Fushun Oil Shale Retorting Plant – came into operation in 1992 under the management of the Fushun Bureau of Mines. Sixty Fushun-type retorts, each having a capacity of 100 tons of oil shale per day, produced approximately 415,000 barrels of shale oil per year at Fushun (Zhou, 1995).

Between 2004 and 2006 China undertook its first national oil shale evaluation, which confirmed that the resource was both widespread and vast. According to the evaluation, it has been estimated that a total oil shale resource of some 720 billion tonnes (795×10^9 US tons) is located across 22 provinces, 47 basins and 80 deposits. Approximately 70% of the deposits are in eastern and middle China, with the remainder largely in the Qinghai-Tibet area and the west. The potentially-producible shale oil resource has been estimated at some 48 billion tonnes (approximately 354×10^9 barrels) of potentially producible shale oil.

During 2007, the Fushun Mining Group Co. was operating 180 retorts, each capable of processing 100 tonnes of oil shale per day. The shale ash by-product is utilized to produce building materials. At the beginning of 2010 it was reported that a 6000 t/d Taciuk retort, imported by Fushun and placed in service by end-2009, had been delayed. Many other retorts are either operating or being planned in the provinces of Gansu, Guangdong, Hainan, Heilongjiang and Jilin.

In 2008 Chinese shale oil production totaled approximately 7600 barrels per day and in 2010 the production of shale oil was reputed to have risen to it has been estimated that production will rise to 10,000 barrels per day. Furthermore, several companies are involved in researching new retorting technologies for processing pulverized or particulate oil shale, with the possibility of constructing a pilot-scale demonstration plant (Qian et al., 2003; Liang, 2006).

In 2015, the in-situ oil shale mining technology in China made a significant breakthrough. Taking into account the characteristics of Chinese oil shale, two in-situ oil shale mining technologies were independently studied and shale oil was successfully extracted in a preliminary test. The *in situ* fracturing and chemical distillation of shale oil and gas extraction were developed and studied at the Unity & Strength Co., Ltd, China, while the TS-A method of shale oil and gas extraction technology was developed and studied at Jilin University, China. These are two successful examples following the in-situ oil shale mining technology of Shell Company. The successful preliminary tests on in-situ mining technology have eliminated the bottleneck in oil shale technology development, aroused enthusiasm for oil shale research, and gave a strong motivation to further develop the oil shale industry. This will not only waive the traditional requirements for mining shallow, thick or high-grade oil shale, but will also solve the serious environmental problems brought about by the current ground dry distillation technology. The Unity & Strength Co., Ltd and Jilin University are looking for a new way to carry out an experiment on in-situ mining technology and systematically evaluate the extracted shale oil. The development and application of in-situ mining technology may signify a new technological revolution in Chinese oil shale industry.

Development of the oil shale sector in China has been sustained partly because of the high level of imports of crude oil and crude oil products, necessary to support indigenous demand with the creation of a middle class and the accompanying demand for automobiles. China also prefers to utilize a national resource in the face of high international oil prices. This competes with the goal of seeking higher production from any one of several heavy oil fields, which has served to keep shale oil production levels low.

3.5 Egypt

Oil shale was discovered during the 1940s as a result of oil rocks self-igniting while phosphate mining was taking place. The phosphate beds in question lie adjacent to the Red Sea in the Safaga-Quseir area of the Eastern Desert.

In Egypt, organic-rich sediments in the Duwi and Dakhla Formations of the Campanian-Danian age are customarily assigned as Boil shaleˆ that occupies the middle latitudes of the country but may extend southward to Kurkur Oases. This oil shale belt has a vast worldwide extension, and it is considered as major oil- and gas-prone source rock in many places, especially in the Middle East. The sedimentation of the oil shale was triggered by the major transgression event that occurred during the Late Cretaceous. The lithology, type of kerogen, organic richness, and thickness of these organic-rich sediments vary markedly both on lateral and vertical scales. In Quseir area, the potentially-producible geological reserves, of oil shale of the 800-kcal/kg quality, is estimated to be more than 9 billion tons (9×10^9 tons) that can produce 5.48 bbls per tonne upon retorting. Very optimistic resources are expected in the unexplored Nile Valley region. The factor analysis of data rank representing 1176 core samples and analysis of 58 major and trace elements besides Rock-Eval analyses point to five main controlling factors that control deposition of oil shale. The terrestrial indicators Al_2O_3, TiO_2, Fe_2O_3, and K_2O and the marine indicators Ca and Sr are oppositely loaded in the first factor. The second factor expresses the reducing conditions that prevailed during the deposition of the organic-rich marine environments.

The euxinity of the basin is recognized by the third factor where sulfide and vanadium seem to be mutual. The fourth factor expresses the role of dolomitization while the fifth factor points to the humble role of oxidation. Considering the metric core samples, the highest TOC content recorded in the borehole drilled in Abu Tartur plateau is 3.6%, but it is approximately 14% for Quseir area. Regarding the spot samples in Quseir area, the highest TOC measured approximately 24%. It is not only the low TOC in Abu Tartur but also the kerogen type that is of type II + III, mostly of terrestrial origin (gas-prone) and lithology dominated by argillites. Organic richness is remarkable in Quseir-Safaga area, where the average TOC of 160-m-thick sequence is approximately 5%, with kerogen of type I or mixed I + II, mostly of marine origin (oil prone). The Dakhla Formation (Maastrichtian-Danian) is the richest in organic matter while Quseir Formation (Campanian) has the least organic richness and lowest kerogen quality. Detailed investigation on biomarkers confirms the relations among transgression, organic richness, kerogen type, and anoxic conditions. The organic matter is immature as witnessed by the low S1 values (<5%, in average), the low Tmax (<430 °C), the low vitrinite reflectance (<0.4%), and biomarker signature. The variation in the S1 values between 1 and 9% is attributed to the influence of tectonics associating the Red Sea rift. In Quseir-Safaga area, there are particular prolific horizons of oil shale that seem to be visible for utilization by different technologies of combustion and retorting. The content of the heavy metals and uranium, as well as the spent, is a significant benefit. The faulting, dragging, and steep tilting of beds in the Quseir-Safaga area shall remain a serious challenge for extensive utilization of the estimated potentially-producible geological reserves (El-Kammar, 2017).

Analysis was at first undertaken in the Soviet Union in 1958 and was followed by further research in Berlin in the late 1970s. This latter work concentrated on the phosphate belt in the Eastern Desert, the Nile Valley and the southern Western Desert. The results showed that the Red Sea area was estimated to have approximately 4.5 billion barrels (4.5×10^9 bbl) of potentially-producible shale oil and that in the Western Desert, the oil shale in Abu Tartour area (which could be mined while mining for phosphates) had the potential to produce up to 1.2 billion barrels (1.2×10^9 bbls) of potentially-producible shale oil.

Although assessment of the oil shale resources continue to establish (or estimate) the potential of the Egyptian resource, the Egyptian government has signed a joint agreement with Jordan, Morocco, Syria and Turkey, together with regional and international companies, will develop the Center with the aims of providing ‘a joint environmental and energy framework, common standards for studying and utilizing oil shale resources and attracting investors to the sector.

While the agreement indicates that Center was to be headquartered in Jordan, the future of the Center and agreement remain unknown at the time of writing) as a result of the recent unrest in Egypt and Syria.

3.6 Estonia

Estonia is unique in the world in that more than 80% of its mined oil shale is used for production of electricity. Estonia has between 0.5 and 1% of the world oil shale reserves, a tiny proportion of the US stocks, but has a history of full-scale production since 1921. Peak oil shale production was in the early 1980s but production of oil shale has been continuously decreasing since that time.

The Baltic Oil Shale Basin is situated near the north-western boundary of the East European Platform (Fig. 12.2) (Baker and Hook, 1979; Lippmaa and Maramäe, 1999; Lippmaa and Maramäe, 2000; Lippmaa and Maramäe, 2001; Loog et al., A., 1996). The Estonia and Tapa deposits are both situated in the west of the Basin, the former being the largest and highest-quality deposit within the Basin. Estonian oil shale resources are currently put at 5 billion tonnes (5.5×10^9 US tons) including 1.5 billion tonnes (1.65×10^9 US tons) of active (mineable) reserves. It is possible that the power production part of the industry will disappear by 2020 and that the resources could last for 30–50 years but scenarios abound on the replacement of oil shale by alternative resources.

The *kukersite* shale is the most important mineral resource of Estonia. There are two principal deposits in the republic: the *Estonian* located in the northeastern part of the republic. The productive seam thickness diminishes from approximately ten feet in the northern part of deposit to approximately six feet in the southern and western parts. The *Tapa* deposit is situated southwest of the *Estonian* deposit with seam depth below the surface 200–600 feet. The seam has maximum thickness six-to-seven feet in the central part of the deposit (Reinsalu, 1998).

Estonian kukersite contains three main components: organic (kerogen), carbonaceous and terrigenous matter. The last two constitute kukersite mineral matter. The content of

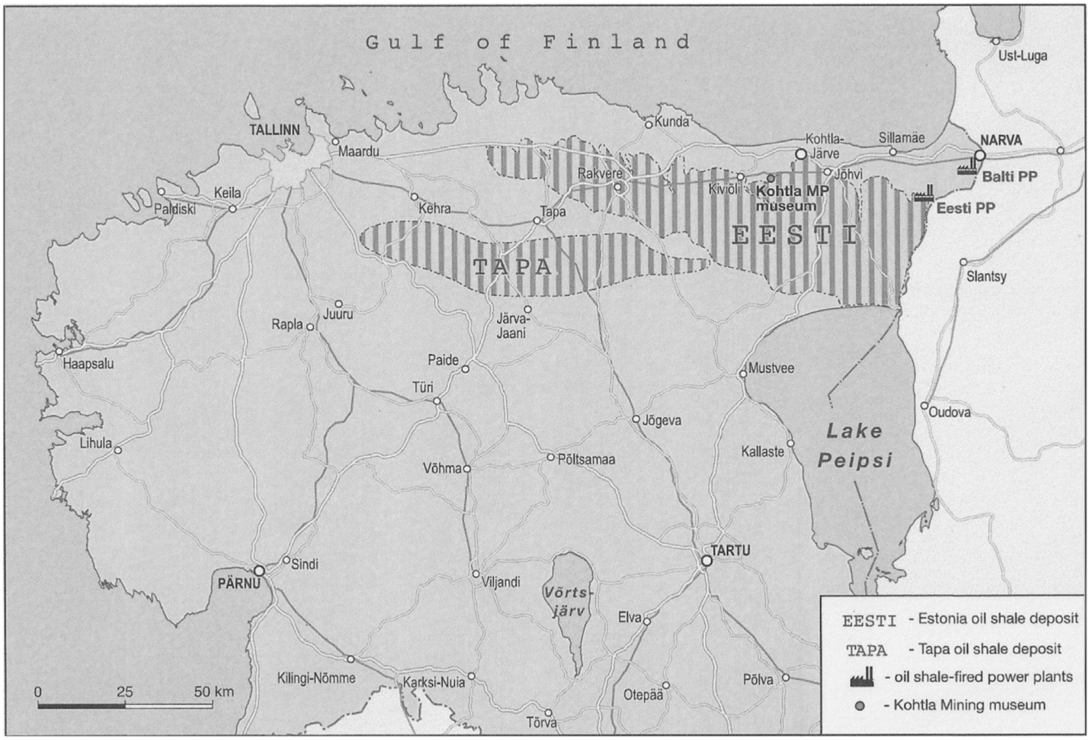

FIGURE 12.2 Estonian oil shale deposits.

kerogen (organic matter of kukersite) varies from 10 to 65% w/w. The content of carbon in the organic matter of kukersite is low (76.7% w/w) and the oxygen and carbon mass ratio is 0.13. Estonian kukersite has a high content of hydrogen (9.7% w/w) and a low content of nitrogen (0.3% w/w) in the organic portion of the oil shale. The hydrogen-to-carbon (H/C) atomic ratio is on the order of 1.25 but the sulfur content in the organic matter of kukersite is 1.6% w/w.

Estonian oil shale was first scientifically researched in the 18th century (Kattai and Lokk, 1998). In 1838 work was undertaken to establish an open-cast pit near the town of Rakvere and an attempt was made to obtain oil by distillation. Although it was concluded that the rock could be used as solid fuel and, after processing, as liquid or gaseous fuel, the *kukersite* (derived from the name of the locality) was not exploited until the fuel shortages created by World War I began to impact.

Permanent mining began in 1918 and has continued until the present day, with capacity (both underground mining and open-cast) increasing as demand rose. By 1955 oil shale output had reached 7 million tonnes (7.7×10^6 US ton) and was mainly used a power station/chemical plant fuel and in the production of cement. The opening of the 1400 MW Baltic Thermal Power Station in 1965 followed, in 1973, by the 1600 MW Estonian Thermal Power Station again boosted production and by 1980 (the year of maximum output) the figure had risen to 31.35 million tonnes (31.35×10^6 tonnes). However, in 1981 the fourth reactor of the Sosnovy Bor nuclear power station opened in the Leningrad District (Russia) thereby reducing demand for Estonian shale. As a result, production of Estonian oil shale has decreased and remains at a lower level than the production in 1980. The decline lasted until 1995, with nominal annual increases in production since that time.

In December 2009, after a construction period of $2^1/_2$ years, a new 3000 tonnes per day oil shale processing plant was officially opened. Located in Kohtla-Järve, the plant is designed to produce more than 100 000 tonnes of shale oil, 30 million m3 of high-calorific gas and 150 GWh of steam. Eesti Energia Technology Industries (operating as Enefit) is currently constructing a 2.26 million tonnes per year oil shale plant in Narva. The plant, planned to produce 290 000 t/yr of oil is due to start up in 2012. Three additional Enefit 280 units and an upgrader plant are scheduled to be started in 2013.

The Estonian government has taken steps toward privatization of the oil-shale industry and is beginning to tackle the air and water pollution problems that nearly a century of oil shale processing has brought. In 1999, 10.7 million tonnes (11.8×10^6 US tons) of oil shale were produced. Imports amounted to 1.4 million tonnes (1.5×10^6 US tons), 0.01 million tonnes (0.011×10^6 US tons) were exported, 11.1 million tonnes (12.2×10^6 US tons) used for electricity and heat generation, and 1.3 million tonnes (1.4×10^6 US tons) were distilled to produce approximately 950,000 barrels of shale oil. Until recently only 16% of Estonian shale was used for crude oil and chemical manufacturing. However, because environmental problems the goal is to decrease oil shale production.

At the time of writing, Estonia is the only country in the world that operates oil shale fired power plants to supply most of its electricity to domestic customers and can export power to neighboring countries. In addition to thermal power plants, Estonia has also oil shale thermal processing plants for shale oil production. Power plants and processing factories in Estonia are supplied with oil shale from two underground mines and two opencast mines (Ots, 2007).

Furthermore, Eesti Energia (also called Enefit, outside of Estonia), the company responsible for more than 90 years of oil shale mining and 50 years of oil shale surface retort production has moved into the United States – on 30 March 2011, Enefit American Oil purchased 100% of Oil Shale Exploration Company (OSEC). With the purchase of Oil Shale Exploration Company, Enefit acquired one of the largest tracts of privately owned oil shale in the United States totaling more than 30,000 acres and reputed to sufficient oil shale to produce approximately 2.1 billion barrels (2.1×10^9 bbls) of shale oil. The company plans to develop a mining, retorting, and upgrading project to produce 50,000 barrels per day of refined shale oil – the first out-of-the-pipe oil is scheduled for 2020.

3.7 Ethiopia

The existence of oil shale deposits in Ethiopia has been known since the 1950s. Although surveys have been undertaken in the past, no projects were proceeded with owing to high mining costs and lack of funding. In 2006 it was reported that the resource, estimated to be 3.89 billion tonnes (4.3 × 109 US tons), in the northern province of Tigray is considered to be suitable for open-cast mining. In the Ethiopian Year 2000 (July 2007–June 2008) the Geological Survey of Ethiopia undertook surveys in the Sese Basin, western Ethiopia to establish the nature and content of the oil shale (and coal) deposits. A certain amount of analysis has been carried out but further research is required.

The oil shale deposits in the Tigray region are found in the northern parts of Ethiopia, Eastern Africa (Girmay, 2006: Yihdego et al., 2018). They are Upper Paleozoic in age, existing as remnants of the Cretaceous erosion period, underlain by tillites and overlain by sandstones. They were formed during the glacial retreat followed by marine deposition of shales in a basin created by the enormous load of the glaciers. The Ethiopian-Tigray oil shale deposits cover an area extending over approximately 10 square miles, with an average mineable bed-thickness up to 200 feet m, showing on the upper part inter-beds and laminations of shaley limestones. The oil shale resources in this region are estimated to be approximately 4 billion tonnes (1 tonne = 2240 lbs).

3.8 France

The French shale oil resources total approximately 500 million barrels of potentially producible shale oil. The resources are of medium quality and yield from 10 to 24 gallons of shale oil per ton of shale. The formations are more properly called bituminous shale, rather than oil shale, because they contain inclusions of asphaltic compounds.

Oil shale was irregularly exploited in France between 1840 and 1957 but at its highest (1950), output only reached 0.5 million tonnes (0.6×10^6 US tons) per year of shale. During its 118 year life, the Government imposed taxes and duties on foreign oil, thus preserving the indigenous industry. In 1978 it was estimated that the potentially-producible shale oil resources amounted to 7 billion barrels (7×10^9 bbls) of producible shale oil. In mid-2009 Toreador Resources Corporation reported that it had a four-phase plan to exploit the oil shale of the Paris Basin.

3.9 Germany

In 1965 it was estimated that potentially-producible shale oil resources in Germany amounted to 2 billion barrels (2×10^9 bbls) of shale oil. The oil shale from this area is a low energy mineral (with a low oil yield and a high ash content) but by using a complex process the complete utilization of both the oil shale energy and all its minerals can be accomplished and incorporated into the manufacture of cement. The heat of this process is used simultaneously to produce electricity.

German oil shale resources were developed as early as 1857, and several retorts were operated in the 1930s. A major development effort was initiated during World War II in response to wartime fuel shortages. The German industry used two types of aboveground retorts and one *in situ* process. A plant with approximately 30 Lurgi above–ground retorts was operated from 1947 to 1949. In 1961, a plant was built in the town of Dotternhausen that burns finely crushed oil shale in a fluidized-bed combustor. The heat of combustion is used for power generation, and the spent shale product is used to make cement. In recent years only a minimal quantity of oil shale (0.5 million tonnes per annum, 0.6×10^6 US tons) of oil shale is produced for use at the Rohrback cement works where it is consumed directly as a fuel for power generation, the residue being used in the manufacture of cement. At the beginning of 2004, Holcim, a Swiss cement and aggregates company, acquired Rohrbach Zement.

3.10 India

Although oil shale, in association with coal and also oil, is known to exist in the far northeastern regions, the extent of the resource and the quality of the oil shale has not yet been determined.

Currently oil shale, recovered with coal during the mining process, is discarded as a waste product. However, the Indian Directorate General of Hydrocarbons has initiated a project designed to assess the reserve and its development. The project covered geological mapping, sampling and analysis in the states of Assam and Arunachal Pradesh. Feasibility and environmental impact assessment studies have also been planned.

3.11 Indonesia

Faced with declining reserves of oil and gas, Indonesia has accelerated its research into identifying, and possibly utilizing, indigenous oil shale resources.

The Center for Geo Resources is currently engaged on surveying and preparing an inventory of occurrences. To date, three main prospective oil shale areas have been found, two on the island of Sumatera and one on Sulawesi.

3.12 Israel

Israel possesses approximately 20 oil shale deposits in a number of different locations, and these, according to Geological Institute estimates, can be expected to produce a total of over 219 billion barrels (219×10^9 bbls) of oil. The most significant of these deposits covers an area of some 1400 square kilometers in the Judean Plain, which is where the 238.1 km licensed to IEI are located. The production potential of the entire Judean Plain deposit is estimated at around 195 billion barrels (195×10^9 bbls), and, on the basis of the calculations by the Geological Institute, the production potential of the licensed area can be claimed to be roughly 33.15 billion barrels (33.15×10^9 bbls).

Marinite deposits of Late Cretaceous age have been identified in Israel (Minster, 1994; Fainberg and Hetsroni, 1996), containing approximately 12 billion tons (12×10^9 tons) of oil shale reserves with an anticipated shale oil yield of 6% w/w of the oil shale. The organic content of the oil shales is relatively low, ranging from 6 to 17% w/w, with an oil yield of 15–17 gallons per ton. Israeli oil shale is generally relatively low in heating value and oil yield, and high in sulfur content, compared with other major deposits.

Sizable deposits of oil shale have been discovered in various parts of Israel, with the principal resources located in the north of the Negev desert. Estimates of the theoretical reserves total some 300 billion tonnes (330×10^9 US tons), of which those considered to be open-pit mineable are put at much less. The largest deposit (Rotem Yamin) has shale beds with a thickness of 35–80 m, yielding 60–71 L of oil per tonne. Generally, Israeli oil shale is relatively low in heating value and shale oil yield, and high in moisture, carbonate, and sulfur content, compared with other major deposits.

Additional significant deposits are to be found in the Negev, where the Rotem Plain possesses a potential of some 1.4 billion barrels (1.4×10^9 bbls) and the Yamin Plain has a potential yield of 2.1 billion barrels (2.1×10^9 bbls). In addition, according to the Institute of

Geology, there are another three areas suitable for *in situ* extraction. These include the deposits of the Zin Valley, which has an extraction potential of around 1.62 billion barrels (1.62×10^{12} tons), of Sde Boker with an extraction potential of 1.08 billion barrels, and Nevatim, which has an extraction potential of around 600 million barrels (600×10^6 bbls or more.

In the Rotem Plain and the Yamin Plain, most of the oil shale layers are situated at a depth of between 30 and 100 m below the surface (at Yamin Plain the depth is slightly greater), and the shale layer itself is between 30 and fifty meters thick, with an organic material content of between 15% and 18%.7 In the Rotem Plain area, oil shale extraction by means of opencast mining and controlled combustion was begun as early as twenty years ago, for purposes of electricity and steam production. These activities were originally conducted by the Energy Resources Development Company of the Government of Israel, but in the past decade both mining operations and management of the power station have been carried out by Rotem Empert. It should be noted that the oil shale mine at the site has suffered spontaneous combustion, and a fire has been burning there for a long time now.

As stated above, at Sde Boker, the Zin Valley and Nevatim, the geological findings indicate possible suitability for the use of *in situ* technology. The production potential for these three deposits alone will probably be sufficient to satisfy the oil needs of Israel for approximately forty years. In the Judean Plain area the oil shale deposit lies at a greater depth than some of the Negev deposits. This deposit is some 200 m below the surface; it is 200 m thick and has an organic content of approximately 20%.9 The depth of the Judean Plain oil shale deposit is thus unsuitable for mining, and the only possible means of extraction is by heating of the shale layer *in situ.*

A commercially exploitable bed of phosphate rock, 25–50 feet thick, underlies the oil shale in the Mishor Rotem open-pit mine and some of the deposits can be mined by open-pit methods. The largest deposit (Rotem Yamin) has shale beds with a thickness of 100–250 feet, yielding 15 to 20 gallons of shale oil per ton. A pilot power plant fueled by oil shale has been technically proven in the Negev region. Annual production of oil shale has averaged approximately 450,000 tonnes (500×10^3 US tons) in recent years.

Following tests in a 0.1 MW pilot plant (1982–6), a 1 MW demonstration fluidized-bed pilot plant was established in 1989. In operation since 1990, the generated energy is sold to the Israeli Electric Corporation, the low-pressure steam to an industrial complex and a considerable quantity of the resulting ash used to make products such as cat litter which is exported to Europe.

During 2006, AFSK Hom-Tov, an Israeli company, presented a scheme to the Ministry of National Infrastructures for the manufacture of synthetic oil from oil shale. The method would entail combining bitumen (from the Ashdod refinery, 80 km north of the proposed plant at Mishor Rotem in the Negev Desert) with the shale prior to processing in a catalytic converter.

While the Government is encouraging development of the oil shale resource, particularly *in situ* underground techniques, it is mindful of the environmental concerns. While the country investigates the possibilities of harnessing its large oil shale deposits for producing shale oil, some of the resource is utilized directly for the production of electricity.

3.13 Jordan

Oil shale is the most abundant fossil energy resource discovered in Jordan, ranking third after the USA and Brazil in terms of oil shale reserves (Abu-Hamatteh and Al-Shawabkeh, 2008.). This asset is considered to be the most extensive domestic fossil-fuel source in Jordan. The identified reserves of this oil shale are huge and sufficient to satisfy the national energy needs for hundreds of years – more than 65 billion tons (65×10^9 tons) have been recorded over all Jordan of which 50 billion tons (50×10^9 tons) are located in central of Jordan.

Oil shale in Jordan was recognized for the first time in the early 20th Century in the Yarmouk region north of Jordan near Al-Maqqarin Village. The German Army during the First World War had used it when they installed the first project to produce oil from the oil shale to operate the Hijazi Railway. Exploration work started after El Lajjun deposit had been discovered by the German Geological Mission in the 1960s. Intensive exploration activities on oil shale in central of Jordan were carried out during the 1980s and resulted in delineating other deposits such as Sultani, Hasa, and Jurf Ed Darawish. Continued exploration resulted in the discovery of other deposits such as Attarat Um Ghudran, Wadi Maghar, Siwaqa, Khan El Zabib, and El Thammad (Jaber et al., 1997; Alali, 2006).

In all, there are at least 24 known occurrences of oil shale, which result in Jordan having an extremely large proven and exploitable oil shale resource. Geological surveys indicate that the existing shale reserves cover more than 60% of the country and amount to in excess of 40 billion tonnes (43×10^9 US tons). The proven and exploitable reserves of oil shale occur in the central and north-western regions of the country (Jaber et al., 1997; Hamarneh, 1998; Bsieso, 2003; Alali, 2006). The major deposits of commercial-scale interest are located approximately 60 miles south of Amman (Bsieso, 2003).

The most important oil shale occurs in the lower part of the Upper Cretaceous Muwaqqar Chalk-Marl (MCM) Formation, which outcrops across much of the central northern and central southern parts of Jordan. Although the oil shale in Jordan is widely spreading, it varies in thickness and in oil content. The Jordanian most significant oil shale deposits are found in more than 25 locations around the country with the 8 most important deposits located in the central region of the country. The Jordanian best-explored oil shale deposits were found in the following regions: El-Lajjun (Al-Lajjun), Sultani, Jurf Ed-Darawish, Attarat Um El-Ghudran, Wadi Maghar, Wadi Thamad (Eth-Thamad), Khan Ez-Zabib, and Siwaga (Siwaqa). The oil shale deposits in these 8 locations exist in the west-central parts of Jordan, meanwhile the oil shale deposits in the Yarmouk region are found in the Yarmouk River region in northern Jordan, which is close to the Jordanian-Syrian borders, extending into the Syrian Territory.

The Jordanian oil shale deposits are kerogen-rich, bituminous, argillaceous limestones, deposited in shallow marine during the Late Cretaceous to early Tertiary (Maastrichtian-Danian) geological ages. The origin of the kerogen is the dead plants and animals that found in the ancient seas and lakes during the Upper Cretaceous geological ages and after the burial process, along with high temperatures and pressures, which caused the change from organic matter to kerogen.

Jordanian shale is generally of quite good quality, with relatively low ash and moisture content. Oil yield (5–12% w/w) is favorably comparable with the oil yields from the oil shale of western Colorado (USA) shale; however, Jordanian shale has exceptionally high sulfur content (up to 9% by weight of the organic content). The reserves are exploitable by opencast mining and are easily accessible (Bsieso, 2003).

The principal mineral component of the oil shale is calcite or more rarely quartz together with kaolinite and apatite and, on occasion feldspar, muscovite, illite, goethite and gypsum as secondary components. Dolomite ($CaCO_3 \cdot MgCO_3$) occurs in some individual carbonate beds as in the Arbid limestone of El-Lajjun. The main elements of the oil shale, if organic carbon is excluded are calcium, and silicon; minor constituents are sulfur, aluminum, iron and phosphorous. The concentrations of the remaining components are generally low. The silicon is derived from two sources: clastic sediment input together with titanium, aluminum and iron; and from sedimentary or early diagenetic silicification.

The amount of phosphorous in the shale increases from the top to the bottom of the sequence. Phosphorous content is not favorable in the utilization of the spent shale for the manufacture of cement. However, certain percentage of the oil shale and/or the spent shale can be used in the cement manufacturing. Molybdenum, chromium and tungsten are significantly enriched in the bituminous marl in comparison to limestone. Zinc, vanadium, nickel, copper, lanthanum and cobalt are also enriched, whereas barium is depleted and the content of arsenic and lead are low to moderate. The uranium content is relatively high but it is clearly associated with phosphorous and not with the bituminous organic matter. The sulfur content ranges from 0.3 to 4.3% w/w (Alali, 2006).

The eventual exploitation of the only substantial fossil fuel resource to produce liquid fuels and/or electricity, together with chemicals and building materials, would be favored by three factors: (i) the high organic-matter content of Jordanian oil shale, (ii) the suitability of the deposits for surface-mining and (iii) their location near potential consumers (i.e. phosphate mines, potash and cement works).

In May 2010, Enefit (Eesti Energia) signed a concession agreement with the Jordanian Government granting the former the right to utilize part of the Attarat Um Ghudran deposit for 50 years. Located in central Jordan and estimated to contain 25 billion tonnes (27.5×10^9 tons), the deposit is considered to be the largest in the country. Enefit will undertake further geological research and an environmental impact assessment. After a maximum period of four years, a decision will be taken regarding the economic feasibility of the project. If commercial development ensues, it is planned that a 900 MW (maximum) capacity oil shale-fired power plant will begin operating in 2016 and a 38 000 b/d shale oil plant in 2017.

3.14 Kazakhstan

The occurrence of oil shale is widespread and the most important deposits having been identified in western Kazakhstan (the Cis-Urals group of deposits) and eastern Kazakhstan (the Kenderlyk deposit). Further deposits have been discovered in both the southern region (Baikhozha and the lower Ili river basin) and the central region (the Shubarkol deposit).

In excess of 10 deposits have been studied: the Kenderlyk Field has been revealed as the largest (in the region of 4 billion tonnes, 4.4×10^9 US tons) and has undergone the greatest investigation. However, studies on the Cis-Urals group and the Baikhozha deposit have shown that they have important concentrations of rare elements (rhenium and selenium), providing all these deposits with promising prospects for future industrial exploitation.

The shale oil resources have been estimated as having the potential to produce approximately 2.8 billion barrels (2.8×10^9 bbls) of shale oil. Moreover, many of the deposits occur in conjunction with hard and brown coal accumulations which, if simultaneously mined, could increase the profitability of the coal production industry while helping to establish a shale-processing industry.

At the beginning of the 1960s successful experimentation was carried out on a sample of oil shale from Kazakhstan – the former Soviet Republic of Kazakhstan. Both domestic gas and shale oil were produced. It was found that the resultant shale oil had a low-enough sulfur content for the production of high-quality liquid fuels.

Beginning in early 1998 and lasting until end- 2001, a team funded by INTAS (an independent, international association formed by the European Community to preserve and promote scientific co-operation with the newly independent states) undertook a project aimed at completely re-evaluating the oil shale resources of Kazakhstan. The resultant report testified that Kazakhstan's oil shale resources could sustain the production of various chemical and power-generating fuel products. In September 2009 it was reported that a high-level bilateral economy, science and technology cooperation agreement had been signed by Estonia and Kazakhstan. Estonia expressed a willingness to share its expertise in the field of oil shale in order to help Kazakhstan develop its own resource.

3.15 Mongolia

Mongolia possesses large mineral deposits which, owing to the political isolation of Mongolia during most of the 20th Century, remain largely undeveloped. Some mining operations were established prior to 1989 with the help of the Soviet Union and Eastern European countries but following the breakup of the USSR, the move by Mongolia to a free economy and the Minerals Law being passed in 1997, the potential is being recognized.

Numbered among the indigenous minerals are oil shale deposits from the Lower Cretaceous Dsunbayan Group, located in the east of the country. Exploration and investigation of the deposits began as long ago as 1930 but it was only during the 1990s and with the help of Japanese organizations that detailed analyses began. Twenty six deposits were studied and found to be associated with coal measures. During 2004, Narantuul Trade Company, the owner of the Eidemt deposit was investigating the possibilities of developing the potential of the field with the aid of international cooperation. It was reported in late-2006 that China University of Petroleum had signed a contract to undertake a feasibility study on the Khoot oil shale deposit.

3.16 Morocco

Morocco has substantial oil shale reserves but to date they have not been exploited to any great extent. The total oil shale resource of Morocco is estimated to have the potential to produce at some 50 billion barrels (50×10^9 bbls) of shale oil, an amount which (if proven) would rank the country among the world leaders in respect of shale oil (Bouchta, 1984). Exploitation of oil shale in Morocco occurred as long ago as 1939, when the Tanger deposit was the source of fuel for a pilot plant (88 US tons per day) which operated until 1945. A preliminary estimate of this resource has been put at some 2 billion barrels (2×10^9 bbls) of oil in place.

During the 1960s two important deposits were located: (i) Timahdit in the region of the Middle Atlas range of mountains in north central Morocco, and (ii) Tarfaya in the south west, along the Atlantic coast. Shale oil potential has been estimated at approximately 16 billion barrels (16.0×10^9 bbls) for Timahdit and 22.7 billion barrels (22.7×10^9 bbls) for Tarfaya. During the early 1980s, Shell and the Moroccan state entity ONAREP conducted research into the exploitation of the oil-shale reserves at Tarfaya, and an experimental shale-processing plant was constructed at another major deposit (Timahdit) (Bouchta, 1984; Bekri, 1992). At the beginning of 1986, however, it was decided to postpone shale exploitation at both sites and to undertake a limited program of laboratory and pilot-plant research.

The technical and economic feasibility studies have resulted in Morocco acquiring a large amount of information — a database which can be used for future projects. With the current need to look at developing alternative sources of liquid fuels, government has stated that any pilot plant should be followed by a demonstration phase during which the commercial evaluation of by-products should also be undertaken.

3.17 Nigeria

Research has shown that the southeastern region of Nigeria possesses a low-sulphur oil shale deposit. The reserve has been estimated to be of the order of 5.76 billion tonnes (6.3×10^9 US tons) with the potential to produce 1.7 billion barrels (1.7×10^9 bbls) of shale oil.

An oil shale deposit, possibly of high economic value and corresponding to the Turonian Ezeaku shale (lower Nkalagu formation) of the Lower Benue Trough, was found in a 1.5×1.0 km belt in Lokpanta near Okigwe, in Imo State, Nigeria (Ekweozor and Unomah, 1990). The characteristically dark-grey, laminated and fissile marlstone contains total organic carbon (TOC) in excess of 7% w/w in some locations and total extractable organic matter generally in excess of 10 000 ppm. The kerogen is type I—II (oil-prone) and at the updip rim it has attained intermediate thermal maturity status. An initial appraisal of the economic potential of the fossil fuel deposit by pyrolysis (modified Fischer assay) indicates an average oil-yield on the order of 40 gallons per ton.

3.18 Russia

In excess of 80 oil shale deposits have been identified in Russia. There are oil shale deposits in Leningrad Oblast, across the border from those in Estonia. Annual output is estimated to be approximately 2 million tonnes (2.1×10^6 US tons), most of which is exported to the Baltic power station in Narva, Estonia. In 1999 Estonia imported 1.4 million tonnes (1.5×10^6 US tons) of Russian shale but is aiming to reduce the amount involved, or eliminate the trade entirely. There is another oil-shale deposit near Syzran on the river Volga (Russell, 1990; Kashirskii, 1996).

Russia has been mining its reserves on a small-scale basis since the 1930s, with the oil shale being used to fuel two power plants, but the operation was abandoned owing to environmental pollution. However, most activity has centered on the Baltic Basin where the kukersite oil shale has been exploited for many years. The exploitation of Volga Basin shale, which has a higher content of sulfur and ash, began in the 1930s. Although the use of such shale as a power-station fuel has been abandoned owing to environmental pollution, a small processing plant may still be operating at Syzran in 1995, with a throughput of less than 50,000 tonnes (50×10^3 tonnes) of shale per annum.

Until 1998, the Slantsy electric power plant (located close to the Estonian border, 91 miles from St Petersburg) was equipped with oil shale fired furnaces but in 1999 its 75 MW plant was converted to use natural gas. The plant continued to process oil shale for oil until June 2003, since when its main activities have been electrode coke annealing and the processing of coals and natural gas oil components.

In 2002 the Leningradslanets Oil Shale Mining Public Company produced 1.12 million tonnes (1.3 × 106 US tons). In June 2003 all shale mined was delivered to the Estonian Baltic power station with the resultant electricity delivered to UES (Unified Energy System of Russia). However, production ceased at the Leningradslanets Mine on 1 April 2005. Oil shale production restarted on 15 January 2007, with the 50,000 tonnes (55,000 US tons) per month being stored. Leningradslanets exported 40,000 tonnes (44,000 US tons) of oil shale to Estonia between May and August 2009.

3.19 Scotland

The oil shale resources of Scotland occur in seams from 4 to 14 feet thick and yield approximately 22 gallons of shale oil ton of shale. The reserves were originally estimated to be capable of producing approximately 600 million barrels of shale oil.

The first retorting plant was built in 1859 but the economic viability of the plant was immediately threatened by the rapid development of conventional crude oil that followed the drilling of the first commercial oil well. The production of shale oil and valuable byproducts such as waxes, ammonia, pyridine derivatives, ammonium sulfate, and building materials enabled the Scottish shale oil industry to survive for over 100 years despite the high cost of the oil in comparison with conventional crude oil. At its peak, the industry processed approximately 3.3 million tons per year of oil shale. The last plant, because of competition from cheap crude oil, closed in 1962.

3.20 Serbia

More than twenty oil shale deposits have been located in Serbia, most numerous in the southern half of the country. The total oil shale resource is estimated to be in the region of 4.8 billion tonnes (5.3×10^9 US tons) with approximately two million barrels of shale oil thought to be recoverable. However, only sections of two of the deposits have received detailed study: (i) Aleksinac in the basin of the same name and (ii) Goč-Devotin in the Vlase-Golemo Selo basin.

Viru Keemia Grupp of Estonia has been collaborating with the University of Belgrade to conduct further research and analysis of the oil shale resource. Technical data are not readily available at the time of writing.

3.21 South Africa

Rich oil shale deposits occur in South Africa that produce a yield of shale oil up to 100 gallons of shale oil per ton of oil shale with 55 gallons of shale oil per ton of oil shale being a more recordable yield of shale oil.

The production of shale oil in South African began in 1935, and the industry attained a maximum throughput of 800 tons of oil shale per day in the 1950s, with a corresponding shale oil production on the order of 800 barrels per day. The industry was located in the interior of South Africa and, although it was not directly subsidized by the government, the economic viability of the project was enhanced when the high cost of transporting competing crude oil from the seacoast ports to interior markets in the vicinity of the plants was given due consideration. The richer deposits were eventually depleted, and the industry ceased operations in 1962 when the country turned more to coal as the source of liquid fuels.

3.22 Spain

The best Spanish resources yield from 30 to 36 gallons of shale oil per ton of oil shale. The reserves have been estimated to be on the order of 280 million barrels of producible shale oil.

The industry began in 1922 using retorts similar to those that had been developed in Scotland. The maximum throughput for these units was 220 tons of oil shale per day that was reached in 1947. In 1955, new retorts from Scotland were installed and in 1960, the enlarged industry processed 1 million tons of oil shale which produced sufficient shale oil to supply more than half of the national requirement of lubricating oil, The industry ceased operation in 1966.

3.23 Sweden

The oil shale resources underlying mainland Sweden are more correctly referred to as alum shale; black shale is found on two islands lying off the coast of south-eastern Sweden (Andersson, 1985). Typical Swedish oil shale formations are approximately 50 feet thick and The potential for shale oil production estimated to be 6.1 billion barrels (6.1×10^9 bbls) of producible shale oil.

The exploitation of alum shale began as early as 1637 when potassium aluminum sulfate (alum) was extracted for industrial purposes. By the end of the 19th century the alum shale was also being retorted in an effort to produce shale oil. The modern Swedish oil shale industry began in the 1920s, with the largest operations near the city of Kvarntorp. These facilities featured two types of aboveground retorts and a unique type of *in situ* process in which the deposits were pyrolyzed with electric heaters. The industry reached a maximum capacity of 2 million tons of oil shale per year (6000 ton/d) and produced as much as 550,000 barrels per year of crude shale oil. Because of the limited quantity of high-quality reserves, and price competition from crude oil, the industry ceased operation in 1966.

The Swedish alum shale has a high content of various metals including uranium, which was mined between 1950 and 1961. At that time the available uranium ore was of low grade but later higher-grade ore was found and 50 tonnes of uranium were produced per year between 1965 and 1969. Although the uranium resource is substantial, production ceased in 1989 when world prices decreased and made the exploitation uneconomic.

Sustained commodity prices in recent years have resulted in a Canadian company, Continental Precious Minerals, conducting a drilling program on the alum shale. The exploration of oil, uranium and various minerals are all possibilities and samples are being analyzed by the Estonian Oil Shale Institute.

3.24 Syria

Although the existence of oil shale has been known approximately for the past 60 years, it is only in the recent years of high oil prices that the widely-distributed deposits have received more detailed study (Puura et al., 1984).

The most significant and evaluated deposits have been located in the southern Yarmuk Valley, close to the border with Jordan, with the Dar'a deposit having had the most detailed study. Further investigative research and evaluation, particularly in the northern areas of the country is being undertaken by the General Establishment of Geology and Mineral Resources.

Current unrest at the time of writing makes the future development of Syrian oil shale resources uncertain.

3.25 Thailand

Some exploratory drilling by the government was made as early as 1935 near Mae Sot in Tak Province on the Thai-Burmese border. The oil-shale beds are relatively thin and the structure of the deposit is complicated by folding and faulting.

Approximately 18.7 billion tonnes (20.6×10^9 US tons) of oil shale have been identified in Tak Province but to date it has not been economic to exploit the deposits. Proved recoverable reserves of shale oil are put at 810 million tonnes (890×10^6 US tons) (Vanichseni et al., 1988).

Exploratory drilling by the Government was made as early as 1935 near Mae Sot (Tak Province) on the Thai-Burmese border. The oil shale beds are relatively thin, underlying the Mae Sot basin and structurally complicated by folding and faulting. Approximately 18.6 billion tonnes (20.5×10^9 US tons) of oil shale, yielding an estimated 6.4 billion barrels (6.4×10^9 bbls) of shale oil, have been identified but to date it has not been economic to exploit the deposits. Another deposit at Li (Lampoon Province) is small, estimated at 15 million tonnes (16.5×10^6 US tons) of oil shale and yielding 10 to 45 gallons of shale oil per ton.

The Thai Government has instituted a 4-year project to study the feasibility of developing and utilizing the Mae Sot oil shale deposit. The potential for both direct use (electricity generation) and indirect use (extraction of shale oil) is being evaluated and there is also an investigation as to the suitability of using the retort ash in the building industry.

3.26 Turkey

Oil shale comprises the second largest potential fossil fuel in Turkey (Güleç; Önen, 1993; Sener et al., 1995; Altun et al., 2006). The main oil shale resources are located in middle and western regions of Anatolia. The amount of proved explored reserves is around 2.22 billion ($2/2 \times 10^9$) tons while the total reserves are predicted to be 3 to 5 billion ($3-5 \times 10^9$) tons. Despite this vast potential, the stated amount cannot be accepted as the amount of commercial reserves. Four major deposits: Himmetoğlu, Seyitömer, Hatildağ, and Beypazari have been studied in detail and found to vary quite widely in quality.

The deposits vary from 500 to 4500 kcal/kg in calorific value, revealing that each deposit requires a detailed study regarding its possible use (Güleç; Önen, 1993). Numerous studies carried out to recover shale oil have ended with positive but unfeasible results. Treating oil shale as a supplement to coal or lignite in power production is a more.

However, it is already considered that in general Turkish oil shale would be most profitably used to supplement coal or lignite as a power station fuel, rather than for the recovery of shale oil.

3.27 United Kingdom

The oil shale industry started in Scotland where, in 1694, oil was produced by heating Shropshire oil shale. The direct combustion of oil shale to produce hot water, steam, and, finally, electricity has developed in accordance with the general trends in solid fuel combustion technology. At the beginning of the 19th century, industrialized countries became more interested in obtaining oil and gas from coal pyrolysis (the decomposition or transformation of the kerogen organic matter into hydrocarbon derivatives by heat).

Thus, the United Kingdom (specifically Scotland) holds an important place in the historical development of oil-shale working. The first oil-shale patent – A way to extract and make great quantities of (quote) pitch, tarr and oyle out of a sort of stone (end quote) (Crown Patent No. 330) – was granted to a group of English entrepreneurs in 1694, and the first substantial shale-oil industry was begun in the Lothians of Scotland (based on Carboniferous oil shales) in 1851 by John Young and others. Production peaked in 1913 when over 3.2 million tons of oil shale was processed. The industry declined slowly but steadily until it closed down in 1962.

No matter what the method of formation, the use of oil shale as a fuel or fuel source is not new and can be traced back to ancient times. But to skip a generation or two, the modern use of oil shale to produce oil dates to Scotland in the mid-nineteenth century (Louw and Addison, 1985). In 1847 Dr. James Young prepared lighting oil, lubricating oil and wax from coal. Then he moved his operations to Edinburgh where oil shale deposits were found and in 1850 he patented the process of cracking the oil into its constituent parts. Thus, oil from oil shale was produced in that region from 1857 but production (albeit small-scale production) was terminated in 1966 because of the availability of cheaper supplies of crude oil.

Oil shale occurs at a number of other stratigraphic levels in Great Britain, notably in the Devonian Caithness Flags and in the Jurassic Lias, Dun Caan and Brora oils shales, Oxford Clay and Kimmeridge Clay. Of these, the Kimmeridge Clay has long seemed the most economically interesting prospect, but repeated attempts at commercial exploitation have ended in failure.

The occurrence of oil shale in the cliffs of Kimmeridge Clay at Kimmeridge Bay, Dorset, has been known since the Iron Age. The most famous seam, the Blackstone, has been used locally as a coal substitute and has yielded at various times products ranging from lubricating oil to sanitary deodorizer. During the latter half of the 19th century 8 companies were set up to exploit this oil shale, but none was lastingly successful. In each case, the failure was blamed on the unacceptably higher sulfur content (4–8% w/w) of the shale-oil combined with the high cost of working thin seams.

Combustible shales have been recorded in the Kimmeridge Clay throughout its English outcrop. Assessments were made of their potential value as fuel in Dorset and Lincolnshire and Norfolk during the World War I, and although substantial quantities of good quality oil shale were reported to be present, no major industry was developed. They were re-assessed by the British Geological Survey in the 1970s as a result of the economic crisis caused by a rapid increase in crude oil prices in 1973.

Oil shale is present throughout the outcrop and subcrop of the Kimmeridge Clay, locally with over 100 seams with potential yields of shale oil ranging from 10 to 90 gallons per ton. However, major economic and environmental problems would need to be solved before they could be worked on a large scale. The seams are thin (most are less than <6 feet) and separated by barren mudstones that would have to be removed before the oil-shale concentrate was retorted at 500 °C (930 °F) to yield shale oil. This pyrolysis produces sulfurous gases and large volumes of spent shale, and the shale oils and spent shale can contain low concentrations of carcinogens. In addition, the shale oil would have to be distilled to make them comparable to naturally occurring crude oils that can be used as a refinery feedstock.

The oil shale in the Kimmeridge Clay have the potential to produce millions of tons of shale oil, but only by removing and processing tens of cubic kilometers of material from open-cast excavations, an impossible task in a densely populated country such as Britain. Even if this was possible, the energy used in the winning and upgrading processes might be greater than the energy value of the finished product. The oil shale in the Kimmeridge Clay could never, therefore, make a major contribution to the energy supply of the United Kingdom.

3.28 United States of America

Deposits of oil shale, ranging from Precambrian to Tertiary age, are present in the United States. The two most important deposits are in the Eocene Green River Formation in Colorado, Wyoming, and Utah (Fig. 12.3) and in the Devonian-Mississippian black shales in the eastern United States (Conant and Swanson, 1961; De Witt et al., 1993; Pitman et al., 1989; Dyni, 2003, 2005; 2006; US DOE, 2007; Johnson et al., 2009). Oil shale associated with coal deposits of Pennsylvanian age is also in the eastern United States. Other deposits are known to be in Nevada, Montana, Alaska, Kansas, and elsewhere, but these not been sufficiently explored to be considered as commercial resources (Russell, 1990). Because of their size and grade, most investigations have focused on the Green River and the Devonian-Mississippian deposits.

The largest of the deposits is found in the Eocene Green River formation in north-western Colorado, north-eastern Utah and south-western Wyoming. The richest and most easily recoverable deposits are located in the Uinta Basin in eastern Utah and the Piceance Creek Basin in western Colorado. The Uinta basin and the Piceance basin underlie approximately 20,000 square miles of terrain, and were once occupied by a second freshwater lake. Most of the Piceance basin lies north of the Colorado River, but it includes oil shale deposits within Battlement Mesa and Grand Mesa on the south side of the river. Colorado oil shale also occurs in the Sand Wash basin, which is north of the Piceance basin near the Wyoming border.

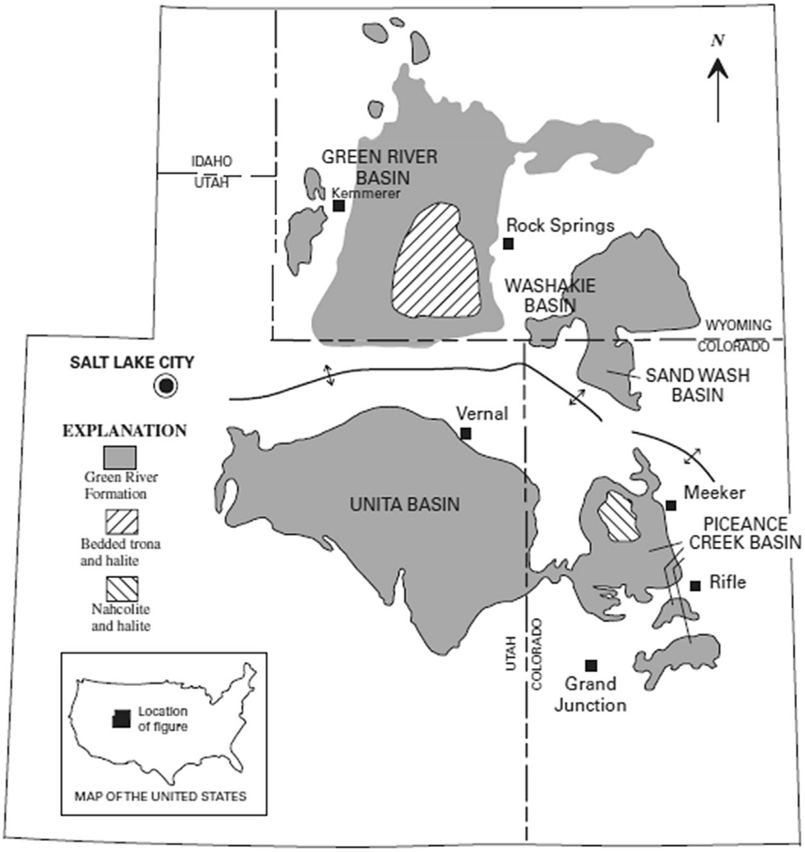

FIGURE 12.3 Main basins of the green river formation.

The shale oil can be extracted by surface and in-situ methods of retorting: depending upon the methods of mining and processing used, as much as one-third or more of this resource might be recoverable. There is also the Devonian-Mississippian black shale in the eastern United States.

Large deposits are also found throughout the Midwestern and Eastern States. However, because of the richness and accessibility, the Green River shales are the ones most likely to be developed on a large scale in the future. The formation has been divided into several distinct geological basins – the richest and most thoroughly explored deposits occur in Piceance basin (Colorado). The resources of the Uinta basin (Utah) are, in general, of somewhat poorer quality. The Wyoming deposits are relatively inferior and often intermingled with rock that does not contain any organic matter.

The quality of the Green River shale is evaluated according to thickness and potential oil yield. Only deposits that yield at least 15 gal/ton and are at least 15 feet thick. This group includes shales containing as much as 1.4 trillion barrels (1.4×10^{12} bbls) of potential shale oil. The high grade shale formations are further defined as shale formations that are at least 100 feet thick that would yield at least 30 gallons of oil per ton of shale.

The potentially-producible oil content is estimated to be an additional 0.4 trillion barrels (0.4×10^{12} bbls) for a total shale oil resource on the order of 1.8 trillion barrels (1.8×10^{12} bbls) of potentially producible shale oil.

The proven amount of US oil shale resources: the proved amount of shale in place is estimated to be on the order of 3680×10^9 US tons of which approximately 89% is located in the Green River deposits and 11% in the Devonian black shale.

By assay techniques (Fischer assay being the commonly used method) oil yields vary from approximately 10 gallons per ton to 50 gallons per ton and, for a few feet in the Mahogany zone, up to approximately 65 gallons per ton. Oil shale yields more than 25 US gallons per ton are generally accepted as the most economically attractive, and hence, the most favorable for development.

Recoverable resources of shale oil from the marine black shale in the eastern United States were estimated in 1980 to exceed 400 billion barrels (400×10^9 bbls). These deposits differ significantly in chemical and mineralogical composition from Green River oil shale. Owing to its lower atomic hydrogen/carbon ratio, the organic matter in eastern oil shale yields only approximately one-third as much oil as Green River oil shale, as determined by conventional Fischer assay analyses. However, when retorted in a hydrogen atmosphere, the oil yield of eastern oil shale increases by as much as twice to three times the Fischer assay yield.

Many pilot retorting processes have been tested for short periods. Among the largest were a semi-commercial-size retort operated by Union Oil in the late 1950s, which processed 1100 tons per day of high-grade shale. A pilot plant operated by Tosco (The Oil Shale Corporation) processed 900 tons per day of high-grade shale in the early 1970s. For a shale grade of 37 - gallons (150 L) per ton, these feed rates correspond, respectively, to production of 43,500 gallons (165,000 L) per day and 357,000 gallons (135,000 L) per day of crude shale oil.

Because of the abundance and geographic concentration of the known resource, oil shale has been recognized in the United States as a potentially valuable energy resource since as early as 1859, the same year Colonel Drake completed his first oil well in Titusville, Pennsylvania. Oil distilled from oil shale was first burnt for horticultural purposes in the 19th Century and early products derived from shale oil included kerosene and lamp oil, paraffin, fuel oil, lubricating oil and grease, naphtha, illuminating gas, and ammonium sulfate fertilizer. However, although the US shale oil industry was a viable part of the economy prior to the strike by Colonel Drake at Titusville, Pennsylvania in 1859, the industry struggled after the Titusville discovery and but practically disappeared within a few years.

However, in the early 1900s, more detailed investigations were made and in 1912 the US government established the Office of Naval Petroleum and Oil Shale Reserves. The oil shale reserves were seen as a possible emergency source of fuel for the military, particularly the United States Navy, which had, at the beginning of the 20th century, converted its ships from coal to fuel oil, and the economy of the United States was transformed by gasoline-fueled automobiles and diesel fueled trucks and trains, concerns have been raised related to assuring adequate supplies of liquid fuels at affordable prices to meet the growing needs of the nation and its consumers.

The abundance of oil shale resources in the United States were initially eyed as a major source for these fuels. Numerous commercial entities sought to develop oil shale resources. The Mineral Leasing Act of 1920 made crude oil and oil shale resources on Federal lands available for development under the terms of federal mineral leases. Soon, however, discoveries of more economically producible and refinable liquid crude oil in commercial quantities caused interest in oil shale to decline.

Interest resumed after World War II, when military fuel demand and domestic fuel rationing and rising fuel prices made the economic and strategic importance of the oil shale resource more apparent (US DOE, 2004a, 2004b; 2004c). After the war, the booming post-war economy drove demand for fuels ever higher. Public and private research and development efforts were commenced, including the 1946 United States Bureau of Mines Anvil Point, Colorado oil shale demonstration project. Significant investments were made to define and develop the resource and to develop commercially viable technologies and processes to mine, produce, retort, and upgrade oil shale into viable refinery feedstocks and by-products. Once again, however, major crude oil discoveries in the continental 48 States, off-shore, and in Alaska, as well as other parts of the world reduced the foreseeable need for shale oil and interest and associated activities again diminished. Lower-48 United States crude oil reserves peaked in 1959 and lower-48 production peaked in 1970.

By 1970, oil discoveries were slowing, demand was rising, and crude oil imports, largely from Middle Eastern states, were rising to meet demand. Global oil prices, while still relatively low, were also rising reflecting the changing market conditions. On-going oil shale research and testing projects were re-energized and new projects were envisioned by numerous energy companies seeking alternative fuel feedstocks. These efforts were significantly amplified by the impacts of the 1973 Arab Oil Embargo which demonstrated the vulnerability of the United States to disruptions in the supply of imported crude oil, and were underscored by a new supply disruption in 1979 that was associated with the revolution in Iran.

By 1982, however, technology advances and new discoveries of offshore oil resources in the North Sea and elsewhere provided new and diverse sources for United States oil imports, and dampened global energy prices. Global political shifts promised to open previously restricted provinces to oil and gas exploration, and led economists and other experts to predict a long future of relatively low and stable oil prices. Despite significant investments by United States energy companies, numerous variations and advances in mining, restoration, retorting, and in-situ processes, the costs of oil shale production relative to foreseeable oil prices, made continuation of most commercial efforts impractical. In addition, the collapse of world oil prices in 1984 did not help the oil shale development cause.

Thus, the prospects for oil shale development in the United States remain uncertain (Bartis et al., 2005). The estimated cost of surface retorting remains high – for surface retorting, it may be inappropriate to contemplate near-term commercial efforts. Meanwhile, the technical groundwork may be in place for a fundamental shift in oil shale economics. Advances in thermally conductive in-situ conversion may cause shale-derived oil to be competitive with crude oil. If this becomes the case, oil shale development could soon occupy a very prominent position in the national energy agenda (Bartis et al., 2005).

4. Utilization

Oil shale utilization will involve several different kinds of technologies. In any case, the major areas will include mining, size reduction, retorting or other means of recovering shale oil from the rock, disposal of the spent shale and upgrading the shale oil into marketable products. Estimates of required selling prices for synfuels have, through the years, been very badly off the mark. However, estimating the potential for lowering shale oil costs by improving the economics of one or another of the various technologies can be useful in assigning priorities for research and development efforts.

It is interesting to note how similar these estimates are, even though their cost bases are obviously different, they differ by years in time (1980 vs. 1987) and were made for shales half a world apart. Yet, in each case the costs of getting the shale out of the ground and ready to process represent fully one-half the total cost. It is also interesting to note that substantial reductions in the cost of the Estonian shale oil were achieved, even though this industry is approximately 80 years old, hence should be relatively mature.

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C H A P T E R

13

Kerogen

1. Introduction

The term *kerogen* will be used here to designate the organic constituent of the sedimentary rocks that is neither soluble in aqueous alkaline solvents nor in the common organic solvents. This is the most frequent acceptance of the term kerogen, and results from a direct generalization to other rock types in carbonaceous shales and oil shale formations (Tissot and Welte, 1984). However, some authors still restrict the name kerogen to the insoluble organic matter of oil shales only, because kerogen originally was applied to the organic material found in Scottish shales, which yielded an oil product upon a destructive distillation.

Sedimentary rocks commonly contain minerals and organic matter with the pore space occupied by water, natural gas, and crude oil. *Kerogen* is the fraction of organic matter remaining after extraction of pulverized rock with organic solvents. Kerogen can be isolated from carbonate-bearing rocks and from silicate-bearing rocks by treatment with inorganic acids, such as hydrochloric acid (HCl aq.) and hydrofluoric acid (HF aq.) (Durand, 1980; Scouten, 1990; Peters and Cassa, 1994) although there are questions related to whether these acids can change the character of the kerogen during the extraction process. However, the term *kerogen* is only an operational definition because the amount and composition of insoluble organic matter or kerogen remaining after extraction depends on the types and polarities of the organic solvents. In fact, the use of the term kerogen, originally described as the organic matter in oil shale, has been extended to include all insoluble solid organic matter in sedimentary rocks (Hutton et al., 1994).

To reaffirm the above, it is important to note that the name kerogen, in opposition with usual chemistry nomenclature, does not represent a substance with a given chemical composition. Indeed kerogen is a generic name, in the same sense as lipids or proteins. Several organic precursors and their mixtures may lead to kerogen incorporation in sediments. Moreover, with geological burial of sediments at temperatures ranging up to 200 °C (390 °F), during time periods from tens to thousands of million years, the chemical composition of kerogen dispersed in sedimentary layers progressively changes. The operational definition of kerogen on the basis of insolubility accounts neither for these compositional variations due to source and evolution, nor for a possible mixture of the substance able to generate petroleum with other insoluble organic compounds like coke for example, resulting from

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further petroleum transformation into source rocks (Vandenbroucke, 2003; Vandenbroucke and Largeau, 2007).

Another major drawback of the definition of kerogen using the insolubility of the material in organic solvents, in contrast with the solubility of crude oil or tar sand bitumen, is that the composition and chemical features of kerogen will be closely dependent on the organic solvent and extraction procedure used for this separation. As a consequence, analytical data on kerogens if the experimental procedure is standardized by use of the same solvent. Thus, there needs to be established standard test method protocols regarding extraction procedures, either in terms of the solvent polarity or for sample grinding, temperature, duration of extraction and stirring efficiency. The result is that extraction can never be considered as complete (or even reliable) since any change in these parameters may result in extraction of further compounds.

In addtion to the solvent extraction procedure needed for separation of soluble and insoluble organic matter in rocks, analytical techniques used for kerogen characterization often require its isolation from minerals, or at least a kerogen concentrate. This can be achieved by efficient physical or chemical methods (Forsman, 1963; Robinson, 1969; Durand and Nicaise, 1980; Whelan and Thompson-Rizer, 1993; Vandenbroucke, 2003; Vandenbroucke and Largeau, 2007). However, when chemical method are employed for elucidation of the chemical structure of kerogen or the identification of structural and functional groups in kerogen, there is the need to implications of using the chemicals and whether or not the chemicals cause any changes to the structural and functional entities in kerogen during the course of the reaction. The potential for such changes is not always acknowledged by the researchers. A similar rationale must also be applied to methods that use thermal decomposition of the kerogen (as a means of deducing structural entities in the kerogen for the products of the thermal reaction) insofar as the potential for changes to the structural and functional entities in the kerogen may (or likely) occur during the course of the reaction.

Kerogen is a mixture of macerals and reconstituted degradation products of organic matter. *Macerals* are the remains of various types of plant and animal matter that can be distinguished by their chemistry and by their morphology and reflectance using a petrographic microscope (Stach et al., 1982). This term was originally applied to components in coal but has been extended to sedimentary rocks. *Palynomorphs* are resistant, organic-walled microfossils such as spores, pollen, dinoflagellate cysts, and chitinozoa (flask-shaped palynomorphs which appear dark, almost opaque when viewed using a light microscope).

Throughout this text, the term *kerogen* is also generally used for organic matter in sedimentary rocks that is insoluble in common organic and inorganic solvents. Thus, the term *kerogen* is used throughout this text to mean the carbonaceous material that occurs in sedimentary rocks, carbonaceous shale, and oil shale. This carbonaceous material is, for the most part, insoluble in common organic solvents. A soluble fraction, *bitumen*, co-exists with the kerogen. The bitumen is not to be confused with the material found in tar sand deposits (Speight, 2008, 2009, 2014). However, like many naturally-occurring organic materials, kerogen does yields a hydrocarbonaceous oil when heated to temperatures sufficiently high (typically >300 °C, 570 °F) to cause thermal decomposition with simultaneous removal of distillate.

The precise details regarding the perennial issues related to the origin and accumulation of kerogen have yet to be fully answered. Therefore, in any text dealing with the science and technology of oil shale, there must, of necessity, be a section dealing with kerogen but it is not the goal of this chapter to deal with the various intimacies of kerogen structure. The chapter is to assist the reader to understand kerogen and its place as a naturally occurring organic material (Durand, 1980; Tissot and Welte, 1984; Scouten, 1990; Vandenbroucke, 2003).

Briefly, Rock-Eval pyrolysis is used to determine the properties of kerogen in rock formations without need to isolate it from minerals. Although the initial objective of Rock-Eval pyrolysis was the screening of source rocks in exploration wells, the method has been used for many other studies, including systematic application to kerogen analysis (Vandenbroucke, 2003; El Nady and Hammad, 2015).

In order to visually assess the quality of the kerogen visually, it can be separated from the mineral matrix through acidification after which the kerogen can be examined using transmitted light through a microscope to determine its form (structured or amorphous) and origin. Visual estimates of kerogen quality are typically presented in terms of the percentage of each type of kerogen in a sample derived from cuttings composites or core (conventional or sidewall). Structured kerogens include woody, herbaceous, vitrine and inertinite. Amorphous kerogens are by far the most prevalent and include most of the algal material (Table 13.2). As an example, the visual estimate of kerogen type might be stated as 50% woody, 45% amorphous, 5% inertinite. In general, the more amorphous kerogen present, the more oil prone the rock.

Thus, the type of kerogen present in a rock formation (such as a shale formation) determines the quality of the formation. From the above presentation, Type I kerogen is the highest quality; Type III is the lowest. Type I has the highest hydrogen content; type III, the lowest. To determine the kerogen type present in a source rock, plot the hydrogen and oxygen indices on a modified Van Krevelen diagram (Fig. 13.1). In terms of quality (i.e. the propensity of gas and oil production, the hydrogen index (HI) represents the amount of hydrogen relative to the amount of organic carbon present in a sample. The Rock-Eval analysis can help in the determination of the total amount of hydrogen in milligrams of hydrogen to grams of sample. The oxygen index (OI) represents the amount of oxygen relative to the amount of organic carbon present in a sample.

However, as with any analytical method, the elemental analyses of oil shale kerogen is subject to differences that arise from contamination and dilution by mineral matter. This often gives to difficulties when attempting to sub-divide kerogen data into clearly defined domains, even where the oil shale type is the same. Thus, classifications of oil shale based

TABLE 13.1 The four basic types of kerogen.

Kerogen type	Predominant hydrocarbon potential	Amount of hydrogen	Typical depositional environment
I	Oil prone	Abundant	Lacustrine
II	Oil and gas prone	Moderate	Marine
III	Gas prone	Small	Terrestrial
IV	Low – primarily composed of vitrinite or inert material	None	Terrestrial (?)

TABLE 13.2 Visual kerogen types and quality are shown in the table below.

Visual kerogen type	Hydrocarbon potential
Woody	Gas prone
Herbaceous	Oil and gas prone
Vitrinite	Gas prone
Inertinite	No gas or oil
Amorphous (dominantly algal)	Oil and gas prone

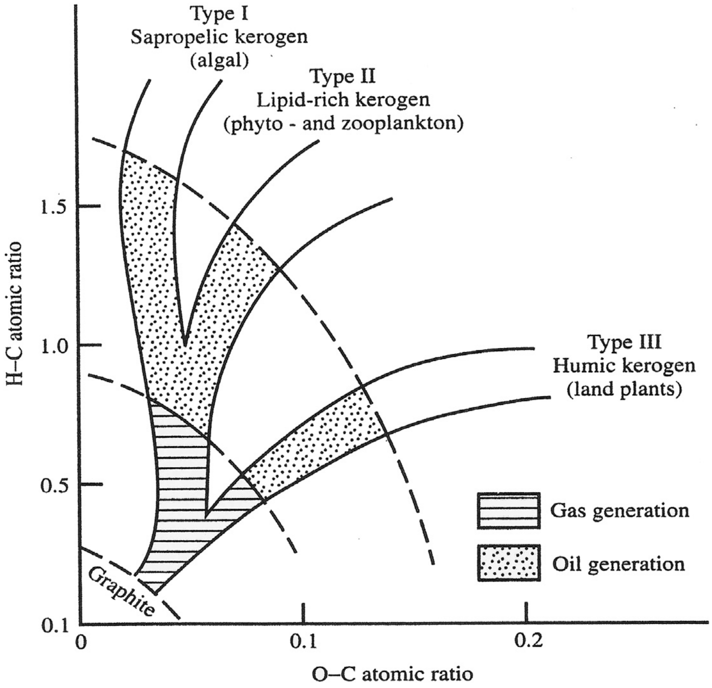

FIG. 13.1 Hypothetical evolutionary pathways (atomic H/C ration vs. atomic O/C ratio) of kerogen.

on elemental composition that groups the oil shales according to the types of the organic matter (i.e. the kerogen) may lead to some confusion. The major limitation of the van Krevelen diagram for oil shale (Fig. 13.1), as it is with any technique that uses bulk rock properties, lies in the very nature of the kerogen (and thus the nature of the oil shales themselves, when the diagram is used for oil shales).

Oil shale kerogen generally is derived from at least two, and commonly many more, chemically different components (Wang et al., 2018). Almost without exception, all oil shales contain liptinite, vitrinite, and inertinite, the latter two groups being minor components in many oil shales. The relative hydrogen content of vitrinite is much lower than that of liptinite and, correspondingly, the oxygen content of vitrinite is higher; the hydrogen content of inertinite is lower than that of vitrinite. Therefore, it is to be expected that the relative abundance of hydrogen and oxygen in any kerogen will be dependent on the relative proportions of vitrinite, liptinite, and inertinite, in addition to factors such as maturation level and weathering (Hutton et al., 1994).

Recall that the use of the term *kerogen*, originally described as the organic matter in oil shale, has been extended to include all insoluble solid organic matter in sedimentary rocks. Kerogen is divided into types based on elemental composition and potential maturation path. *Maceral* nomenclature, originally developed to describe the organic components of coal, has also been extended to source rocks and, later, oil shale. The extension and overlap of these two fields creates problems as attested to by the proliferation of vitrinite terminology and the application of the term vitrinite to organic matter that is not clearly derived from woody tissue.

Maceral terminology was first developed for coal and then extended to include source rocks and oil shale (Hutton et al., 1994; Speight, 2013). Macerals are analogous to the minerals of rocks, are the elementary microscopic organic constituents of a rock, and form from plant cells or tissue during coalification. The type, quantity, and association of the floral components, as well as the environmental conditions and burial history, determine the chemical, physical and technological properties of a coal. A maceral group comprises several macerals each of which has chemically similar properties. Thus, for macerals in any group, the properties of macerals are more closely related to each other than they are to the properties of the macerals in another maceral group.

Maceral terminology is based on the direct observation of the morphological and optical properties of the organic matter which ultimately reflects their internal chemistry. Issues that arise form the use of maceral terminology notwithstanding, the fundamental framework of organic matter in sedimentary rocks is best served by maceral nomenclature. This is consistent with observations that kerogen, or solid sedimentary organic matter, is clearly composed of macerals (Hutton et al., 1994).

Oil shale, kukersite, and torbanite (Chapter 1) represent types of mineral materials that contain various amounts of organic matter (kerogen), which has been assumed to be an organic (albeit complex) polymer completely that is dispersed through a complex of minerals. Most torbanite (or boghead coal) kerogen fall into the range of the Type I kerogen (Fig. 13.1). However, petrographic analysis of torbanite shows that this oil shale type contains vitrinite and inertinite. In addtion, a lamosite is a lacustrine oil shale that contains predominantly lamalginite. A tertiary lamosite generally falls within the range of a Type I kerogen (Fig. 13.1), and in the alginite field. However, exceptions are common. Kerogen derived from marine oil shales mostly plots as Type II or fall into a range between Types I and II (Fig. 13.1).

The concept of kerogen is rooted in oil shale nomenclature and has been refined into categories and extended to include other forms of sedimentary matter. The purpose of kerogen classification was to provide a framework for comparison using the popularization of the van Krevelen diagram (Fig. 13.1). However, each kerogen type does not define a physical or chemical entity but rather a broad compositional field which defines a path taken by the organic matter type during diagenesis and catagenesis. The questions that arise from this system are illustrated by Type II kerogen which is often found to consist of many different kinds of organic matter, each of which has a different maturation path. On the other hand, using the concept of macerals may present an alternate method to describe the type of kerogen.

Thus, the solution to the classification of organic matter is not a choice between kerogen type and maceral, but rather the use of both, that is, maceral nomenclature to describe the physical entities which compose kerogen. This does not mean that the suggested solution will provide a clear path to the classification of kerogen but it may provide a more logical approach since it takes into account the individual components of kerogen, which (classification notwithstanding) is best described a complex naturally-occurring organic heterogeneous material.

In summary, the precise structure of kerogen is unknown and the precise role of kerogen-rock interactions in determining the properties of oil shale is also unknown.

2. Origin

Kerogen is formed during sedimentary diagenesis from the degradation of living matter which can include lacustrine algae, marine algae and plankton, as well as terrestrial higher-order plants. Algae are simple, nonflowering, and typically aquatic plant of a large group that includes the seaweeds and many single-celled forms. Algae contain chlorophyll but lack true stems, roots, leaves, and vascular tissue. Plankton are the diverse collection of organisms that live in large bodies of water and are unable to swim against a current.

The formation of the kerogen is subject to the preservation (in one form or another) of the original organic matter in the formation. Moreover, the actual chemical mechanism and pathways of the maturation of the organic matter are not definitively established. Pathways have been suggested but various factors play a role in the preservation of organic matter, notably the oxygen content of the water column and sediment (oxic vs. anoxic), primary productivity of new organic matter by plants, water circulation, and sedimentation rate (Demaison and Moore, 1980; Emerson, 1985; Peters and Cassa, 1994).

Moreover, for ancient sediments, the oxygen content of the overlying water column is unknown, but it can be interpreted from the presence or absence of laminated or bioturbated sediments and organic matter content in the sediment (Demaison and Moore, 1980). The oxygen content of water is determined by availability and solubility of oxygen (which depends upon the temperature, pressure, and salinity). *Oxic* water (saturated with oxygen) has been estimated to contain 2.0–8.0 mL oxygen per liter of water (Tyson and Pearson, 1991). *Dysoxic* water has been estimated to contains 0.2–2.0 L of oxygen per liter of water, and *suboxic* water has been estimated to contain 0.0–0.2 L of oxygen per liter of water. *Anoxic* water, as the name implied, lacks oxygen. Below the 0.5 mL oxygen per liter of water threshold, the activity of multicellular organisms as agents in the oxidative destruction of organic matter is severely limited (Demaison and Moore, 1980).

Anoxic sediments are typically thinly laminated (distinct alternating layers <2 mm thick) because of the lack of bioturbation by burrowing, deposit-feeding organisms. It has been suggested (Pederson and Calvert, 1990) that anoxia is less important than primary productivity in determining quantities of organic matter preserved. However, the effect of anoxia on the quality rather than quantity of organic matter preserved, that is, anoxia favors preservation of all organic matter, including hydrogen-rich, oil-prone organic matter (Peters and Moldowan, 1993).

During diagenesis, macromolecular compounds (sometimes referred to as *biopolymers*) that are formed from proteins and carbohydrates in the original organic matter decompose partially or completely. These resulting products units can then react with each other to form other macromolecular compounds (often referred to as *geopolymers* because the formation takes place under geological conditions). The formation of the geopolymers in this way is often assumed to be associated with the large high molecular weight and diverse chemical compositions associated with kerogen. The diversity in the chemical composition of kerogen is ascribed to (i) the types of precursors in the pre-kerogen mix, (ii) the distribution of the precursors in the pre-kerogen mix, and (iii) maturation parameters, such as the temperature and the pressure. The reactions occur simultaneously with the formation and/or the sedimentation of one or more mineral components resulting in an organic-containing sedimentary rock like such as oil shale.

Sedimentary organic matter is formed by diagenesis (reactions in sediments up to 60 °C, 140 °F) (Tegelaar et al., 1989) and catagenesis (those reactions that occur at temperatures in excess of >100 °C (212 °F) by the thermal cracking of biological material introduced during deposition from primary producers (Tissot and Welte, 1984). More than 90% w/w of this sedimentary organic matter is a non-hydrolyzable (i.e., immune to acid−base hydrolysis) kerogen (sometimes arbitrarily referred to as a macropolymer that does not dissolve in organic solvents and produces crude oil upon catagenesis (Tissot and Welte, 1984; de Leeuw and Largeau, 1993). The composition and type of kerogen is heavily dependent on the nature of the biological input the environment of deposition and the preservation pathway (Goth et al., 1998; Briggs, 1999). Both diagenesis and catagenesis can be simulated in the laboratory using P-t apparatus (Stankiewicz et al., 2000) and environmental decay experiments (Briggs, 1999; Gupta et al., 2009).

Kerogen formation is generally attributed to neogenesis (Tissot and Welte, 1984), in which sedimentary organic matter is formed by random intermolecular polymerization and polycondensation of biological residues (e.g., amino acids, sugars, and lipids) including melanoidins or the Selective Preservation of resistant biosynthesized macromolecules that undergo limited chemical change during diagenesis (i.e., they remain morphologically and chemically recognizable as organic remains in the sedimentary rock (Goth et al., 1998). Selective preservation which has gained widespread acceptance as a counter thesis to neogenesis since the mid-1980s suggests that aliphatic derivatives in fossil organic matter are derived from highly aliphatic and resistant (insoluble and non-hydrolyzable) biopolymers in living organisms, such as algaenan (present in algae) (Goth et al., 1998), cutan (present in plant leaves) (Mösle et al., 1998), and suberan (present in suberinized vascular tissue (de Leeuw and Largeau, 1993). These survive decay more readily than labile biopolymers such as polysaccharides, proteins, and nucleic acids (Tegelaar et al., 1989).

The microstructure of kerogen also evolves during thermal maturation. Analysis by gas sorption demonstrated that the internal specific surface area of kerogen increases by an order of magnitude (~40−400 m^2/g) during thermal maturation (Craddock et al., 2015). X-ray and neutron diffraction studies have examined the spacing between carbon atoms in kerogen, revealing during thermal maturation a shortening of carbon-carbon distances in covalently bonded carbons (related to the transition from primarily aliphatic to primarily aromatic bonding) but a lengthening of carbon-carbon distances in carbons at greater bond separations (related to the formation of kerogen-hosted porosity). This evolution is attributed to the formation of kerogen-hosted pores left behind as segments of the kerogen molecule are cracked off during thermal maturation leading to the assumption of the structure of kerogen (Vandenbroucke and Largeau, 2007; Bousige et al., 2016).

A thorough geochemical analysis of organic fossil matter using high-resolution spectroscopy in conjunction with mass spectrometry [such as in Goth et al. (1998)] and laboratory analytical chemistry methods (de Leeuw and Largeau, 1993) establishes the diagenetic pathway degree of biological preservation (Briggs, 1999) and insights into geochemical transformation of biomolecules to geomolecules (Gupta et al., 2009). Organic sulfurization (Kok et al., 2000) and oxidative reticulation of unsaturated cross-linkages in reacting molecules (Riboulleau et al., 2001) offer mechanistic insights through analysis and case study of modern (extant) and fossil material (discrete) or those disseminated in sediment as kerogen. In consideration of this aspect, this synthesis opinion article focuses on complimentary and conflicting arguments from plant fossil analysis, their widespread relevance, the biochemical description of contributors, insights from controlled laboratory experiments (decay), and simulated autoclave experiments in pressure–temperature regimes from 270 to 350 °C (520–650 °F) (Stankiewicz et al., 2000).

Thus, kerogen is formed during sedimentary diagenesis from the degradation of living matter. The original organic matter can comprise lacustrine and marine algae and plankton and terrestrial higher-order plants. During diagenesis, large biopolymers from constituents such as protein and carbohydrates in the original organic matter decompose partially or completely and the resulting units can then condenses to form geopolymers. The formation of geopolymers in this way accounts for the high molecular weight and diverse chemical composition associated with kerogen. The smallest units are the fulvic acid derivatives, the medium units are the humic acid derivatives, and the largest units are the humin derivatives. This polymerization usually happens alongside the formation and/or sedimentation of one or more mineral components resulting in a sedimentary rock of which oil shale is a prime example.

When kerogen is contemporaneously deposited with geologic material, subsequent sedimentation and progressive burial provide elevated pressure (overburden pressure) and temperature owing to lithostatic and geothermal gradients in crust of the Earth. Resulting changes in the burial temperatures and pressures lead to further changes in kerogen composition including loss of hydrgoen, oxygen, nitrogen, and sulfur and their associated functional groups as well as subsequent isomerization and aromatization. These types of changes are indicative of the thermal maturity state of kerogen (Requejo et al., 1992; Keleman et al., 2006; Budinova et al., 2014).

During the process of thermal maturation, kerogen breaks down in high-temperature pyrolysis reactions to form lower-molecular-weight products including bitumen, oil, and gas. The extent of thermal maturation controls the nature of the product, with lower thermal maturities yielding mainly bitumen/oil and higher thermal maturities yielding gas. These generated species are partially expelled from the kerogen-rich source rock and in some cases can charge into a reservoir rock. Kerogen takes on additional importance in unconventional resources, particularly shale. In these formations, oil and gas are produced directly from the kerogen-rich source rock (i.e. the source rock is also the reservoir rock). Much of the porosity in these shales is found to be hosted within the kerogen, rather than between mineral grains as occurs in conventional reservoir rocks.

The microstructure of kerogen also evolves during thermal maturation, as has been inferred by scanning electron microscopy (SEM) imaging showing the presence of abundant internal pore networks within the lattice of thermally mature kerogen. Analysis by gas sorption demonstrated that the internal specific surface area of kerogen increases by an order of magnitude ($\sim 40-400\ m^2/g$) during thermal maturation. X-ray and neutron diffraction studies have examined the spacing between carbon atoms in kerogen, revealing during thermal maturation a shortening of carbon-carbon distances in covalently bonded carbons (related to the transition from primarily aliphatic to primarily aromatic bonding) but a lengthening of carbon-carbon distances in carbons at greater bond separations (related to the formation of kerogen-hosted porosity). This evolution is attributed to the formation of kerogen-hosted pores left behind as segments of the kerogen molecule are cracked off during thermal maturation.

These changes in composition and microstructure result in changes in the properties of kerogen. For example, the skeletal density of kerogen increases from approximately 1.1 g/mL at low thermal maturity to 1.7 g/mL at high thermal maturity. This evolution is consistent with the change in carbon speciation from predominantly aliphatic (similar to wax, density < 1 g/mL) to predominantly aromatic (similar to graphite, density > 2 g/mL) with increasing thermal maturity.

3. Composition and properties

It is important to keep in mind that the name kerogen, in opposition with usual chemistry nomenclature, does not represent a substance with a given chemical composition. Indeed kerogen is a generic name and several organic precursors and their mixtures may lead to kerogen incorporation in sediments. As a consequence, analytical data on kerogens can be compared only if the same solvent is used.

Typical oil shale formations are non-porous, impermeable rocks containing 80%–95% w/w mineral constituents and 5%–20% w/w organic matter. Of the organic matter, only a minor part, the bitumen, is extractable into organic solvents. By far the major part of the organics in most oil shales is present as kerogen, an insoluble solid of variable composition which is usually finely dispersed throughout the mineral matrix.

The difficulty of achieving quantitative and selective reactions of insoluble organic solids under mild conditions and the scarcity of good methods for probing the structures of such materials have discouraged attempts to characterize the organic material. As a result many of the speculative concepts regarding the structures of oil shale kerogens have been derived from the many reported studies of bitumen (in this case, oil shale extracts and not the soluble material found in tar sand formations) and thermally generated shale oils. Nevertheless, over the past twenty-five years several research groups have begun to probe the chemical structures of oil shale kerogens.

Kerogen is a solid, waxy, organic substance that forms when pressure and heat from the Earth act on the remains of plants and animals. Kerogen is a complex mixture of organic chemical compounds that make up the most abundant fraction of organic matter in sedimentary rocks. As kerogen is a mixture of organic materials, it is not defined by a single chemical formula. Its chemical composition varies substantially between and even within sedimentary formations. For example, kerogen from the Green River oil shale deposit contains elements in the proportions carbon: 215, hydrogen: 330, oxygen 12, nitrogen, 5, and sulfur 1 (Robinson, 1976).

Kerogen is insoluble in typical organic solvents in part because of its high molecular weight of its component compounds, some of which are in the form of polar functional groups. Overall, changes in kerogen composition with respect to heteroatom chemistry occur predominantly at low thermal maturities (bitumen and oil windows), while changes with respect to carbon chemistry occur predominantly at high thermal maturities (oil and gas windows).

However, detailed structural information on kerogen is limited because of the heterogeneous composition of kerogen and the difficulties associated with the chemical analysis of solid organic matter. Kerogen has been described as a *geopolymer,* which has been formed (by polymerization) from a random mixture of lower molecule weight chemical species (monomers). These chemical species are derived from the diagenetic decomposition of *biopolymers,* including proteins and polysaccharides (Tissot and Welte, 1984).

In fact, the discovery of insoluble biopolymers in living organisms, sediments, and sedimentary rocks has led to a reappraisal of the structure of kerogen (Rullkotter and Michaelis, 1990). In the modified scheme, more emphasis is placed on selective preservation of biopolymers and less on reconstitution of monomers. Progress has been achieved by the application of specific chemical degradation (Mycke et al., 1987), pyrolysis (Larter and Senftle, 1985), and spectroscopic techniques (Mann et al., 1991). In addtion the asphaltene constituents in the bitumen (the soluble organic portion of oil shale) may be the lower molecular weight fragments of kerogen and may be intermediates between bitumen and kerogen. For example, although the asphaltene constituents are soluble in polar solvents, they show elemental compositions similar to associated kerogens (Orr, 1986) and similar distributions of hydrocarbon derivatives (Bandurski, 1982; Pelet et al., 1985), including sterane derivatives and triterpane derivatives (Cassani and Eglinton, 1986). In addtion, lipid derivatives can be incorporated into kerogen during diagenesis, but many survive as free constituents in the kerogen-related bitumen and are known as molecular fossils, biological markers, or biomarkers. *Biological markers* are complex organic compounds composed of carbon, hydrogen, and other elements which show little or no change in structure from their parent organic molecules in living organisms (Peters and Moldowan, 1993).

In more general terms, the hydrogen content of kerogen falls between that of crude oil and that of coal (Speight, 2013, 2014), but this varies considerably with the source so that a range of values is found. This has been suggested as reflecting an overlap between terrestrial and aquatic origin. In fact, high lipid content, consistent with the occurrence of aquatic plants in the source material, appears to be diminished in kerogen by lignin of terrestrial origin (Scouten, 1990). In fact, kerogen and is best represented as a macromolecule that contains considerable amounts of carbon and hydrogen (Scouten, 1990). Furthermore, it is the macromolecular and heteroatom nature of kerogen with up to 400 heteroatoms (nitrogen plus oxygen plus sulfur) for every 1000 carbon atoms occurring as an integral part of the macromolecule that classifies kerogen as a naturally occurring heteroatomic material (Hutton et al., 1994).

Given geological time, it is believed that kerogen converts to various liquid and gaseous *hydrocarbon derivatives* at a depth of approximately 4.5 miles or more (approximately 7 km) and a temperature between 50 and 100 °C (122 and 212 °F) (USGS, 1995), which has been assigned to the presence of the *geothermal gradient*, which is the variation of temperature with depth in subterranean formations of the Earth (Chapter 1). Although the geothermal gradient varies from place to place, it is generally on the order of (22 °F per 1000 feet of depth or 12 °C per 1000 feet of depth, i.e. 0.022 °F per foot of depth or 0.012 °C per foot of depth). This would require a depth on the order of 25,000 to attain temperatures of 300 °C (570 °F).

Geological time not being available to the laboratory scientist, much of the laboratory work has focused on increasing the temperature to increase the reaction rate to study the thermal evolution of kerogen (Khatibi et al., 2018). However, the application of high temperatures (>250 °C, <480 °F) to a reaction not only increases the rate of reaction (thereby making up for the lack of geologic time) but can also change the *chemistry* of the reaction. Furthermore, introduction of a pseudo-activation energy in which the activation energy of the kerogen conversion reactions are reduced leave much to be desired because of the assumption required to develop this pseudo-activation energy equation(s). Nor is it valid to use a fixed set of kinetic parameters within each of these groups (Whelan and Farrington, 1992). Suffice it to state that the thermal evolution of kerogen is unknown and the role of kerogen in crude oil formation is at best, highly speculative.

Thus, once incorporated into sediments, the organic matter is buried under increasing depths as deposition of the mineral matter continues (sedimentation). Within the sediment, the physicochemical and biological environment is then gradually modified by the following events: (i) compaction, (ii) decrease in water content, (iii) cessation of bacterial activity, (iv) transformation of the mineral phase; and to some extent, but largely unknown, (v) an increase in temperature. Under these conditions, the skeletal structures of the lignin and lipids could be preserved to a significant degree. Should this be the case, there is the distinct possibility that oil and kerogen are produced from the organic material by simultaneous or closely consecutive processes. There is also the theory that lignin derivatives do not usually form oil but are more likely to produce coal (Speight, 2013). However, it must be remembered that these statements are theories, and proof, other than that obtained by laboratory experiments, is difficult to obtain.

As already noted, kerogen has an implied role in the formation of crude oil and the term *kerogen* has also been used generally to indicate that the material that is a precursor to crude oil. However, caution is advised in choosing the correct definition since there is the distinct possibility that kerogen, far from being a precursor to crude oil, is one of the by-products of the crude oil generation and maturation processes and may not be a direct precursor to crude oil.

The role played by kerogen in the crude oil maturation process is not fully understood, although it is believed to be considerable (Durand, 1980; Pelet and Durand, 1984; Tissot and Welte, 1984; Hunt, 1996). What obviously needs to be addressed more fully in terms of kerogen participation in crude oil generation is the potential to produce crude oil constituents from kerogen by low-temperature processes rather than by processes that involve the use of temperatures in excess of 250 °C (>480 °F).

In terms of the formation of kerogen, it can only be assumed that the similar types of plant debris that went into the formation of crude oil and coal may have played a role in the formation of kerogen (Tissot et al., 1978; Erdman, 1981; Scouten, 1990; Speight, 2013, 2014). Thus, once incorporated into sediments, the organic matter is buried under increasing depths as deposition of the mineral matter continues (sedimentation). Within the sediment, the physicochemical and biological environment is then gradually modified by the following events: (i) compaction, (ii) decrease in water content, (iii) cessation of bacterial activity, (iv) transformation of the mineral phase, and (v) to some extent, but largely unknown, an increase in temperature. Under these conditions, the skeletal structures of the plant materials could be preserved to a significant degree. Should this be the case, there is the distinct possibility that oil and kerogen are produced from the organic material by simultaneous or closely consecutive processes (Fig. 13.2). There is also the theory that lignin derivatives do not usually form oil but are more likely to produce coal (Speight, 2013, 2014). However, it must be remembered that these statements are theories, and proof, other than the questionable proof obtained by laboratory experiments, is difficult (perhaps even impossible) to obtain.

In the reverse route — the thermal decomposition of kerogen — there are several issues to consider not the least of which is the type or the types that are contained in the kerogen that are undergoing decomposition and the effects of each type of kerogen on the other types of kerogen in the overall kerogen mix.

In gernal terms, the decomposition of kerogen to bitumen and volatile products as a result of the application of heat takes place through series of complex chemical reactions, predominantly first order kinetic reactions and can be simplified into two step mechanism as shown below.

$$\text{Kerogen} \rightarrow \text{bitumen} \rightarrow \text{shale oil}$$

In the equation, the rate constant for the kerogen to bitumen conversion can be represented by k^1 and the rate constant for the bitumen-to-shale oil conversion can be represented by k^2

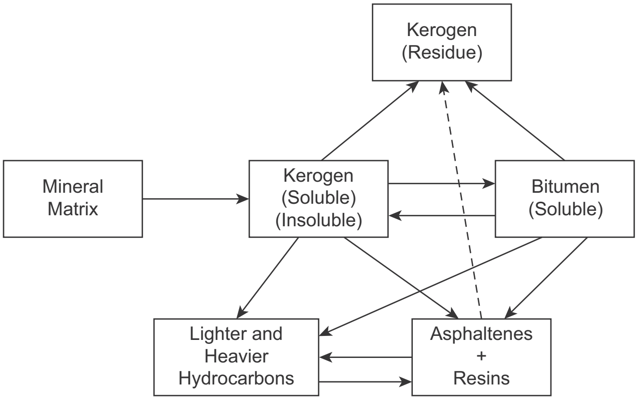

FIG. 13.2 Hypothetical representation of petroleum formation from kerogen.

and $k^1 > k^2$ at $T < 300$ °C (<570 °F). Two different mechanisms, low temperature and high temperature kerogen conversion are proposed for production of hydrocarbon from oil shales (Hill and Dougan, 1967). However, these equations make no allowance for the production of shale oil constituents directly from (without the bitumen intermediary) kerogen.

In the lower temperature range of 260–370 °C (500 to 700 °F), kerogen decomposes to bitumen, which then finally decomposes to form oil, gas and carbonaceous residue with a pour point in the range of -20 °C (68 °F) and an API gravity on the order of 40^o. When heated at higher temperatures (>425 °C, >800 °F), bitumen produces a stabilized polymer product that thermally decomposes to yield different type of oil, gas and residue with pour point on the order of 27 °C (80 °F) and API gravity of approximately 20^o. Low temperature oil shale conversion results in liquids with lesser aromatic and polar compounds and also has insignificant nitrogen content because of low polymerization of nitrogen containing compounds (Wen and Kobylinski, 1983). Almost 95% of the kerogen in oil shale deposits of Green River formation is decomposed to bitumen by two parallel competing first order kinetic reactions, one at higher temperature (>350 °C, 660 °F) with an activation energy of 45.7 kcal/mol and another at lower temperature (<350 °C, >660 °F) with an activation energy of 20.8 kcal/mol (Leavitt et al., 1987).

4. Types

Kerogen is the naturally occurring, solid, insoluble organic matter that occurs in source rocks and can yield oil upon heating. Typical organic constituents of kerogen are algae and woody plant material. Kerogen has a high molecular weight relative to tar sand bitumen and is generally insoluble in typical organic solvents (Speight, 2009, 2014).

After the relatively rapid alterations that take place shortly after the initial deposition of organic matter in a sediment, the surviving (preserved) organic matter undergoes additional changes (kerogen maturation). Oil shales contain relatively immature kerogen; that is the kerogen has not been extensively modified, except where exposed to an unusual geothermal gradient, such as an intrusion of volcanic magma (geologic sill or dike). Over geologic time, however, further alteration does occur.

As the maturation process proceeds, there is a loss of hydrogen and oxygen from the kerogen. Oil shales are generally immature and only the earlier stages of maturation, termed diagenesis, need be considered. During diagenesis, hydrogen is lost primarily as methane and other hydrocarbon gases, water and hydrogen gas, while oxygen is lost primarily as water and carbon oxides. These losses are, however, significant in determining the processing characteristics of the oil shale kerogen in retorting for liquid fuel production. Thus, in order to understand the chemical structure and reactivity of the organic constituents of oil shale, it is necessary to know not only the origin but also the maturity of the kerogen in the form of the various types that are a result of the maturation process(es).

Most schemes for the types of kerogen (a form of kerogen classification) are based on the chemical properties of kerogen, usually isolated by demineralization techniques, and belong to one of the following types: (i) elemental analysis, (ii) the amount of soluble bitumen, (iii) chemical degradation, which included oxidation, hydrogenolysis, and pyrolysis, (iv) functional analysis, (v) electron spin resonance studies, and (vi) nuclear magnetic resonance studies (Scouten, 1990; Lee, 1991; Hutton et al., 1994).

One particular classification scheme (Massoud and Kingdom, 1985) that has been proposed for the components of kerogen, separates the phytoclasts (microscopic plant fragment present in the fossil record) into four groups: (i) kerogìnite, (ii) liptinite, (iii) vitrinite, and (iv) inertinite. The keroginite group includes the finely comminuted or structureless sapropelic material which constitutes the main organic components of hydrogen-rich oil-prone kerogens (Type I and Type II kerogen). The liptinite group encompasses all structured sapropelic phytoclasts which are derived from the remains of waxy and fatty plant tissues, such as algae, spores, pollen and cuticles. When found in marine sediments, they are usually hydrogen depleted and gas prone (Type III kerogen) due to their degradation during transportation from land. The vitrinite group incorporates structured and unstructured woody tissues which correspond to first and second cycle vitrinite macerals and form the main constituents of the gas-prone Type III kerogen. The inertinite group comprises the high-carbon type (charcoal- or graphite-like) phytoclasts which have undergone natural carbonization prior to incorporation into sediments, and have no potential for conversion to hydrocarbon product.

Many of the chemical classifications of kerogen in shales are based on the elemental composition of organic matter. On method uses advocates the use of the elemental ratios as more suitable method of classification rather than the use of elemental percentage method because (i) it requires no preliminary standardization (Hutton et al., 1994). This has led to the classification in which kerogen is conveniently divides kerogen into four types (Table 13.1): (i) Type I, which consists mainly algal and amorphous constituents, (ii) Type II, which consists of mixed terrestrial and marine source material, (iii) Type III, which consists of woody terrestrial source material, and (iv) Type IV, which consists mostly of decomposed organic matter in the form of polycyclic aromatic hydrocarbon derivatives and has a low (<0.5) hydrogen-to-carbon (H/C) atomic ratio.

The Van Krevelen diagram (a plot of the atomic hydrogen-carbon ratio vs. the atomic oxygen-carbon ratio) (Fig. 13.2), derived from the elemental analysis of kerogen and coal, is a practical means of studying kerogen composition and properties (Speight, 2013, 2014). The position of kerogen in the H/C–O/C diagram is related to the total quantity of hydrocarbon derivatives, which in turn is a function of the relative amounts of aromatic hydrocarbon structures. The data for kerogen analysis in the H/C–O/C diagram can be considered to describe the evolutionary path for kerogen from different precursors. Analysis of the minor elements, sulfur and nitrogen, is much more difficult to simulate and may require a more detailed framework. In general, there are four types of kerogen that have been recognized and each is sufficiently different from the other types to be recognizable by elemental analysis (Table 13.3).

Type I kerogen (sapropelic kerogen) is rich in lipid-derived aliphatic chains and has a relatively low content of polynuclear aromatic systems and of heteroatomic systems. The initial atomic hydrogen-to-carbon (H/C) ratio is high (1.5 or more), and the atomic oxygen-to-carbon (O/C) ratio is generally low (0.1 or less). This type of kerogen is generally of lacustrine origin. Organic sources for the type I kerogen include the lipid-rich products of *algal blooms* and the finely divided and extensively reworked lipid-rich biomass deposited in stable stratified lakes.

TABLE 13.3 Characteristics of the four general types of kerogen.

- Type I Kerogen:
  - Alginite
  - Hydrogen/carbon atomic ratio >1.25.
  - Oxygen/carbon atomic ratio <0.15.
  - Tendency to readily produce liquid hydrocarbons.
  - Derived principally from lacustrine algae.
  - Has few cyclic or aromatic structures.
  - Formed mainly from proteins and lipids.
- Type II kerogen
  - Hydrogen/carbon atomic ratio <1.25.
  - Oxygen/carbon atomic ratio 0.03 to 0.18.
  - Tends to produce a mix of gas and oil.
  - Several types: Exinite, cutinite, resinite, and liptinite.
  - Exinite is formed from pollen and spores.
  - Cutinite is formed from terrestrial plant cuticle.
  - Resinite is terrestrial plant resins, animal decomposition resins.
  - Liptinite is formed from terrestrial plant lipids and marine algae.
- Type III kerogen
  - Hydrogen/carbon atomic ratio <1.0.
  - Oxygen/carbon atomic ratio 0.03 to 0.3.
  - Material is thick, resembling wood or coal.
  - Tends to produce coal and gas.
  - Has very low hydrogen because of the extensive ring and aromatic systems.
  - Formed from terrestrial plant matter that is lacking in lipids or waxy matter.
  - Formed from cellulose (the carbohydrate polymer that forms the rigid structure of terrestrial plants), lignin (another carbohydrate polymer that binds the strings of cellulose together), terpene derivatives, and phenol derivatives in the plant.
- Type IV kerogen
  - Hydrogen/carbon atomic ratio <0.5.
  - Contains mostly decomposed organic matter in the form of polycyclic aromatic hydrocarbon derivatives.
  - Little or no potential to produce hydrocarbons.

Thus, Type I kerogen is predominantly is aliphatic kerogen with a relatively high atomic hydrogen-to-carbon (H/C) ratio (>1.5) and a relatively low atomic oxygen-to-carbon (O/C) ratio (<0.1). Type I kerogens are rich in lipid-derived material and is commonly, but not always, from algal organic matter in lacustrine (freshwater) environments. On a mass basis, rocks containing type I kerogen yield the largest quantity of hydrocarbons upon pyrolysis. Hence, from the theoretical view, shales containing type I kerogen are the most promising deposits in terms of conventional oil retorting.

Type I kerogen is predominantly composed of the most hydrogen-rich organic matter preserved in the rock record. Often the organic matter is structureless (amorphous) alginite and, when immature, fluoresces golden yellow in ultraviolet (UV) light. A large proportion of Type I kerogen can be thermally converted to petroleum and therefore is rarely recognizable in thermally mature or postmature rocks. Sometimes in thermally immature rocks, morphologically distinct alginite is structurally or chemically assignable to specific algal or bacterial genera. These organic-walled microfossils have high hydrogen-to-carbon (H/C) ratios because they formed hydrocarbons biologically. Some examples of pure assemblages with Type I kerogen properties include the following: (i) the lacustrine alga Botryococcus braunii, which sometimes retains its diagnostic cup-and-stalk colonial morphology and/or its unique chemical compound, botryococcane, (ii) Tasmanites spp., which are low-salinity, cool water, marine algal phyto-plankton with unique physical features, and (iii) the Ordovician marine organic-walled colonial microfossil Gloeocapsomorpha prisca, with its diagnostic physical appearance and unique chemical signature. Where Type I kerogen is widespread, it is mapped as organic facies A. It usually forms in stratified water columns of lakes, estuaries, and lagoons.

Type I kerogen is concentrated in condensed sections where detrital sediment transport is low and primarily pelagic i.e. relating to the open sea. Condensed sections occur in offshore facies of transgressive systems tracts in marine and lacustrine settings. Although this extension of terminology from marine to lacustrine environments may be unfamiliar at first, lacustrine rocks are formed by the same dynamic processes that form marine rocks (i.e., sediment supply, climate, tectonics, and subsidence), although changes in lake levels often reflect local changes in runoff, evaporation, and sediment basin filling rather than the global and relative sea level changes postulated for marine sediments.

Type II kerogen (planktonic kerogen) is characteristic of the marine oil shales. The organic matter in this type of kerogen is usually derived from a mixture of zooplankton, phytoplankton, and bacterial remains that were deposited in a reducing environment. Atomic H/C ratios are generally lower than for type I kerogen, but the O/C atomic ratios are generally higher for type II kerogen than for type I kerogen. Organic sulfur levels are also generally higher in the type II kerogen. The oil-generating potential of type II kerogen is generally lower than those of the type I kerogen (i.e., less of the organic material is liberated as oil upon heating a type II kerogen at the same level of maturation).

Type II kerogen has a lower atomic hydrogen-to-carbon (H/C) ratio (on the order of 1.0−1.4) than Type I and a wider range of atomic oxygen-to-carbon (O/C) ratio (on the order of (0.05−0.15). Type II kerogen is principally derived from marine organic materials, which are deposited in reducing sedimentary environments. The sulfur content of type II kerogen is generally higher than in other kerogen types and sulfur is found in substantial amounts in the associated bitumen. Although pyrolysis of type II kerogen yields less oil than type I, the amount yielded is still sufficient for type II-bearing sedimentary deposits to be petroleum source rocks. Polyaromatic nuclei, heteroatomic ketones, and carboxylic acid groups are more numerous in Type II kerogen than in Type I kerogen. Other data indicate the fundamental complex and wide-ranging nature of Type II kerogen which is now acknowledged to be a highly heterogeneous material.

Type II kerogen, in its pure (mono-maceral) form is characterized by the relatively hydrogen-rich maceral exinite. Examples include spores and pollen of land plants, primarily marine phytoplankton cysts (acritarchs and dinoflagellates), and some land plant components such as leaf and stem cuticles. As with Type I kerogen, the occurrence of Type II kerogen depends on high biological productivity, low mineral dilution, and restricted oxygenation. The pure exinite Type II kerogen II is preserved in condensed sections and represents macerals that are slightly less hydrogen rich than Type I kerogen.

Type II kerogen can also be formed from partial degradation of Type I kerogen or from varying mixtures of Type I kerogen and Type II, III, and IV. For example, organic matter formed in different provenances can be combined, such as when planktonic algal material falls into sediments containing transported woody macerals (Type III kerogen). Type II kerogen type II is recorded in transgressive systems tracts, sometimes landward deposition of Type I kerogen.

Type II-S (sulfurous) kerogen is similar to Type II kerogen but has a high sulfur content — this type of kerogen contains organic sulfur (8%–14% w/w, atomic S/C ratio ≥ 0.04) and begins to generate oil at a lower thermal maturity than typical type II kerogens with less than 6% w/w sulfur (Orr, 1986). It has been suggested that in kerogen from the Miocene Monterey formation that the precursor moieties of the alkylthiophenes derivatives generated upon pyrolysis were released upon cleavage of sulfide-bonds indicating that their precursors, probably sugars, were sulfur-bound to the kerogen. When ether bond as well as sulfur bonds are cleaved, alkyl pyrrole derivatives were released indicating that their precursors, probably tetrapyrrole pigments, occur as ether-as well as sulfur-bound in the kerogen. It was also suggested that ether-bound tocopherol deroivatives are probably a major source of pristene-1 in kerogen the oil (Höld et al., 1998).

Also, maceral fractions of the Type II-S kerogens from the Monterey Formation (Miocene. California. USA) and Duwi Formation (Campanian/Maastrichtian, Egypt) were separated by density gradient centrifugation. The kerogen sample from the Monterey formation was comprised chiefly of light red-fluorescing amorphous organic matter and the flash pyrolysis liquids from this kerogen was characterized by a predominance of alkyl benzene derivatives, alkyl thiophene derivatives, and alkyl pyrrole derivatives. In contrast, the pyrolysis liquid of the alginite concentrate showed a highly aliphatic character, typical of this maceral, with the series of n-alkene derivatives and n-alkane derivatives (C_6 to C_{26}) predominating. The pyrolysis liquid of the dominant light brown-fluorescing AOM of the Duwi Fm. Kerogen had a relatively high concentration of alkylbenzenes and alkylthiophenes, while the elginite concentrate from this kerogen showed a more aliphatic character upon pyrolysis. There was a marked enrichment of thiophenic sulfur in the light-colored amorphous organic matter of both samples (and also pyrrole-type nitrogen in the case of the Monterey) relative to the alginite. The results support a bacterially-mediated, degradative origin for Type II-S amorphous organic matter, with algal remains as the primary source of the kerogen.

Finally, sulfur-sulfur (S—S) and carbon-sulfur (C—S) bonds are abundant in high sulfur kerogens and are more prone to cleavage at lower temperatures than carbon-carbon (C—C) bonds. This results in sulfur-rich source rocks generating oil at lower maturities (lower temperatures) than other kerogens (Martin, 1993). This corresponds to a shift in the average activation energy distribution from a higher range (taking more energy to begin the chemical reaction) in a typical Type II kerogen (on the order of 52—55 kcal/mol) to a lower range (on the order of 48—51 kcal/mol) for a Type II-S kerogen. It is also suggested that the formation of active sulfur radicals generated during the initial stages of thermal maturation is the main controlling factor on increased petroleum formation rates, rather than the relative weakness of carbon-sulfur bonds (Lewan, 1998).

Oil shales that contain Type I kerogen include the Autun and Campine boghead shales, and torbanite (Scotland), as well as the Green River oil shales. Tasmanite is a marine sediment that contains Type I kerogen. Type II kerogens include most of the marine oil shales, of which many are important petroleum source rocks. Atomic hydrogen-to-carbon (H/C) ratios are generally lower than for Type I kerogens, while generally higher oxygen-to-carbon (O/C) ratios reflect more ketones, carboxylic acids and esters. Organic sulfur levels are also generally higher, generally reflecting more thiophenes and in some cases sulfides, as well. The oil-generating potential of the Type II kerogen is generally lower than the oil-generating potential of the Type I kerogen because less of the organic material is liberated as oil upon heating a Type II kerogen (at the same level of maturation).

Type III kerogen (humic kerogen) is characteristic of coals and coaly shales. Easily identified fossilized plants and plant fragments are common, indicating that this type of kerogen is derived from woody terrestrial material. These materials have relatively low atomic H/C ratios (usually <1.0) and relatively high atomic O/C ratios (>0.2). Aromatic and heteroaromatic contents are high, and ether units (especially of the diaryl ethers) are important, as might be anticipated for a lignin-derived material. Oil-generating potentials are low, but gas-generating potentials are high.

At the beginning of the Type I path, the kerogen types have a strongly aliphatic nature; at the beginning of the Type III path the kerogen consists largely of aromatic structures that carry oxygen functions. At the beginning of the Type II path, and in general for intermediate paths between Type I and Type III, elemental analysis supplies little information about the chemical structure.

Type III kerogen has low a low atomic hydrogen-to-carbon (H/C) ratio (0.6—0.9) and an atomic oxygen-to-carbon (H/C) ratio (>1.5) O/C ratio (typically on the order of 0.1—0.3. Type III kerogen is derived from terrestrial plant matter, specifically from precursor compounds including cellulose, lignin (a non-carbohydrate polymer formed from phenylpropane units that binds the strings of cellulose together); terpene derivative, and phenol derivatives. Coal is an organic-rich sedimentary rock (Speight, 2013) that is composed predominantly of this kerogen type. On a mass basis, Type III kerogens generate the lowest oil yield of principal kerogen types.

Type III kerogen contains sufficient hydrogen to generate gas by pyrolysis but not enough hydrogen to generate substantial amount of oil. In the pure form, Type III kerogen is composed of vitrinite, a maceral formed from land plant wood. As with other intermediate kerogen types, however, various maceral mixtures or degradational processes can contribute to the formation of Type III kerogen. Coal-forming environments represent several different kerogen types. Most coals form in paralic swamps (swamps laid down on the landward side of a coast) and abandoned river channels. In regions where sediment supply is low, incised valleys contain these sediments as estuarine or coastal plain deposits.

Type IV kerogen is the least aliphatic kerogen and has the atomic hydrogen-to-carbon (H/C) ratio (<.0.6) but similar atomic oxygen-to-carbon (H/C) ratio (O/C) ratio (>0.1) to Type II kerogen. Type IV kerogen comprises mostly inert organic matter in the form of polynuclear aromatic hydrocarbon derivatives (PNAs, sometime referred to as polycyclic aromatic hydrocarbon derivatives, PNAs) with a low propensity to produce shale oil. Type IV kerogen is difficult to distinguish from Type III kerogen using only Rock-Eval pyrolysis. It is an inert (does not generate hydrocarbons) end-member on the hydrocarbon generative spectrum. Type IV kerogen is composed of hydrogen-poor constituents such as inertinite, which is detrital organic matter oxidized directly by thermal maturation including fire (charcoal) or by biological or sedimentological recycling.

In summary, the chemical and physical structure of immobile organic matter partially controls both the thermal evolution of organic rich shale formations and hydrocarbon production from these unconventional fossil fuel resources. This organic matter is typically classified into two fractions: (i) kerogen, which is defined as insoluble in organic solvent and (ii) bitumen, which is soluble in conventional organic solvents. Kerogen and bitumen are complex materials that are not yet completely characterized and often considered to be compositionally similar except for molecular weight.

5. Isolation

The first step in any study of the behavior and structure of kerogen has generally been the isolation of a kerogen concentrate (Forsman and Hunt, 1958; Forsman, 1963; Robinson, 1969; Saxby, 1976; Durand, 1984; Goklen et al., 1984). A variety of methods can be employed to isolate fractions of organic material without altering the structure of the native kerogen. There are also those methods intended for degradation of the organic material in a controlled manner. The terminology of the material isolated by such methods is often based upon the method employed. Therefore, an understanding of these methods assists in understanding the terminology. For example, a particular method may result in the generation of hydrocarbon products as well as more complex products that are heteroatomic and/or high in molecular weight.

However, as a word of caution, because of their low permeability, oil shales do not weather as rapidly as coal samples (Scouten, 1990; Lee, 1991; Speight, 2013). Nevertheless, weathering can alter oil shale kerogens that have been exposed to the atmosphere. Whenever possible, core samples or samples taken more than 12 inches below an exposed surface should be used for kerogen isolation to avoid weathering effects. Storage under nitrogen has not been found necessary for oil shale samples that are larger than 1/2 inch.

By far the most common technique for kerogen isolation involves acid demineralization of the shale to produce the kerogen concentrate. In the procedure, larger pieces of oil shale are crushed in a jaw crusher to pass 8-mesh, then ground to pass 100-mesh in a hammer mill or disc mill. Care should be taken to keep temperatures low during fine grinding, and grinding under an inert atmosphere (e.g. nitrogen) is recommended to avoid possible oxidation. Finely ground oil shale should be stored under nitrogen.

To dissolve the mineral matrix, a series of successive treatments with a hydrochloric acid-hydrofluoric acid mixture (at approximately 65C, 150F) is employed (Durand, 1984). On the other hand, demineralization with a reduced chance of organic alteration has been achieved by carrying out the treatment at a lower temperature (20C, 70F) and for shorter times (Scouten et al., 1987). The use of base to dissolve silicates has also been investigated followed by an acid treatment to dissolve carbonates (McCollum and Wolff, 1990).

In the acid demineralization method, in order to dissolve the minerals, a series of series of successive treatments at 65–70 °C (149–159 °F) is recommended (Durand, 1980; Scouten, 1990): (i) treatment with 6 N hydrochloric acid for 2 h, (ii) washing with distilled water containing a small amount of hydrochloric acid, (iii) treatment overnight with 6 N hydrochloric acid, (iv) three washings with distilled water containing a small amount of hydrochloric acid, (v) treatment for 2 h with a mixture containing 2 N HCl and 15.5 N hydrofluoric acid, (vi) washing with distilled water containing a small amount of hydrochloric acid, (vii) treatment overnight with a mixture containing 2 N hydrochloric acid, and 15.5 N hydrofluoric acid, (viii) washing with distilled water containing a small amount of hydrochloric acid, (ix) treatment with 6 N hydrochloric acid for 2 h, (x) two washings with distilled water, and (xi) filtration to recover the kerogen concentrate.

The initial treatments with hydrochloric acid and the use of the hydrochloric acid-hydrofluoric acid mixture were designed to minimize the formation of complex alkaline earth fluorides, such as ralstonite [$Na_xMg_xAl_{2-x}$ $(F,OH)_6H_2O$] while washing with acidulated water is claimed to avoid the flocculation of clay minerals that would plug the filter. Pyrite is not removed by this procedure. In many cases, equivalent demineralization with less chance of organic alteration has been obtained by carrying out the treatments at 20 °C (68 °F) and for shorter times (Durand, 1980; Scouten, 1990). In another method, the demineralization is carried out using base which avoids the long sequence of steps required in the acid-treatment method. The base dissolves the silicate minerals and is followed by an acid treatment to dissolve carbonates. When used for the treatment of Green River oil shale, aqueous caustic digestion at 150–160 °C (300–320 °F), followed by acid extraction, can remove as much as 95% w/w of the minerals from without (it is speculated) appreciably altering the kerogen from its initial state. Pyrite would not be removed by this procedure.

The isolation of kerogen from mineral matrices also depends upon the extent of the interactions between the kerogen and the various minerals. From the results of model compound-model mineral tests, interactions between acid clay minerals and nitrogen-containing organic compounds have been identified as much stronger than other likely candidates for kerogen-mineral interactions (Siskin et al., 1987a,b). The importance of this finding led to the use of differential wetting, a phenomenon typically associated with physical separation methods, as critical to the success of kerogen separation. Thus, efficient kerogen recovery can be achieved by adding an organic solvent that wets and swells the kerogen, thereby diminishing some of the nitrogen-mineral interactions and aiding the physical sink-float separation. Thus both chemical and physical aspects are important for the production under mild conditions of a kerogen concentrate with, presumably, minimal structural alterations.

Physical methods to produce an organic-rich kerogen concentrate are of interest because exposure of the kerogen to the strong acid and/or base is avoided, thereby lessening the chance of chemical alteration. Such methods generally involve the potential for contamination of the kerogen with materials used to effect the separation. However, in many cases the potential impact of such contaminants can be limited by using only one or a small number of known and easily identified chemical species. Among the more important physical methods for kerogen concentration are sink-float, oil-agglomeration and froth flotation methods.

In the sink-float method, finely ground oil shale is suspended in an aqueous calcium chloride ($CaCl_2$) — the density of the calcium chloride solution can be varied to optimize kerogen recovery and residual mineral content for a specific oil shale, but is generally in the range of 1.06—1.15 g/mL The resulting suspension is centrifuged to enhance separation. The recovered kerogen is then washed with water to remove calcium chloride.

Another method, used on Green River oil shale, involves centrifugation in benzene-carbon tetrachloride mixtures. In this method, the finely ground oil shale was first extracted to remove benzene-soluble material, dried, then subjected to successive sink-float separations in solvent mixtures having densities of 1.40, 1.20 and 1.15 g/mL. The concentrate that floated in the 1.20 g/mL mixture represented approximately 6% w/w of the starting organics and contained 14% w/w mineral matter (identified as mineral ash). The concentrate from the last stage contained 9% mineral matter (again, identified as mineral ash) but represented only 1% w/w of the starting organic material. In this case the constancy of atomic H/C ratios and the assay oil/C_{org} ratio may indicate that little fractionation of the kerogen occurred.

An oil-agglomeration method relies on the selective wetting of kerogen particles by an oily pasting material, such as hexadecane ($C_{16}H_{34}$) — as a side note this the highest molecular weight n-paraffin derivative that is in the liquid state at room temperature). The success of this method is questionable (Hubbard et al., 1952; Vadovic, 1983).

From the results of model compound-model mineral tests (Siskin et al., 1987a,b) interactions between acidic clay minerals and nitrogen-containing organic compounds have been identified as being much stronger than other likely candidates for kerogen-mineral interactions in Green River oil shale. Ammonium sulfate [$(NH_4)_2SO_4$]was selected to serve both as a source of ammonia, a base, and as a source of acid, bisulfate ion, to generate porosity by attacking carbonate minerals. Treatment of 80—100 mesh Green River oil shale with aqueous ammonium sulfate at 85 °C (185 °F) for 72 h effectively disrupted kerogen-mineral interactions. Nearly all (98% w/w) of the oil shale organic material were recovered in the kerogen liberated by this procedure and 85% of the mineral matter present in the starting shale was rejected. Nevertheless, the kerogen fraction still contained 38% w/w mineral matter. Efficient kerogen recovery was only obtained by adding an organic solvent that would wet and swell the kerogen, thereby aiding the physical sink-float separation. Thus, both chemical and physical aspects are important in this new method for concentrating kerogen under mild conditions. Toluene was used in the laboratory tests for swelling and floating the liberated organics. A shale-derived naphtha or distillate would probably be used in any larger scale application of this method. The important role of differential wetting (a phenomenon that is dependent upon the chemical proeprties of the oil shale inserted and the proeprties of the kerogen within the shale) is critical to the success (and general applicability) of the method.

Briefly and by way of clarification, mesh size is the mesh number (a US measurement standard) and its relationship to the size of the openings in the mesh and thus the size of particles that can pass through these openings. Understanding the mesh number is simple involves counting the number of openings in one linear inch of screen which is the mesh number. As an example, a 4-mesh screen has four square openings per inch of the screen and, as another example, a 100-mesh screen has 100 openings per inch of the screen.

Thus, among the more important physical methods for kerogen concentration are sink-float, oil agglomeration, and froth flotation method (Hubbard et al., 1952; Vadovic, 1983) which remove the potential for changes in the kerogen composition and structure by omitting treatment with acid and base. The sink-float methods offer mild conditions to minimize chemical alteration and can produce a kerogen concentrate with low ash content. There are disadvantages to this technique, however, which include (i) rejection of organic compounds (leading to low recovery of the kerogen) and (ii) the possibility of kerogen fractionation along with mineral rejection. The oil agglomeration method relies on selective wetting of kerogen particles by an oily paste material such as hexadecane (see also Himus and Basak, 1949; Smith and Higby, 1960; Robinson, 1969).

Thus, the sink-float methods offer mild conditions to minimize chemical alteration and, in favorable cases, kerogen concentrates with low ash contents. Also, elemental analyses can be carried out at each step and the results extrapolated to zero ash to obtain an estimate of the mineral-free kerogen composition. Disadvantages include (i) high rejection of organics, leading to low recovery of the kerogen, and (ii) the possibility of kerogen fractionation along with mineral rejection.

In summary, the ideal method for isolating kerogen (in which there is any assurance that the isolation procedure has not changes the structure of the kerogen) remains elusive. All of the methods involve comminution as the initial step and it is important to select samples that have not been unduly altered by weathering.

6. Methods for probing kerogen structure

Kerogen is a complex mixture of organic compounds and, since kerogen is a mixture of organic constituents, it is cannot defined by a single chemical formula. In fact, the chemical composition varies substantially between and even within sedimentary formations. Thus, the structure of kerogen is predominantly speculative and largely unknown. The complexity of the kerogen structure lies in the formation of kerogen from dead biomass. Not all kerogens are the same but very much dependent upon the source of the biomass material and the conditions under which the biomass changed and evolved. Kerogen is considered to be random-network macromolecular solids; that is, they are composed of macromolecular constituents of heterogeneous structure that are randomly aggregated to form a three-dimensional phase. This phase is hydrated to a degree depending on the type of humic substance and relative humidity, and may contain metal ions that are coordinated to charged groups, such as carboxylate functions ($-COO^-$). As the molecular weight of the kerogen increases, there appears to be a trend in non-polarity, carbon content, fused ring size, density, and cross-linking.

Inferences regarding kerogen structure drawn from the results of bitumen and shale oil analyses are generally based on the premise (i) that the bitumen is analogous to residual monomer in a polymer, i.e. the bitumen represents units of the precursor that did not become bound into the insoluble three-dimensional macromolecular network of the kerogen, or (ii) that the bitumen comprises units of the kerogen structure that have been cleaved more or less intact from the kerogen by thermal treatment. In either case, it is assumed (with some tongue-in-cheek speculation) that the kerogen is structurally similar to the extractable bitumen.

Some of the compound types present in oil shale bitumen and the geochemical inferences that have been drawn from these results were discussed in an earlier section. Much more information can be drawn from bitumen composition in cases where the analysis is comprehensive. There have been comprehensive analyses of the bitumen from Green River oil shale which included were reports on paraffin derivatives, the changes in the character of the paraffin derivatives with depth, sterane derivatives, as well as cycloalkane derivatives, aromatic derivatives, and polar compounds. Extensive analyses of the bitumen in the British Kimmeridge oil shale, Australian oil shale, French oil shales, and Brazilian oil shale have also been reported. While there is a remarkable similarity in the types of compounds found by these analyses — which is not surprising, given the origin of the bitumen from plant debris — there are differences in the details of the composition of the bitumen and these differences can be shown to be related to (i) the origin of the oil shale, (ii) the depositional environment of the oil shale, and (iii) the thermal history of the oil shale.

Most oil shale formations contain only small amounts of bitumen which rarely exceed 15% w/w of the total organic matter. Moreover, oil shale bitumen is typically (comparted to the corresponding insoluble kerogen) richer in hydrogen and has a lower content of aromatic derivatives as well as a lower content of nitrogen-containing, oxygen-containing and sulfur-containing compounds. This limits the usefulness and reliability of any structural inferences drawn from the bitumen composition.

On the other hand, shale oil, on the other hand, typically represents a much larger fraction of the organic matter. Methods for shale oil analysis are generally similar to those used for conventional crude oil. The structural inferences drawn from the results of shale oil analyses typically parallel those from bitumen analyses. However, as a consequence of the thermal generation of the shale oil, the oil is usually richer in aromatic derivatives and olefin derivatives than the starting kerogen, and has a lower content of nitrogen-containing and sulfur-containing compounds poorer in nitrogen-containing and sulfur-containing compounds since these become concentrated in the non-volatile char — which parallels the fate of these heteroatom compounds during refining conventional crude oil (Speight, 2014). Thus, the thermally-produced shale oil tends to reflect the thermal treatment used to produce the oil. Consequently, consideration of the methods of production of shale oil throws some doubt upon the reliance of such analytical investigations to present an accurate estimation of the structure of the corresponding kerogen.

While many useful inferences about kerogen structure have been drawn from bitumen and shale oil analyses, the limitations outlined above have led to the development of more direct methods for probing kerogen structure.

From the perspective of natural gas and crude oil and gas formation — if kerogen is indeed the precursor to crude oil and natural gas (Speight, 2014) — as well as the production of shale oil by thermal processes, the precise molecular structure of kerogen is of lesser importance than the general structural characteristics which determine the nature and the yield of the product that a particular kerogen generates. At one time it was thought that kerogens had a homogeneous structure and showed little structural variation from basin to basin. However, it is now clear that kerogen is a very heterogeneous and complex agglomerate of maceral-type constituents (Hutton et al., 1994) – in a similar manner to coal (Speight, 2013) – such that variations in the kerogen structures can be anticipated over relatively small distances within a source facies.

By way of explanation, the term facies (in geology) refers to a body of rock with specified characteristics, which can be any observable attribute of rocks (such as their overall appearance, composition, or condition of formation), and the changes that may occur in those attributes over a geographic area. It is the sum total characteristics of a rock including its chemical, physical, and biological features that distinguishes it from adjacent rock (Reading, 1996). On the other hand, macerals are discrete particles of insoluble organic material which can be identified under the microscope and represent residual detritus from the various sources of organic material. Once the organic origin for oil and gas and the importance of kerogen as an intermediate became accepted, it was clear that a routine method was necessary to characterize and classify source rocks and their associated kerogens.

In the 1970s kerogen was were often thought of as polymeric structures with repeating subunits. Significant time and effort were invested in unraveling the structure of kerogen through stepwise degradation studies. However, the degradation products obtained in this manner, typically carboxylic acid derivatives were rarely successfully reconstructed into viable kerogen structures and other approaches to kerogen identification were needed (Rullkötter and Michaelis, 1990; Scouten, 1990).

Thus, unraveling the chemical constitution of kerogen is the most challenging objective in molecular organic geochemistry. Some compositional constraints are obtained from elemental analysis and from the determination of functional groups or the degree of aromaticity by IR or NMR spectroscopy. Pyrolysis of kerogen or related materials yields small structural units, some of which may be representative of moieties originally present in the macromolecules whereas others may have been formed by secondary reactions. In any case, there is no information on the mode of connection of the various structural units among each other.

The chemical degradation of kerogen and related materials so far commonly involved the application of strongly oxidizing reagents (e.g. $KMnO_4$), but also was done by reductive cleavage (hydrogenolysis). Although a variety of methods has been used over the years, much of the work lacked adequate detailed analysis of the reaction products and/or the reactions were not sufficiently specific to allow a reconstruction of larger structural entities. Nevertheless, a combination of elemental analysis, spectroscopic information and chemical data from pyrolysis, bitumen composition in natural rocks and sometimes chemical degradation were used to develop constitutional models of kerogen of different origins and different levels of thermal evolution (Rullkötter and Michaelis, 1990; Scouten, 1990). Recently, specific chemical degradation reactions like ether cleavage with boron trichloride followed by lithium aluminum deuteride reduction of the halides or oxidation with ruthenium tetroxide have shown how certain low-molecular-weight products are linked to kerogen macromolecules (Rullkötter and Michaelis, 1990).

In fact, any attempt to achieve substantial progress in kerogen structure elucidation will require the concerted efforts of (i) consecutive specific chemical degradation reactions, (ii) the detailed quantitative molecular analysis of small degradation products, (iii) a study of the degradation residues by spectroscopy and pyrolysis, and (iv) the application of refined concepts of the preservation of biological macromolecules (e.g. aliphatic biopolymers).

The following sections present indications of the methods that can be used to identify structural types within kerogen. There must always be a word of caution when drawing conclusions from the data insofar as isolation of the kerogen from the rock matrix must be attained using a method that does not alter in any way the chemical composition or the microstructure of the kerogen.

6.1 Elemental analysis

Although not strictly a method for probing the structure of kerogen, elemental (ultimate) analysis offers valuable information about the atomic constituents of kerogen. The elemental analysis of kerogen is a method for characterizing the origin and evolution of sedimentary organic matter. Elemental analysis also establishes a framework within which other physicochemical methods can be used more effectively.

The Van Krevelen diagram (a plot of the atomic hydrogen-carbon ratio vs. the atomic oxygen-carbon ratio) (Fig. 13.2), derived from the elemental analysis of kerogen and coal, is a very practical means of studying kerogen composition. The position of kerogen in the H/C—O/C diagram is related to the total quantity of hydrocarbon derivatives, which in turn is a function of the relative amounts of aromatic hydrocarbon structures. The data for kerogen analysis in the H/C—O/C diagram can be considered to describe the evolutionary path for kerogen from different precursors. Oil and gas are believed formed during this evolutionary path. Analysis of the minor elements, sulfur and nitrogen, is much more difficult to simulate and may require a more detailed framework.

Inferences regarding kerogen structure are drawn from the results of bitumen (kerogen extract) analyses. The conclusions are generally based on the premise that the bitumen is analogous to original organic matter, that is, the bitumen represents units of the precursor that did not become bound into the insoluble three-dimensional macromolecular network of the kerogen. It is also assumed that the bitumen is representative of units of the kerogen structure that have been cleaved more or less intact, with little or no structural alteration, from the kerogen by thermal treatment.

Many different compound types have been identified (by extraction procedures) as part of the kerogen matrix but their mode of inclusion in kerogen is remains open to speculation. For example, the compounds isolated from kerogen include paraffins (Cummins and Robinson, 1964; Anderson et al., 1969), steranes (Anderson et al., 1969), cycloalkanes (Anders and Robinson, 1971), aromatics and polar compounds (Anders et al., 1975). Kerogen generally contains only a small amount of bitumen (<15% w/w/of the total organic matter), but the bitumen usually has a higher hydrogen content than the corresponding kerogen. This corresponds to a lower proportion of aromatics, as well as nitrogen-, oxygen-, and sulfur-containing compounds. This is an obvious limitation to due usefulness of structural inferences drawn from the bitumen composition.

The volatile oil generally represents a much larger fraction of the original organic material (usually 50% or more of the available organic carbon). The methods employed for analysis of the product oils are similar to those used for crude oil (Uden et al., 1978; Fenton et al., 1981;

Holmes and Thompson, 1981; Williams and Douglas, 1981; Regtop et al., 1982). As a consequence of their thermal treatment, the volatile oils are usually richer in aromatics and olefins than the starting kerogen but are relatively deficient in nitrogen-containing and sulfur-containing compounds. As for crude oil coking (Speight, 2014), the nitrogen- and sulfur-containing species are concentrated in the nonvolatile char. The volatile oils are a greater reflection of the thermal treatment used to produce the oil and, consequently, are not too reliable in terms of an accurate picture of kerogen structure. Thus, although many inferences about kerogen structure have been drawn from bitumen and oil analyses, their limitations must be recognized.

6.2 Functional group analysis

Attempts to characterize the oxygen functional groups in kerogen have focused on acid demineralization (successive treatments with hydrochloric acid and hydrofluoric acid) to prepare a kerogen concentrate. The concentrate has then been treated by wet chemical methods to determine the distribution of oxygen functional groups (Fester and Robinson, 1966; Robinson and Dineen, 1967).

An attempt to characterize the oxygen functional groups in Green River oil shale kerogen involved the use of acid demineralization (successive treatments with hydrochloric acid and hydrofluoric acid) to prepare a Green River kerogen concentrate containing 14% w/w mineral matter, and wet chemical methods to determine the distribution of oxygen functional groups. Application of the method to other oil shale kerogen sample failed to take into consideration the possibility of structural changes which may have occurred during the preparation of the kerogen concentrate or during the derivatization reactions, nor was there any consideration of the inability of the aqueous reaction media to wet and swell the non-porous kerogen concentrates. This leaves the matter of kerogen structure unsolved in the absence of reliable experimental data.

The organic material in oil shale from the Ramsay Crossing seam of the Rundle Deposit of Queensland, Australia (RXOS) was characterized and modeled using an integrated, multi-technique approach (Scouten, 1990). All of the work is not reproduced here but is available in the corresponding publications (Scouten, 1990).

Acid demineralization yielded the kerogen concentrate (RXOS-KC) and the chemistry that accompanied this demineralization was studied. Selective derivatizations under mild conditions with isotopically labeled reagents followed by solid state ^{13}C and ^{29}Si-NMR analysis enabled a comprehensive study to chemically characterize the organic functionalities in the kerogen concentrate. Combining this data with in depth MS and NMR analyses on shale oils produced under mild conditions from the Ramsay Crossing oil shale and variable-temperature X-ray diffraction studies on the kerogen concentrate led to the development of a detailed structural model of the organic material. This work is summarized to illustrate both the features of the Ramsay Crossing kerogen and the power of the closely integrated characterization-modeling-reactivity approach.

The Ramsay Crossing oil shale used in this work contained 18.69 wt% organic material finely dispersed in a mineral matrix. Solid state ^{13}C NMR employing CP/MAS indicated an aromaticity of 23% which includes contributions from olefin and carbonyl carbon types.

Exhaustive extraction (in a Soxhlet unit) with tetrahydrofuran removed 8.5% w/w of the organic materials as bitumen with an as-received moisture content in excess of 20% w/w. After drying at 50 °C (122 °F) in a nitrogen purged vacuum oven, the oil shale had little surface area (16.6 m^2/g) or porosity insofar as the shale was impermeable to organic solvents and reagents. As a result, organic reactions which do not dissolve the minerals proceed slowly and often do not go to completion. To circumvent this mass transport limitation, Ramsay Crossing oil shale was demineralized, using an aqueous mixture of hydrochloric and hydrofluoric acids at 20 °C (68 °F) 247 to produce the corresponding swellable kerogen concentrate prior to chemical reactions for derivatization of organic functionalities. The aromaticity derives from investigations using ^{13}C nuclear magnetic resonance and the bitumen content of the kerogen concentrate were unchanged from the raw shale values. However, elemental analysis indicated that the bitumen had a significantly higher hydrogen content, was lower in nitrogen and sulfur than kerogen concentrate. The major portion of the bitumen included aromatic derivatives as well as carboxylic acid derivatives, ester derivatives, and amide derivatives with long paraffinic chains The elemental composition of the ground (-80 mesh) Ramsay Crossing oil shale and the kerogen concentrate give empirical formulas (normalized to 100 carbon atoms) for the organic material of $C_{100}H_{161}N_{2.3}S_{0.7}O_X$ and $C_{100}H_{161}N_{1.85}S_{0.7}O_{9.2}$, respectively, thereby indicating that 0.45 nitrogen atoms per 100 carbon atoms were lost during the preparation of the kerogen concentrate.

Nitrogen bases liberated during the acid washings would be retained in the acid solutions as the corresponding ammonium salts. To recover and identify these free bases all of the acid washings were basified with 50% aqueous potassium hydroxide under a nitrogen sweep. Any volatile free base evolved during basification was swept through aqueous hydrochloric acid where it was trapped as the corresponding hydrochloride. Complete evolution of bases was ensured by heating the basic mixture until a small of water had distilled into the flask containing the hydrochloric acid solution. Solvent extraction of the basic solutions and evaporation of the hydrochloric acid solutions to dryness under reduced pressure afforded 0.52 g of dissolved salts (C: 0.39% w/w, H: 7.63% w/w, N: 25.79% w/w. K: 0.21% w/w, Cl: 65.43 w/w; theoretical for ammonium chloride, NH_4Cl, H: 7.54% w/w. N: 26.18% w/w, Cl:, 66.28% w/w). The very low carbon content ruled out the presence of major amounts of organic amine hydrochlorides. Over 75% of the total ammonia was liberated during the treatment with hydrochloric acid indicating the presence of primary amides which are hydrolyzed by the aqueous acids. The rest of the ammonia liberated during the hydrogen fluoride treatment is due to ammonium ions associated with silicate minerals.

Quaternization of unhindered basic nitrogen compounds (e.g. pyridines) with iodomethane at 50 °C (122 °F) in tetrahydrofuran gives the corresponding quaternary ammonium methiodides. Under these conditions hindered nitrogen bases (e.g., 2,6-disubstituted pyridines) do not react, or (at best) react slowly. Non-basic nitrogen compounds (e.g., pyrroles) do not react. Thus, methylation with iodomethane (90% ^{13}C enriched) was used to quantify unhindered nitrogen bases. The reaction was followed for 28 days by ^{13}C NMR. Most of the methyl groups were added to oxygen (as esters) appearing at 51 ppm and to carbon sites at approximately 15 ppm. Nitrogen methyl groups were added slowly, but after 14 days 0.1 N-methyl groups per 100 carbon atoms had been added at approximately 40 ppm and this value did not increase with additional reaction time.

A sample of 0.1 N potassium washed (to remove any amine hydrochloride derivatives) Ramsay Crossing kerogen concentrate was treated with anhydrous hydrogen chloride in methylene chloride at -78 °C (-108 °F) for times of 5 min, 10 min, and 15 min. The number of chlorine atoms added at each reaction time was obtained by elemental analysis. At the low temperature used, olefin hydrochlorination to give the corresponding alkyl chloride should be much slower than protonation (neutralization) of the basic nitrogen groups. Consequently, the data were extrapolated to zero time to correct for the small interference of the olefin reaction. This gave 1.0 basic nitrogen atoms per 100 carbon atoms as an estimate of the total basic nitrogen atoms in the kerogen concentrate. As discussed above, 0.1 unhindered nitrogen per 100 carbon atoms/and the he remainder (0.9 nitrogen atoms per 100 carbon atoms) were assigned to sterically hindered basic nitrogen functionality.

Combining the hydrolyzable nitrogen results with the characterizations on the Ramsay Crossing kerogen concentrate enables a comprehensive description of the distributions of hydrocarbon, and oxygen heteroatom and nitrogen heteroatom functionalities in the solid Ramsay Crossing oil shale. Any functionalities that could not be converted to derivatives, such as ether derivatives and N-alkyl pyrrole derivatives, were obtained by difference. From this, a structural model of Ramsay Crossing kerogen was derived.

The model with a formula weight of 30,000 (and an empirical formula of $C_{100}H_{160}N_{2.25}S_{0.68}O_{9.22}$) was required to accommodate the large range of heteroatom functionalities and long side chains present in Ramsay Crossing oil shale. It was not possible to accurately represent the range of compound types in the bitumen because of its small amount (8.5%) and the need to maintain a finite model size. Because carboxylic acid derivatives comprise the major part of the bitumen, all of the bitumen in the model was represented as carboxylic acid derivatives.

This type of model offers more than the previously presented (and highly speculative models) and serves to illustrate the potential of the closely integrated characterization modeling-reactivity approach to provide a model of the functionalities structure in sufficient detail to be useful as a tool for guiding oil shale research and interpreting experimental results (Scouten, 1990; Siskin et al., 1987a,b, 1995).

Workers at the Institut Français du Petrole (IFP) have taken a distinctly different approach to kerogen modeling and have constructed generalized models representative of the three types of kerogen and the of the asphaltenes from the corresponding oils, as a function of maturity. Emphasis in this work was placed on elucidating the chemistry of maturation for the three kerogen types – in the context of the IFP approach to the organic aspects of crude oil geochemistry.

The latest IFP models (Behar and Vandenbroucke, 1987) represent the kerogen at the beginning of diagenesis (excluding the early stages of diagenesis which is probably dominated by microbial action), at the beginning of catagenesis (start of the oil generation window) and at the end of catagenesis where late gas begins to be generated. Type I kerogen was modeled only at the beginning of diagenesis and the end of catagenesis, while models of Types II and III kerogen were constructed at each stage of maturation. The corresponding asphaltene constituents were modeled only at the end of diagenesis/beginning of catagenesis, where they become most abundant. For the asphaltene fraction, a molecular weight of 8000 was selected chosen. These models are based on the results of elemental analysis, infrared spectroscopy, ^{13}C nuclear magnetic resonance analyses, pyrolysis (the Rock Eval method) and electron microcopy (fringe analysis) results.

The IFP models provide an interesting view of the structural relationships between the three types of kerogen. However, many oil shales contain Type I kerogen at a maturation state corresponding roughly to that IFP designates Stage b. Thus, it is unfortunate that the IFP workers chose to omit this model from their publication. However, the IFP models are generalized and not intended to precisely represent the structure of any particular kerogen but there is general agreement that most condensed ring systems are small in Type I kerogen and few of the larger systems are fully aromatized until late in the maturation sequence. Also, in all of the IFP models aromatics are shown parallel sheets. But, even pure aromatic derivatives, especially those system having of 1−4 rings are likely to of some important in oil shale kerogen, these types of aromatic derivatives do not crystallize in such parallel sheets, but rather in a herringbone arrangement that maximizes edge-to-face interactions. The highly substituted aromatic units in kerogens are even less likely to arrange in parallel sheets.

Finally, in the IFP models, the trends in functional group distributions are not unreasonable but it must be remembered that the details of the IFP models reflect an average distribution and structural moieties over many samples and were not intended to represent any particular kerogen.

6.3 Oxidation

Oxidative degradation, one of the primary methods of structural determination used in natural product chemistry, has also been employed to examine kerogen structure (Vitorovic, 1980). Alkaline permanganate and chromic acid have been the two most widely used oxidants, although ozone, periodate, nitric acid, perchloric acid, air or oxygen, hydrogen peroxide, and electrochemical oxidation (among many other reagents) have also been used.

Alkaline permanganate oxidation of kerogen has been carried out in two very different ways. Older work generally involved use of the *carbon balance* method developed for studies of coal. The products of this exhaustive oxidation are carbon dioxide, oxalic acid ($HO_2C{-}CO_2H$, from aromatic rings), nonvolatile benzene polycarboxylic acids, and unoxidized organic carbon. However, because aliphatic material is oxidized mainly to carbon dioxide, this method is not well suited to probe the structure of kerogen that is highly aliphatic. This led to the development of stepwise procedures to give products that retain more structural information about the starting kerogen.

The careful development of the stepwise alkaline permanganate method represented attempts to minimize unwanted secondary oxidation of the first-formed product by adding the oxidant − potassium permanganate in aqueous potassium hydroxide ($KMnO_4$ in 1% aqueous KOH) in small portions. In some cases, the acids obtained from stepwise oxidation proved to be of such high molecular weight that they precipitated upon acidification, were insoluble in ether, and were difficult to characterize. In these cases, the precipitated acids were subjected to further stepwise oxidation to produce the desired ether-soluble acids of lower molecular weight.

In general terms, alkaline permanganate oxidizes alkylbenzenes, alkylthiophenes, and alkylpyridines (but not alkylfurans) to the corresponding carboxylic, acids. This is not true when the aromatic ring bears an electron-donating group (e.g., $-OH$, $-OR$, or $-NH_2$). In such cases degradation of the aromatic portion is usually rapid. Condensed aromatics are also attacked and benzene polycarboxylic acids are produced. In addition, caution is advised since benzene itself also reacts (slowly) in hot alkaline permanganate solutions. Olefins are rapidly converted into the corresponding glycol, which are then cleared to carboxylic acids.

$$RCH = CHR^1 \rightarrow RCH(OH)CH(OH)R^1 \rightarrow RCO_2H + RCO_2H$$

Cyclic olefins yield dicarboxylic acids. Enolizable ketones are also cleaved, presumably via the enol.

Tertiary and benzylic carbon-hydrogen groups are reacted to afford tertiary, alcohols. In simple alkyl systems, the presence of an alcohol group markedly accelerates the rate of this reaction. Primary and secondary alcohols are oxidized to the corresponding acids and ketones, and alkaline permanganate oxidation degrades the porphyrin nucleus, giving pyrrole-2,4-dicarboxylic acid derivatives under mild conditions. The porphyrin side chains $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CO_2H$, $-COCH_3$, and $-CH(OH)CH_3$ persist in the degradation products, but the $-CH{=}CH_2$ and $-CHO$ side chains are both oxidized to $-CO_2H$.

The structural information obtained from the oxidation of kerogen by chromic acid (and other chromium-containing oxidants) is usually similar to that obtained with alkaline permanganate (Lee, 1980; Vitorovic, 1980). However, for any particular technique the recovery of organic carbon in the oxidation products may be as low as 10% of the original carbon (Simoneit and Burlingame, 1974). Consequently, the alkaline permanganate procedure is often considered superior for elucidating structural moieties in kerogen.

Nitric acid has also been used for the oxidation of kerogen (Robinson et al., 1963). However, it must be recognized that nitric acid reacts in different ways depending upon the temperature, time, and concentration. Thus, in addition to the anticipated oxidation reactions, aromatic structures in the kerogen or even in the products are nitrated. However, nitric acid has been successfully used for investigating aliphatic structural units, and the data are often complementary to other structural studies.

Oxidants such as ozone (Rogers, 1973), air (Robinson et al., 1965), oxygen (Robinson et al., 1963), and hydrogen peroxide (Kinney and Leonard, 1961) have also been used for the oxidative degradation of kerogen. As in other cases, it is strongly recommended that structural data not be compiled in an absolute manner on the basis of one oxidant. The data from the various methods should be employed in a complementary manner so that an overall model can be compiled that explains the behavior of the kerogen under different reaction conditions.

However, considerably less attention has been paid into defining the susceptibility of kerogen structural features to oxidation and the precise relationships between oxidation products and kerogen structure. For example, permanganate is a vigorous, and in some cases a drastic, oxidant which has long been used in the organic laboratory. The literature on permanganate oxidation is extensive and, in addtion, the permanganate oxidation of about model compounds illustrates the susceptibility of organic compounds under oxidation conditions, and this does not include the potential for the interference of mixed model compounds (with each other) in the reaction mixture.

Generally, alkaline permanganate will oxidize alkylbenzene derivatives, alkylthiophenes derivatives and alkylpyridine derivaitves — but not alkylfurans derivatives — the corresponding carboxylic acid derivatives. This is not true in cases where the aromatic ring bears an electron donating group (such as a hydroxy substituent, —OH, an ether substituent, —OR, or an amino substituent, —NH2). In such cases degradation of the aromatic moiety is typically rapid. Condensed aromatics are also attacked and produce benzene polycarboxylic acids. The need for caution in the interpretation of the product data (and the subsequent reverse chemical projection to the chemical character of the starting material, in this case kerogen) cannot, however, be overemphasized.

In fact, even when oxidation is applied using mild (supposedly) selective techniques — such as the stepwise alkaline permanganate method — the information provided about kerogen structure is also questionable. It should be clear that much additional information is needed to define the reactivity of different structural features and establish clear relationships between oxidation products and the structure of the starting kerogen. And this information cannot be guaranteed to be reliable when the potential exists for the method to introduce undefined chemical changes to the structure of the kerogen.

6.4 Thermal methods

While oxidation under (as yet to be defined) favorable conditions, oxidation methods can give reasonably high recovery of organic material but structural alteration does occur and some features are obliterated. A particularly attractive approach to minimize the formation of intractable residues-and the obliteration of important structural features-has been to heat the kerogen at moderate temperatures for prolonged periods and then to extract the degraded kerogen (Hubbard and Robinson, 1950).

Thus it may be possible to achieve complete conversion of the kerogen and recover >90% w/w as lower molecular weight (liquid) products. However, product alteration is also a feature of thermal reactions, but there is the distinct possibility that the thermal fragments that were allowed to escape from the reaction zone (by virtue of their volatility) would preserve some of the original (skeletal) features of the kerogen. Overall, the mild heat-soak-extraction method is a complementary method to the oxidation studies for providing lower molecular weight products for structural studies.

One approach has been to minimize the formation of intractable residues has been to heat the shale at a moderate temperature for a long time, then extract the depolymerized kerogen. Another approach is to heat the oil shale at a low temperature for a time, then increase the temperature to the conventional retorting temperature, cool, then extract. In either case, the conceptual goal is to depolymerize the kerogen with minimal condensation to intractable material, then recover even non-volatile oil by extraction. The concept of depolymerization is based on the idea that kerogen is an organic polymer and the mild thermal condition produce the monomers — it is doubtful that this is a realistic approach.

Whether or not there is an optimum time-temperature window for thermal depolymerization remains unproven. For example, a two-step process (two heating plus extraction cycles) was deemed to be unnecessary for Green River oil shale, since the same conversions could be obtained by simply heating for a longer period before extraction. However, because of the relatively mild conditions, absence of added reagents and controlled time, alteration of the recovered organics should be minimal it was deduced that the mild heat-soak/extraction method is an attractive alternative to oxidation for providing liquid products for structural studies. However, no consideration was given to the potential changes in the chemistry of the process or the manner in which the process conditions (such as temperatures on the order of 300 °C+ (570 °F+) influence the reaction products.

The use of micropyrolysis coupled with gas chromatography-mass spectrometry (GC–MS) can also provide valuable information about the structural units in kerogen (Schmit-Collerus and Prien, 1974). In addition to the on-line micropyrolysis-GC-MS studies, larger samples of kerogen have been pyrolyzed to obtain products that were fractionated by chromatography (ion exchange, complexation with ferric chloride ($FeCl_3$), and silica gel) into compound classes, and then by gel permeation chromatography into fractions of increasing molecular weight. These samples can then be investigated by conventional mass spectrometric techniques as well as by other spectroscopic studies.

These studies led to the conclusion that Green River kerogen contains two distinct types of material: (i) alpha-kerogen, which is an alginite-like material of low aromatic content and (ii) beta-kerogen with a much higher content of aromatic (probably polycondensed) material. The latter, representing approximately 5% w/w of the total, was a reddish-brown color. The alpha-kerogen yielded several types of products: normal and branched alkane derivaitves, alkyl naphthalene derivatives, tetralin derivatives, alkyl-substituted tricyclic derivatives or phenanthrene derivatives. These results led to the important conclusion that most of the cyclic units (alicyclic derivatives, naphthenic derivatives, aromatic derivatives) in the Green River kerogen are small, containing 1 to 3 rings.

Backing tracking to the potential natural product contributors to kerogen, these conclusion are not invalid but do not adequately describe the intimate structure of kerogen. They do indicate the potential size of the ring systems in the kerogen.

6.5 Acid-catalyzed hydrogenolysis

The use of hydrogenolysis in the presence of stannous chloride ($SnCl_2$) to degrade kerogen (Hubbard and Fester, 1958) affords good yields of liquid products for characterization purposes. Under these conditions, the majority of the heteroatoms are generally removed: nitrogen as ammonia, oxygen as carbon dioxide or as water, and sulfur as hydrogen sulfide. From these data it was concluded that the nitrogen, oxygen, and sulfur functionalities comprise internuclear links (as opposed to their existence in ring systems) in the kerogen structure. These conclusions may appear to be at variance with other data – from which it has been posited that these heteroatoms exist in ring structures – but this may be a result of the severe degradation conditions employed in the experiments, and examination under milder conditions is warranted.

7. Structural models

Unraveling the chemical constitution of kerogen is the most challenging objective in molecular organic geochemistry. Some compositional constraints are obtained from elemental analysis and from the determination of functional groups or the degree of aromaticity by infrared spectroscopy or by nuclear magnetic resonance spectroscopy. In addtion, the pyrolysis of kerogen or related materials yields small structural units, some of which may be representative of moieties originally present in the macromolecules whereas others may have been formed by secondary reactions. In any case, there is little information about the method by which the various structural units are interconnected (Rullkötter and Michaelis, 1990).

The need to gather the very large mass of information about kerogen structure into a compact form useful for guiding research and development has led to models for kerogen structure. These models are not intended to depict the molecular structure of kerogen. At least not in the sense that the double helix describes the structure of deoxyribonucleic acid (DNA) or even in the sense that synthetic polymers are described in terms of monomers joined to form chains that have well-defined structures. The kerogen models represent attempts, based on the available data, to depict a collection of skeletal fragments and functional groups as a three-dimensional network in the most reasonable manner possible.

Nevertheless, much work has been performed to construct conceptual models of kerogen. However, considering the complex macromolecular structure of kerogen, comprising both resistant biomacromolecules and recombined biodegradation products, any detailed chemical model represents only an average structure — and whether or not this structure really represents the proeprties and behavior of kerogen is open to much debate.

Any chemical structure, in spite of the high level of detail, is more than likely, not a true representation of the chemical structure of kerogen has no meaning and only conceptual models representing at best the largest possible set of physicochemical analytical data, but including also many assumptions, can be obtained. Although it is very difficult to describe such complex macromolecular mixtures by any chemical structures, many structural or chemical models of sedimentary organic matter have been presented in an attempt to visualize a number of the properties of kerogen. In fact, a model aimed at representing physical or spectral properties can be a structural model whereas a model for describing chemical interactions or cracking reactions will rather be a molecular model and the weighting and detail of input and output data will depend on the use for which these models are constructed (Vandenbroucke, 2003).

Several models have been proposed for the structure of kerogen in which a multidimensional approach has been employed. Such approaches are extremely valuable since they bring together the results of several analytical methods. Indeed, the success of such approaches in the deduction of structural types in kerogen is also paralleled by the use of a similar approach to the deduction of the structural types that occur in the asphaltene fraction of crude oil (Speight, 2014). Such structural models are of interest to consider here because they give an overall picture of the perception of the kerogen structure and the models may even allow predictions of properties and behavior. If the model does not match such behavior and properties, the model must be reworked since it then becomes of little if any value.

Models for oil shales such as the Green River shale (Yen, 1976; Siskin et al., 1995), then for the three main types of kerogen at various maturity stages (Behar and Vandenbroucke, 1986, 1987). Finally, the development of computerized molecular modeling enabled to build 3D molecular models satisfying not only bond lengths and directions but also minimum energy configurations (Vandenbroucke, 2003). Although it will never be possible to represent a true kerogen structure, because it is a mixture of various nonpolymeric macromolecules that cannot be analyzed separately, such models of average kerogen structure, by accounting for a great amount of information from various analyses, can provide a synthetic view of the main resemblances and differences among sedimentary organic matter from different sources. Therefore, it must be recognized that no single analytical technique provides sufficient information to construct a precise model of the macromolecular structure of kerogen. Thus, most workers now use a multidimensional (multiple-technique) approach, but as is quite often the case, the techniques used by different workers have different strengths and may emphasize different features of kerogen structure. Sample-to-sample variation and the use of different isolation techniques also complicate the issue.

A model derived for kerogen was based on the oxidative degradation using chromic acid (Simoneit and Burlingame, 1974). Additional information was provided by studies of the bitumen, again primarily by mass spectrometry, and was incorporated into the structural model that included regions of undefined structure containing trapped organic compounds of unknown nature and bearing side chains linked to the main structure by non-hydrolyzable carbon-carbon bonds and hydrolyzable ester linkages. Ester linkages were also believed to be present and the model also includes an alicyclic (naphthene) ring. To understand this model it is important to recall that the oxidation products (acids and ketones) − upon which most of this structure is based − represented only a fraction of the total organic carbon.

Another model for kerogen was developed on the basis of the data derived from the stepwise alkaline permanganate oxidation of kerogen, which produced high yields of carboxylic acids. Based on the oxidation results, a cross-linked macromolecular network structure was proposed. The most striking feature of this model is the predominance of straight-chain groups in the backbone of the network. The network bears both linear and branched side chains; branching points are indicated in the model by open circles. This model accommodates many important experimental observations, including reversible swelling and gel-like *rubbery* behavior in the swollen state, but does not satisfactorily account for the aromatic carbons observed by carbon 13 magnetic resonance spectroscopy or the nitrogen and sulfur contents determined by elemental analysis.

Another kerogen model (Schmidt-Collerus and Prien, 1974) was assembled from the sub-units identified by micropyrolysis-mass spectrometry studies. Key features of this model include formulation as a three-dimensional macromolecular network and a very uniform hydrocarbon portion comprised mostly of small alicyclic and partially hydrogenated aromatic sub-units with few heterocyclic rings. Long-chain alkylene and isoprenoid units and ethers serve as interconnecting bridges in this structure. Entrapped species (bitumen) include long-chain alkanes and both n-alkyl and branched-chain carboxylic acids. This model provides a useful view of the types and role of hydrocarbon units but de-emphasizes heteroatom functional groups and rings, presumably because groups containing these elements would not be detected efficiently by the micropyrolysis technique.

Another model for the structure of kerogen was developed using a variety pf The structure of kerogen has also been probed by a wide variety of techniques, including stepwise alkaline permanganate and dichromate-acetic acid oxidation, electrochemical oxidation and reduction (in non-aqueous ethylenediamine-lithium chloride), and x-ray diffraction techniques (Barakat and Yen, 1988). It was concluded for that particular sample of kerogen that: (i) aromaticity was low but isolated carbon-carbon double bonds were possible, (ii) the structure was largely comprised of three-to-four-ring naphthene derivatives, (iii) oxygen was present mostly as esters and as ether, (iv) the kerogen structure comprises a three-dimensional network and ethers serve as cross-links in this network, and (v) additional linkages provided by disulfides, nitrogen heterocyclic groups, unsaturated isoprenoid chains, hydrogen bonding, and charge-transfer interactions. Using these components as building blocks, a *multipolymer* network was envisaged. It was also pointed out that the extractable bitumen molecules could resid, more or less freely depending on their size, within the network.

To further account for the observed variations in the products obtained from the individual steps of stepwise permanganate oxidation, it was suggested that a *core plus shell* arrangement existed for the individual kerogen particles. The core was visualized as a cross-linked region containing most of the alkyl and alkylene chains and the bulk of the kerogen as naphthenic ring structures. On the other hand, the shell is more tightly cross-linked and contains most of the heteroatom functional groups and heterocyclic rings. This is interesting from the geochemical viewpoint since the outer shell of this model is that part of the kerogen in contact with the mineral matrix; heteroatom functions tend to interact more strongly with minerals than do the hydrocarbon chains. Organic-mineral interactions in the resulting composite would then be ideally situated to hinder physical separation of minerals from kerogen. This picture is consistent with the data of other workers (Siskin et al., 1987a,b) on chemically assisted oil shale enrichment.

Another hypothetical model for kerogen is based on the results of a multidimensional approach to probing kerogen structure, which also included a detailed analysis of the functional groups in the kerogen (Scouten et al., 1987; Siskin et al., 1995). A comparison with other kerogen models serves to illustrate some of the key features of this model for kerogen. Aliphatic material is the most obvious feature of this model, and the aliphatic moieties are longer and more linear than those in other kerogen models. In addition, the aliphatic moieties are present both as alkylene bridges and as alkyl side chains and secondary structures due to paraffin-paraffin interactions are important in the kerogen. Naphthenic and partially hydrogenated aromatic rings also make an important contribution to the aliphatic moieties. The typical ring system is only slightly larger than that in other kerogen models, but the size distribution is appreciably broader; a significant number of the larger four-to five-ring systems are present.

Yet another approach to deriving models for kerogen structure involves a more generalized procedure in which models representative of the three types of kerogen and of the asphaltene constituents from the corresponding oils as a function of maturity were developed (Tissot and Espitalie, 1975; Behar and Vandenbroucke, 1987). Emphasis in this work was placed on elucidating the chemistry of maturation for the three kerogen types and representing kerogen at the beginning of diagenesis (excluding the early stages of diagenesis, which is probably dominated by microbial action) (Behar and Vandenbroucke, 1987). These models provide an interesting view of the structural relationships between the three types of kerogen (Vandenbroucke, 2003).

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CHAPTER

14

Mining and retorting

1. Introduction

Shale oil can be produced from oil shale by a retorting process either above-ground (*ex-situ*) or underground (*in-situ*) processing.

When overburden is too great, underground mining processes are required. Underground mining necessitates a vertical, horizontal or directional access to the kerogen-bearing formation. Consequently, a strong roof formation must exist to prevent collapse or cave-ins, ventilation must be provided, and emergency egress must also be planned. Room and pillar mining has been the preferred underground mining option in the Green River formations. Advanced technologies have already been developed, tested, and demonstrated, safely and successfully, by Cleveland-Cliffs, Mobil, Exxon, Chevron, Phillips and Unocal (Burnham and McConaghy, 2006). Technology currently allows for cuts up to 27 m in height to be made in the Green River formation, where ore-bearing zones can be hundreds of meters thick. Mechanical continuous mining machine have been selectively tested in this environment, as well. Depending on the ore size limitations of various retorting processes, mined oil shale may need to be crushed using gyratory, jaw, cone or roller crushers, all of which have been successfully used in oil shale mining operations.

Underground mining is more generally applicable to the Piceance basin resources but mining conditions in other areas are considerably different. Underground mining is especially affected by the physical properties of the ore and by the presence of ground water. Underground mining was used at the Anvil Points Oil Shale Research Facility (APF) that was operated from 1944 to 1956 by the US Bureau of Mines, then by others until 1984 after which it was decommissioned. Underground mining was also used successfully by Union Oil, Mobil Oil and Colony Development, and was planned for Exxon Colony Shale Oil Project (now terminated). In these cases, the mine was of a room-and-pillar design.

In the process, the permeability of the oil shale deposit is increased by mining some shale from the deposit and then blasting the remainder into the void thus created. In the first step, a tunnel is dug to the bottom of an oil shale bed, and enough shale is removed to create a room with the same cross-sectional area as the future retort. Holes are drilled through the roof of the room to the desired height of the retort and the holes are packed with explosives that are detonated in the second step. A chimney-shaped underground retort filled with broken shale results after which the access tunnel is then sealed, an injection hole is drilled from the surface

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(or from a higher mining level) to the top of the rubble pile. The pile is ignited by injecting air and burning fuel gas, and heat from the combustion of the top layers is carried downward in the gas stream. The lower layers are pyrolyzed, and the oil vapors are swept down the retort to a sump at the bottom from which they are pumped to the surface. The burning zone moves slowly down the retort, fueled by the residual carbon in the retorted layers. When the zone reaches the bottom of the retort, the flow of air is stopped, causing combustion to cease. The product of either process – crude shale oil – can be burned as a boiler fuel, or it can be further converted into syncrude by refining through hydrogenation.

Thus, shale oil is produced from oil shale by the thermal decomposition of the kerogen component of oil shale. Oil shale must be heated to temperatures between 400 and 500 °C (750–930 °F). This heating process is necessary to convert the embedded sediments to kerogen oil and combustible gases. Generally, with solid fossil fuels, the yield of the volatile products depends mainly on the hydrogen content in the convertible solid fuel. Thus, compared with coal, oil shale kerogen contains more hydrogen and can produce relatively more oil and gas when thermally decomposed (Speight, 2008, 2013, 2014). From the standpoint of shale oil as a substitute for crude oil products, the composition is of great importance.

The thermal processing of oil shale to oil has quite a long history and various facilities and technologies have been used. In principle, there are two ways of the thermal processing: (i) low-temperature processing – semi-coking or retorting – by heating the oil shale up to approximately 500 °C (930 °F), and (ii)·high-temperature processing – coking – heating up to 1000–1200 °C (1830–2190 °F).

A high yield deposit of oil shale will yield 25 gallons of oil per ton of oil shale. Approximately 8 million tons of ore would need to be mined daily to meet one-quarter of the US demand of 17–20 million barrels of oil per day, resulting in large quantities of spent shale that would need to be handles in an environmentally acceptable manner.

Production processes for the thermal treatment of oil shale deposits to produce shale oil fall into two categories as oil sands production processes: (i) ex situ production, which involves surface mining and processing and (ii) in situ production methods, which involves heating the shale in place (underground) (Yen, 1976; Scouten, 1990). In the first option (ex situ production), oil shale is mined, crushed, and then subjected to thermal processing at the surface in an oil shale retort. Both pyrolysis and combustion have been used to treat oil shale in a surface retort. In the second option (in situ production), the shale is left in place and the retorting (e.g., heating) of the shale occurs in the ground.

Generally, surface processing consists of three major steps: (i) oil shale mining and ore preparation, (ii) pyrolysis of oil shale to produce kerogen oil, and (iii) processing kerogen oil to produce refinery feedstock and high-value chemicals. For deeper, thicker deposits, not as amenable to surface or deep-mining methods, shale oil can be produced by in-situ technology. In-situ processes minimize, or in the case of true in situ, eliminate the need for mining and surface pyrolysis, by heating the resource in its natural depositional setting.

The advantages of in situ processing are that mining is not required, spent shale is not produced on the surface, and the surface facilities needed are minimal. However, the principal disadvantages are that the technology is not well advanced, that it is applicable only to deposits that are not deeply buried, that oil recovery is lower than by other methods, and that the retorted shale is left underground where it may be leached by groundwater.

Another option is to use a modified in situ (MIS) process. In the process, the permeability of oil the shale deposit is increased by mining some of the shale from the deposit and then blasting the remainder into the void thus created. In the first step, a tunnel is dug to the bottom of an oil shale bed, and enough of the oil shale is removed to create a room with the same cross-sectional area as the future retort. Holes are drilled through the roof of the room to the desired height of the retort and the holes are packed with explosives that are detonated in the second step and a chimney-shaped underground retort filled with broken shale results. The access tunnel is then sealed, an injection hole is drilled from the surface (or from a higher mining level) to the top of the rubble pile. The pile is ignited by injecting air and burning fuel gas, and heat from the combustion of the top layers is carried downward in the gas stream. The lower layers are pyrolyzed, and the oil vapors are swept down the retort to a collection area (the sump) at the bottom from which condensed vapors are pumped to the surface. The burning zone moves slowly down the retort, fueled by the residual carbon in the retorted layers. When the zone reaches the bottom of the retort, the flow of air is stopped, causing combustion to cease.

The modified in situ process requires mining 20% to 40% of the deposit to be retorted, and involves more facilities and waste disposal on the surface. More oil is recovered per ton of rock processed than with the conventional in situ process, but less than with aboveground processing. Oil recovery per acre is probably higher with the modified in situ process than with a combination of underground mining and aboveground processing, but lower than with surface mining and aboveground processing. The principal advantage of ex situ processing (above-ground processing) is the relatively high recovery of shale oil. The principal disadvantage is that ex situ processing requires large mining and waste disposal operations and substantial surface facilities.

A horizontal modified in situ process might be practical if a technique could be developed to remove large sections of oil shale strata. One possibility is to use solution mining: the injection of fluids into the formation to dissolve soluble salts from among the oil shale layers. The result would be a honeycomb pattern of voids that could then be distributed throughout the area to be retorted by injecting and detonating an explosive slurry. This method would be limited to areas like the Leached Zone or the Saline Zone that contain significant concentrations of soluble salts. Other methods, such as longwall mining or mechanical under-reaming, could be used in other areas. It might be possible to operate mechanical under-reaming machines by remote control from the surface, thereby reducing or even eliminating the need for miners to work underground.

Of the available methods for development of oil shale resources (Table 14.1), surface mining is generally considered to be economically attractive for large, low-grade ore deposits because it permits high recovery of the resource and allows sufficient space for very large and efficient mining equipment. Open pit mining allows large-scale, economic development and maximizes the recovery of the resource. The application of open pit mining is, however, limited to a few areas in the Piceance basin and to several in the Uinta basin. Alterations to the surface of the land are substantial, and the stripped overburden must be disposed of along with the processing wastes.

Theoretically, an open pit mine could recover almost 90% w/w of the oil shale in a very thick deposit. In the strip mining option, the overburden is removed with a dragline—a massive type of scraper shovel. When the dragline has filled its scoop, it pivots and dumps

TABLE 14.1 Methods of oil shale resource development.

Method	Comment
Surface mining with surface retorting	The ore is produced from open cast surface mines, crushed, and processed in surface retorts.
Underground mining with surface retorting	The ore is mined, transported to the surface, crushed, and then heated in surface vessels to produce liquids and gases, after which the processed shale is disposed of in the mine and other disposal areas.
Modified in situ (MIS)	The process has improved the pyrolysis and recovery efficiency of in situ combustion processes by fracturing the resource to improve heat transfer and fluid flows through the shale.
True in-situ (TIS)	Heat is applied to the subsurface oil shale resource without mining; the focus is on applying heat without any combustion of the resource as earlier some of the shale was combusted at one end of the deposit to generate heat at pyrolysis temperatures to produce liquids and gases.

the burden into an adjacent mined-out area. One difference between open pit and strip mines is that in strip mining, the burden is simply cast into a nearby area; in open pit, it must be moved far from the mine site to prevent interfering with the development of the pit. Strip mining could provide high recovery of the oil shale.

Depending on the depth and other characteristics of the target oil shale deposits, either surface mining or underground mining methods may be used. Each method, in turn, can be further categorized according to the method of heating (Burnham and McConaghy, 2006). Another way in which the various retorting processes differ is the manner by which heat is provided to the shale by hot gas — (i) by a solid heat carrier or (ii) by conduction through a heated wall.

After mining, the oil shale is transported to a facility for retorting after which the oil must be upgraded by further processing before it can be sent to a refinery, and the spent shale must be disposed of, often by putting it back into the mine. Eventually, the mined land is reclaimed. Both mining and processing of oil shale involve a variety of environmental impacts, such as global warming and greenhouse gas emissions, disturbance of mined land, disposal of spent shale, use of water resources, and impacts on air and water quality.

Finally, it is noteworthy at this point that any development of western oil shale re-sources will require water for plant operations, supporting infrastructure, and the associated economic growth in the region. While some new oil shale technologies are claimed to significantly reduce process water requirements, stable and secure sources of significant volumes of water may still be required for commercial-scale oil shale development. The largest demands for water are expected to be for land reclamation and to support the population and economic growth associated with oil shale activity.

In many cases, the technologies developed to produce and process kerogen oil from shale have not been abandoned and not forgotten but held-in-reserve for adaptation and application at a future date when market demand for shale oil would increase, oil price risk would attenuate, and major capital investments for oil shale projects could be justified. Many of the companies involved in earlier oil shale projects still hold their oil shale technology and resource assets. The body of knowledge and shale industry, including the addition of larger scale retorts and advanced retorting technologies to increase output and reduce environmental impacts. Additional projects in other regions plan to retort an additional 10,000 tons per day of oil shale to produce about l 000 tons per day of shale oil, quadrupling shale oil production (Burnham and McConaghy, 2006).

2. Mining

The recovery of oil shale from shallow resources has traditionally focused on mining from either surface (open pit mines) or underground mines. Over the past 70—80 years, a variety of technologies for recovering shale oil from oil shale and processing it to produce fuels and byproducts have been developed. Both surface processing and in-situ technologies have been examined. Generally, surface processing consists of three major steps: (i) oil shale mining and ore preparation (ii) pyrolysis of oil shale to produce shale oil, i.e., kerogen-derived oil, and (iii) processing the shale oil to produce refinery feedstock and high-value chemicals. For deeper, thicker deposits, not as amenable to surface- or deep-mining methods, the shale oil can be produced by in-situ technology. In-situ processes minimize, or in the case of true in-situ, eliminate the need for mining and surface pyrolysis, by heating the resource in its natural depositional setting (Chapter 15).

The criteria used to decide on the type of mine operations is similar to that used for coal resources and is a function of ore depth, seam thickness and quality and the ratio of overburden to ore which drive mining economics. Historically oil shale has been mined and used as fuel and/or petrochemicals for centuries, but usually cannot compete economically with lower cost coal and oil energy resources. Currently all commercial oil shale operations are based on mining with approximately 70% of those operations being located in Estonia, with other commercial operations found in China and Brazil, and new large scale operations actively being considered for Jordan. There have been a range of smaller pilot and demonstration projects in the US, Australia and other countries, however, the recent development and rapid growth of hydraulic fracturing to produce shale oil, and the subsequent drop in international oil prices, has reduced interest in oil shales in many locations.

Estonia is unique in having few coal, oil or gas resources of its own, and the low lying and flat topography of this small country makes hydropower and many other renewable energy sources uneconomic. It does, however, have extensive oil shale deposits which have been exploited since before the Second World War and allowed it to be independent of energy imports. In 1997 oil shale provided over 75% of the total primary energy supply for Estonia – primarily for electrical power generation through direct firing, with smaller volumes of oil shale directed toward production of liquid distillates and petrochemicals through surface retorting processes of various types. Like Estonia, the commercial oil shale operations in China began in the 1930s for liquid fuels but were largely displaced with the discovery of oil, until oil prices increased in the 1990s which encourage China to restart production in 1992 and it is now the largest producer of crude oil from oil shale in the world. The national oil company of Brazil, PetroBras, started commercial production of liquid fuels by retorting oil shales in 1992.

In the case of the United States and using the Green River oil shale as the example, the deposits are characterized by the extreme thickness and the extent of the deposits. Very thick seams of well-consolidated oil shale are characteristic of the Green River Formation. Around the basin rims (especially of the Piceance Basin), outcrops are numerous, while considerable overburden covers the rich seams near the basin center. As a result, both underground mining and surface (open-pit) techniques may have economic advantages in different locations. In some locations, in situ methods may have advantages, but even in these cases some mining will probably be required to provide a void into which rubble can be blasted. Several general reviews have been made of the mining technology applicable to oil shale.

The richer shale zones in the Piceance basin are more than one thousand feet thick in places and are continuous over an area of approximately 1200 square miles. The deposits are amenable to either surface mining (strip mining or open pit mining) or to underground mining methods (such as room and pillar mining), depending on factors such as (for example) topographical features, accessibility, overburden thickness, and the presence of groundwater in the mining zone. Surface mining may be feasible for very thick oil shale zones that are not deeply buried, especially if the average oil yield is not high, Because of the thickness of the overburden, only a limited area of the Piceance basin and somewhat more of the Uinta basin and the Wyoming basins is amenable to surface mining. In other areas, streams have eroded gulleys and canyons through the shale beds, exposing some of the richer shale zones. Shale that outcrops in these areas, plus the shale in all deeply buried beds, will probably be extracted by underground mining.

The two principal types of surface mining — open pit mining and strip mining — have been widely used to develop coal seams (Speight, 2013) but the feasibility and effect of each type vary with the nature of the shale formation. For example, surface mining is economically attractive for large, low-grade ore deposits because the process permits high recovery of the resource and allows sufficient space for very large and efficient mining equipment. An open pit mine could recover almost 90% of the oil shale in a very thick deposit. Strip mining could provide even higher recovery of the oil shale whereas, in contrast, underground mining would recover much less.

In the first step of open pit mining, the overburden is drilled and blasted loose over a large area above the oil shale zone. The overburden is carried by trucks or conveyors to an offsite disposal area. When sufficient overburden has been removed to expose the shale formation, the shale itself is drilled and blasted, and is hauled from the pit for processing in aboveground retorts. As mining proceeds, a huge hole is formed, extending from the top of the overburden to a point deep into the oil shale deposit. On the other hand, strip mining involves removal with a dragline that is able to dump the overburden into an adjacent mined-out area. Thus, one difference between open pit and strip mines is that in strip mining, the burden is simply cast into a nearby area; in open pit, it must be moved far from the mine site to prevent interfering with the development of the pit.

However, surface mining of most of the Green River oil shale deposits is made difficult by the great thickness of the overburden that covers them. In the center of the Piceance basin, for example, the 2000-feet thick oil shale zones are buried under approximately 1000 feet of inert rock and very lean oil shale. This does not necessarily preclude surface mining, because the deposits are generally characterized by a favorable stripping ratio — the ratio of overburden thickness to orebody thickness. The thick beds in the center of the Piceance basin have 1 foot of overburden for every 2 feet of oil shale — a stripping ratio of 1:2. Open pit mining would be favored if the stripping ratio was on the order of 2:1 and 5:1; strip mining would be favored for smaller ratios and underground mining for larger ratios than 5:1.

The mine at the Anvil Points facility was begun as a three-level mine, but in later operations only two levels were mined. Nevertheless, the mining at the Anvil Points facility provided a wealth of information related to the safe design, operation and maintenance of an underground oil shale mine in the unique environment of the Green River Formation. Variations on this basic design can be tailored to mine the rich strata, while selectively leaving the lean ones. Such designs, however, leave much of the shale in place, hence are not suited for zones that are both thick and uniformly rich. Bulk underground mining methods, such as sublevel stoping (i.e., the process of extracting the desired ore or other mineral from an underground mine, leaving behind an open space known as a *stope*) with full subsidence or block caving methods, can provide more complete recovery of rich oil shale from thick zones.

However, spent shale cannot easily be disposed of in the mined void. A stoping method with spent shale backfill may be a compromise that is both reasonably efficient and environmentally acceptable. Longwall mining, a method widely used in underground coal mining, is another alternative. Longwall methods have been used for oil shale mining in the USSR and its use in the US has been contemplated. Given the high cost of mining, it is clear that, even incremental, improvements in oil shale mining technology could have a major impact on the economics of a proposed oil shale project. However, it must be realized that mine design is very much site specific and an improvement applicable at one site may be inappropriate for another. Moreover, safety considerations dictate a conservative policy with respect to the amount of rock that must be left in place. Perhaps improvements in subsurface imaging can be made to enable more precise three-dimensional modeling of subsurface features using computer techniques. This will require a much better fundamental understanding of wave propagation in homogeneous media. However the benefits should be both lowered cost of mine design and more efficient designs that significantly increase the amount of rich oil shale that can be removed without compromising mine safety.

From 1981 to 1984, an extensive oil shale fragmentation research program was conducted at Anvil Points by a consortium comprised of Cities Service, Getty Oil, Mobil Research & Development, Phillips Petroleum, Sohio Shale and Sunoco Development. Science Applications, Inc. (SAI) managed the program and provided technical direction. Los Alamos National Laboratory, and in later stages Sandia National Laboratory, participated with SAI and the consortium and shared the experimental work. This program included a wide range of tests, ranging from single level/single borehole tests to obtain basic fragmentation data, to multiple level/multiple borehole tests to explore fragmentation as a function of explosive type, charge placement and detonation sequencing. Some of the heavily-instrumented tests carried out late in the program provided results that were used to verify and refine computer programs that simulate with remarkable precision, the behavior of the Green River oil shale under explosive stress. These results should prove invaluable in designing new, more efficient mines and in formulating efficient operating procedures for these mines of the future.

At Fushun, in Manchuria (PRC), there is a very large open-pit mine where 450 feet of low-grade oil shale (15 gal/ton) overlies one of the thickest coal deposits in the world. Oil shale processing has accompanied coal production since the Japanese initiated large-scale operations at Fushun in 1929. Surface (open-pit) mining is also practiced on a large scale in the

USSR, especially in Estonia. Surface mining was planned for the (now deferred) Rundle Project (Queensland, Australia) by a consortium comprised of Esso Exploration and Production Australia, Central Pacific Minerals and Southern Pacific Petroleum. Surface (strip) mining has also been envisioned for the Toolebuc shale, largest oil shale resource in Australia, especially along the St. Elmo Structure where the shale is 22–45 feet thick below a nearly barren oxidized zone approximately 60 feet thick.

Surface mining of Green River oil shale has never been practiced on a large scale, though approximately 15% of the total reserve is potentially recoverable by surface mining methods. A detailed engineering economics study was carried out to explore the potential of open-pit mining of Green River oil shale. Surface mining of Eastern U.S. (Indiana, Kentucky) shales was evaluated as one part of an effort to develop plans for Devonian oil shale utilization. Surface mining is used extensively in ore recovery and for mining coals, especially low-rank coals. It is anticipated that technology developed for these applications will be adaptable to oil shale mining.

For above-ground retorting, oil shale has to be removed from the deposit by mining. The shale excavated from a mine varies greatly in size, from several mm to hundreds of mm, and even larger than one thousand mm. Pretreatment by crushing and screening is necessary to meet the demands of retorting operation – commercial retorts have strict demand on the size range of oil shale charge. Usually shale fraction is divided to lump shale and/or particulate shale, as the feed for different types of retorts.

In general, for lump shale, an internal hot gas carrier is usually used for supplying heat whereas for particulate oil shale (less than 10 mm in size), an internal hot solid carrier is usually employed. Combustion gas, pyrolysis gas, or retorted shale char can serve as the heat source(s). However, due to the low heat conductivity coefficient of lump oil shale, it takes longer time for retorting because of the low heating up rate (only several degrees per minute) and can take several hours to reach the desired temperature. For particulate oil shale, due to its smaller size, the heating rate is higher, the time required for retorting the oil shale is much shorter, only approximately several minutes or little more than 10 min.

In general, the developers of deposits in the United States are likely to use surface mining for those oil shale zones that are near the surface or that are situated with an overburden-to-pay ratio of less than approximately 1:1. Economic optimization methods can be used to select stripping ratios, optimum intercept, and cutoff grades.

Oil shale exhibits distinct bedding planes. These bedding planes can be used to an advantage during mining and crushing operations. Shear strength along the bedding planes is considerably less than across the planes, thereby, reducing operational demands. Thin overburden, attractive for surface mining, tends to be found along part of the mar-gins of the southern Uinta Basin and the northern Piceance Creek Basin (Cashion, 1967). The choice of how deep or selective to mine is an economic optimization issue. Numerous opportunities exist for the surface mining of ore averaging better than 25 gal/ton, with overburden-to-pay ratios of less than 1, especially in Utah. In general, room and pillar mining is likely to be used for resources that outcrop along steep erosions. Horizontal adit, room and pillar mining was used successfully by Unocal.

In a mining-surface retorting process (*ex situ process*), oil shale rock is crushed, and then conveyed to a retort. At the temperature in the retort (500–550 °C, 930–1020 °F) the organic constituents of the oil shale are converted to lower molecular weight distillable shale oil, which can also be a source of chemical products.

Open-pit mining has been the preferred method whenever the depth of the target resource is favorable to access through overburden removal. In general, open-pit mining is viable for resources where the over burden is less than 150 feet in thickness and where the ratio of overburden thickness to deposit thickness ration is less one-to-one. Removing the ore may require blasting if the resource rock is consolidated but in some cases exposed shale seams can be mined using a bulldozer. The physical properties of the oil shale, the volume of operations, and project economics determine the choice of method and operation.

When the depth of the overburden is too great for economic surface mining, underground mining processes are required, which will necessitate a vertical, horizontal or directional access to the kerogen-bearing formation. Consequently, a strong *roof formation* must exist to prevent collapse or cave-ins, ventilation must be provided, and emergency egress must also be planned. Many underground mining procedures have been proposed for oil shale deposits. As an example, room-and-pillar mining some of the oil shale is removed to form large rooms and some is left in place, as pillars, to support the mine roof. The relative sizes of rooms and pillars are determined by (i) the physical properties of the shale, (ii) the thickness of the overburden, and (iii) the height of the mine roof. Most of the Green Rover deposits of commercial interest are very thick and have relatively few natural faults and fissures. The oil shale resists compression and vertical shear stresses. These properties allow the use of large rooms, and relatively little shale needs to be left as unrecoverable pillars.

Room and pillar mining, as practiced in coal mining operations (Speight, 2013) has been the preferred underground mining option in the Green River formations. Technology currently allows for cuts up to 90 feet in height to be made in the Green River formation, where ore-bearing zones can be hundreds of feet thick. Mechanical *continuous miners* have also been selectively tested in this environment, with some degree of success.

Suitable locations in Colorado are at the north end and along the southern flank of the Piceance Creek basin where zones with a thickness of at least 25 feet and with yields of 35 -gallons of shale oil per ton of oil shale exist throughout the area. In Utah, opportunities for 35 gallons of shale oil per ton of oil shale ore exist along Hell's Hole canyon, the White River, and Evacuation Creek. Because the pay zone is more than 1500 feet thick in some places, it is conceivable that open pit mining could be applied even with 1000 feet of overburden.

It is worthy of note here that in recent years, Shell has experimented with a novel in-situ process that shows promise for recovering oil from rich, thick resources lying beneath several hundred to one-thousand feet of overburden (Chapter 5). There are locations that could yield of 1 million barrels of shale oil per acre of oil shale deposit and require, with minimum surface disturbance, fewer than 23 square miles to produce as much as 15 billion barrels (15×10^9 bbls) of shale oil over a 40-year lifetime of the project.

It also deserves mention that in the northern Piceance Creek basin, zones of high grade oil shale also contain rich concentrations of nahcolite (a mineral composed of sodium bicarbonate, $NaHCO_3$, also called thermokalite) and dawsonite [a mineral composed of sodium aluminum carbonate hydroxide, $NaAlCO_3(OH)_2$], which are high-value minerals that could be recovered through solution mining. For deeper, thicker deposits, not as amenable to surface- or deep-mining methods, the shale oil can be produced by in-situ technology (Chapter 5). In-situ processes minimize, or in the case of true in-situ, eliminate the need for mining and surface pyrolysis, by heating the resource in its natural depositional setting.

Advances in mining technology continue in other mineral exploitation industries, including the coal industry. Open-pit mining is a well-established technology in coal mining, tar sand mining, and hard rock mining. Furthermore, room and pillar and underground mining have previously been proven at commercial scale for oil shale in the western United States. Costs for room and pillar mining will be higher than for surface mining, but these costs may be partially offset by having access to richer ore. Indeed, current mining advances continue to reduce mining costs, lowering the cost of shale delivered to conventional retort facilities. Restoration approaches for depleted open-pit mines are demonstrated, both in oil shale operations and other mining industries.

The advantages of *ex-situ* processes include: (i) high efficiency for organic matter recovery (approximately 70–90% w/w of the total organic content of the shale), (ii) control of process operating variables, (iii) undesirable process conditions can be minimized, (iv) product recovery is relatively simple, and (v) process units can be used repeatedly for a large number of retorting operations. However, there are disadvantages, which include: (i) high operating cost because of the need to mine, crush, transport, and heat the oil shale, (ii) because of the costs, the process is somewhat limited to rich shale resources accessible for surface mining, (iii) spent shale disposal, (iv) the potential for underground water contamination, (v) the costs of revegetation of the site, and (vi) high capital investment for large-scale units, and (vii) once the mine is depleted, some of the investment may have to be forsaken.

The liberated compounds from oil shale retorting include gas and shale oil, which is collected, condensed, and upgraded into a liquid product that is considered, by some, to be equivalent to crude oil although this is not really the case (Chapter 6). This oil can be transported by a pipeline or by a tanker to a refinery, where it is refined into the final product.

Advances in mining technology continue in other mineral exploitation industries, including the coal industry. Open-pit mining is a well-established technology in coal mining, tar sand mining, and hard rock mining. Room and pillar and underground mining have previously been proven at commercial scale for the western oil shale formation of the United States. In fact, Current mining advances continue to reduce mining costs, lowering the cost of shale delivered to conventional retort facilities. Restoration approaches for depleted open-pit mines are demonstrated, both in oil shale operations and other mining industries.

3. Size reduction

In situ retorting DOES not require size reduction past that obtained by blasting to rubblize the shale, however size reduction by crushing and grinding will be required for above-ground processing. Moreover, size reduction is expensive and becomes rapidly more so as the target particle size decreases below approximately one-half inch. Nevertheless, closely controlled size reduction is a necessary preliminary to the use of heavy medium cycloning and other of the newer, more efficient methods for oil shale beneficiation. In addition, most current above-ground retorts have severe particle size restrictions, especially with respect to fines.

In the case of the size reduction of Green River oil shale, three types of crushers (gyratory, impact, roll) were studied, using 200-ton samples collected from the R-6 (20.7 gal/ton) and R-5 (24.9 gal/ton) zones of the Rio Blanco Mine (Tract C-a). However, caution is advised for the extrapolation of the results to leaner shales (approximately 15 gal/ton) should be done with caution and that extrapolation to appreciably richer shales should be made only with trepidation. Major findings of this work are: (i) the variations in feed grade (20–25 gal/ton) have little or no effect on the performance of the three crusher types for product having a top size of 3/8-inch or larger, (ii) when a crusher is producing 3/8-inch or finer top size product, the richer oil shale tends to have a significantly finer size distribution, (iii) the relative ability to process larger pieces of oil shale was in the order: gyratory > impact > roll, (iv) the grinding of these relatively rich shales was roughly equivalent to grinding a moderately hard limestone, and wear during oil shale grinding is anticipated to be similar to that suffered during grinding such a limestone.

Processing oil shale in surface facilities causes spent shale to increase in volume by as much as thirty percent, primarily because of the void space created by crushing and size reduction. As such, the disposal area needed for the spent shale exceeds the original capacity of the geological formations from which it is extracted, whether from deep underground mines or open pit surface mines.

Once the shale is crushed to size (which is process dependent), it is then transported to the above-ground retort. Although aboveground retorts differ widely with respect to many technical details and operating characteristics, they can be grouped into four classes, aptly named: Class, 1 retorts, Class 2 retorts, Class 3 retorts, and Class 4 retorts.

In the Class 1 retorts, heat is transferred by conduction through the retort wall. The Pumpherston retorts used in Scotland, Spain, and Australia were of this class, as is the Fischer assay retort that was developed in the 1920s. It is a laboratory device for estimating potential shale oil yields. The oil yield is the standard to which the retorting efficiencies of all other retorts are compared.

In the Class 2 retorts, heat is transferred by flowing gases generated within the retort by combustion of carbonaceous retorted shale and pyrolysis gases. Retorts in this class are also called directly heated and include the Nevada-Texas-Utah (NTU), the Paraho direct process, the also USBM gas combustion retort, and the Union A retort. Class 2 retorts produce a spent shale low in residual carbon and low-Btu retort gas. The thermal efficiency of these retorts are high because energy is recovered from the retorted shale. However, recovery efficiencies are relatively low (on the order of 80–90% w/w of the Fischer assay yield).

In the Class 3 retorts, heat is transferred by gases that are heated outside of the retort vessel. Retorts in this class are also called indirectly heated. They include the Paraho indirect, Petrosix, Union "B," and Superior retorts discussed below, and also the Union SGR and SGR-3, the obsolete Royster design, the Soviet Kiviter, the Texaco catalytic hydrotort, and others. These retorts produce a carbonaceous spent shale and a high-Btu gas. Thermal efficiencies are relatively low because energy is not recovered from the residual carbon, but oil recovery efficiencies are high, from 90% to over 100% of Fischer assay (Crawford et al., 2008).

In the Class 4 retorts, heat is transferred by mixing hot solid particles with the oil shale. They include the TOSCO II and Lurgi Ruhrgas retorts described below, and also the Soviet Galoter retort. Class 4 retorts achieve high oil yields (about 100% of Fischer assay) and produce a high-Btu gas. The spent shale may or may not contain carbon, and thermal efficiencies vary, depending on whether the spent shale is used as the heat carrier. The retorts are sometimes referred to as indirectly heated, as in class 3, because they also lack internal combustion, and produce a similar gas product. Several other conversion methods have been developed that cannot easily be placed in these classes, which include microwave heating, bacterial degradation, gasification, and circulation of hot solids slurries. Although some of these processes have potentially valuable characteristics, they will not be discussed in this section because they have not yet been proposed for near-term commercial application.

4. Direct retorting

Unlike the bitumen derived from tar sand (Speight, 2014, 2017, 2019a), the kerogen in oil shale is a solid that does not melt and is insoluble in organic solvents. Therefore, other process for the production of liquid products from kerogen have been developed. The obvious option is the application of heat (retorting) to cause the kerogen to thermally decompose into a distillable product − shale oil.

Retorting is the process of heating oil shale in order to recover the organic material as shale oil + gas (less commonly, just as gas). Thus, in order to create other fuels, the kerogen must be converted from a solid to a liquid product. In general, releasing organic material from oil shale and converting it into a liquid form requires heating the shale in an anoxic environment (i.e., in the absence of oxygen) to temperatures on the order of 400−600 °C (750−1110 °F) in order to convert the kerogen to a condensable vapor which, when cooled, becomes liquid shale oil.

Depending on the efficiency of the process, a portion of the kerogen may not be vaporized but deposited as a carbonaceous product (coke) on the remaining shale, or converted to other hydrocarbon gases. In some processes, residual carbon and hydrocarbon gases may be captured and combusted to provide process heat. For the purposes of producing shale oil, the optimal process is one that minimizes the thermodynamic reactions that form coke and hydrocarbon gases and maximizes the production of shale oil. Maximum oil production requires pyrolysis at the lowest possible temperature (about 480°C) to avoid unnecessary cracking of hydrocarbon molecules, which reduces oil yields.

To avoid unwanted combustion a retort in its simplest form is a vessel in which the shale can be heated without exposure to air and from which the product gases and vapors can escape to a collector − the retorts used in early oil shale processes were that type. Modern retorts are usually tailored to meet the needs of an integrated oil shale process, hence are somewhat more complicated. Therefore, this section outlines not only the major features of the different retorts, but also of the corresponding integrated processes that have been developed/improved during the past two decades.

Shale oil extraction process decomposes oil shale and converts the kerogen into shale oil by pyrolysis (Scouten, 199091). The oldest and the most common extraction method involves pyrolysis (also known as *retorting* or destructive distillation). In this process, oil shale is heated in the absence of oxygen until its kerogen decomposes into condensable shale oil vapors and non-condensable but combustible gas. Oil vapors and oil shale gas are then collected and cooled, causing the shale oil to condense. In addition, oil shale processing produces spent oil shale, which is a solid residue.

Spent shale consists of minerals and char – a carbonaceous residue formed from kerogen. Burning the char off the spent shale produces oil shale ash. Spent shale and shale ash can be used as ingredients in cement or brick manufacture. The composition of the oil shale may lend added value to the extraction process through the recovery of by-products, including ammonia, sulfur, aromatic compounds wax derivatives, and resid.

Heating the oil shale to pyrolysis temperature and completing the endothermic kerogen decomposition reactions require a source of energy. Some technologies burn other fossil fuels such as natural gas, oil, or coal to generate this heat and experimental methods have used electricity, radio waves, and microwaves or reactive fluids for this purpose (Burnham and McConaghy, 2006). Two strategies are used to reduce, and even eliminate, external heat energy requirements: the oil shale gas and char by-products generated by pyrolysis may be burned as a source of energy, and the heat contained in hot spent oil shale and oil shale ash may be used to pre-heat the raw oil shale.

For *ex situ* processing, oil shale is crushed into smaller pieces, increasing surface area for better extraction. The temperature at which decomposition of oil shale occurs depends on the time-scale of the process. In *ex situ* retorting processes, the conversion of the kerogen it begins at 300 °C (570 °F) and proceeds more rapidly and completely at higher temperatures. The amount of oil produced is the highest when the temperature ranges between 480 and 520 °C (900 and 970 °F). The ratio of oil shale gas to shale oil generally increases along with retorting temperatures. For an in situ process, which might take several months of heating, decomposition may be conducted at temperatures as low as 250 °C (480 °F). Temperatures below 600 °C (1110 °F) are preferable, as this prevents the decomposition of limestone ($CaCO_3$) or dolomite ($CaCO_3 \cdot MgCO_3$) in the rock and thereby limits emissions of carbon dioxide and energy consumption.

Hydrogenation and thermal dissolution (reactive fluid processes) extract the oil using hydrogen donor solvents. Thermal dissolution involves the application of solvents at elevated temperatures and pressures, increasing oil output by cracking the dissolved organic matter. Different methods produce shale oil with different properties (Baldwin et al., 1984; Koel et al., 2001; Gorlov, 2007).

In the above-ground processing option, the shale is mined, transported to a processing facility, and then heated in retorting vessels. Above-ground retorting processes fall into three broad classes depending on whether the process heat is generated internally (direct heated retort), externally (indirect heated retort), or have the potential for both. Currently, only the Kiviter retort used in the USSR for retorting of Estonian kukersite simultaneously derives major fractions of its process heat from both internal and external sources. On the other hand, underground retorting processes does not require mining and can be classified into two categories: (i) the true-in-situ process in which the oil shale deposit is first fractured by explosives and then retorted underground and (ii) the modified-in-situ process.

Oil derived from shale is referred to as a synthetic crude oil insofar as the constituents of derived oil do not occur naturally within the oil shale matrix. The retort is typically a large cylindrical vessel, and early retorts were based on rotary kiln ovens used in cement manufacturing. In situ technology involves mining an underground chamber that functions as a retort. A number of design concepts were tested from the 1960s through the 1980s.

Retorting essentially involves destructive distillation (*pyrolysis*) of oil shale in the absence of oxygen. Pyrolysis (temperatures in excess of 480 °C, >900 °F) cracks (thermally decomposed) the kerogen to release the hydrocarbon derivatives and then cracks the higher molecular weight products into lower-weight products. Conventional refining uses a similar thermal cracking process, termed *coking*, to break down a high-molecular weight residuum or tar sand bitumen (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017).

Surface retorting involves (i) transporting mined oil shale to the retort facility, (ii) crushing the mined shale, (iii) retorting, (iv) recovering the raw shale oil, (v) upgrading the raw oil to marketable products, (vi) disposing of the *spent* shale, and (vii) reclamation of the mined land (Bartis et al., 2005).

Retorting processes require mining more than a ton of shale to produce one barrel of oil. The mined shale is crushed to provide a desirable particle size, injected into a heated reactor (*retort*), where the temperature is increased to approximately 450 °C (850 °F). At this temperature, the kerogen decomposes to a mixture of liquid products and gaseous product. However, the surface retorting technique can be divided into two broad categories which is based on the size range of oil shale particles: lump oil shale retorting and particulate oil shale retorting. Lump oil shale retorting is preferred with grain size ranging from 25 to 125 mm and particulate oil retorting is preferred with grain size less than 25 mm. Though there are many retorting technologies developed since the discovery of oil shale, only few are able to retain its position as an economically viable.

The United States, Russia, Estonia, Brazil, and China have developed several oil shale retorting technologies. In the united States some companies have paid considerable attention on the development work and the Union Oil Company of California developed the rock-type (lump) retorting process with oil shale processing capacity on the order of 10,000 tons − the highest capacity in the world (Barnet, 1982). Another company − TOSCO − developed moving bed particulate retorting. However, all of the retorts developed in the United States have not seen long time continuous service in commercial production.

Numerous approaches to oil shale pyrolysis have been tested at pilot and semi-commercial scales during the 1980s (Scouten, 1990; Speight, 2008). The principal objectives of any retorting process are high yields, high energy efficiency, low residence time and reliability. Retorting conditions for oil shale have a significant effect on the properties of the shale oil and on the oil yield. Among them, heating of the individual shale pieces is the prime consideration in developing retorting concepts and in operating oil shale retorts. Therefore, the method of heat transfer to the raw shale provides a convenient way to classify the retorts. In a very broad sense, two different retorts can be distinguished: (i) directly and indirectly gas heated retort, and (ii) directly solid heated retort.

In direct heat retorting, some of the oil shale, char-bearing spent shale from previous retorting cycles, or some other fuel is combusted to provide heat for pyrolysis of the remaining oil shale, with the flame impinging directly on the oil shale undergoing retorting. Indirect heating, the more widely practiced alternative, involves the use of gases or solids that have been heated externally using a separate imported fuel or energy source and then introduced into the retort to exchange heat with the oil shale. Indirect heat sources include hot combustion gases or ashes from combustion of an external fuel, ceramic balls that have been heated by an indirect source, or even the latent heat contained in retort ash from previous retort cycles. The flammable hydrocarbon gases and hydrogen produced during retorting are also sometimes burned to support the heating process.

In the directly solid heated retort, heat is transferred by mixing hot solid heat carriers with fresh shale. This method involves a more complex heat carrier circulation system but has the advantages of high oil yield, easy scale-up, undiluted product gas, direct use of spent shale, etc. The Lurgi-Ruhrgas retort, the Tosco retort, the Taciuk retort and the Galoter retort are typical examples of directly solid heated retorts.

In the directly gas heated retort, heat is transferred by passing hot gases directly through the shale, mostly in a vertical shaft kiln. This kind of retort can be subdivided into the following two modes: (i) internal combustion mode and (ii) external combustion mode. In the internal combustion mode retort, hot gases are generated either by combustion of residual carbon in spent shale within the retort or by combustion of some retort gases. However, the main disadvantage of a direct retort is that recovery efficiencies (80%–90%) are lower than when indirect retorting is used (US OTA, 1980).

Almost all of the commercial retorts and the retorts in development are the internal heating retorts, i.e., direct heating retorts. The external heating retorts, i.e., indirect heating retort, are such that heat is supplied from a hot medium to oil shale through a wall – this retorting method if less popular because of the small unit capacity, expensive heat transfer, and low thermal efficiency.

At the present, the mature commercial technologies are: (i) Kiviter lump shale retorting, used in Estonia, (ii) Galoter particulate oil shale retorting, also used in Estonia, (iii) Petrosix lump shale retorting, used in Brazil, (iv) the Fushun retorting system, used in China, and (v) the scaled up Taciuk particulate shale retort, called AOSTRA Taciuk Processing (ATP), used in Australia.

Initial attempts at oil shale pyrolysis were conducted in above-ground retorts by using designs and technical approaches that had been adapted from technologies developed for other types of mineral resource recoveries. There are numerous configurations for above-ground retorts these are differentiated by the manner in which they produce the heat energy needed for pyrolysis, how they deliver that heat energy to the oil shale (Table 14.2). The manner and extent to which excess heat energy is captured and recycled, and the manner and extent to which initial products of kerogen pyrolysis are used to augment subsequent pyrolysis. Technologies include both direct and indirect heating of the oil shale. While all retorts will produce crude shale oil liquids, hydrocarbon gases, and char, some have been designed to further treat these hydrocarbon fractions to produce syncrude. Other retorting processes contain auxiliary features to treat problematic by-products such as nitrogen- and sulfur-containing compounds; in some cases, they even convert these compounds to saleable by-products.

In this section, various surface retorting processes are described. In order not to show any preference, the retorts are listed alphabetically.

4.1 Alberta Taciuk process

The Alberta (AOSTRA) Taciuk Processor (ATP) was originally designed to extract bitumen from tar sand (oil sand) (Speight, 2011, 2014) but has found application in oil shale processing

TABLE 14.2 Characteristics of the retorts.

Retort type	Description
Class 1:	Heat is transferred by conduction through the retort wall.
	Example: Pumpherston retort.
	Products: variable oil yield, carbonaceous shale.
Class 2:	Heat is transferred by flowing gases generated within the retort by combustion of carbonaceous retorted shale and pyrolysis gases.
	Examples: Nevada-Texas-Utah (NTU) retort, Paraho direct heating retort, USBM gas combustion retort, Union A retort.
	Products: medium-to-high oil yield, a spent, shale low in residual carbon, low-Btu gas.
Class 3:	Heat is transferred by gases that are heated outside of the retort vessel.
	Indirectly heated.
	Examples: Paraho indirect, Petrosix retort, Union B retort, Superior Oil retort, Union SGR retort and SGR-3 retort, Kiviter retort, Texaco catalytic hydrotort.
	Products: high oil yield, carbonaceous spent shale and a high-Btu gas.
Class 4:	Heat is transferred by mixing hot solid particles with the oil shale.
	Examples: TOSCO II retort, Lurgi-Ruhrgas retort, Galoter retort.
	Products: high oil yield, high-Btu gas, spent shale may be carbon-free.

(Taciuk and Turner, 1988; Koszarycz et al., 1991; Schmidt, 2002, 2003; Taciuk, 2002). This retorting technology has been tested Australia to process oil shale deposits found in Central Queensland but has been superseded by the Paraho retort (Schmidt, 2003).

In the unit, the rotary refractory is a high melting point material that lines furnaces. In a well-integrated process, approximately 30% of the energy from raw shale is sufficient to support the process energy requirements. With the Taciuk technology, approximately 20% of the energy from raw shale is sufficient to support the process energy requirements. The rotary kiln retort combines direct and indirect heat transfer through recirculation of gas and of hot solids. Some of the processed shale is mixed with the fresh feed to provide the energy, through solid-to-solid heat transfer, for combustion and retorting. This technology improves on previously explored retorting methods by increasing oil and gas yields, improving thermal efficiency, reducing process water use, and minimizing the residual coke on the spent shale. The system has been designed to reduce both gaseous and particulate emissions and to make disposal of the spent shale straightforward and efficient.

The Taciuk technology has not been tested and demonstrated on western US oil shale reserves and there is uncertainty regarding the use of the Taciuk technology domestically due to the different composition of Colorado shale relative to the Australian shale (Johnson et al., 2004). Another potential difficulty in applying the Taciuk technology is that Colorado oil shale will generate more fine particles than Australian oil shale (Andrews, 2006). However, other researchers have concluded that due to their richness, Colorado oil shales will be easier to process using Taciuk technology with some process modifications (Berkovich et al., 2000).

The Oil Shale Exploration Company (OSEC) planned to apply the Taciuk technology to the processing of oil shale from the Green River Formation in Utah. The company was awarded a 160-acre (0.65 square kilometer) research, development, and demonstration lease by the Bureau of Land Management (BLM) in December 2006 for the White River Mine site in Uintah County, Utah. The plans were to produce shale oil from the approximately 50,000 tons (45,000 metric tons) of previously mined oil shale available at the site. However, on 9 June 2008, OSEC announced it had signed an agreement with Petrobras and Mitsui according to which Petrobras agreed to undertake a technical, economic and environmental commercial feasibility study of the Petrosix shale oil technology for oil shale owned or leased by OSEC in Utah. Few results of the study were disclosed.

In March 2011, it was announced that Eesti Energia (an Estonian Energy Company) (Chapter 2) would acquire all of the shares of OSEC. On 15 March 2011 the transaction was approved by the Committee on Foreign Investment in the United States. After acquiring the OSEC shares, Eesti Energia announced it would conduct a new commercial study using its Enefit process.

The Australian Stuart project implemented the Taciuk technology in a multi-stage strategy − originally, the technology was chosen because of (i) the simple design and energy self-sufficiency, (ii) minimal process water requirements, (iii) ability to handle fines, and (iv) high shale oil yield (Johnson et al., 2004). In Stage 1, the production level was 4500 barrels of shale oil per day and produced 1.3 million barrels of shale between 1999 and 2004. By Stage 3, production levels were projected to be 200,000 barrels of shale oil per day. However, the Taciuk processor achieved only 55% capacity in a sustained trial due to mechanical problems and plugging by fine solids. The project was stopped in late 2004 for the further evaluation and the operation subsequently went out of business.

Queensland Energy Resources (Australia) assessed the possibilities for the future commercial operation of the Stuart project and spent the 2005−07 period testing indigenous Australian oil shale at a pilot plant in Colorado. The results of the tests showed that, by using the Paraho process, an oil shale-to-shale oil and liquid products business could be operated in Queensland.

4.2 Allis-Chalmers roller grate process

The roller grate process is traveling grate process in which heat transfer occurs in zones of the grate from the cross flow of process gas (hot air) repeatedly passed through the feedstock pellet bed in a modified countercurrent fashion. The traveling grate is typically comprised of chain that carries the pellets like a conveyor. The difference is that the grate chain allows air to pass through it. The grate chain travels flat and strait. There are several compartments the pellets are exposed to different heat. Once the pellets are discharged into the kiln the grate chain returns underneath. The grate is driven by a motor with gearbox or hydraulic drive and the grate is supported by rollers. Thus, the process for oil shale processing grew out of experience in design and construction of large iron ore and cement plants on the scale of 10,000 tons/day, approximately one-fifth the size needed for a 50,000 bbl/day shale oil retorting plant. In this process, the shale is conveyed along a straight-line path by a series of closely-spaced slotted rollers.

In the process, raw shale crushed to 1-3/4″ × 1/4″ is fed into the roller grate. Fines (-1/4″) are screened from the feed, agglomerated and fed on top of the bed of crushed shale. Bed depth can be up to three feet. The rollers impart a mild tumbling motion to the shale particle. This has two important benefits in retorting: by exposing new surface to the hot gas sweep it speeds heat-up and it causes fines to quickly migrate down through and out of the bed, thereby preventing pockets of fines that would cause gas channeling.

In the preheater, the shale is heated by off-gas from the retorting zone. This dries the shale and liberates some low-boiling oil. Next the shale moves into the first retorting zone where it is further heated by recycled non-combustible retort gases in the temperature range of 482−538 °C (900−1000 °F). The heating gas flows down through the shale bed and slotted rollers, sweeping liberated oil into the preheat zone where it is partially condensed. In the second retorting zone, a 650 °C (1200 °F) gas stream completes the retorting process to give a high-boiling oil that is taken through a heat exchanger and condenser. Sealing between the retorting and combustion zone is accomplished by the use of solid rollers (instead of slotted ones), drag plates at the entrance and exit of the sealing zone, and careful maintenance of equal overbed pressures.

In the combustion zone, air flow is upward through the grate and shale bed in order to keep the grate temperature as low as possible. The two cooling zones are kept separate, since the hotter gases from the first cooling zone are combined with the hot off-gas from the combustion zone and passed through a heat exchanger where their heat is transferred to the non-condensable retort gas stream used in the retorting section.

4.3 Chattanooga process

Central to the Chattanooga Process is the pressurized fluid bed reactor and associated fired hydrogen heater. Conversion reaction occurs in a relatively low temperature (<535 °C, 1000 °F) non-combustion environment. With modifications only to its feed system, the reactor can convert oil bearing material such as oil sand, oil shale and liquid bitumen via thermal cracking and hydrogenation into hydrocarbon vapors and spent solids.

Hydrogen is used as the heat conveyor to the reactor, reactor bed fluidizing gas, and reactant. Hydrogen is heated in an adjacent fired heater fueled by process off-gases and either supplemental gas or product oil, depending upon economic conditions. This flexibility minimizes or eliminates natural gas requirements.

Combustion air for the heater and the associated hydrogen plant reformer is preheated by cooling the spent sand or shale discharged from the reactor. Reactor overhead gases are cleaned of particulate solids in a hot gas filter, cooled and hydrocarbon products condensed and separated from the gas stream. The liquid product produced at this stage may be lightly hydrotreated to produce a very low sulfur high grade synthetic crude oil.

The excess hydrogen, low-boiling liquids and acid gases are passed through an amine scrubbing system to remove hydrogen sulfide which is converted to elemental sulfur. Excess hydrogen and the low-boiling liquids, now stripped of the acid gases, together with new make-up hydrogen are admitted to a turbine-driven centrifugal compressor for recompression and recycling. Steam for the turbine is generated by recovering waste heat from the fired heater. Compressor power requirements are minimized by maintaining a low pressure drop around the process loop.

A slip stream of recycle gases is taken from the compressor discharge and passed through a purification system to remove hydrocarbon gases produced in the reactor. The purified hydrogen gas stream is returned to the compressor inlet. The hydrocarbon gases may be used as feedstock to the integrated hydrogen plant thus again minimizing the requirement for purchased natural gas.

Use of hydrogen in the initial phase of the process greatly enhances the quality of the product and reduces the need for extreme hydrotreating in downstream operations. Recovery of waste heat, power co-generation and the utilization of the hydrocarbon gases produced in the reactor as feedstock for the hydrogen plant make the Chattanooga Process virtually self-sufficient by obtaining its energy requirements from the primary plant feedstock.

4.4 Chevron retorting process

The Chevron staged turbulent bed (STB) oil shale retort represents a very different approach to fluidized bed retorting from that taken by the workers at Shell and Exxon. To approach plug flow performance in an open fluidized bed reactor requires minimizing the backmixing associated with circulation around rising bubbles. Also, to avoid generating shale fines in the retort little turbulence is desirable. For these reasons the Shell and Exxon workers chose to avoid the turbulent bed regime. In contrast, the STB retort operates in the turbulent flow regime and staging by restricting the flow at intervals is used to approach plug-flow conditions for the solids. Solids move down through the STB retort against a countercurrent of the fluidizing gas.

Like the Shell retorts, the STB is a small-particle retort, hence can process the entire oil shale resource. However, top size of the shale feed to the STB retort is 1/4 inch (6.4 mm). Grinding to for lump shale processes, but is considerably less expensive than fine grinding (to bed processes). Locally, the bed of solids in the STB appears to be fluidized, but the superficial gas flow is well below that required for fluidization of the larger particles. However, rapid local mixing and good solid-solid heat transfer help avoid local overheating. This minimizes cracking and coking reactions that lower oil yields.

The STB retort is flexible with respect to fluidizing/stripping gas; it can be operated with steam, a recycle gas stream, or a mixture of the two. The superficial gas velocity is in the range of 0.3–1.5 m/sec (1–5 ft/s) at the bottom of the retort, but increases up the retort as product vapors add to the gas volume.

A combination of thermal shock as particles enter the bed, the removal of kerogen, and turbulence in the bed, causes some breakage to generate fines within the retort. Particles smaller than approximately 200 mesh are elutriated with the product vapors, but most are recovered before the oil is condensed. These fines are rich in carbon, hence are sent to the combustor for recovery of their fuel value.

4.5 Dravo circular traveling grate

The Dravo circular traveling grate retort also comes from a firm that is well-established as a leader in material-handling equipment and processes for the mining and mineral industries.

The retort design is similar to traveling grate machines supplied by Dravo for the sintering or pelletizing of iron ore. The grate is a continuous chain of wheeled pallets that can accommodate a bed of shale up to 95 inches thick as it travels around a circular track. The shale would be crushed and screened to give a -1-inch +1/4-inch shale feed.

Unlike the Allis-Chalmers roller grate, the shale bed is not agitated on the Dravo grate. This minimizes the generation of fines during retorting. Some of the fined generated in crushing could be burned if needed to heat the recycle gas streams. The remainder and oily fines collected throughout the process would be agglomerated and fed as pellets or briquettes onto the top of the shale bed. This capability enables processing of the entire resource and avoids the expense of environmentally acceptable disposal of oily fines. Retorting takes place in four zones. In the first zone, the shale is heated by oxygen-free gases produced by combustion of gas recycled from the heat recovery section (natural gas is used for start-up and additional natural gas is added if needed to maintain temperature). The upper 20%–30% of the bed is retorted in this zone.

A major part of the process heat is generated in the second zone, which is fed with a mixture of recycle gas and air to burn the carbon in the spent shale. As the combustion front moves down through the shale bed, the retorting front moves ahead of it to retort the middle portion of the bed. The amount of air is controlled to limit combustion and prevent breakthrough of oxygen-rich gas into the product collection system. In Zone 3, oxygen-free gases are used to transfer heat from the hot combusted shale in the upper part of the bed to the cooler shale at the bottom of the bed. Thus, the bottom of the bed is retorted adiabatically. Finally, oxygen-free gases cool the bed to below 120 °C (250 °F) before the grate is tipped to dump the spent shale into a water-sealed discharge hopper.

In the oil recovery section, oil and water are condensed from the retort off-gas, using direct contact quench towers or air heat exchangers. Heavy oil mist is recovered by electrostatic precipitation. Desalting and deashing of the raw shale oil is accomplished using (Petrolite) technology developed for crude oil applications. Overall oil recoveries in the range of 95%–100% of Fischer Assay are reported, depending upon the grade and type of shale fed.

The quality of shale oil obtained from the Dravo retort is very similar to that obtained from the Paraho retort operating with direct heating. Pour point is high, as are the contents of nitrogen, arsenic, iron and nickel. In several cases, samples of raw shale oil were sent to Gulf Oil for upgrading via 2-stage hydrotreating.

4.6 EcoShale In-Capsule process

The EcoShale In-Capsule process integrates surface mining with a relatively low-temperature roasting method that occurs in an impoundment that is constructed in the void space created by the shale mining excavation. A similar low-temperature concept was used in Germany during World War II (Kogerman, 1997).

When filled with shale, the capsule is heated using pipes circulating hot gases derived from burning natural gas or its own produced gases. To maximize energy efficiency, the process heat used in one capsule can be recovered by circulating lower temperature gases which transfer remaining heat into adjacent capsules. The lower-temperature slower roasting approach also minimizes carbon dioxide emissions and is amenable to carbon capture and sequestration. The unique impoundment approach allows for rapid reclamation and approximate restoration of the topography.

4.7 Enefit process

The Enefit process is a modification of the Galoter process being developed by Enefit Outotec Technology. In this process, the Galoter technology is combined with proven circulating fluidized bed combustion technology used in coal-fired power plants and mineral processing. Oil shale particles and hot oil shale ash are mixed in a rotary drum as in the classical Galoter process. The primary modification is the replacing of the Galoter semi-coke furnace with a fluidized bed combustion furnace. The Enefit process also incorporates fluid bed ash cooler and waste heat boiler commonly used in coal-fired boilers to convert waste heat to steam for power generation.

Compared to the traditional Galoter technology, the Enefit process allows complete combustion of carbonaceous residue, improved energy efficiency by maximum utilization of waste heat, and less water use for quenching. According to promoters, the Enefit process has a lower retorting time compare to the classical Galoter process and therefore it has a greater throughput. Avoidance of moving parts in the retorting zones increases their durability.

4.8 Fushun generator type retorting

The Fushun process is similar to the Kiviter process but with a slightly different hot gas flow direction and has some aspects of an external hot gas process (Crawford et al., 2008). It was developed in China in the 1920s and first commercialized in the 1930s. At one point there were over 250 retorts in operation in the 1950s producing 100–200 tons of shale oil per day. Once heavy oil was discovered in China, oil shale production became less economic and was shut down in the 1990s, but was soon restarted and grew to where China is the largest shale oil producer in the world from mined oil shale The retort has been developed and utilized in commercial production for more than seventy years in Fushun, China (Zhou, 1995; He, 2004; Hou, 1986; Zhao and He, 2005). The retort is of vertical cylindrical type, with outside steel plate lined with inner fire bricks; its inner diameter is approximately ten feet with a height of approximately 30 feet.

In the process, the oil shale is fed from the top of the retort, with the size of 10–75 mm; at the upper section (pyrolysis section) of the retort, the oil shale is dried and heated by the hot ascending gaseous heat carrier, and pyrolyzed at approximately 500 °C (930 °F), the oil-gaseous vapor produced exits from the top of the retort, the oil shale is converted to shale coke, and goes to the lower part (gasification section) of the retort, it is reacted with the ascending air-steam (coming from the bottom of the retort), it is gasified and combusted to shale ash; the air-steam react with the coke to form hot gas and flows to the upper part of the retort to heat the oil shale; at the middle of the retort a hot recirculating gas as the supplementary hot gas carrier is introduced to heat the oil shale, this recirculating gas is part of the retort exit gas, after it is cooled in condensation system (shale oil is condensed) and it is again heated in a recuperator to 500−700 °C, then back to the retort. The shale ash exits from the water dish at the bottom of the retort.

Twenty Fushun retorts share one condensation system, i.e., the exit gas evolved from 20 Fushun retorts flows together to a collecting tube, then successively to washing tower, gas blower, and cooling tower, where shale oil is condensed; part of retort gas coming from the gas blower is introduced to the recuperator as fuel, meanwhile a part of retort gas is introduced to another recuperator, where it is heated and recirculated to the middle of the retort as hot gas carrier for heating the oil shale in the retort; the remaining retort gas coming from the cooling tower is introduced out of the condensation system as surplus gas.

The characteristics of Fushun retort is: the potential heat of the fixed carbon of the shale coke is partly utilized, thus high thermal efficiency is obtained, but due to the addition of air into the retort, after combustion, the nitrogen dilutes the pyrolysis gas, makes the retort-exit gas having low calorific value; furthermore, the excess oxygen coming to the upper part of the retort will burn out a part of the shale oil produced, thus reducing the shale oil yield greatly.

The oil yield of the Fushun retort accounts for approximately 65% of Fisher Assay. The daily capacity of the retort is only 100−200 tons, Fushun type retort is suitable for small oil shale retorting plant, and for processing lean oil shale with low gas yield.

4.9 Galoter retort

The Galoter retort process uses an inclined hot cylindrical rotating kiln as the retort vessel (Crawford et al., 2008). Solid oil shale particles are separated from the dried crushed feed in a cyclone separator. A mixing chamber combines the feed with hot recycled ash from combustion of the spent shale. Then the mixture is added to the kiln where the oil and gas vapors are removed and condensed to products. The spent shale is burned in an external furnace with some solids returned to the mixer while the remainder are cooled and sent to disposal, while the hot gases from combustion are used to dry and preheat the feed stream. The process has a high thermal efficiency and high oil recovery. Commercial scale units were first online in the 1950s and 1960, but were shut down and replaced with two larger 3000 tonne/day units in 1980. Between 2009 and 2015 three additional units with slight modifications were built but were called Petroter plants. All units were in Estonia.

The newest modifications of the Galoter retort are the Enefit process and the Petroter process is a technology for a production of shale oil. In this process, oil shale is decomposed into shale oil, gas, and spent residue. The process was developed in 1950s and it is used commercially for the shale oil production in Estonia. There are projects for further development of this technology and for expansion of its usage, e.g., in Jordan and the United States.

The retort is a near-horizontal- slightly-inclined cylindrical rotating retort and the feed oil shale is crushed and sized to approximately 25 mm. The shale ash is used as solid heat carrier. In the horizontal cylindrical retort, the dried oil shale mixed with the hot ash carrier, and is heated to 500 °C, it is pyrolyzed at the interval approximately 20 min, shale coke is formed, it comes out from the retort with the ash into the vertical fluidized combustion chamber, where it is combusted with incoming up-flowing air, shale coke is converted into shale ash, having a temperature on the order of 700−800 °C (1290−1470 °F).

The shale ash is separated from the hot flue gas in the cyclone, and is mixed with dried oil shale, both are introduced into the retort, the dried oil shale is heated and pyrolyzed, the shale ash with the shale coke is recirculated. The hot flue gas leaving from the cyclone is introduced to the waste heat boiler and then to the fluidized drier for drying the oil shale feed. The shale oil vapor exits from the retort, is cooled successively, thus high-boiling oil, low-boiling oil, naphtha fractions, and high calorific gas are obtained.

Two Galoter solid heat carrier retorts, each with processing capacity of 3000 tons of oil shale per day were built at Estonia Narva Power Plant (Golubev, 2003; Opik et al., 2001). Technological chemical efficiency accounts for 73%–78% with an oil yield of 85%–90% of Fisher Assay. The retort gas contains low-boiling olefins 30% and may be used for producing petrochemicals or as town gas; besides the oil shale as feed (Senchugov and Kaidalov, 1997).

This retorting technology is complex, having more equipment and machines, the operation is not easy, Estonia and Russia have spent much money and time for developing; more than 50 years for scaling up from laboratory to pilot plant and at last to the commercial scale.

Overall, the Galoter Process is similar to the Lurgi-Ruhrgas, Tosco II and Shell (SPHER, SSRP) processes in using hot spent shale as the heat carrier. Dried oil shale (smaller than 1-inch at about 110 °C, 230 °F) is mixed with hot spent shale (at 800 °C, 1470 °F) in a screw mixer, then passed into a 500 °C (930 °F) rotary kiln after which the retorted shale and product vapors pass into a gas-solid separator, from which the vapors are sent to the product recovery section and a part of the spent shale is discarded. The balance of the spent shale is fed into an air-blown riser combustor where burning of residual carbon raises the temperature of the solid to 800 °C (1470 °F). The hot shale stream is used to provide heat for retorting, while the hot gases are used to raise steam and then to dry the wet incoming shale.

Oil yields on the order of the 85%–90% of the theoretical (Fischer assay) yield and an 82% overall thermal efficiency are claimed for Galoter process operations with 40 gal/ton wet Baltic shale.

4.10 Gas combustion retorting process

The US Bureau of Mines gas combustion retorting process uses a vertical, refractory-lined vessel (similar in operating concept to a moving bed reactor used for coal gasification) through which crushed shale moves downward by gravity, countercurrent to the retorting gases (Fig. 14.1) (Matzick et al., 1966; US OTA, 1980). Recycled gases enter the bottom of the retort and are heated by the hot, spent shale as they pass upward through the vessel. Air and some additional recycle gas are injected into the retort through a distributor system located above the heat recovery zone to mix with the rising hot recycled gases. Combustion of the gases and of some residual carbon heats the shale immediately above the combustion zone to retorting temperature. Oil vapors and gases are cooled by the incoming shale, and the oil leaves the top of the retort as a mist (Burnham and McConaghy, 2006).

Vertical -shaft retorts can be traced back to Scottish oil shale retorts that evolved from coal gasification technologies (Speight, 2013). This retort is a vertical, refractory-lined vessel through which crushed shale moves downward by gravity. Recycled gases enter the bottom of the retort and are heated by the hot retorted shale as they pass upward through the vessel. Air is injected into the retort at a point approximately one-third of the way up from the

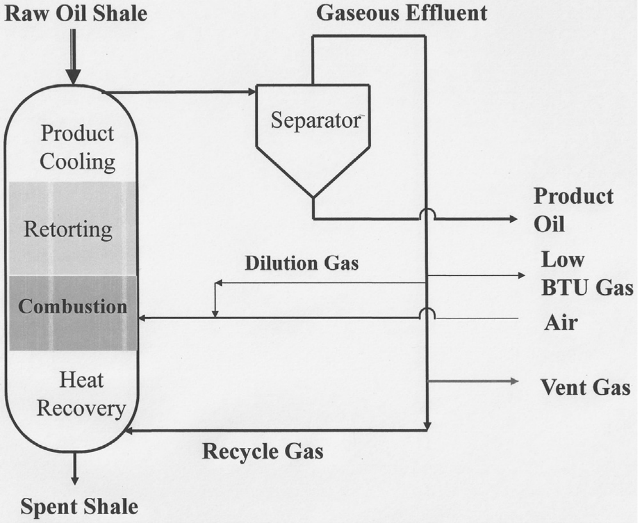

FIG. 14.1 Gas combustion retort.

bottom and is mixed with the rising hot recycle gases. Combustion of the gases and some residual carbon from the spent shale heats the raw shale immediately above the combustion zone to retorting temperature. Oil vapors and gases are cooled by the incoming shale and leave the top of the retort as a mist. The novel manner in which retorting, combustion, heat exchange and product recovery are carried out gives high retorting and thermal efficiencies. The process does not require cooling water, an important feature because of the semi-arid regions in which the oil shale targets occur.

Design objectives for the Gas Combustion Process grew out of the USBM work described above. These included gravity flow to minimize mechanical complexity, heating of the raw shale by hot gas, and generation of this hot gas by burning the residual carbon on retorted shale within the retort vessel. Work began in 1949 on the first version, known as the dual-flow retort. A second and much improved version, the countercurrent retort soon followed. By flowing combustion gases up and shale down, oil recoveries above 90% of Fischer Assay were obtained from 25 to 20 gal/ton shale at throughputs of 200 lb/h/ft^2. However, having the combustion zone at the bottom of the retort led to the spent shale being discharged at high temperature, thereby wasting valuable heat. Also, handling the hot shale was a problem. The Gas Combustion Process was developed to alleviate these problems.

In the retort, the are no internal baffles divide the zones and the flow of shale from the retort is controlled by a movable grate at the bottom. Shale fed into the top of the retort through a rotating lock is heated by the hot product vapors. This serves to cool the oil vapors past the dew point into a mist that is swept out into the collector by the up-flowing gases. The preheated shale then moves down into the retorting zone where, upon further heating, kerogen decomposition yields the oil and gas products and a carbonaceous residue that adheres to the spent shale. Next the shale moves into the hottest part of the system where air is introduced for combustion of the residue and of the hydrocarbon derivatives in the recycle gas. In the lowest part of the retort, heat from the combusted shale is transferred to the recycled gas as it flows upward. Finally, the cooled, combusted shale is discharged from the bottom of the retort.

Three gas combustion retorts were constructed by the United States Bureau of Mines at the Anvil Points facility: (i) a 6-ton/day unit, (ii) a 25-ton/day pilot unit, and (iii) a 150-ton/day unit designed to furnish engineering design data for a commercial unit. The benefits of this system include (i) energy is recovered from the retorted shale fiving the unit high thermal efficiency and (ii) an important consideration in arid regions (such as the western United States) is that there are no requirements for cooling water. However, there were several problems of the gas combustion retort: (i) oil yields were in the range of 85%–90% of Fischer Assay, approximately some 5%–10% lower than desired, (ii) the poor control of oil mist and the design of air-gas distributors were persistent problems, and (iii) the inability to efficiently process shale fines (smaller than 1/4-inch) was a considerable drawback.

The first stage in development of the Gas Combustion Process ended in 1955 when work was halted by USBM. Stage II began in 1961 with the passage of Public Law 87–796 empowering the Secretary of the Interior to lease the facility, in order to encourage further development of oil shale technology. After evaluating several proposals, the Interior Department leased the Anvil Points facility to the Colorado School of Mines Research Foundation (CSMRF). Under the terms of the lease, the Colorado School of Mines Research Foundation became lessor, provided administrative and logistic support, and made the facility available to a consortium that eventually included Mobil Oil (project manager), Humble Oil & Refining, Pan American Petroleum Corp., Sinclair Research, Inc., Continental Oil Co. and Phillips Petroleum Co. Under this agreement, the facility was reactivated in 1964 and was operated for approximately one year in 1966–67. During this time, nearly 300 runs were made, mostly in the 25-ton per day unit and in the 150-ton per day units. Improvements made in Stage II solved many problems and throughput was almost doubled to 500 lbs/h/ft^2. However, oil yields remained a disappointing 85%–90% of Fischer Assay despite efforts to achieve improvement. Nevertheless, progress was made and many of the results were incorporated into the Paraho project. No work was carried out on the Gas Combustion Process after 1967, but the Paraho Process in its directly heated mode is nearly identical, so Paraho results can be used as a guide to the potential of the Gas Combustion Process.

The US Bureau of Mines developed and tested this retorting system during the 1980s specifically for the Green River Shale Formation. However, the project was terminated prior to the operation of the largest of three pilot plants (Dinneen, 1976; US OTA, 1980).

4.11 Hytort process

The Institute of Gas Technology (IGT) has been a leader in exploring the use of a hydrogen atmosphere in retorting (hydroretorting). Initially, the objective was gasification at high temperatures, however most of the products obtained below the carbonate decomposition temperature were liquids. Next, IGT devised and patented a process for gasifying the shale liquids. More recent hydrogen retorting studies at IGT have focused on obtaining high liquid yields and improved product quality, especially from Eastern shales. In addition to IGT, Texaco was active in this area during the 1960s and Phillips Petroleum studied process response for hydroretorting Indiana New Albany shale in a recirculating loop reactor system. Phillips also participated with IGT, Bechtel and Hycrude Corp. in process design studies aimed at the commercial use of the IGT technology with Eastern US shales. Work at Mobil Research & Development has resulted in the development of a Rapid Heat-Up (RHU) Assay, especially designed to evaluate Eastern shales.

Some of the more efficient fluidized bed processes have achieved oil yields of 110%, or so, of Fischer Assay. However, Fischer Assay recovers only a small part of the organic matter in many of the oil shale formations of the world. Thus, potential oil yield is several times Fischer Assay in these cases, notable among which are the Devonian shales of the Eastern US Hydrogen retorting affords greatly enhanced oil yields in many such cases. The quality, in comparison to Fischer Assay oil, of the oils obtained by hydrogen retorting depends markedly upon the type of shale. The oil produced from Green River oil shale by the HYTORT process is very similar to the Fischer Assay oil; the main differences in elemental composition are a somewhat lower oxygen content. Nitrogen content was slightly higher and this seems to a general phenomenon in hydrogen retorting. In sharp contrast, the oils from hydrogen retorting of the two Eastern shales were quite different from their Fischer Assay counterparts. Moreover, the two Eastern shales were quite different in their response to hydrogen (though oil yield increased in both cases). In both cases, the HYTORT oils had appreciably lower atomic H/C ratios than the Fischer Assay oil. However, the sulfur content was approximately the same and the oxygen content only slightly lower for the New Albany HYTORT oil, while both sulfur and oxygen contents were much lower for the Sunbury HYTORT oil. The reason for this behavior is not known.

Most hydrogen production involves the production of synthesis gas, which is further processed to produce hydrogen. In coal liquefaction, synthesis gas in the presence of liquid water has been shown superior to hydrogen alone for improving reaction rates and oil yields. Hydrogen retorting was compared to retorting in a mixture of synthesis gas and steam for three Eastern shales.

The oil yields and organic carbon conversions achieved with the synthesis gas mixture were approximately those that would have been obtained by hydrogen retorting at the hydrogen partial pressures used. However, the synthesis gas mixture yielded oils with appreciably higher H/C ratios and API gravities, and lower nitrogen contents. 404 Sulfur contents were, however, higher for the oils produced with synthesis gas.

Early work at IGT (1972–79) focused on moving bed hydroretorting, the HYTORT process. Tests were made with selected shales at rates up to 1 ton/h. Additional progress was made during 1980–83 by the joint Hycrude-IGT-Bechtel-Phillips Petroleum effort, especially in reducing hydrogen consumption. Based on these results, an engineering design study was made for a commercial HYTORT facility.

The HYTORT effort served to bring into focus the advantages of hydrogen retorting for Eastern oil shales. However, the HYTORT moving bed technology is mechanically complex and its large, high-pressure vessels are expensive to construct. Moreover, fines are not readily processed in the moving bed system, hence are usually discarded. Therefore, the emphasis of more recent work at IGT has shifted to a pressurized fluidized bed hydroretorting (PFBH) concept.

The pressurized fluidized bed hydroretorting process will use a vertically-staged fluidized bed and the pressurized fluidized bed hydroretorting is projected to afford higher throughput, hence lower reactor capital costs, than the moving bed HYTORT process. Moreover, for Eastern shales the use of smaller shale particles in the pressurized fluidized bed hydroretorting should boost oil yields, while decreasing gas yields and having little effect on overall carbon conversion. Thus, not only should the pressurized fluidized bed hydroretorting process more shale per capital dollar than the moving bed, it should also give approximately one-third more shale oil per unit weight of shale. As a result, the pressurized fluidized bed hydroretorting is expected to substantially reduce the cost of producing shale oil from oil shale.

Other advantages of the pressurized fluidized bed hydroretorting process compared to the moving bed HYTORT process stem from the characteristics of the fluidized bed. The efficient gas-solid contacting and good heat transfer characteristics of the fluidized bed should improve thermal efficiency and the need to briquette beneficiated shale (required for moving bed hydroretorting) will be eliminated.

Additional work is underway to develop a fluidized bed gasification system that will utilize the carbon content of the fines to produce hydrogen. However, the shale processing facility will require process heat and steam, and the carbon on spent shale is usually the energy source that meets these needs. Therefore, even if technically successful, the impact of gasification as a hydrogen source may not be dramatic. However, if chemistry can be found that will enable the use of synthesis gas to increase the rate and/or lower the overall pressure requirement for hydroretorting, the impact of gasification may be very important.

Finally, it should be pointed out that the molecular chemistry responsible for the striking yield enhancements often obtained by hydrogen retorting are not yet well understood. Nor, for that matter, are the reasons why shales that are remarkably similar in elemental and mineral composition sometimes respond very differently to hydrogen pressure.

4.12 Kiviter retort

The Kiviter retort (Sonne and Doilov, 2003; Yefimov and Doilov, 1999; Crawford et al., 2008) is used in Estonia in a number of retorts and was previously used for oil shale processing in Russia. The retort is a vertical cylindrical retort, having rectangular combustion chambers at the middle of upper part of the retort and also at the two sides of the middle part of the retort. The combustion chambers are equipped with air and recirculating gas nozzles, the combustion takes place, and the hot combusted gas formed horizontally comes to the two pyrolysis chamber, where the oil shale fed from the top of the retort goes vertically downward and is heated by the hot combusted gas in the mode of thin layer pyrolysis, the oil-gaseous vapor horizontally escapes to the two sides of the upper part of the retort, and comes out of the retort top.

The shale coke is cooled down at the lower part of the retort by the upward cooled circulating gas, and is discharged from the bottom water seal; meantime the cooled circulating gas is heated and goes upward as supplementary heat source, combined with the combusted gas for pyrolysis of feed shale. The discharged shale coke contains fixed carbon, it is not utilized in the retort, therefore the retorting thermal efficiency is not high, approximately 70%, and the retort exit gas is diluted by nitrogen in air, its heating value is not high, and the Fisher assay oil yield is also not high, approximately 75%–80%, due to the fact that air (with oxygen) introduced into the retort for combustion is in excess, and the excess oxygen burns out some shale oil produced, or mainly due to the fact that part of the shale oil produced is pyrolyzed by the hot combusted gas.

The Kiviter retort handles coarse oil shale lumps of 1 inch–5 inches in size in a single multi-function retort that is generically similar to the direct-fired Paraho and Gas Combustion retorts. As started above, oil shale is gravity-fed downward through the Kiviter retort. However, relatively rich kukersite (like very rich Colorado shale) becomes plastic on slow heating and the resulting agglomeration can lead to uneven gas and solids flows and/or plugging of the retort. Gas flow patterns selected to avoid these problems, the retort design to accommodate these flows, and the water-sealed spent shale discharge with mechanical shovel unloading are distinctive features of the Kiviter retort.

Large amounts of gas for cooling the spent shale, and for gasification, are injected into the lower part of the Kiviter retort. This gas must travel a long path before passing through the annular retorting zone at the retort top. Even though care may be taken to maintain bed permeability, the bottom of the retort operates under appreciable pressure. Also, to provide sealing against in-retort pressures, the retort uses discharge chutes that project down into a water trough that is fitted with a reciprocating mechanical shovel. However, other methods for controlling solids flow have proven better suited for continuous operations on a large scale.

The daily capacity of the retort accounts for 1000 tons oil shale with the size of 10–125 mm (mainly 25–100 mm), the electricity consumption for processing one ton oil shale is approximately 14–18 kwh, steam (5–8 bars) 15–20 kg, and water 0.2–0.5 m^3. Two Kiviter retorts each with daily capacity of 1000 ton of oil shale have been well operated at Estonia Viru Keemia Group (VKG), in Kohtla Yarve. This retort is suitable for medium and small shale oil plant.

4.13 Lurgi-Ruhrgas process

The Lurgi-Ruhrgas technology was developed in Germany for the production of pipeline-quality gas through the devolatilization of coal fines (Fig. 14.2). The process was designed not only to retort kerogen but also to refine the resulting hydrocarbon derivatives into saleable liquid fractions similar to the products from crude oil.

The Kiviter retort is a vertical cylindrical vessel that heats coarse oil shale with recycled gases, steam, and air. To supply heat, the process uses internal combustion technology, The raw oil shale is fed into the top of the retort, and is heated by the rising gases, which pass laterally through the descending oil shale causing decomposition of the rock. Pyrolysis is completed in the lower section of the retort, where the spent shale contacted with more hot gas, steam and air is heated to about 900 °C (1650 °F) to gasify and burn the residual carbon (char). Shale oil vapors and evolving gases are delivered to a condensing system, where condensed shale oil is collected, while non-condensable gases are fed back to the retort. Recycled gas enters the bottom of the retort and cools the spent shale, which then leaves the retort through a water-sealed discharge system.

The technology has operated at commercial scales for the devolatilization of lignite fines, the production of char fines for briquettes from sub-bituminous coal, and the cracking of

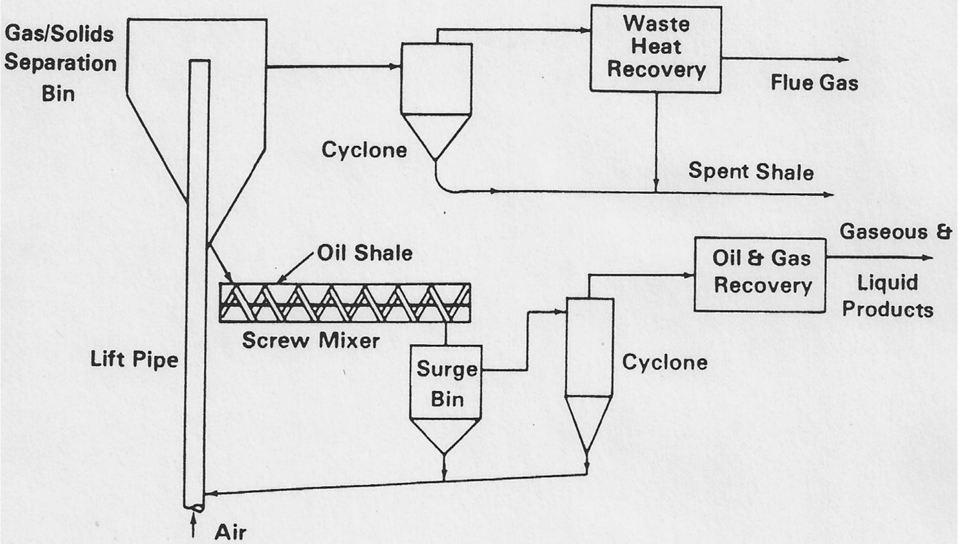

FIG. 14.2 Lurgi-Ruhrgas process.

naphtha and crude oil to produce olefins (Speight, 2008, 2013, 2014). The technology features a lift pipe in which residual carbon is burned off spent hot solid feedstock to provide process heat. Burned feedstock is carried to the retort for solid-to-solid heat transfer to the raw feedstock. It has been successfully tested for processing Green River Oil Shale.

In the process, crushed and sized oil shale (<0.25 inch) is fed through a feed hopper and mixed with as much as six to eight times its volume of a mixture of hot spent shale and sand with a nominal temperature of 630 °C (1165 °F) and conveyed up a lift pipe. This mixing raises the average temperature of the raw shale to 530 °C (985 °F), a temperature sufficient to cause the evolution of gas, shale oil vapor, and water vapor. The solids mixture is then delivered to a surge hopper to await additional processing in which more residual oil components will be distilled off. The sand, introduced as a heat carrier, is recovered and recycled. The mixture is then returned to the bottom of the lift pipe and allowed to interact with hot combustion air at 400 °C (750 °F). The carbonaceous fraction is burned as the mixture is raised pneumatically up the lift pipe and transferred to a collection bin where the spent shale fines are separated from gases.

The hydrocarbon gases and oil vapors are processed through a series of scrubbers and coolers to eventually be recovered as condensable liquids and gases. Because the particle size of the oil shale feedstock is small, management of fines is critical throughout the process and involves the use of sedimentation and centrifuging as well as numerous cyclones and electrostatic precipitators.

Retorted shale from the mixer passes through a hopper to the bottom of a lift pipe, with the dust from the cyclone. Preheated air introduced at the bottom of the pipe carries the solids up to the surge bin. Solids are heated by the combustion of the residual char in the shale to approximately 550 °C (1020 °F). In the case when the residual char is not sufficient for this, fuel gas is added. In the surge bin, the hot solids separate from the combustion gases and return to the mixer, where they are brought in contact with fresh oil shale, completing the cycle − a surge bin with baffles facilitates uniform flow of feedstock (Kennedy and Krambeck, 1984).

The Lurgi-Ruhrgas oil shale process (LR process) grew out of an earlier Lurgi process for making high-BTU gas from coal fines. Initially, a solid heat carrier (e.g., sand) was mixed with the coal fines, but later the hot coal char product was recycled to supply the needed heat. The process was tested on a variety of coals, and was used commercially in Germany, England, Yugoslavia, Argentina and Japan. Application to oil shale was a logical extension.

In the LR shale retort, hot solids recycled from a combustor and the raw shale are fed (ratio 6−8:1) to a screw type mixer. Retorting takes place in the mixer and in the surge bin (accumulator) that follows. Gas-solid separation takes place in the surge bin and the following cyclone. Most of the solids are diverted to the lift pipe combustor where burning of the residual carbon raises the temperature to related to 650 °C (1200 °F). The hot solids are separated from the gases and returned to the retort, which is maintained at an optimum retorting temperature in the neighborhood of 535 °C (1000 °F).

The use of the mixer provides rapid heat transfer and allows very short residence times for the product vapors in the hot zone to minimize unwanted cracking. The forced mixing also reduces the tendency for rich shales to agglomerate upon heating, thereby enabling high throughputs. Significantly, this section, which must withstand both heat and abrasion, is not large. As a result, the critical materials problems are confined to a small, manageable section of the overall facility. Also, it is important that no part of the LR retorting system operates at high pressure; maximum pressures are a few inches of water. The product collector section is designed in stages to provide two, and preferably three or more, product fractions. This is not to give fractions defined by boiling range, but rather to avoid oil/water emulsions and for improved dust control. The first section is an underflow scrubber, where the product stream is concurrently cooled and scrubbed by injection of the aqueous product and high-boiling oil. Fine dust not collected in the cyclone is concentrated in the high-boiling oil and the subsequent fractions are essentially dust-free.

For commercial use, provision would be made to recover process heat from spent shale and heat exchangers would be used to recover additional heat. Also, two or three cyclones may be staged for more complete dust removal from the product vapors; and scrubbing would be used in all stages to give efficient cooling and condensation of the product vapors. Electrostatic precipitators would probably be added to reduce particulate emissions in the flue gas from the lift-pipe combustor.

One of the important features of the LR process is its ability to process shale fines; the entire oil shale resource can be utilized in a single type of reactor. Good material balances were obtained in pilot plant operations and oil yields were high from a variety of oil shales; yields were commonly above 95% of Fischer Assay. In favorable cases oil yields went as high as 110% of Fischer Assay. The product oil is 85%−90% volatile, though nitrogen and sulfur levels are high, and pour points are desirably low. Dust in the high-boiling oil is troublesome, but Lurgi has a patented process for oil dedusting. Alternatively, the dust-laden high-boiling oil can be recycled to the mixer. Thus, The LR retort solved two of the most persistent problems of the gas combustion retort, namely low oil yields and inability to process shale fines (i.e., the entire oil shale resource).

Gas products from the LR process are not diluted with combustion gas, so BTU content is high and the gas should be suitable for reforming to produce the hydrogen needed in product upgrading. The aqueous product is only slightly basic and should not require special materials of construction. It does contain phenols and ammonia that may be recovered by steam stripping, however further treatment (e.g., biological oxidation) may be required before the process water is environmentally acceptable for moistening the spent shale.

After removal of the kerogen by retorting and decomposition of some of the carbonates during combustion, the spent shale is friable. Shear applied in the mixer retort does reduce particle size. On the one hand, these characteristics make the combusted shale a very good SOx acceptor, while on the other, the fine particle size means that special care must be exercised in above-ground disposal. This should not normally be a problem, since most of the spent shale would be returned to the mine. Moreover, when moistened, the spent shale acts like a cement and gives a hard, rock-like mass. This will reduce the tendency for dusting of the spent shale, hence should simplify environmentally acceptable disposal.

In summary, the LR process uses relatively simple, inexpensive and reliable hardware to achieve high oil shale throughput and high oil yields with the ability to process the entire oil shale resource. Major environmental concerns, save leachate, have been addressed. On the other hand, the high nitrogen and sulfur contents of the LR shale oil product will make upgrading difficult and expensive. Several suggestions were advanced by workers at Monash University to improve overall efficiency of the LR process when handling oil shale from the Rundle Deposit in Australia. These suggestions included (i) using a fluidized bed solid-solid heat exchanger for improved heat recovery from spent shale, (ii) staged drying of the raw shale with the added benefit of raising low pressure steam, (iii) the use of fluidized bed combustion to give better temperature control than the lift-pipe combustor and thereby lower heat requirements for carbonate decomposition, and (iv) co-pyrolysis of coal with shale to obtain higher liquid yields from a retort of a specific size.

4.14 Nevada-Texas-Utah retort

The Nevada-Texas-Utah retort (NTU retort) is a modified downdraft gasifier that is similar to the gasifier units used in the 19th Century to produce low-Btu gas from coal (Speight, 2013). The retort is a vertical steel cylinder, lined with refractory brick and equipped with an air supply pipe at the top and an exhaust pipe at the bottom. The top may be opened for charging a batch of shale; the bottom for discharging the spent shale after retorting. The batch retort is relatively simple to operate and inexpensive to construct and proved to be durable in operation. The retort is relatively simple to operate, and require no external fuel except for small amounts of gas to start the retorting. The unit can process a wide variety of oil shale with oil recovery on the order of 60%–90% of the Fischer assay yield.

In the process, the retort unit is loaded with crushed oil shale and sealed after which the gas burner is lighted, and air is blown in. Once the top of the shale bed is burning, the fuel gas is shut off but the air supply continues. As the air flows through the burning layer, it is heated to approximately 815 °C (1500 °F) which heats the shale in the lower layers and induces the pyrolysis of the kerogen. The gaseous products and the shale oil are swept down through the cooler portions of the bed to an exhaust port. The solid product from the conversion of the kerogen (residual carbon) remains on the spent shale and is consumed as the combustion zone moves down the retort, thereby providing fuel for additional combustion and heat for additional pyrolysis. When all of the carbon is burned from the upper layers of the bed, the four zones are formed: the top layer contains burned and decarbonized spent shale, the second layer is burning, releasing heat for pyrolysis in the third layer. In the bottom layer, the oil shale is being heated but is not yet at pyrolysis temperatures.

During the 1920s, the NTU Company constructed a 40-ton retort near Santa Maria, California and the US Bureau of Mines (USBMs) constructed a small retort at its Anvil Points facility. This first phase ended in 1930, but interest was revived by the fuel demands of WWII. In Australia, these retorts were used by Lithgow Oil Pty. Ltd. at their facility at Mangaroo. Three 35-ton retorts were constructed, but seldom operated simultaneously due to lack of feed shale. Nevertheless, nearly 2 million gallons of liquids were produced during 1944–45. Interest was also revived in the US Upon passage of The Synthetic Liquid Fuels Act of April 5, 1944, the USBM constructed two identical 40-ton NTU retorts at Anvil Points to provide design data and quantities of shale oil sufficient for refining studies. By the time these retorts were dismantled in 1951, each retort had operated nearly 7000 h to process approximately 18,000 tons of oil shale and produce 6000 barrels of shale oil. Inspection showed that the retorts were still in good condition.

In the 1960s, a 10-ton retort was constructed at Laramie Energy Technology Center (LETC of the United States Bureau of Mines, later the Laramie Energy Research Center (LERC) of the Energy Research and Development Administration (ERDA) and now the Western Research Institute). This retort, and the 150-ton version added in 1968, have been used extensively to study many of the parameters important to in-situ retorting. The 150-ton retort, located just north of Laramie, Wyoming, had an internal diameter of just over 6 feet and height of 45 feet.

To simulate an in-situ retort, the 150-ton unit is generally charged with ungraded shale selected to simulate the wide range of sizes obtained by blasting to produce a rubblized shale bed in an underground retort. Individual shale blocks weighing up to 10,000 lb have been retorted successfully. Oil recovery from shale in the range of 1/2 to 3-1/2 inches ranged from 80% of Fischer Assay for 30 gal/ton grade to 87.5% of Fischer Assay for 50 gal/ton grade. Even very large pieces of shale could be retorted.

The NTU retorts served well as research tools, but as batch units they were not well suited for commercial use. This led to a search for a more efficient and continuous retorting process.

4.15 Oil Shale Exploration Company process

The Oil Shale Exploration Company (OSEC) process has used the Alberta Taciuk process (ATP), a horizontal rotating kiln process, for development of Utah oil shale. This technology was originally developed for mineable oil sands in Alberta, Canada where it went through extensive development and testing in the late 1970s, but its first commercial use in the late 1980s was for clean-up of contaminated soils. From 1999 to 2004 it was used at the Stuart Shale Oil Project in Australia, but the plant has since been closed and dismantled. The process has been considered for a number of other applications in Estonia, China and Jordan. The process is a hot recycled solids process with the main feature of the process being that most of the process steps occur within a single rotating horizontal retort, through the use of multiple chambers. This provides energy efficiency and high yields with process simplicity and a robust design.

The continuous-flow retort, as proposed for production of shale oil shale from Australian oil shale, comprised three stages (Taciuk and Turner, 1988; Schmidt, 2003). In the first stage partially dried oil shale is dried at approximately 250 °C (480 °F) and surface and crystalline waters are liberated from the oil shale. The second stage is the retort stage and is carried out at approximately 500 °C (930 °F) and the kerogen in the oil shale is decomposed to produce shale oil and hydrocarbon. The third and final stage involves combustion of retorted oil shale at 750 °C (1380 °F) and is coupled with hot solids recycle to heat the preceding stages.

The retort has been used in the Stuart oil shale project Australia which produced more than 1.5 million barrels of shale oil (US DOE, 2007). However, the Stuart project has recently opted for the Paraho retort in place of the Taciuk retort.

4.16 Paraho retort

The Paraho retort has been in service in oil shale fields in both Colorado and Brazil. Two versions exist: (i) the direct heating mode retort and (ii) the indirect heating mode retort – both retorts utilize vertical retorting chambers. The retort is typical of vertical-shaft retorts in which crushed shale with the fines removed descends through the retort under the influence of gravity. Zones for each step in processing the shale are maintained by managing gas flow in the retort. This retort can also be operated in an indirect combustion (Section 5.2).

In the direct mode retort (Fig. 14.3), some of the raw shale is ignited in the combustion zone of the retort to produce the heat that pyrolyzes the remaining oil shale present in higher zones. In the indirect mode retort, heat is generated in a separate combustion chamber and delivered to lowermost portion of the retorting chamber.

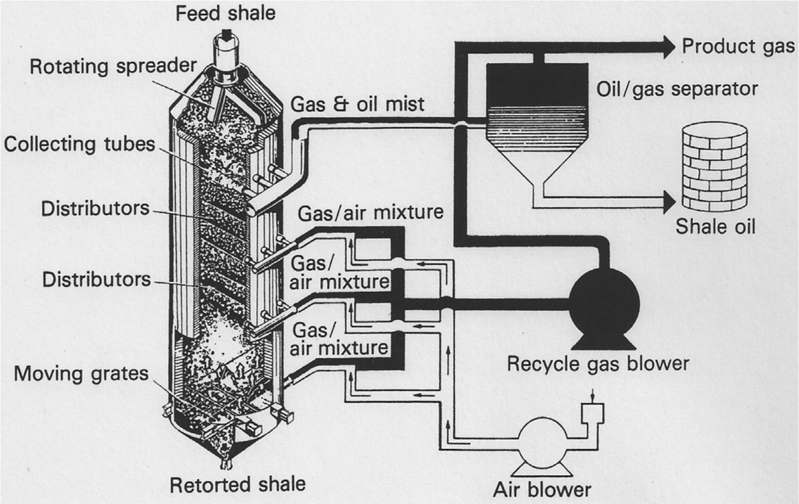

FIG. 14.3 Paraho retort – direct heating mode.

In the direct mode Paraho retort, crushed and sized oil shale is fed into the top of the vertical retorting vessel. At the same time, spent shale (previously retorted oil shale that contains solid carbonaceous char) is ignited in a lower level of the retort. Hot combustion gases rise through the descending raw shale to decompose the kerogen. Shale oil vapor formed in the uppermost portion of the retort are removed for further upgrading in independent facilities. Any gases are cleaned for sale, while a small portion is returned to the retort and combusted together with the spent shale.

4.17 Petroter retort

Petroter technology uses a modified Galoter retort for a pyrolysis (semi-coking) process to treat fine-grained oil shale (0—25 mm fraction) with a solid heat carrier. Through a mixture of oil shale and heated ash in the absence of air, the heating and (by sufficient temperature) decomposition of the oil shale organic matter occurs to produce shale oil and gases.

The oil shale pyrolysis process is effected in a drum rotating reactor in the absence of air, at a temperature of 450—500 °C, (840—930 °F) due to the mixture of oil shale with hot ash — which is used as a as a solid heat carrier. The vapor-gas product mixture that appears in the reactor during the process is fed through several process vessels to for removal of ash and any other mechanical impurities after which the liquid and gases are subject to a distillation process to produce liquid products and gas with high calorific value.

Liquid products are fed to other units for loading as final products or for further processing. Gas is fed to the heat power plant for heat and power production. Steam is fed to the heat power plant for power production. The by-products of this process include phenol water, flue gases and ash from thermal processing.

4.18 Shell shale retorting process

The Shell shale retorting process (SSRP) uses a gas-solid system to achieve rapid heat-up to a temperature where retorting proceeds rapidly will require the use of small particles, due to the low volumetric heat capacity of the gas. Based on the results of 2—3 mm particles would give acceptable average heating rates of 100—600 °C (212—1110 °F) per minute. This requirement for small particle size is expected to lead to a substantial penalty in both capital and operating costs for size reduction in SSRP versus processes that can use larger particles.

Retorting kinetics vary with shale type, due in large part to differences in heat and mass transport within the individual oil shale particles. Because of the need for a relatively long solids residence time (8—12 min) to achieve complete retorting, selection among the various fluidized bed designs was driven by ability to maximize particle holdup. Whereas a dense bed offered particle holdup in the range of 0.45—0.55 and a turbulent bed holdup would be approximately 0.4, holdup in a riser bed design would only be in the range of 0.1—0.2. Moreover, it was found desirable to minimize turbulence to narrow the distribution of particle residence times, hence minimize the reactor volume required to achieve 99% retorting of the average particle. Thus, for both its higher holdup and its narrower distribution of residence times, the dense bed was favored. However, gas fluidized beds are inherently unstable and tend to have a large degree of backmixing associated with the circulation patterns around rising gas bubbles. Beds with large height/diameter ratios (L/D) restrict this circulation, hence tend to lower backmixing. To obtain desirable L/D, while keeping the bed height (hence vapor residence time) at an acceptably low value, would require multiple trains or horizontal staging. For its lower capital cost, the Shell workers chose the latter option with steam as the fluidizing gas.

In order to facilitate close-coupling the various stages within a single housing, the use of rectangular bed sections (instead of the usual circular bed cross-section) was suggested. This suggestion emphasizes the importance Shell attaches to a single train/single unit design in minimizing capital cost. The report indicates that a single unit capable of processing 100,000 tons of oil shale to produce 50,000 barrels of crude shale oil per day could be constructed using the SSRP design.

Other important features of the horizontally-staged design include the following: (i) the fluidizing gas has the primary function of keeping the solids fluidized, (ii) product vapors leave the reactor along a short path, thereby minimizing unwanted cracking, (iii) a large bed area can be made available without incurring a severe penalty from backmixing due to turbulence, (iv) the linear vapor velocity can be kept low enough to minimize fines carry-over, without sacrificing vapor residence time, (v) different sections could be operated at different conditions selected for optimum product yield/quality and a high-boiling product might be recycled to one or more sections for additional cracking to lower-boiling distillates, (vi) products from the different sections could be collected separately by partitioning the gas space without compromising solids staging.

Heat for process can be provided by burning the carbon on the spent shale and three types of fluid bed combustors (FBCs) were indicated as candidates. A bubbling dense bed fluidized bed combustor, similar to those in use for coal combustion (Speight, 2013), but with a gas velocity somewhat below the 2 m/s typical for coal, is an option, which would require a large bed height and a large shale inventory, due to the limited amount of air available for combustion. On the other hand, a dilute phase riser fluidized bed combustor would offer high shale throughput and no shortage of air, but would require a tall reactor to provide sufficient residence time for complete combustion. As a compromise, the use of a fast circulating fluid bed combustor, similar to those now being commissioned for coal combustion, can also be employed. The fast circulating fluid bed combustor combines good lifting power making gravity flow of the hot combusted shale possible with good contacting and burn-out, while maintaining a moderate reactor size.

It is not clear from the cited reports how much experimental work backs up the SSRP design. However Shell, like other major oil companies, has extensive experience in the design, construction and operation of very large fluidized beds (e.g., for catalytic cracking). As with other fluidized bed retorts, the success of the process design may well rest on its ability to control fines. The available reports show that Shell is well aware of this problem, but past the obvious measures of controlling gas velocities and installing high-efficiency cyclones for fines removal, give little hint of the envisioned fines management strategy.

4.19 Superior oil circular grate retorting process

This retort (also called the Superior Oil/Davy-McKee circular grate retort) was developed as a joint effort of Superior Oil (at the time, a subsidiary of Mobil Corporation) and

Davy-McKee, another firm well-established in the material handling and mineral processing field. This retort − a counterflow, gas-to-solid heat exchange process conducted in an enclosed circular grate, which has been used for processing various ores with a relatively high reliability factor − offers environmental advantages over other retorts. The retort is not designed just to recover fuel; it is but one part of the Superior Multi-Mineral approach to efficient oil shale utilization. The retort design is based on the mineral processing technology of Davy-McKee.

The distinctive feature of the Superior Oil/Davy-McKee retorting process is the way crushed shale is fed onto the grate in three layers; the smallest particles (+1/4 inch, the -1/4 inch material is not retorted, but may be burned in a separate unit) are fed directly onto the slotted grate, intermediate sized particles form the center layer and the largest particles are placed on top of the bed. As a result, the largest particles that heat up slowest are exposed to the hottest recycle gases for the longest time. This minimizes the residence time needed to achieve complete retorting, and has the added benefit of minimizing overheating which would be detrimental to subsequent recovery of soda ash and aluminum trihydrate. Laboratory tests carried out in an adiabatic batch reactor were followed by testing of the retorting step in a 250 ton/day pilot plant. Product quality from Colorado oil shale retorted in the Superior retort seems somewhat inferior to that from the Paraho retort.

In the process, oil shale (0.25−4.0 inch) is added, rotated to the first segment of the retort, and heated by a continuously circulating gas medium. Volatilized shale oil mixes with the circulating gas and, together with water, is periodically removed from the gas stream. The partially pyrolyzed shale rotates to the next segment of the retort where it is partially oxidized to complete the kerogen pyrolysis and oil evolution. The spent shale cools in the next segment of the grate as it yields heat to the circulating gas. Additional heat is added to the first segment of the grate where initial pyrolysis of raw shale takes place either through direct or indirect combustion of gases recovered from previous shale retorting. Temperature control results in high hydrocarbon recovery rates and relatively minor amounts of sintering of the inorganic phase of the shale. Recovery yields of shale oil are on the order of 98% w/w of Fisher assay data.

From an environmental perspective, the circular grate it is a sealed operation with hooded enclosures above the grate to capture hydrocarbon gases and shale oil vapor − water troughs (water seals) are installed below the grate where the spent shale is discharged. The water seals not only prevent gas and vapor mist leakage but also provide for the moistening the spent shale that is necessary for safe handling and disposal.

4.20 Superior oil multi-mineral process

The Superior Oil multi-mineral process (also known as the McDowell-Wellman process or circular grate process) heats oil shale in a sealed horizontal segmented traveling grate retort to produce shale oil, gas, and spent residue. The process is suitable for processing of mineral-rich oil shales, such as in the Piceance Basin and has a relatively high reliability and high oil yield.

The multi-mineral process also produces minerals such as nahcolite alumina (Al_2O_3), and soda ash in addition to shale oil and gas (Matar, 1982). The process is basically a four-step operation for oil shale that contains recoverable concentrations of shale oil, nahcolite ($NaHCO_3$), and dawsonite [a sodium-aluminum salt, $Na_3Al(CO_3)_3 \cdot Al(OH)_3$] (Matar, 1982).

The process was originally developed as a stirred-bed, low-Btu coal gasifier. The continuously-fed, circular-moving-grate retort used in this process is a proven, reliable piece of hardware that provides accurate temperature control, separate process zones, and a water seal that eliminates environmental contamination.

The nahcolite has been tested as a dry scrubbing agent to absorb sulfurous and nitrous oxides. The dawsonite in the shale is decomposed in the retort to alumina and soda ash. After the shale is leached with recycled liquor and makeup water from the saline subsurface aquifer, the liquid is seeded and the pH is lowered to recover the alumina. This alumina can be extracted and recovered at a competitive price with alumina from bauxite. The soda ash is recovered by evaporation. The soda ash can be used for a variety of industrial applications such as neutralizing agents. The leached spent shale is then returned to the process.

4.21 Union B retort

This retort was developed by the Union Oil Company of California (Unocal) and is an example of hot inert gas retorting and represents the evolution of Retort A.

In Retort A, with once-through air as combustion gas, peak temperatures at the top of the retort reached 1195−1205 °C (2000−2200 °F). As a result, cracking limited the oil yields to about 75% v/v of the theoretical (Fischer assay) yields. Moreover, heating value of the gas product was low, about 120 BTU/scf, because of dilution with nitrogen and CO_2 from combustion and carbonate decomposition.

Efforts to improve oil yield and heating value of the gas product led to the development of the second generation concept (Retort B) in which case the heat required for retorting is provided indirectly, using a recycle gas stream heated to 510−540 °C (950−1000 °F) in an external furnace. Rundown oil yields are high, were close to the theoretical (Fischer assay yield and the C4+ oil yields) were significantly above Fischer Assay. Moreover, the gas product has a high heating value of over 800 BTU/scf.

In Retort B, the space above the freestanding pile of spent shale is enclosed by a dome to exclude air and heat is provided by a recycle gas stream that is heated in an external furnace. Spent shale falls off the retort by gravity and down discharge chutes through the dome wall into a vessel where it is cooled by a water spray. Steam generated during cooling helps to strip products from pores in the spent shale. The cooled shale is then moistened before being discharged.

The B Retort was tested at a demonstration scale between 1956 and 1958. This retort consists of a vertical refractory-lined vessel. It operates on a downward gas flow principle, and the shale is moved upward by a unique charging mechanism usually referred to as a rock pump. Heat is supplied by combustion of the organic matter remaining on the retorted oil shale and is transferred to the raw oil shale by direct gas-to-solids exchange. The oil is condensed on the cool incoming shale and flows over it to an outlet at the bottom of the retort. The process does not require cooling water (Burnham and McConaghy, 2006).

In the process, crushed shale (0.13−2.00 inch) is fed through two chutes to a solids pump that moves shale upwards through the retort. The shale is heated to retorting temperatures by interaction with a counterflow of hot recycle gas (510−538 °C, 950−1000 °F), resulting in the evolution of oil shale vapor and gas. Heat is supplied by combustion of the organic matter remaining on the retorted oil shale and is transferred to the (raw) oil shale by direct gas-to-solids exchange. This mixture is forced downward by the flow of recycle gas and cooled by contact with cold shale entering the retort in the lower section of the retort. Gas and condensed liquids are separated at the bottom of the retort. The liquids are removed and are further treated for removal of water, solids, and arsenic salts. The gases are sent to a pre-heater and returned to the retort for recovery of heat energy by burning. The captured liquids.

As in Retort A, the Retort B shale oil and the gas stream containing product gas, vapors and mist exit at the bottom of the retort through slots that lead into the disengaging section. Gases from the disengaging section are scrubbed and cooled. Oil and water collected as mist and condensate are separated. The oil is returned to the disengager, while the water is used to moisten spent shale. Part of the scrubbed gas is compressed and heated before being recycled to the retort. The balance is processed by compression and scrubbing to remove heavy ends and sweetened using the Unisulf Process to remove hydrogen sulfide. The sweetened gas is then suitable for use as plant fuel. However, hydrogen requirements for shale oil upgrading are substantial and the made gas is rich in hydrogen. As a result, fractionation to recover this hydrogen may be desirable.

Retort B produces a very high quality shale oil. Pour point, a very important parameter if the oil is to be pipelined, is notably low and the Conradson carbon value also has a very desirable low value. Treatment of this crude shale oil involves water washing (2 stages) to remove solids, removal of chemically bound arsenic to a level of 1 ppm (using a proprietary absorbent), and stripping of light ends to stabilize the oil. Unocal plans to upgrade the crude shale oil by hydrotreating to produce a syncrude that is a premium quality feedstock for a conventional refinery. Thus, the high quality of the Retort B shale oil will eliminate the need for the coking step used to remove refractory material in upgrading Retort A shale oil.

Pollution control devices are integrated into the design for removal of hydrogen sulfide (H_2S) gas and ammonia (NH_3) gas produced during retorting and for treatment of process waters recovered from oil/water separations. Treated waters are recycled, used for cooling the spent shale, or delivered to mining and handling operations and used to moisten the shale for fugitive dust controls.

The reducing atmosphere maintained in the retort results in the removal of sulfur and nitrogen compounds through the formation of hydrogen sulfide and ammonia, respectively, both of which are subsequently captured. Forcing the hot newly-formed oil vapors to contact the cooler shale as it enters the retort results in rapid quenching of the vapors. Additional treatment of the initially formed shale oil and the removal of heavy metals, such as arsenic, results in a final product recovered from the retort that can be used directly as a low-sulfur fuel or delivered to conventional refineries for additional refining.

The retort achieves high yields of shale oil and the retort gas has a high heating value.

5. Indirect retorting

In the indirectly gas heated retort, oil shale is heated through a barrier wall. This type of retort was used mainly before 1960 and is not being developed further because of (i) the small capacity, (ii) expensive heat transfer, and (iii) low thermal efficiency.

5.1 Lurgi-Ruhrgas retort

The Lurgi-Ruhrgas retorting system uses a class 4 retort (Table 14.2) in which hot retorted shale carries pyrolysis heat to oil shale. The process was developed jointly by Ruhrgas A. G. and Lurgi Gesellschaft fur Warmetechnik mbH. The process was developed in the 1950s for low-temperature coal carbonization of coal (Speight, 2013).

In the process, finely crushed oil shale is mixed with hot retorted oil shale in a mechanical mixer that resembles a conventional screw conveyor. Retorting takes place in the mixer, and gas and shale oil vapors are withdrawn. Dust is removed from these products in a cyclone separator and oil is separated from the gas by condensation. Retorted shale leaves the mixer and is sent to a lift pipe where it is heated to approximately 595 °C (1100 °F) in a burning mixture of fuel gas and air. The hot retorted shale is then sent back to the mixer, and the process is repeated. High oil yields have been reported for the retort, and the product gas is of high quality.

5.2 Paraho retort

The Paraho Development Corporation developed new vertical shaft kiln hardware and process techniques and confirmed new technology in the 1960s by building three large commercial lime kilns. In the 1970s the company adapted their lime kiln technology to oil shale retorting. Paraho obtained a lease from the US Department of the Interior in May 1972 for the use of the US Bureau of Mines oil shale facility at Anvil Points near Rifle, Colorado, to demonstrate their retorting technology. The indirect combustion mode bums process gas in a separate furnace and hot gases carry heat to the retort. This retort can also be operated in a direct combustion (Section 4.16).

In the *indirect mode* Paraho retort (Fig. 14.5), the portion of the vertical retorting chamber that was used for oil shale combustion in the direct mode is now the region of the retort chamber into which externally heated fuel gas is introduced. No combustion occurs within the retorting chamber. That separate combustion process is typically fueled by commercial fuels (natural gas, diesel, propane, etc.) that are often augmented with a portion of the fuel gas recovered from the retorting operation.

In the process, finely-ground oil shale enters a feed hopper on top of the retort after which, in a continuous moving bed, the oil shale flows downward consecutively through the mist formation, retorting, combustion, and cooling zones. As the shale descends, heat is efficiently exchanged with a countercurrent flow of recycle gas, which is introduced into the retort at different levels by three specific-purpose gas-air and gas distributors. Near the top of the retort the ambient temperature shale is warmed by rising hot oil vapors and gas, which, in turn, are cooled to form an oil mist that is entrained in the gas.

While they are very similar in operation, the direct and indirect mode Paraho retorts offer sufficiently different operating conditions so as to change the composition of the recovered crude shale oils and gases. Oil vapors and mists leave the direct mode retort at approximately 60 °C (140 °F), while the vapors and gases in the indirect mode leave the retorting vessel at 135 °C (280 °F) and have as much as nine times higher heating values than gases and vapors recovered from the direct mode retort (102 and 885 Btu/ft^3) — oil vapor and mists recovered from the direct mode are diluted with combustion gases from the combustion of the spent shale at the bottom portion of the retort.

The characteristics of the recovered raw shale oil are somewhat different for the direct and indirect mode retorts, but each has characteristics similar to shale oils recovered from other retorts using similar shale heating mechanisms (direct vs. indirect). In addition, gases from the indirect mode retorts have much lower levels of carbon dioxide but generally higher levels of hydrogen sulfide, ammonia, and hydrogen, which are thought to be the result of the indirect mode retort having much less of an oxidizing environment than the direct mode retort (EPA, 1979).

5.3 Pumpherston retort

The Pumpherston retort emerged as the most successful retort of the Scottish oil shale industry in the second half of the nineteenth century. The plant was established in Scotland in 1947, and consisted of two benches with 52 retorts — each with a capacity of 10 tons per day and daily oil production was approximately 530 barrels. Acid was recovered from the acid tars and used to produce ammonium sulfate and the tar was used as refinery fuel.

The Pumpherston retort had the advantages of producing undiluted shale gas and few restrictions on the grain size of the feed shale. The retort was closed down in 1963 because of competition from cheap and imported crude oil.

5.4 Petrosix retort

The Petrosix Process was developed in Brazil, especially for processing oil shale from the Irati Formation (Crawford et al., 2008). The Petrosix process is indirectly heated. In the demonstration plant, a hot recycle gas stream is further heated by gas and injected into the retort to heat and retort the shale. Although the process was developed for the Brazilian Irati shales, the Petrosix technology has also been considered for use with the Eastern US Devonian shale formations.

In the process, crushed shale is fed into the retort at the top, through a feeder designed to prevent horizontal segregation. The shale moves downward through drying, heating and retorting zones against an up-flowing stream of heated recycle gas. The retorted shale then moves down into the lowest section of the retort, where it is cooled by an unheated recycle gas stream before being discharged through one of the hydraulically sealed spent shale hoppers.

Gases and product vapors are carried out of the top of the retort by the recycle gas stream and pass successively through a cyclone for fines removal, an electrostatic precipitator for collection of high-boiling oil mist, heat exchangers where the low-boiling oil and water are condensed, and into the gas treatment section for removal of hydrogen sulfide and recovery of liquefied petroleum gas (LPG) and low-boiling naphtha. Non-condensable gases are compressed and part is used to cool the spent shale, part is heated and injected into the retorting zone, and the balance is used as fuel. Sulfur is recovered in a conventional Claus plant.

Atmospheric and vacuum distillation are used to recover distillate from a composite of the high-boiling and low-boiling oils. The vacuum bottoms will be used as fuel within the oil shale complex. Most oil shale facilities planned for the US have included on-site hydrotreating to stabilize the crude shale oil before pipelining. In contrast Petrosix plans to pipeline a composite of distillate and naphtha to a refinery for hydrotreating. The hydrotreated shale oil will then be refined along with crude oil.

The Brazilian Petrosix retort is also a vertical cylindrical retort (Fig. 14.4) (Scouten, 1990; Hohman et al., 1992; Martignoni, 2002). The retort is 18 ft in diameter, and has a capacity of 2200 tons per day of Irati oil shale. Escape for mechanical differences, the Petrosix retort is similar to the Paraho indirect retort. One operational difference is that the Petrosix spent shale is discharged into a water bath and pumped in a slurry to a disposal pond. Paraho shale is discharged dry, with only a little water added prior to disposal.

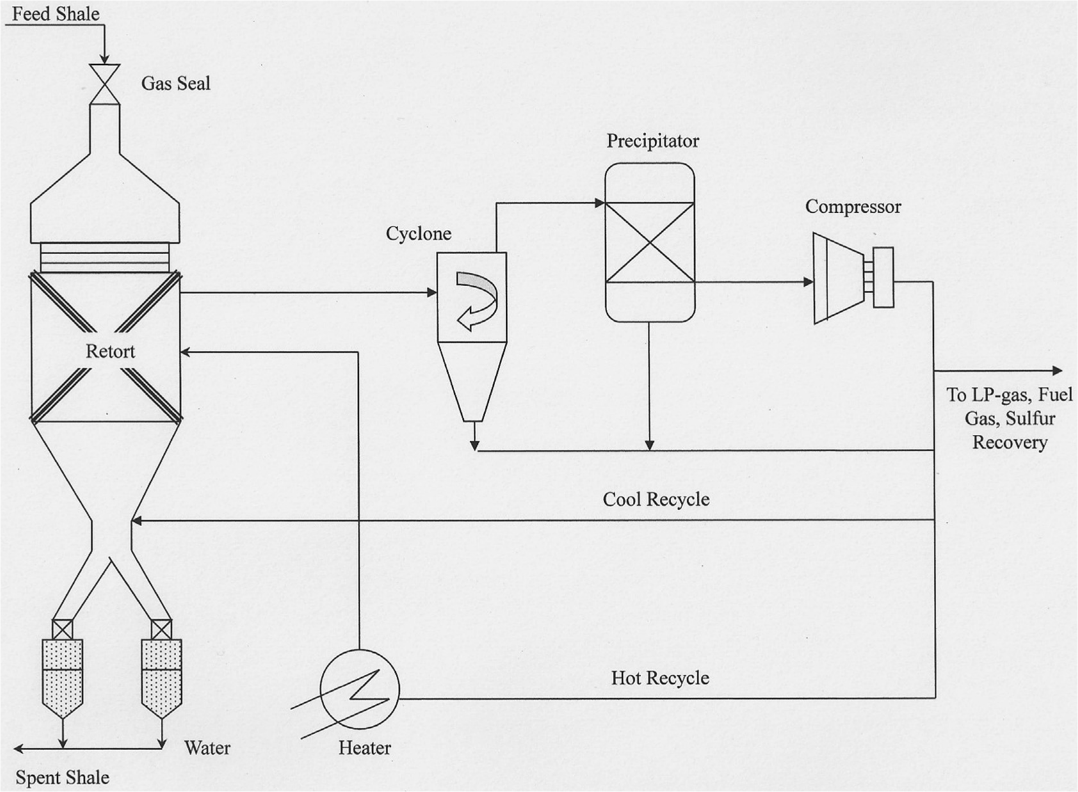

FIG. 14.4 Petrosix retort.

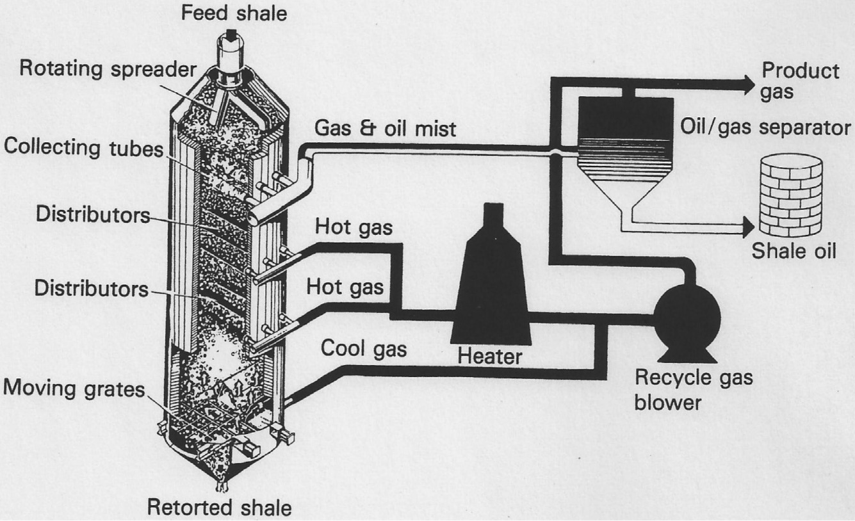

FIG. 14.5 Paraho retort – indirect heating mode.

The Petrosix retort has the upper pyrolysis section and lower shale coke cooling section. Shale oil is produced at 500 °C (930 °F) and is recovered at the top of the retort. The retort off gas is cooled successively by cyclone, electric precipitator, and spraying tower for condensation and part of the cooled retort gas is used as fuel in a tubular heater. Another part of the cooled retort gas is heated to a temperature is excess of 500 °C (930 °F) and recirculated back to the middle of the retort as hot gas carrier for heating and pyrolyzing the oil shale feed. Another part of the cooled retort gas is circulated and enters into the bottom of the retort where it cools the hot shale and, the gas now heated up again, ascends into the pyrolysis section as supplementary heat source for heating the oil shale feed. The cooled shale is discharged from the water seals at the retort bottom.

The advantages of the Petrosix retort are: (i) the retort capacity is high, (ii) the off gas has high calorific value – it is not diluted by nitrogen, and (iii) the oil yield is high, reaching as high 85%–90% of Fischer Assay. However, the thermal efficiency is variable depending upon whether or not the carbon deposited on the shale is utilized.

Petrobras Company at Sao Mateus do Sul built two large Petrosix retorts, one with an inside diameter of 18 feet (built in 1981), for processing lump (6–50 mm) oil shale, the other with an inside diameter of 38 feet (built in 1991). The 38-feet diameter retort has a daily capacity of 1600 tons, with the capital cost of US$35,000,000. The 38-feet diameter retort has a daily capacity of 6200 tons, with the capital cost of US$93,000,000.

5.5 Salermo retort

In the Salermo retort, small oil shale particles (<25 mm) were progressively shoveled through a series thirty six of semicircular troughs (sixteen inches in diameter) heated from the underside by combustion of non-condensible gases. Each of the ten externally-heated retorts processed approximately 670 to 70 tons of oil shale per day to produce 810 barrels of shale oil per day − approximately 90% of Fischer assay. The spent shale containing large quantities of residual carbon (up to 40%) was discarded (Steele, 1979).

This type of retort was operated near Ermelo, Transvaal (South Africa), in 1935. The plant was closed in 1962; by that time it had exhausted its oil shale resources. At present, one Salermo retort is still in operation in Clerbagnoix, France, to produce high sulfur shale oil.

5.6 Shell pellet heat exchange retorting process

The Shell Development Company addressed the Tosco drawbacks of high capital cost, mechanical complexity and heat inefficiency in their design of the Shell Pellet Heat Exchange Retorting (SPHER) Process. While never progressing past the experimental stage, a brief discussion of this process is worthwhile, since it was an important conceptual bridge in the evolution of the newer fluidized bed processes. The SPHER design grew out of the experience of Shell with fluidized beds in refinery processes, such as riser transport and catalytic cracking in dense beds, the former operating at relatively high and the latter at relatively low superficial gas velocities. The key features of the SPHER process are countercurrent flows of shale and the heat exchange pellets for improved heat efficiency and the use of fluidized beds for low capital cost.

As conceived, the SPHER process uses two loops for circulation of the heat transfer pellets or balls. In the cool ball loop, balls fall from the preheater into a countercurrent fluidized bed for recovery of heat from the spent shale. A pneumatic riser transports the balls to the top of the cool ball loop, where they rain down through the up-flowing shale in the preheater. In the hot ball loop, after heating in a ball heater (riser/lift-pipe combustor or Tosco-type) the heated balls fall through a dense bed of shale fluidized by superheated steam in the retorting vessel. Segregation of the two ball loops allows the size of the different elements and the size and material of the balls to be tailored to each specific task, while high throughput and mechanical simplicity are maintained throughout. Projected thermal efficiency of the SPHER process was 67%, giving it a 4% advantage over Tosco II and a 9% advantage over the Paraho process.

While preliminary Shell economics indicated that shale oil from the SPHER process would be approximately 15% less expensive than Tosco shale oil, due primarily to lower capital cost, the retorting operation was still relatively complex and required heat transfer pellets. To obtain reliable fluidization in the SPHER beds was found to require grinding to -1/16 inch size. Such grinding would be expensive, even using staged grinding with oversize recycle, especially for hard, relatively rich shales, such as those from Green River and Jordan. Also, agglomeration of small particle of relatively rich shale would seriously impair the operability of the fluidized beds. Balanced against these factors are the benefits of fast heat-up and low vapor residence time in the retort, both of which contribute to increased yields of high-value liquids. Other workers at Shell and at Exxon have realized the capital cost advantages of fluidized bed retorting and have begun to study ways of further reducing costs and improving operability in fluidized bed retorting.

5.7 Tosco II process

The Tosco (The Oil Shale Corporation) process used a rotating kiln that was reminiscent of a cement kiln in which heat was transferred to the shale by ceramic balls heated in an exterior burner (Fig. 14.6) (Whitcombe and Vawter, 1976). The process, which was initiated in the 1960s and 1970s and is more correctly described as a retorting/upgrading process (US OTA, 1980).

This process employed a rotary type kiln utilizing ceramic balls heated in external equipment to accomplish retorting. Shale reduced to one-half inch size or smaller is preheated and pneumatically conveyed through a vertical pipe by flue gases from the ball-heating furnace. The preheated shale then entered the rotary retorting kiln with the heated pellets where it is brought to retorting temperature of 500 °C (930 °F) by conductive and radiant heat exchange with the balls. Passage of the kiln discharge over a trommel screen permits recovery of the balls from the spent shale for reheating and recycling. The spent materials are then routed to disposal.

Development of the Lurgi-Ruhrgas process by Tosco Corporation (formerly The Oil Shale Corporation) began in 1955 as an attempt to overcome the shortcomings of the USBM gas combustion retorting process. Exploratory work proceeded through a 25 ton/day pilot plant built in 1957 at Golden, Colorado and a 1000 ton/day semi-works plant constructed at Parachute Creek, Colorado in 1965 to detailed engineering design work completed in 1968 for a 66,000 ton/day commercial facility – the Colony project. To implement the recommendations of the 1968 study, a second phase of developmental work was carried out in the 1000 ton/day plant for acquisition of the data necessary for construction of the commercial facility.

Initially, the commercial facility was a joint venture of Tosco (40%) and Arco (60%), with Arco as the operator, but in 1980 Exxon acquired the interest owned by Arco and assumed the role of operator. Construction of the facility and the associated town of Battlement Mesa, began in 1980. However, faced with increasing project cost estimates, ultimately reaching approximately $7 billion (nearly twice the original estimate, due in large part to high

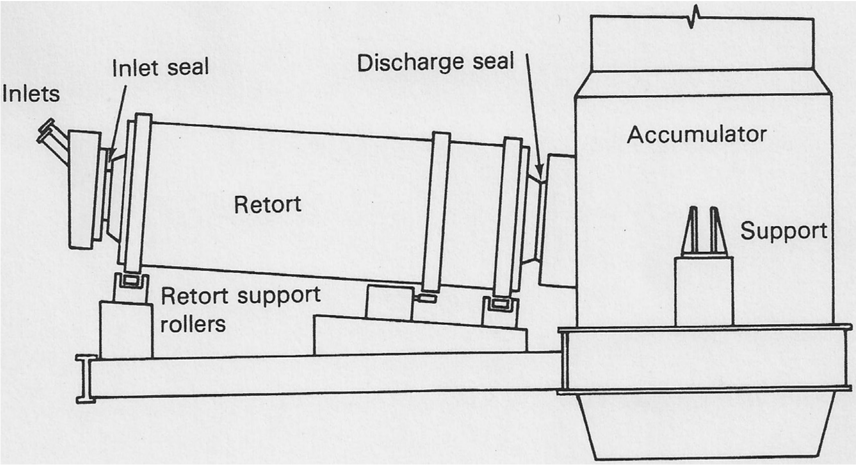

FIG. 14.6 Tosco retort.

interest rates) and lower crude oil prices, the project was terminated early in 1982. At that point, Exxon acquired interest (amounting to 40% of the project) owned by in the Colony project.

In the process, oil shale — crushed and sized (nominally to 112 in.) raw oil shale and preheated to 260 °C (500 °F) by interaction with flue gases from the ceramic ball heater — is introduced into a horizontal rotary kiln together with 1.5 times its weight in previously heated ceramic balls. The temperature of the shale is raised to its minimal retort temperature of 480 °C (900 °F). The kerogen is converted to distillable shale oil that is fed to a fractionator for hydrocarbon recovery and water separation. Spent shale and the ceramic balls are discharged and separated; the ceramic balls are returned to their heater; and the spent shale is cooled, moistened for dust control, and removed for land disposal. The fractionator separates the shale oil hydrocarbon vapors into gas, naphtha, gas oil, and higher-boiling *bottom oil*.

The gas, naphtha, and gas oil are sent to various upgrading units, while the bottom oil is sent to a delayed coking unit, where it is converted to lower-boiling products and by-product coke. Gas oil and raw naphtha are both upgraded in separate hydrogenation units through reaction with high-pressure hydrogen (produced on-site from steam reforming of the fuel gas originally recovered from the retort) (Dinneen, 1976; US OTA, 1980).

In the Tosco process, hot ceramic balls are mixed with smaller oil shale particles in a rotating drum retort. After retorting, the ceramic balls are separated from the spent shale and reheated in a separate ball heater using gas as the fuel. The feed streams to the Tosco retort are 1/2-inch ceramic balls heated to approximately 690 °C (1270 °F) and the oil shale crushed to pass a 1/2-inch screen and preheated by contact with hot flue gases from the ball heater. The streams are rapidly mixed under an inert atmosphere. Heat transfer is rapid and at the exit of the retort the shale and ceramic balls are essentially the same temperature and the shale is fully retorted. Retorting in the Tosco process is carried out in a rotating drum that is mechanically a simpler device than the screw mixer of the Lurgi process, but like the Lurgi retort is only a small part of the total facility.

However, unlike the Lurgi process heat for the Tosco retort is provided by gas, not combusted shale. The independence of gas flow and shale flow effectively decouples retorting from heat generation and gives the Tosco retort unusual latitude for processing shales of widely varying grades. Oil yields from the Tosco retort generally exceed Fischer Assay. An oil yield nearly 108% of the Fischer Assay was obtained from one 7-day test in the semiworks plant. Product vapors from the retort are passed through a separator to remove fines, then into a fractionator that yields high-boiling oil, distillate, naphtha and product gas streams. Because combustion is separated from retorting in the Tosco process, the product gas is a high-BTU stream that may be used as plant fuel or reformed to give hydrogen for liquid product upgrading.

The ceramic balls and spent shale discharged from the retort are fed into a cylindrical screen (trommel) inside the spent shale accumulator housing. The ceramic balls, being larger than the holes in the screen, pass through the accumulator and are recycled to the ball heater by a bucket elevator. The spent shale falls into the accumulator at approximately 480 °C (900 °F) and passes into a rotating heat exchanger where its heat is used to raise steam in water-filled tubes. The spent shale is further cooled in the moisturizer where is water content is increased to 12%—13% to reduce dusting before disposal.

One commercial-size Tosco retort would process approximately 11,000 tons of oil shale/day to produce 4500 barrels of crude shale oil. Properties of a typical oil produced from Mahogany zone Green River oil shale are similar to those of a low-sulfur crude – with three very important exceptions: olefin and nitrogen contents are high, which make the oil very unstable with respect to sludge and sediment formation. Like other oils from Green River shales, the Tosco oil also has a high content of arsenic that is a powerful poison for the catalysts needed for efficient upgrading.

The typical spent shale produced by the TOSCO-II process was a fine-grained material (containing approximately 4.5% w/w of organic carbon via char formation) comprising approximately 80 mass% of the raw oil shale feedstock. The mineral constituents of spent shale consisting of principally dolomite, calcite, silica, and silicates are mostly unchanged by the retorting process treatment, except that some carbonate minerals such as dolomite have decomposed to oxides liberating carbon dioxide. During the retorting process, significant size reduction is also taking place, yielding the particle (grain) size of most spent shale finer than 8 mesh. One problem with the system was slow destruction of the ceramic balls by contact with the abrasive shale particles.

Shale fines could be processed, making it possible to utilize the entire shale resource. The gas by-product was not diluted with combustion gases, hence had a high value for heating or hydrogen production. The process design afforded both good operability and an unusually high degree of flexibility in control and in ability to handle shales of varying richness. However, operability and flexibility were obtained only at the cost of expensive hardware, making the Colony Project very capital-intensive. This last factor, coupled with the high interest rates of the early 1980s and uncertain crude oil prices ultimately led to the demise of the Colony Project that would have used Tosco II retorting technology. Finally, even though flue gas heat was recovered in preheating the shale and spent shale heat was used to raise steam, the Tosco II process was relatively heat inefficient because of the concurrent flows of heated balls and cooler shale.

In summary, the Tosco II Retorting Process achieved several important technical goals: Oil yields were high; consistently at or above Fischer Assay.

6. Other processes

While mining followed by retorting in the *conventional* method of converting the kerogen in oil shale to products, there is also the need for alternative options such as the use of extraction by supercritical fluids or the gasification of the kerogen in the mined shale. These options, while not being the complete answer to the issues of oil shale use to provide fuel and chemicals, do offer reason for further consideration as processes for the future and are presented below.

6.1 Extraction using supercritical fluids

White not a retorting process in the strictest sense, there is another thermal option for oil shale extraction/conversion to liquid products using supercritical fluids.

A fluid is subcritical if it exists at a temperature between its atmospheric boiling point and critical temperature. For example, water has a critical temperature and pressure of 400 °C (750 °F) and 3200 psi respectively and supercritical fluids have lower viscosity and higher diffusivity, compared to normal liquid solvents. This leads to increased penetration capacity of supercritical fluids into shale samples, thereby promoting higher kerogen decomposition. This extraction process is carried out in a fixed bed reactor equipped agitation (Deng et al., 2012).

In such a process, mined oil shale is crushed to very small particles and kept inside the reactor. The reactor is heated externally to the desired temperature. Supercritical fluid pump is used to pump the solvent into the reactor at a high pressure (Allawzi et al., 2011). The solvent changes from pressurized liquid to supercritical fluid by the end of the process due to external heating at a constant rate. The amount and composition of the extract depends on many process parameters such as (i) grain size of the oil shale, (ii) reactor temperature, (iii) duration of the extraction process, and (iv) water to oil shale ratio.

The yield of extract decreases with an increase in grain size due to a reduction of the diffusion ease with an increasing surface area and inter-particle path blockage (Allawzi et al., 2011). An increase in temperature leads to increase in solubility of extract in solvent, which leads to a higher yield of liquid extract, which later reduces as solvent density decreases. Supercritical water extraction leads to an increase in the yield of paraffin and aromatics and a decrease in asphaltene yield with an increase in temperature.

Increase in extraction time for supercritical water extraction leads to increase in oil yield, particularly concentration of paraffin and aromatics, and a decrease in concentration of polar compounds. However, no significant increase in yield was observed by increasing the extraction time for supercritical carbon dioxide extraction with co-solvents, hexane and acetone (Allawzi et al., 2011). In oil shale extraction using gases (carbon monoxide, hydrogen, nitrogen), increasing the water to oil shale ratio to 3:1 resulted in a decrease in oil yield, an increase in hydrocarbon gas yield and carbon dioxide yield due to calcium carbonate decomposition (El Harfi et al., 1999; Fei et al., 2012).

A better conversion rate and higher composition of light oil extract are obtained by using water as supercritical fluid compared to toluene (Hu et al., 1999). Polar components are more easily decomposed with water than with toluene but, however, the yield of nonpolar hydrocarbons is unaffected by solvent (Funazukuri et al., 1988). Co-solvents like hexane and acetone assist in extraction, reducing the required operating conditions needed (pressure, temperature etc.), thus lowering the operating cost (Allawzi et al., 2011).

The subcritical water extraction process has been used to extract hydrocarbons from Huadian oil-shale (Deng et al., 2012). On comparing the subcritical water extraction and retorting methods carried out under exactly similar process conditions, it was found that subcritical extraction technique is more advantageous. It has a promising future in the industry as it promotes an eco-friendly technology (Deng et al., 2012).

Oil shale extraction using supercritical and subcritical solvents have the advantages of lower energy requirements, higher efficiency, selective extraction, good quality of yield with higher hydrogen/carbon ratio and lower olefin content. However, these processes are still mostly in experimental stages and have a long way to go to be used commercially due to the high cost of solvent requirement and its processing.

6.2 Gasification

A conventional gasification process involves the reaction between organic carbon and steam in a limited oxygen environment; the reaction products are mainly synthesis gas with impurities which are usually separated from the product to produce a clean synthesis gas (a mixture of carbon monoxide and hydrogen) that can be used to produce a wide variety of hydrocarbon derivatives and chemicals as well as for the generation of steam and electricity (Speight, 2013, 2019b; Luque and Speight, 2015).

Gasification in dense pressurized bed or burning in a circulating fluidized bed is the most promising means for extracting low grade oil shale (Simonov et al., 2007). Gasification of oil shale has been in existence for many decades. In Estonia, gases from oil shale gasification were used to be mixed with natural gas from Russia, but the low price of natural gas wiped the gas out of the market. The first oil shale gasification was carried out in a coal gasification retort, this led to a low conversion rate on the order of 38–40% w/w.

Another type of gasification uses a plasma arc of air or steam to break down oil shale (Al-Amayreh et al., 2011; Janajreh et al., 2013). The process requires the use of plasma to provide the heat required for gasification in a process known as plasma gasification. Plasma is an ionized gas that is an excellent conductor of heat and electricity and can be generated from a plasma torch.

Efficiency and environmental impact of gasification depends on the method used. Conventional gasification processes have an average efficiency on the order of 72%, while plasma gasification processes have an average efficiency on the order of 42% (Janajreh et al., 2013). Plasma gasification reduces significantly the pollutant generated compared to conventional gasification processes.

7. The future

The fundamental issue with all above-ground oil shale retorting technologies is the need to provide large amounts of heat energy to thermally decompose the kerogen to liquid and gas products. More than one ton of shale must be heated to temperatures in the range 425–525 °C (850–1000 °F) for each barrel of oil generated, and the heat supplied must be of relatively high quality to reach retorting temperature. Once the reaction is complete, recovering sensible heat from the hot rock is very desirable for optimum process economics.

This leads to three areas where new technology could improve the economics of oil recovery: (i) recovering heat from the spent shale, (ii) disposal of spent shale, especially if the shale is discharged at temperatures where the char can catch fire in the air, and (iii) concurrent generation of large volumes of carbon dioxide when the minerals contain limestone, as they do in Colorado and Utah.

Heat recovery from hot solids is not always efficient – the major exception to this generalization is in the field of fluidized bed technologies where the technologies are mature and practiced in several industries, particularly in the crude oil industry. However, to apply fluidized bed technologies to oil shale would require grinding the shale to sizes less than approximately 1 mm, an energy intensive task that would result in an increased disposal problem. Such fine particles might be used in a lower temperature process for sequestering carbon dioxide, with the costs of grinding now spread over to the solution of this problem.

Disposal of spent shale is also a problem that must be solved in economic fashion for the large-scale development of oil shale to proceed. Retorted shale contains carbon as *char*, which may represent more than 50% w/w of the original carbon value in the oil shale feedstock. The char is potentially pyrophoric and can burn if disposed into the open air while hot. In addition, the process results in a solid that occupies more volume than the fresh shale because of the problems of packing random particles. This is analogous to the tar sand (plants) in northern Alberta (Canada) where the sand from the process occupies more space than the original tar sand there being an approximate 120% increase in volume (Speight, 2009, 2014).

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CHAPTER

15

In situ retorting

1. Introduction

An attractive alternative to surface retorting processes is the in situ retorting process (*underground retorting process*) (Scouten, 1990; Lee, 1991; Lee et al., 2007; US DOE, 2010, 2011). There are many reasons to develop in situ techniques for recovering oil from the oil shale. In surface processing, approximately 80% w/w of the material mined must also be disposed of as inert inorganic material, which presents serious environmental problems and adds considerably to the cost of the oil produced. In addition, half or more of the shale oil reserves are contained in the lower grade shale, ranging down to 10 gallons of shale oil per ton of oil shale. Only by in situ retorting can oil be economically recovered with high grade sections. The in situ retorting process involves (i) hydraulic pressure, (ii) chemical explosives, and, in the more risky schemes, (iii) the use of the more unconventional nuclear explosives which, if contained correctly, generate sufficient heat to convert the kerogen to liquid product that remains in the ground until pumped to the surface. Typically, the heat necessary top convert the kerogen to liquid products is supplied either by underground combustion or by introducing heated gases or liquids into the oil shale formation.

Thus, in situ retorting is usually carried out by introducing air to burn and pyrolyze the underground oil shale layer in order to obtain shale oil and offers the potential of recovering shale oil from deeply buried oil shale (Scouten, 1990; Lee, 1991). In-situ processes can be technically feasible where permeability of the rock exists or can be created through fracturing. *True in-situ* processes do not involve mining the shale. The target deposit is (i) fractured, (ii) air is injected, (iii) the deposit is ignited to heat the formation, and (iv) the resulting shale oil is moved through the natural or man-made fractures to production wells that transport it to the surface. In true in-situ processes, difficulties in controlling the flame front and the flow of pyrolyzed oil can limit the ultimate oil recovery, leaving portions of the deposit unheated and portions of the pyrolyzed oil unrecovered.

In-situ processing is attractive because the requirements for mining, hauling, crushing and grinding the oil shale rock are eliminated or greatly reduced. Thus, in situ retorting offers the potential for corresponding savings in both capital and operating expenses. Above-ground retorting, on the other hand, generally affords better control of retorting conditions that can minimize heat loss due to carbonate decomposition and lead to a better yield of higher-quality products. Novel processes, using supercritical solvent extraction or

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TABLE 15.1 Methods of oil shale resource development.

Method	Comment
Surface mining with surface retorting	The ore is produced from open cast surface mines, crushed, and processed in surface retorts.
Underground mining with surface retorting	The ore is mined, transported to the surface, crushed, and then heated in surface vessels to produce liquids and gases, after which the processed shale is disposed of in the mine and other disposal areas.
Modified in-situ (MIS)	The process has improved the pyrolysis and recovery efficiency of in situ combustion processes by fracturing the resource to improve heat transfer and fluid flows through the shale.
True in-situ (TIS)	Heat is applied to the subsurface oil shale resource without mining; the focus is on applying heat without any combustion of the resource as earlier some of the shale was combusted at one end of the deposit to generate heat at pyrolysis temperatures to produce liquids and gases.

bioleaching to recover shale oil, are still in the early experimental stages, but appear to have the potential for use either above- or underground.

As opposed to the mining methods (Table 15.1) (Chapter 14), the in situ production methods target deep, thick shale formations which may initially produce shale oil but still contain large amounts of kerogen and shale oil trapped by residual kerogen blocking the fine pores in the shale rock. Directionally these methods will provide access to a much larger volume of oil shale, can be applied incrementally as there is no major investment in mine development, and should result in lower land, air and water impacts. None of these processes are yet commercial so it is unclear which process is most likely to proceed, although the Shell in-situ conversion process seems to be furthest along and has been piloted in both oil shale and oil sands formations (Crawford et al., 2008a).

However, both conventional and in situ retorting processes result in inefficiencies that reduce the volume and quality of the produced shale oil. Depending on the efficiency of the process, a portion of the kerogen that does not yield liquid is either deposited as *coke* (a carbonaceous residue) on the host mineral matter or is converted to hydrocarbon gases. For the purpose of producing shale oil, the optimal process is one that minimizes the regressive thermal and chemical reactions that form coke and hydrocarbon gases and maximizes the production of shale oil.

Nevertheless, considering the magnitude of the shale resources and the continuing depletion of crude oil resources. There are many reasons to develop in situ techniques for recovering the oil from oil shale. In surface processing, as already stated, approximately 80% w/w of the material mined must also be disposed of as inert inorganic matter, which presents serious environmental problems and adds considerably to the cost of the oil produced. In addition, half or more of the shale oil reserves are contained in the lower grade shale, ranging down to 10 gallons of shale oil per ton of oil shale. Only by in situ retorting can oil be economically recovered with high grade sections. The in situ retorting process involves hydraulic pressure, chemical explosives, and the more unconventional nuclear explosives. Heat is supplied either by underground combustion or by introducing heated gases or liquids to the oil shale formation.

In-situ retorting is usually carried out by introducing air to burn and pyrolyze the underground oil shale layer to obtain shale oil (Scouten, 1990; Lee, 1991). This process obviates the problems of mining, handling, and disposing of large quantity of material, which occurs for aboveground retorting. In-situ retorting offers the potential of recovering the deep buried oil shale. However, the true in-situ method is not usually successful, because oil shale lacks permeability, thus hindering the inflow of air and outflow of produced oil and gases and also lowering the heat transfer into the oil shale deposit.

In the in situ retorting process, heat is supplied either by underground combustion or by introducing heated gases or liquids to the oil shale formation. Two methods of in situ oil shale retorting have been tested. The ″true″ in situ method consists of fracturing, retorting, and recovering the products through the use of boreholes from the surface. The modified in-situ method involves subsurface mining to create a void, blasting the adjacent oil shale into this void area and then retorting it.

Modified in-situ retorting is a variant of the in situ approach and has made some progress. In this process, a volume of the formation beneath the retort zone is mined and the shale to be retorted is rubblized by a series of staged explosions. This process provides improved access for the air needed for combustion. The rubblized shale is retorted in place, and the mined shale is sent to surface retorts. Occidental Petroleum was the principal developer of modified in-situ retorting technology. During the early 1980s, several companies expressed interest in using the Occidental technology in commercial operations.

In-situ processing presents the opportunity of recovering shale oil from deep, even low-grade, these low-grade deposits, and the main idea in in-situ combustion is burning a portion of the oil shale to produce sufficient heat to retort the remainder. In-situ processes introduce heat to the kerogen while it is still embedded in the natural geological oil shale formation. There are two general approaches to the in-situ production of shale oil: (i) *true in-situ processes* in which there is minimal or no disturbance of the ore bed and (ii) *modified in-situ processes* in which the bed is given a rubble-like texture (rubbelized), either through direct blasting with surface up-lift or after partial mining to create void space.

Both conventional and in-situ retorting processes result in inefficiencies that reduce the volume and quality of the produced shale oil. Depending on the efficiency of the process, a portion of the kerogen that does not yield liquid is either deposited as *coke* (a carbonaceous residue) on the host mineral matter, or is converted to hydrocarbon gases. For the purpose of producing shale oil, the optimal process is one that minimizes the regressive thermal and chemical reactions that form coke and hydrocarbon gases and maximizes the production of shale oil.

The advantages of in-situ processing include: (i) oil can be recovered from deep deposits of oil shale formation, (ii) mining costs can be eliminated, or minimized, (iii) issues related to solid waste are eliminated, (iv) shale oil can be extracted from leaner shale, e.g., deposits containing less than 15 gallons of shale oil per ton of oil shale, (v) the process is ultimately more economical due to elimination or reduction of costs involved with mining, transportation, and crushing.

However, disadvantages are also evident in in-situ processing (Fang et al., 2008) and these include: (i) subsurface combustion is difficult to control due to insufficient permeability within the shale formation, (ii) drilling costs are still high, (iii) recovery efficiencies are generally low, (iv) it may be difficult to establish the required permeability and porosity in the shale formation, and (v) there is the potential for aquifer contamination − if not controlled or treated, effects may linger for an extended period of time even after the project completion.

Modified in-situ retorting is a more amenable approach to solve the problems related to low-to-zero permeability and low-to-zero porosity. In the process, an upper portion of the oil shale bed is taken out to the surface by conventional mining to provide the desired void volume of the resulting underground retort. Then the oil shale deposit adjacent to the void portion is fractured, by using conventional explosion, to rubble which expands to the void volume. Combustion is initiated with inflow of air at the top of the shale rubble in the underground retort, with the burning front descending through the rubble bed at the rate of several feet per week. Ahead of the combustion zone, the hot combustion gas creates a pyrolysis zone, where oil shale is thermally decomposed. The produced shale oil produced flows to the bottom of the rubble and is pumped to the surface.

This chapter will provide a basic description (with some degree of detail) of the principles and processes that lie behind the in situ development and the production of oil of from oil shale formations. The processes that were considered before abandonment of the projects, although being shelved during the current economic situation, may not have been fully abandoned and other methods that were under development in the early 1980s may be taken off the shelf and reactivated in the same forms or in modified forms, when the occasion arises. As will surface processes all methods require the heating of the in-situ kerogen to temperatures above 300−350 °C (70−660 °F) to accelerate maturation of the kerogen in the oil shale rock. The temperature of the process, which can have a significant effect in an ex situ retort and an institute retort, on the character of the products (Lan et al., 2015), s needed are generally lower than surface retorts as resident time and vessel size are not as critical to the economics.

2. Principles

In situ retorting involves heating the shale in-place to produce shale oil and gas. This process eliminates (or, at least, greatly reduces) the obvious problems of mining, handling, and disposing of large quantities of material, which occurs for above-ground retorting. In-situ retorting offers the potential of recovering deeply deposited oil shale.

In the process, heat (various forms are employed from combustion to radio frequency heating) is injected into the formation or the use of linear or planar heating sources followed by thermal conduction and convection to distribute heat through the target area of the formation after which shale oil is then recovered through vertical wells drilled into the formation (Scouten, 1990; Lee, 1991). These technologies are potentially able to extract more shale oil from a given area of land than conventional ex situ processing technologies, as the wells can reach greater depths than surface mines and present the opportunity to recover shale oil from low-grade deposits that would be physically and economically inaccessible using mining techniques.

True in situ retorting also eliminates the costs of an above-ground retort. Thus, in situ retorting offers the potential for corresponding savings in both operating and capital costs. However, making an in situ retort work is generally difficult because most oil shales have very low porosity and almost no permeability. Without permeability, getting combustion air into the oil shale formation, or oil and gas products out of the formation is not possible.

Permeability can be induced, for example, by blasting or by injecting high pressure air or water. However, maintaining such induced permeability is difficult because shale oil tends to fill the void space in the bed and because oil shale swells (exfoliates) upon heating. Attempts to induce and maintain permeability have led to the two main in situ retorting approaches: (i) true in situ methods − sometimes referred to as TIS methods − that involve blasting and/or other fracturing techniques, but no mining, and (ii) modified in-situ methods − sometimes referred to as MIS methods − that involve mining part of the shale to generate free underground space followed by blasting to generate a permeable zone of rubblized oil shale for retorting. Both true and modified in-situ methods use a moving flame front to generate heat for retorting, hence are similar in basic principle to the above-ground NTU Retort described later.

In a few areas of the Green River Formation, leaching of water-soluble minerals affords a porous zone of high permeability. One such case is the *leached zone*, located below the rich *mahogany zone* and extending across much of the Piceance Creek Basin. The BX In Situ Oil Shale Project was an attempt to take advantage of this natural permeability.

In the early 1960s, Laramie workers began to lay the foundation for development of in situ retorting technology for Green River oil shale. Data obtained from the above-ground 10- and 150-ton NTU Retorts at Laramie provided basic information related to the ignition of rubblized shale beds and the use of a moving combustion front to provide heat for retorting. A series of nine field experiments to explore true in situ retorting were carried out in the Green River Basin near Rock Springs, Wyoming. The major object of these experiments was to demonstrate that fracturing of the oil shale formation could induce sufficient permeability to support underground combustion. A variety of techniques − electrical, hydraulic and explosive − were evaluated for inducing permeability.

The major objective of the Laramie studies was met and sufficient permeability was induced for combustion to be initiated, and for the combustion front to be maintained and moved through the rubblized shale bed. Although post-burn coring established that significant amounts of shale were heated in the retort, in the cases where in situ combustion was sustained, oil recoveries were poor. In part, this was due to recurring problems with pumps that plugged with shale debris. However, non-uniform combustion and inadequate product containment also contributed to low oil recovery in these exploratory studies.

In parallel with, and following, the test burns, Laramie workers carried out an extensive program of environmental studies. These studies identified the disposition of the produced retort water as a key environmental concern. This water is produced during thermal retorting and is derived from dehydration of shale minerals, as well as from combustion. The intrusion of ground water may also contribute to the water recovered with the oil. Retort water is odoriferous, yellow to brown in color and contains high levels of both organic and inorganic dissolved constituents. It is usually basic, with a pH in the range of 8−9.5. The amount of retort water is large; approximately equal to the volume of oil produced, in favorable cases. However, testing revealed that the retort water is not particularly toxic, and indicated that standard purification techniques should be adequate for its environmentally acceptable disposal.

The true in situ retorting processes discussed above involved drilling, but no underground mining. In contrast, the modified in-situ methods discussed below involve mining approximately 15%−40% of the shale to create void space within the formation, then blasting to rubblize the remaining shale to fill the resulting retort. The retort is ignited at the top and burned with a downflow of air.

3. Processes

During the oil shale boom of the 1970s and 1980s, in situ retorting was selected as alternative to surface retorting processes because the method does not generate the amount of waste disposal that accrues from mining and surface retorting. In surface processing, approximately 80% w/w of the material mined must also be disposed of as inert inorganic matter, which presents serious environmental problems and adds considerably to the cost of the oil produced. Only by in situ retorting can oil be economically recovered with high grade sections. The in situ retorting process involves hydraulic pressure, chemical explosives, and the more unconventional nuclear explosives. Heat is supplied either by underground combustion or by introducing heated gases or liquids to the oil shale formation and recovering any oil and gases produced from the heated deposit through wells, and transporting the liquid to an upgrading facility (US OTA, 1980). The most widely tested in situ retorting technology involved burning a portion of the shale underground to provide the heat necessary to retort the remaining shale. This method achieved little success due to temperature and combustion instabilities (US OTA, 1980; Bartis et al., 2005).

The advantages of in-situ processing include: (i) oil can be recovered from deep deposits of oil shale formation, (ii) mining costs can be eliminated, or minimized, (iii) issues related to solid waste are eliminated, (iv) shale oil can be extracted from leaner shale, e.g., deposits containing less than 15 gallons of shale oil per ton of oil shale, (v) the process is ultimately more economical due to elimination or reduction of costs involved with mining, transportation, and crushing. However, disadvantages are also evident in in-situ processing (Fang et al., 2008) and these include: (i) subsurface combustion is difficult to control due to insufficient permeability within the shale formation, (ii) drilling costs are still high, (iii) recovery efficiencies are generally low, (iv) it may be difficult to establish the required permeability and porosity in the shale formation, and (v) there is the potential for aquifer contamination – if not controlled or treated, effects may linger for an extended period of time even after the project completion. The most notable disadvantage is that oil shale is a relatively hard impermeable formation through which fluids will not flow is of extreme importance in the in situ processing option. Also of interest is the specific gravity of the oil shale since much of the inorganic material must be disposed. The specific gravity of the Green River kerogen is approximately 1.05 and the mineral fraction has an approximate value of 2.7 (Baughman, 1978).

In-situ processes can be technically feasible where permeability of the rock exists or can be created through fracturing. The target deposit is (i) fractured, (ii) air is injected, (iii) the deposit is ignited to heat the formation, and (iv) resulting shale oil is moved through the natural or man-made fractures to production wells that transport it to the surface, thence to the refinery (Bartis et al., 2005). However, difficulties in controlling the flame front and the flow of the produced shale oil can limit the ultimate oil recovery, leaving portions of the deposit unheated and portions of the shale oil unrecovered.

While in situ processes avoid the need to mine the shale, they do require that heat be supplied underground and that product be recovered from a relatively non-porous bed. As such, the in situ processes tend to operate slowly, behavior that the Shell in-situ process exploits by heating the resource to approximately 345 °C (650 °F) resulting in high yields of liquid products, with minimal secondary reactions (Mut, 2005; Karanikas et al., 2005; Crawford et al., 2008a).

The process involves use of ground-freezing technology to establish an underground barrier (*freeze wall*) around the perimeter of the extraction zone. The freeze wall is created by pumping refrigerated fluid through a series of wells drilled around the extraction zone. The freeze wall prevents groundwater from entering the extraction zone, and keeps hydrocarbon derivatives and other products generated by the in-situ retorting from leaving the project perimeter.

In situ processes avoid the spent shale disposal problems because the spent shale remains where it is created but, on the other hand, the spent shale will contain uncollected liquids that can leach into ground water, and vapors produced during retorting can potentially escape to the aquifer (Karanikas et al., 2005).

Modified in-situ processes are designed to improve performance by exposing more of the target deposit to the heat source and by improving the flow of gases and liquid fluids through the rock formation, and increasing the volumes and quality of the oil produced. These processes involve mining beneath the target oil shale deposit prior to heating and also requires drilling and fracturing the target deposit above the mined area to create void space of 20%—25%, which is needed to allow heated air, produced gases, and produced shale oil to flow toward production wells.

The process uses a vertical burn configuration in which the combustion zone progresses vertically through the shale bed. It is also theoretically possible to advance the burn front horizontally, in much the same way as it occurs in a true in situ process. A crude version of this approach was implemented in Germany during World War II, when a few modified in-situ retorts were created by digging tunnels into oil shale deposits and then collapsing their walls into the void volume. However, these operations produced a low recovery of the shale oil and were difficult to control.

In this process, some of the shale was removed from the ground and explosively shattered the remainder to form a packed bed reactor within the mountain. Drifts (horizontal tunnels into the mountain) provided access to the top and bottom of the retort. The top of the bed was heated with burners to initiate combustion and a slight vacuum pulled on from the bottom of the bed to draw air into the burning zone and withdraw gaseous products. Heat from the combustion retorted the shale below, and the fire spread to the char left behind. Key to the success of the process is the formation of shattered shale of relatively uniform particle size in the retort.

If the oil shale contains a high proportion of dolomite (a mixture of calcium carbonate and magnesium carbonate; $CaCO_3 \cdot MgCO_3$) such as occurs in Colorado oil shale, the limestone decomposes at the customary retorting temperatures to release large volumes of carbon dioxide.

$$CaCO_3 \cdot MgCO_3 \rightarrow CaO + MgO + 2CO_2$$

This consumes energy and leads to the additional problem of sequestering the carbon dioxide to meet global climate change concerns.

The development of a commercial oil shale industry in the United States would have significant social and economic impacts on local communities. Other impediments to development of the oil shale industry in the United States include the relatively high cost of producing oil from oil shale and the overall lack or uniformity of regulations to lease oil shale tracts.

Hydrocarbon products of successful in situ heating are similar in character to the products recovered from above-ground retorts: gases, hydrocarbon liquids, and char. Field experiences with the first generation in situ retorts indicate that the gases tend to be of lesser quality than gases recovered by above-ground retorts. The condensable liquid fraction, however, generally tends to be of better quality than the liquid hydrocarbon fractions recovered from above-ground retorts with higher degrees of cracking of the kerogen macromolecules and elimination of substantial portions of the higher boiling fractions typically produced in above-ground retorts.

Overall yields with any in situ retorting tend to be lower than yields from equal amounts of oil shale of equivalent richness processed through above-ground retort. Various explanations have been advanced for these observed differences. Some of the loss of quality for recovered gases may be the dilution that results when heat is introduced to the formation by injection of combustion gases and/or steam, by advancement of a flame front as a result of combustion of some portion of the shale, or when high-pressure gases are used to sweep retorting products from the formation to recovery wells.

The quality improvements for the liquid fraction may be due to the relatively slow and more even heating that can be attained in a properly designed and executed in situ retorting process. Such quality improvements also may be indicative of further refining of initial retorting products when sweep gases such as natural gas or hydrogen are used. Finally, and importantly from an environmental perspective, the char and the mineral fraction to which it is adsorbed are not recovered but remain in the formation, significantly reducing (but not completely eliminating) environmentally-related disposal issues.

The overall success of any in situ retorting technology results from the ability of the technology to distribute heat evenly throughout the formation. Indiscriminate formation heating that allows portions of the formation to reach 590 °C (1100 °F) can result in technological problems, as well as the thermal decomposition of mineral carbonates and the formation and release of carbon dioxide.

From an operational standpoint, such decompositions are endothermic and will result in the energy demands of such uncontrolled in situ retorting quickly becoming insurmountable. As noted above, environmental consequences of carbonate decomposition during in situ retorting can be expected to be mitigated to a large extent by the natural carbon dioxide sequestration that can also be anticipated. Nevertheless, the lack of precise heat control will devastate both the yields and the quality of recovered hydrocarbon derivatives and must be avoided. However, in situ retorting with good thermodynamic controls can product pyrolysis products of equal or even greater quality than above-ground retort.

Another potential disadvantage to in situ retorting involves the time that it takes to heat substantial masses of formation materials to retorting temperature (on the order of months or years) and the energy costs over that period. Field experiences are limited, and, because every formation accepts heat differently, it is difficult to define a universal time line or perform precise, reliable energy balances except on a site-specific basis.

Other largely unanswered questions involve long-term impacts from retorted segments of oil shale formations.

3.1 American Shale Oil process

The American Shale Oil, LLC (AMSO), originally known as EGL Oil Shale, LLC, was a developer of in-situ shale oil extraction technology based in Rifle (Colorado). The company was owned by Genie Energy and Total SA. The American Shale Oil LLC (AMSO) has developed a new process for in-situ retorting of Green River oil shale (Burnham et al., 2009; US DOE, 2010, 2011). The American Shale Oil process involves the use of proven oil field drilling and completion practices coupled with a unique heating and recovery technology.

The process combines horizontal wells, which are heated by a downhole burner or other means, and other horizontal or vertical wells, which provide both heat transfer through refluxing of generated oil and a means to collect and produce the oil. At the start of the heating process, oil is injected to improve heat transfer. The company has proposed that permeability of the formation sufficient for convection will be achieved by thermomechanical fracturing. In the process, closed-loop in-situ retorting is used which has the advantage of energy efficiency and manageable environmental impacts. The oil shale is heated with superheated steam or other heat transfer medium through a series of pipes placed below the oil shale bed to be retorted. Shale oil and gas are produced through wells drilled vertically from the surface and *spidered* to provide a connection between the heating wells and production system. Convection and refluxing are mechanisms that improve heat transfer to retort the oil shale.

After initial start-up, the process uses the gas produced from retorting to supply all the heat required to extract the shale oil and gas from the deposit. Surface disturbance is minimized with this process by heating through lateral piping. Energy efficiency is optimized by recovery of heat from the shale rock after retorting is completed (US DOE, 2007). In May 2016, Genie Energy announced that the AMSO project was closing.

3.2 Chevron process

The Chevron technology for the recovery and upgrading of oil from shale (CRUSH) process is an in situ conversion process which involves the application of a series of fracturing technologies which rubbelized the formation, thereby increasing the surface area of the exposed kerogen (Crawford et al., 2008a). The process is based on fracturing or preferably rubblizing the shale to increase the surface area of oil shale kerogen exposed to flow through the fractures. High temperature gas, preferably carbon dioxide, is injected through the fractures then reheated at surface or by being passed through previously depleted portions of the shale zone. There does not appear to have been much recent activity on this technology and Chevron appears to be mainly focused on shale oil developments.

In the process, which involves creation of controlled horizontal fractures at shallow depth through vertical wells, the exposed kerogen in the fractured formation is then converted through a chemical process resulting in the kerogen changing from a solid material to a liquid and gas. Hot carbon dioxide is used to heat the oil shale. The hydrocarbon fluids are then recovered and improved to refinery feedstock specifications (US DOE, 2007).

Vertical wells are drilled into the oil shale formation and applying horizontal fractures are induced by injecting carbon dioxide through drilled wells and then pressured through the formation for circulation through the fractured intervals to rubbelize the production zone. For further rubbelization propellants and explosives may be used. The used carbon dioxide then be routed to the gas generator to be reheated and recycled. The remaining organic matter in previously heated and depleted zones is combusted in-situ to generate the heated gases required to process successive intervals. These gases would then be pressured from the depleted zone into the newly fractured portion of the formation and the process would be repeated. The hydrocarbon fluids are brought up in conventional vertical oil wells (US DOE, 2007, 2010).

3.3 DOW process

The interest by the Dow Chemical Company interest in oil shale was directed in the 1950s toward in situ processes and local shales, specifically the Antrim, a black Devonian shale formed some 260 million years ago during the Devonian and Mississippian ages and which underlies most of the lower peninsula of Michigan. The shale occasionally produces natural gas and which yields produces natural gas and which yields 9 to 10 gallons of retorted shale oil per ton of oil shale when retorted. The Michigan Antrim shale is believed to contain an equivalent hydrocarbon volume of 2500 billion barrels. Even applying a 10% w/w recovery factor, this resource is approximately nine times the amount of the US proven oil reserve.

Various field studies by Dow of the Antrim shale have resulted in the drilling of some 21 wells and the cutting of over 5000 feet of core. Both high pressure air and oxygen have been used underground as reactants. Hydraulic fracturing and chemical explosives have been used on a massive scale in attempts to generate the necessary fracture permeability for in situ retorting. The costs have been large and the technological problems yet to be solved are formidable, however the potential of the eastern oil shale is so large that a continuing effort has been recommended to the Federal Government.

As early as June 1955, research planners for The Dow Chemical Company were suggesting that underground processes, including in situ retorting, be studied with specific attention to the essential problem of rubbelizing the strata, because the long range availability of energy and organic raw materials was not favorable at some Dow plant sites.

A block of Colorado oil shale was purchased, however, interest soon shifted to a local oil shale a little more than half a mile below the DOW power plants at Midland, Michigan. This shale, the Antrim of Michigan, is a Chattanooga-type shale that represents only a small part of the very extensive oil shale deposits of Devonian age in the Eastern and Mid-eastern parts of the United States. The US Geological Survey estimates that these shales underlie an area of over 400,000 square miles.

Thus, the Dow Chemical Company, under a contract with the US Department of Energy, conducted a four-year research program to test the feasibility of deep, in-situ, recovery of low-heat content gas from Michigan Antrim Shale (Matthews and Humphrey, 1977; McNamara and Humphrey, 1979).

In the process, extensive fracturing (rubbelizing) of the oil shale is considered essential to adequate in-situ retorting and recovery of energy from the Antrim shale. Two wells were explosively fractured using metalized ammonium nitrate slurry. The test facility was located at 75 miles NE of Detroit, Michigan, over one acre of field – the process used was true in-situ (TIS) retorting.

Combustion of the shale was started using a 440-V electric heater (52 kW) and a propane burner (250,000 Btu/h). The special features of the process include shale gasification and severe operating conditions. The test data also showed that explosive fracturing in mechanically under-reamed wells did not produce extensive rubbelization. They also tested hydrofracturing, chemical under-reaming, and explosive under-reaming.

As a final note, an alternative to electrical heating is to heat the shale by down-hole natural gas burning. Compared with using electric power produced by natural gas, this approach halves natural gas use. Implementing downhole gas burning requires the development of appropriate combustion technology. At this time, the net impact on shale oil production costs remain uncertain.

3.4 Equity Oil/Arco process

Equity Oil/Arco BX Project took advantage of prior work in the leached zone of the Piceance Basin in which the dissolution of water-soluble minerals has led to a relatively rich oil shale of high natural permeability. The Equity Oil BX Project took advantage of this permeability for in situ retorting, using injected superheated steam to heat the oil shale. The project was carried out on a 1000-acre fee property jointly owned by Equity Oil and Atlantic Richfield (ARCO) and located in Rio Blanco County, CO, approximately midway between Tracts C-a (Rio Blanco) and C-b (Occidental). At the project site, the leached zone averages 540 feet thick with shale assaying 24 gal/ton. The project comprised a pattern of eight injection wells, five production wells and three observation wells covering an area of 0.7 acres.

Initial plans were to inject steam at 535 °C (1000 °F), 1500 psi, and a total pattern rate of 974,000 lb steam/day (2784 bbl/day water). This was to be maintained over a 2-year period to produce a total of 650,000 bbl of shale oil (100% of Fischer Assay). Because of equipment limitations and mechanical problems, these injection targets were not met. As a result, very little shale oil was actually produced. The initial oil observation was made only after a year of steam injection and 18 months of steam injection yielded 46 barrels of crude shale oil.

However, the permeability of the leached zone shale is not uniform; it is appreciably lower in the vertical direction, than in the horizontal direction (bedding plane). The effects of this anisotropic permeability shows that efficient heating was confined to the two steam injection zones. These results do not preclude using the Equity Oil steam injection scheme, but does mean that more complicated and expensive injection equipment would be needed for distribution of the steam into multiple injection zones to provide uniform heating of the shale formation. In summary, the BX Project attempt to take advantage of the natural permeability of the leached zone for in situ retorting by superheated steam injection did not result in high oil recoveries. In large part, the BX results were traced to equipment limitations. However, the results also showed clearly that the anisotropy of leached zone permeability is a factor to be reckoned with in any future work along these lines.

3.5 Exxon/Mobil Electrofrac process

The Electrofrac process (ExxonMobil) uses a method of heating oil shale in situ based on established principles of oil and gas well horizontal drilling and hydraulic fracturing (Crawford et al., 2008a). The process involves the fracturing of oil shale hydraulically and filling the fractures with an electrically conductive material such as calcined petroleum coke which acts as a heating element. The electric heat is applied, and this heat is conducted through the heating element changing kerogen to oil.

Electricity flowing through the conductive medium turns the fracture into a resistive heating element which will gradually heat the shale and convert the kerogen into oil and gas which can then be produced by conventional means. This process is supported by on-going research and technology development for production of shale oil and gas is conducted from one end of the fracture to the other, making the fracture a resistive heating element. Heat flows from the fracture into the oil shale formation, gradually converting the solid organic matter of the oil shale into oil and gas. ExxonMobil indicates that field tests have been initiated to test the concept but it will be many years before the technology could be shown to be technically, environmentally and economically feasible.

The proppant used in fracturing is highly electrically conductive and is a means of extending heat beyond the borehole and into the fractures. The proppant creates an electrically conductive pathway the length of the fracture system, turning it into a large, plate-like electrode. ExxonMobil has conducted a 100-ft scale test (which it calls "The Giant Toaster") at its Colony Mine near Parachute, Colorado.

The process uses a series of hydraulic fractures created in the oil shale formation. The fractures should be preferably longitudinal vertical fractures created from horizontal wells and conducting electricity from the heel to the toe of each heating well. For conductibility, an electrically-conductive material such as calcined coke is injected into the wells in fractures, forming a heating element. Heating wells are placed in a parallel row with a second horizontal well intersecting them at their toe. This allows opposing electrical charges to be applied at either end. Planar heaters require fewer wells than wellbore heaters and offer a reduced surface footprint. The shale oil is extracted by separate dedicated production wells (US DOE, 2007; Plunkett, 2008; Symington et al., 2006, 2008).

3.6 Geokinetics process

The Geokinetics horizontal in situ retorting process (HISP) is a true in situ process, designed to retort shallow shale seams with no mining. Because no mine construction is involved, a key feature of the process was the very low initial capital cost. In 1974, process development began as a joint effort of Geokinetics Inc. and Aminoil USA. In 1976, US ERDA (United States Energy Research and Development Administration, later US DOE) joined the effort. In 1978, Aminoil withdrew, leaving Geokinetics and US DOE as the remaining participants. In 1984, US DOE withdrew and Geokinetics completed the project at its own expense.

In the process, the soil and subsoil are first removed using earthmoving equipment, then a pattern of holes is drilled through the overburden and shale formation to be retorted. Explosive charges are then loaded and detonated sequentially to create the in situ retort. The blasting pattern is precisely designed so that the initial blast lifts its rubble some 10−20 feet at the surface. While this rubble is still aloft, approximately 0.5 s after the initial blast, the subsequent rows of charges fire at approximately 0.1 s intervals to laterally displace rich shale into the void. The result is a disruption of the surface (spalling) only at one end of the retort. Offgas well are then drilled at the disrupted end and air injection wells at other. Oil production wells are associated with sumps to facilitate oil collection. Observation, thermocouple and gas sample wells complete the required drilling. The subsoil is then replaced and thoroughly tamped to seal the retort before ignition.

Oil recoveries from were on the order of 59% and 51% of Fischer Assay, respectively, where superficial gas velocities were maintained at or above 0.8. Due to substantially lower air injection rates, oil recoveries and production rates from the other retorts were much lower. Quality of the oil produced by the process varied from retort to retort, due to variations in shale composition, and also varies with time during production from a given retort. However, a composite analysis of oils showed that oil quality was acceptable − in particular, the metals, asphaltenes and residuum contents were low.

3.7 Illinois Institute of Technology Research Institute process

The Illinois Institute of Technology Research Institute developed the concept of oil shale volumetric heating using radio frequency (radio waves) processing during the late 1970s. This technology was further developed by Lawrence Livermore National Laboratory. The concept presumes that a radio frequency at which the depth is in excess of thirty feet (perhaps 30–300 feet), thereby overcoming the thermal diffusion times needed for conductive heating (Sresty, 1982; Bridges et al., 1983).

In the process, oil shale is heated by vertical electrode arrays. Deeper formations could be processed at slower heating rates by installations spaced at approximately thirty feet apart.

3.8 Occidental Modified In-Situ process

Starting in 1972, Occidental Oil Shale, Inc., a subsidiary of Occidental Petroleum, began research on a shale oil extraction process, ending research in 1991. The company conducted the first modified in-situ oil shale experiment in 1972 at Logan Wash, Colorado.

In 1972, Occidental began field development of the vertical modified in-situ (VMIS) retorting process at the Logan Wash oil shale mine north of DeBeque, Co. Early work at Logan Wash included the construction and processing of three small retorts and one commercial-sized retort. The small retorts were approximately 30 feet square by 72–113 feet in height. Retorts 1E and 2E used a vertical raise in the center of each retort, with a single room at the bottom to provide void volume. Three horizontal rooms were spaced vertically to distribute void volume in Retort 3E, which improved yield relative to 1E and 2E. Retort 4, with two vertical slots parallel to each other across the retort width, was an attempt to scale up the vertical void concept. The lower yields obtained from Retort 4 were ascribed to limitations imposed by rock mechanics that led to non-uniform flows and bed stability problems.

Retorts 5 and 6 were commercial-sized units that were developed under a 1976 cooperative agreement with United States Department of Energy. Retort 5 used a single vertical slot mined across its width to provide void volume, while Retort 6 was a scale-up of the Retort 3 design with three horizontal rooms. The latter design again afforded a superior oil yield. Retorts 7 and 8 were constructed under the second phase of the cooperative agreement with the United States Department of Energy. These were identical, commercial-sized retorts, measuring 165 × 165 feet across × 241 feet tall. They were constructed side-by-side, using the Retort 6 design, and burned at the same time in order to obtain reproducibility data not available from single retort tests. Retorts 7 and 8 afforded even higher oil yields than Retort 6.

The amount of oil produced in Retorts 7 and 8 by the amount of shale mined gives a value of 0.88 bbl/ton. This value compares very favorably with the value of 0.41 bbl/ton that would have been obtained if the mined shale had been retorted under conditions affording 100% of Fischer Assay. In a commercial operation, the mined shale would probably be processed in such an above-ground retort. In this scenario, for maximum overall efficiency the bulk of the shale would be retorted using the cost-effective underground method, while surface retorting of the mined shale would provide nearly complete resource utilization.

The distance between Retorts 7 and 8 was 160 feet. To assess the effect of a shorter inter-retort distance, the partial height Retort 8× was constructed 50 feet behind Retort 8. Retort 8 had the 165 × 165 foot cross-section of Retorts 7 and 8, but was only 63 feet tall. It was blasted first, so that blasting of Retort 8 could provide information relayed to the deformation, stresses and fracturing that would occur at the shorter distances called for in the commercial development plan. No specific problems associated with the 50-foot inter-retort distance have been mentioned, and Retort 8 performance does not seem to have suffered. However, rock structure is highly site-specific and it would be unwise to assume that such a short distance would be acceptable in any other site.

Modified in-situ processes attempt to improve performance by exposing more of the target deposit to the heat source and by improving the flow of gases and liquid fluids through the rock formation, and increasing the volumes and quality of the oil produced. Modified in-situ involves mining beneath the target oil shale deposit prior to heating. It also requires drilling and fracturing the target deposit above the mined area to create void space of 20%−25%. This void space is needed to allow heated air, produced gases, and pyrolyzed shale oil to flow toward production wells. The shale is heated by igniting the top of the target deposit. Condensed shale oil that is pyrolyzed ahead of the flame is recovered from beneath the heated zone and pumped to the surface.

The Occidental vertical modified in-situ process was developed specifically for the deep, thick shale beds of the Green River Formation. Approximately 20% of the shale in the retort area is mined; the balance is then carefully blasted using the mined out volume to permit expansion and uniform distribution of void space throughout the retort. A combustion zone is started at the top of the retort and moved down through the shale rubble by management of combustion air and recycled gases. Full-scale retorts would contain approximately 460,000 cubic yards of shale rubble (Petzrick, 1995).

In a modified in-situ retorting method, a portion of the underground shale was mined and then the remaining portion was crushed through a series of explosions. This method overcame many of the difficulties of burning shale underground by allowing the necessary combustion air to permeate the crushed shale. The underground shale was then retorted in place and the mined shale was sent to surface retorts for processing. There were several companies interested in this technology in the early 1980s, but that interest faltered when oil prices collapsed (US OTA, 1980; Bartis et al., 2005).

The process used explosives to create underground chambers (retorts) of fractured oil shale. Approximately 20% was mined out after which blasting was used to fracture oil shale. The commercial-sized retort covered 333 by 166 feet area and had height of 400 feet. Oil shale was then ignited on the top by external fuel and air or steam was injected to control the process. As a result, combustion moved from the top to the bottom of retort (US DOE, 2004a,b,c, 2007).

The retorting technology involved creating a void in the oil shale formation using conventional underground mining techniques. Explosives (ammonium nitrate and fuel oil) were then introduced to cause the rubbelizing of some of the shale on the walls of the void and to expand existing fractures in the formation, improving its permeability. Access to the void was sealed and a controlled mixture of air and fuel gas (or alternatively, commercial fuel such as propane or natural gas) was introduced to initiate controlled ignition of the rubbelized shale. Combustion using this external fuel continued until the rubbelized shale itself was ignited, after which external fuel additions were discontinued and combustion air continued to be provided to the void to sustain and control combustion of the shale. The resulting heat expanded downward into the surrounding formation, heating and retorting the kerogen.

Retort products collected at the bottom of the retort void and were then recovered from conventional oil and gas wells installed adjacent to the void. Careful control of combustion air/fuel mixtures was the primary control over the rate of combustion occurring in the heavily instrumented and monitored void. Once recovery of retorted oil shale products equilibrated, a portion of the hydrocarbon gases was recycled back into the void to be used as fuel to sustain in situ combustion. Two separate retorts were constructed and operated during Phase II of the project, with the last two retorts shutting down in February 1983.

Ultimately, oil recovery was equivalent to 70% of the yield predicted through Fisher assay. Design of the experiment was directed toward potential future commercial applications so numerous that such in situ retorts were operated simultaneously to demonstrate the practicability of an approach that would likely have been desirable in commercial development ventures.

Differences in approaches among modified in-situ technologies center on the manner in which formation voids are formed, the shape and orientation of such voids (horizontal vs. vertical), and the actual retorting and product recovery techniques employed. Retorting techniques can include controlled combustion of rubbelized shale, or formation heating by alternative means such as the introduction of electromagnetic energy. Product recovery techniques have included steam leaching, chemically assisted or solvent leaching, and displacement by high-pressure gas or water injection. Some of these formation sweeping techniques also can be seen as aiding or promoting additional refining of the initial retorting products. It is beyond the scope of this summary to discuss in detail all or even a majority of the designs that have been developed (Lee, 1991).

3.9 Petroprobe process

Petroprobe (subsidiary of Earth Search Sciences, Inc.) developed technology in which air is super-heated in a burner on the surface that moves down the borehole; interacts with the organic rich rock and brings hydrocarbons to the surface with minimal surface footprint. Drilling is done into oil shale deposits as deep as 3000 or more feet and super-heated air is injected through a processing inlet conduit within the hole that heats the rock and converts the kerogen to a gaseous state.

The portable design of surface plant allows it to be dismantled easily and moved to the next site.

3.10 Rio Blanco Oil Shale process

The Rio Blanco Oil Shale Company (RBOSC) was originally a 50/50 joint venture of Gulf Oil Corporation and Standard Oil Company (Indiana), and is now a division of Amoco Corporation. It was formed after winning a bid in January 1974 for Federal Oil Shale Lease C-a. Site preparation for modified in-situ (MIS) development on Tract C-a began in late 1977. Two retorts were designed, constructed, then successfully rubblized and burned to demonstrate the modified in-situ (RBOSC-MIS) technology of which the MIS retorting phase was completed during the first part of 1982. Following successful completion of the effort, an extensive study of above-ground retorting based on Lurgi technology, was made at the Gulf Oil Research Center at Harmarville, Pennsylvania. Because Tract C-a is suitable for open-pit mining, future interest has may shift to the above-ground technology. The Tract C-a operation has now been suspended until the Rio Blanco Oil Shale Company can obtain off-tract land for disposal of overburden and spent shale. During suspension, the Rio Blanco Oil Shale Company maintained the leasehold and continuing environmental monitoring work, while proceeding with internal oil shale research and development programs at the Amoco Research Centers.

Key features of the Rio Blanco Oil Shale Company mine include the production shaft which was constructed first using conventional shaft-sinking equipment, the exhaust shaft which was then raise-bored to the surface to establish a conventional ventilation system for the mine, and the service/escape shaft which was also raise-bored to the surface. A separate circuit for supplying air and steam to the retorts through the surface-drilled blastholes, and for piping off-gases back to the surface through the offgas shaft, was sealed off from the working areas of the mine. A unique feature of the Rio Blanco Oil Shale Company design is the underground oil-water separator that is a mined cavity, that minimizes the capital cost of large above-ground tankage. The main production level is the G-level, 850 feet below the surface. The G-level provided access to the bottoms of the retorts before bulkheads were installed to seal off the mine from the retorts.

Retort 1 extends through the Upper Aquifer of the Piceance Basin in which the pressure is several hundred feet of water. Initially a ring of surface wells was drilled to dewater the area around the production shaft; later the sub E level was mined and drain holes were drilled into the aquifer. After water production rates as high as 3600 gal/min, water rates stabilized near 1100 gal/min and only 10−30 gal/min was entering Retort 1 at its ignition.

The Rio Blanco Oil Shale Company proprietary rubblizing procedure that affords high void-volume, hence high permeability, is felt to be the single factor most responsible for the success of the process. The first step in this procedure is to drill blast holes from the surface to the full depth of the planned retort and undercut a room that will serve as a product drain is then mined. In Step 2, the lower part of each blast hole is loaded with explosive that is detonated to blast a segment of roof down into the room at the bottom. Part of the rubble is mucked, leaving the rubble at its angle of repose. The load, blast and muck sequence is repeated until the desired void space is obtained. In Step 3, the remaining roof rock is rubblized without mucking, until the entire retort is constructed with only a small free space at the top to serve as a feed gas distributor.

The Rio Blanco Oil Shale Company rubblizing procedure was found to give a relatively small average particle size with a random size distribution that is conducive to high, even and maintainable permeability. This was confirmed by extensive cold flow tests with Freon tracer gases. These tests indicated an overall sweep efficiency of 85% for both retorts. Sweep efficiency in Retort 1 could be investigated in more detail, because of its instrumentation. In this case, it was found that sweep efficiency in the top two-thirds was 100%, while that in the lower third was only 60%. Leak rates were measured under stable pressure conditions and void volumes were calculated from pressure changes with the effluent valves closed. Cold flow pressure drop as a function of flow rate could be calculated from the Ergun Equation, using the experimental void volume and a calculated effective mean particle size.

Ignition of the retorts was achieved within 28 h, using gas-fired burners lowered downhill. Durability of the burners, a problem in some other in situ studies, was demonstrated by repeated shut-down/re-ignition cycles. It was found that the higher pressure drop in ignited rubble tended to direct flow to unignited rubble, and thereby to promote even spreading of the flame front.

Air and steam were fed to the ignited retort through the same boreholes used for blasting. Products flowed to the underground separator, from which oil and water were pumped separately to the surface. The philosophy for operation was to maximize the flame front advance within the safe operating limits of the available equipment. Consequently, the advance rate decreased with time, due to the increasing pressure drop from the top of the bed to the front. Even though some problems that limited advance (air leakage, sulfur emission limits) were encountered, the front advance averaged approximately 3 ft/day and were considerably higher during the early stages.

Oil production, which totaled 24,444 bbl for Retort 1, includes liquid oil from the separator room, the C6+ condensable liquids from the exit gas, and any oil mist found as an aerosol in the exit gas. The first liquid oil appeared approximately 15 days after ignition, and thereafter oil production tended to mirror the flame front advance. Oil recovery in the Rio Blanco Oil Shale Company tests was very good, 68% of Fischer Assay from each retort. The maximum yield value was calculated using a computer model from Lawrence Livermore National Laboratory which takes into account the shale grade, particle size, air/steam ratio and front advance rate. The maximum calculation assumes 100% sweep efficiency. However, it will be recalled that efficiency was only approximately 85% for these retorts. Thus, the experimental values are in reasonable accord with expected behavior.

In summary, the Rio Blanco effort led to a simple design that approaches laboratory results in oil recovery efficiency. The high void-volume retorts are suitable for MIS retorting at high burn rates. The entire retort can be developed from a single mine level (e.g. the G-level); no access to the upper part of the retort is needed for ignition. Safe and very effective ignition was achieved using downhole burners. In addition, it has been demonstrated that successful retorting can be achieved in the dewatered Upper Aquifer. Even though current Tract C-a interest has shifted, the success of the Rio Blanco Oil Shale Company-modified in-situ project suggested that the technology may be applicable to other deposits situated even deeper beneath the surface than that at Tract C-a.

3.11 Schlumberger/Raytheon-CF radio-frequency technology

This *in-situ* method is based on the application of radio frequencies (RFs) to heat the buried shale to high temperatures (pyrolysis) and then hydrocarbon is extracted from production wells by pumping supercritical fluid (CF) carbon-dioxide into the shale formations (Crawford et al., 2008a).

Radio frequency electromagnetic (microwave) can do work directly on medium molecule of oil shale and change into heat energy, the transmission of which allows both inner and outer molecules heating simultaneously without heat conduction (Pan et al., 2012). Meanwhile, oil shale is a poor microwave absorbing material and microwave absorbents must be added to reach pyrolysis temperature. By this means, shale oil could be heated at a higher speed and kerogen will gradually be cracked into gas and oil. Then shale oil and gas will flow into the production wells through fractures generated by heating and be pumped up to the surface.

Microwave heating has dielectric thermal effect on materials, by which the migration of ion and the rotary of polarity molecules that make the molecules moving insofar as the relatively static transient of polarity molecules changes into dynamic and produces thermal effect by the dipolar high-speed rotating of molecules. The change happens in the inner part of the rolled substance that is internal heating. Since oil shale is a poor conductor of heat, the utilization of conduction heating and convection heating will lead to low speed.

The adoption of radio frequency heating overcome the difficulties of heating underground oil shale, which makes the retorting easier and more effectively. Thus, one of the advantages of this process is that it can yield quick production of oil and gas in terms of months whereas other methods take longer time; may years to heat the shale in-situ. Due to lower heating requirements, this in-situ process is very much applicable in recovery of tar sands and heavy oil and the yield will be in order of 10–15 barrels of oil equivalent per barrel consumed (Pan et al., 2012).

3.12 Shell In Situ Conversion process

In the early 1980s, Shell proposed the in situ conversion process (ICP) for in situ retorting (Bartis et al., 2005; Crawford et al., 2008a). In the process, a volume of the shale formation is heated by electric heaters placed in vertical holes drilled through the entire thickness (more than a thousand feet) of a section of oil shale. To obtain even heating over a reasonable time frame, between 15 and 25 heating holes need to be drilled per acre. After heating for two to three years, the targeted volume of the deposit will reach a temperature of between 345 and 365 °C (650 and 700 °F). This very slow heating to a relatively low temperature (compared with the >480 °C (>900 °F) temperatures common in surface retorting) is sufficient to cause the chemical and physical changes required to release oil from the shale. On an energy basis, about two-thirds of the released product is liquid and one-third is a gas similar in composition to natural gas. The released product is gathered in collection wells positioned within the heated zone.

The main characteristic of this method is the use of electric heaters in drilled wells which heat the surrounding oil shale. The heaters are inserted into the wells which are 1000–2000 feet deep, and the rock formation is heated slowly to 400 °C (750 °F), changing the kerogen present in oil shale into oil and gas. This method yields high quality oil and it has been estimated that potential yields in rich deposits could vary from 100,000–1,000,000 barrels of oil per acre (Crawford et al., 2008a).

A unique aspect of the project was the use of subsurface *ice-walls* to isolate the test volume from surrounding groundwater aquifers and to allow the shale to be dewatered before heating began. The ice-walls required surface refrigeration systems on relatively close spacing. Vertical wells were then drilled within the ice wall perimeter and heaters installed to heat the rock to ∼350° C which slowly converts the kerogen into shale oil and gases, which could then be produced from a pattern of producing wells. With vertical heating and producing wells in close proximity the initial pilot had a large footprint. ICP requires further development to address issues related to shales, such as low permeability and water impacts.

Thus, the process is comprised of a series of underground heaters drilled into an oil shale deposit and the field size for this method is typically one square mile. Approximately 15–25 holes are drilled per acre at a distance of 35–42 feet (10.7–12.8 m) apart in a variety of configurations. The wells reach a depth of up to 2000 feet, depending on the deposit location (Bartis et al., 2005). The target depth zone is 1000–2000 feet (Andrews, 2006). The fracturing step is achieved by existing and induced fractures – as in crude oil recovery processes, fracturing increases shale permeability (Scouten, 1990; Lee, 1991; Speight, 2014).

The electrical resistance heaters inserted into the holes reach temperatures of 760 °C (1400 °F) in order to raise the surrounding shale deposit to an average temperature of 345–370 °C (650–700 °F). Although this temperature is significantly lower than that required for conventional surface retorting (482–538 °C, 900–1000 °F), it is sufficient to induce the chemical and physical changes that release the oil from the shale.

After heating the deposit for 2–3 years, the oil and any associated gas are pumped out of the ground using conventional methods (Bartis et al., 2005). The hydrocarbon mixture generated from this procedure is of a very high quality and quite different from traditional crude oils in that it contains light hydrocarbon derivatives and almost no heavy ends. The mixture quality can be controlled by adjustment of the heating time, temperature and pressure in the subsurface shale layer. A typical mixture is two-thirds liquid (30% naphtha, 30% jet fuel, 30% diesel and 10% heavier oil) and one-third gas (propane and butane). The liquid hydrocarbon fractions can easily be converted into a variety of finished products, including gasoline, naphtha, jet fuel and diesel (Andrews, 2006). On a 30 × 40 foot (9.1 × 12.2 m) test area, Shell recovered 1700 barrels of light oil plus associated gas from shallower, less-concentrated oil shale layers.

To protect groundwater, a freeze wall is constructed around the heating grid at a distance of 300 feet (91 m) from the heaters. The coolant is a 40% ammonia-water mixture. The freeze wall establishes an underground barrier to fluid movement, thus preventing groundwater contamination and the escape of the freed shale oil. Shell calculated that of the 3.5 units of energy gained from the oil shale for every unit of energy consumed through the electrical heating process assumes electricity is produced by an advanced, 60% efficient, combined cycle gas power plant. Shell is also considering gas-fired heating, which will utilize the natural gas being recovered from the drilling process, potentially improving the energy balance.

In the period 2004 to 2010, Shell conducted a test of a similar process at their Viking pilot in the Peace River Oil Sands called an *In-situ Upgrading project* which was followed by a Grosmont pilot in a bitumen in carbonate formation. In this case freeze-walls were not required and heaters were installed in layers of horizontal wells alternating with layers of producing wells. A second project in the Grosmont Carbonate Bitumen formation has continued work mainly on developing and proving downhole heater technology while upgrading bitumen to lighter fractions. This work in parallel with the oil shale work should be complementary but may result in bitumen conversion moving ahead before oil shale conversion.

3.13 Vertical Modified In-Situ process

The basic premise of the modified in-situ processes is improvement in performance by exposing more of the target deposit to the heat source and by improving the flow of gases and liquid fluids through the rock formation, and increasing the volumes and quality of the oil produced. To do this, the oil shale is heated by igniting the top of the target deposit. Condensed shale oil that is thermally decomposed ahead of the flame is recovered from beneath the heated zone and pumped to the surface.

As an example, the vertical modified in-situ process was developed by Occidental Oil Shale, Inc., a subsidiary of Occidental Petroleum (Oxy) was developed specifically for the deep, thick shale beds of the Green River Formation. Approximately 20% of the shale in the retort area is mined; the balance is then carefully blasted using the mined out volume to permit expansion and uniform distribution of void space throughout the retort (Petzrick, 1995; Hulsebos, 1988).

3.14 Other options

An interesting concept – while not a in situ retorting process which could be used prior to any process in which the kerogen is thermally decomposed and which is certainly worthy of mention here – is the soluble salt process. This is a process in which permeability and porosity are developed by dissolution of soluble salts. The process consists of two steps that may be conducted simultaneously or sequentially: leaching of soluble salts and conversion of kerogen (Prats et al., 1977).

The approach is to develop the permeability and porosity of the formation using is based on the leaching of leaching of water-soluble salts (primarily nahcolite) that have been found to be interspersed in the oil shale in a formation. The use of hot water and steam sed to leach the nahcolite (NaHCO3, also called thermokalite) and in which steam was used to retort the oil shale to produce shale oil. In-situ combustion and hot-gas pyrolysis methods for converting kerogen to shale oil are suggested as alternatives to pyrolysis with steam and are discussed briefly. Pyrolysis with steam and are discussed briefly. However, prior to the leaching operation, it is necessary to include items such as: (i) Identification of the nature and distribution of the soluble salts and of the oil-shale richness of the formation, (ii) measurement of the subsurface properties under simulated process conditions, (iii) experimental determination of the kinetics of kerogen decomposition and oil production under simulated process conditions, and (iv) solubility measurements under simulated process conditions.

4. The future

In 1970s, during the period of world oil crisis, different oil shale retorting technologies, including underground retorting were actively developed by oil companies. In the second half of the 20th Century, extensive research and development efforts had been devoted to the commercialization of in-situ pyrolysis of oil shale. However, most of these efforts were either halted or scaled sown in the late twentieth century due to the unfavorable process economics in a short term. In fact, until the 1990s, due to the depletion of oil price, many in-situ projects were closed or plans abandoned and, even at the time of writing, although the crude oil price is much higher than decades ago, only the Shell Company in the USA is conducting an in-situ oil shale retorting pilot test.

In-situ retorting obviates the any issues related to mining, handling, and disposing of large quantities of material, which occurs for aboveground retorting. In-situ retorting offers the potential of recovering deeply deposited oil shale. However, in order to mitigate the potential disadvantages of in situ processes, novel and advanced retorting and upgrading processes should seek to modify the conversion chemistry to improve recovery and/or create high-value by-products. Approaches such as (i) the use of lower heating temperatures, (ii) the use of higher heating rates, (iii) a shorter residence time, (iv) the use of additives such as hydrogen or hydrogen transfer/donor agents, and (v) use of solvents.

Several emerging technologies for extracting oil from shale are currently being tested and refined in Utah and Colorado in an effort to determine their commercial viability. These efforts range from application of new surface mining and processing technologies to modified in-situ methods.

The basic idea is to create an in situ environment in an ex situ process. The shale is mined from the richest and largest deposits and then crushed and piled into an embankment lined with clays or other impervious material. The embankment is capped with an appropriate impermeable layer. Horizontal wells are drilled into the structure and then heaters are inserted into the wells to provide a slow, steady heating source. The concept is to mimic in situ conditions in this embankment structure. As the source rock heats up, appropriately placed wells are used to collect the oil. Once oil production ceases, a heat scavenging program is used to scavenge/divert waste heat to adjacent embankments. Then, the structure is shut down.

Reclamation is engineered to ensure no further environmental impact from the embankment. The advantages of the technology are that features of in situ and ex situ methods are combined to process the oil shale. In fact, it may be possible to engineer improved "in situ" conditions in the embankment to produce better quality oil. However, mining would require its own infrastructure and remediation activities and the long-term environmental security of the embankment would have to be ensured.

The main difference between using horizontal drilling and hydraulic fracturing for crude oil or natural gas and using them for oil shale is the time frame – to convert the kerogen to shale oil, heat delivered electrically via the calcined coke proppant subjects the surrounding rock to the effects of pyrolysis over a period of around five years in order to yield its liquid oil.

A process has been proposed to convert oil shale by radio frequency heating over a period of months to years to create a product similar to natural crude oil (Burnham, 2003). Electrodes would be placed in drill holes, either vertical or horizontal, and a radio frequency chosen so that the penetration depth of the radio waves is of the order of tens to hundreds of meters. A combination of excess volume production and overburden compaction drives the oil and gas from the shale into the drill holes, where it is pumped to the surface. It could well be that the comparative economics of shale oil will change substantially to be more favorable in the 21st Century. Several of noteworthy processes are described below.

In any discourse on the future of oil shale processing, there must be acknowledgment of the environmental aspects (Chapter 18). It is acknowledged that the production and processing of oil shales can have significant environmental impacts depending on the shale composition the extraction process used and the region in which the operation occurs.

The greenhouse gas emissions (GHG emissions) vary widely depending on the process. Power generation in Estonia is treated the same as a coal power plant when compared to European emissions. Limestone in the oil shale feed can reduce SO_x emissions but will increase carbon dioxide emissions. Other air emissions depend on the shale processing may produce SO_x emissions, VOCs and high particulate emission levels into the air which could impact workers and nearby residents and other industries. These may in some cases be similar to coal power plant emissions, other types of mines, refineries or in-situ production operations in other case they may be better or worse than other energy processes so there is no clear generic statement which could be made related to air emissions from oil shale operations.

In terms of water use and contamination, the impact will vary widely across the various shales and extraction processes. All oil shale mining operations will tend to impact ground water and surface drainage. Power generation water use would likely be similar to an equivalent sized coal fired plant. Internal combustion retorting plants tend to use a lot of water for quenching the spent shale, and minerals found in the spent shale can also contaminate the water. In contrast the hot recycles solids processes mostly operate dry so there is little water consumption and minerals in the spent shale would be less soluble when contacting water at lower temperatures. For in-situ conversion processes the main water concerns will be with any water used for hydraulic fracturing and flowback treatment and the protection of underground aquifers if the shale is shallow or as a result of potential well failures due to high temperatures and corrosive conditions in the production wells and gathering lines.

As with other energy resource operations oil shale operations will have land impacts from mining and well development footprints, as well as the processing units, truck haulage, pipelines and waste disposal operations associated with the chosen extraction method. Land impacts are also impacted by the geographic location of the operations, and any potential to impact sensitive landscapes or ecosystems.

At the time of writing and because of the lack of development over the past three decades, significant uncertainties still remain in regard to the impact of in-situ retorting on the quality of groundwater. Retorting and removing hydrocarbon derivatives and hydrocarbonaceous derivatives (as shale oil) will change aquifer properties and which could cause an increase in hydraulic conductivity and any changes in properties of the aquifer could result in the leaching and transport of mineral salts and trace metals that are commingled with oil shale deposits. Questions also arise about the fate of any hydrocarbon gases that may have migrated beyond the retort zone and whether there should be any cause for concern regarding their interaction with groundwater or release into the atmosphere. Until these critical uncertainties are satisfactorily addressed, the technical viability of any method of in-situ retorting cannot be fully guaranteed or established. If and when any such in situ projects are initiated, there will be the necessity for environmental monitoring of the subsurface to gather the data required to support a decision to begin initial commercial operations.

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CHAPTER

16

Refining shale oil

1. Introduction

The characteristic feature of oil shale is the presence of kerogen (organic matter) from which oil is obtained by thermal treatment (thermal decomposition) in the absence of oxygen. Shale oil is the main product of oil shale thermal treatment or processing (retorting). As the demand for precursor fractions (blending stock) to produce fuels (such as gasoline and diesel) increases, there is much interest in developing economical methods for recovering liquid distillate fraction hydrocarbon derivatives from oil shale. However, the recovered distillates from oil shale processing are not yet economically competitive against distillates from crude oil (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). Furthermore, the value of hydrocarbon derivatives recovered from oil shale is diminished due to the presence of undesirable contaminants. The major contaminants of concern are oxygen-containing, sulfur-containing, nitrogen-containing and metallic (and organometallic) compounds which cause detrimental effects to the catalysts used in the subsequent refining processes. These contaminants, when present in the actual fuel, are also undesirable because of their disagreeable odor, corrosive characteristics, and emission when combusted that further cause environmental problems (Scouten, 1990; Lee, 1991; Kundu et al., 2006; Tsai and Albright, 2006; Lee et al., 2007; Speight, 2014, 2017, 2019a). Oil-shale distillates also had a higher content of olefins than crude oil, as well as higher pour point and viscosity.

Crude shale oil (sometimes referred to as *retort oil*) is the liquid oil condensed from the effluent from oil shale retorting. Crude shale oil typically contains appreciable amounts of water and solids, as well as having a high propensity to form a sediment. As a result, crude shale oil must be upgraded to a synthetic crude oil (syncrude) before being suitable for pipelining or substitution for (or blending with) crude oil as a refinery feedstock. However, for the most part, shale oil is sufficiently different from conventional crude oil and, in fact, from other shale oils (Tables 16.1 and 16.2) that processing shale oil presents some unusual problems (Scouten, 1990; Lee, 1991, Speight, 2014, 2017).

Generally, shale oil has a high content of nitrogen (typically on the order of 1.5–2.5% w/w) compared to a conventional crude oil (typically 0.2 to 0.3% w/w nitrogen). Furthermore, because retorted shale oil is produced by a thermal cracking process, olefin and diolefin contents are high and, it is the presence of these olefin derivatives and diolefin derivatives in conjunction with the high nitrogen content that gives crude shale oils their characteristic

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TABLE 16.1 Properties of shale oil from various sources.

Location	Specific gravity (API)	Elemental analysis, % w/w					Composition of <350 °C % w/w		
		C	H	O	N	S	Saturates	Olefins	Aromatic
Colorado, USA	0.943 (18.6)	84.90	11.50	0.80	2.19	0.61	27	44	29
Kukersite, Estonia	1.010 (9.0)	82.85	9.20	6.79	0.30	0.86	22	25	53
Rundle, Australia	0.64 (0.91)	79.50	11.50	7.60	0.99	0.41	48	2	50
Irati, Brazil	0.92 (22.5)	84.30	12.00	1.96	1.06	0.68	23	41	36
Maoming, China	0.903 (24.0)	84.82	11.40	2.20	1.10	0.48	55	20	25
Fushun, China	0.912 (26.0)	85.39	12.09	0.71	1.27	0.54	38	37	25

TABLE 16.2 Properties of shale oil from different formations in China.

Producing area:	Fushun	Maoming	Huadian	Yaojie
Properties				
Specific gravity	0.9033	0.9122	0.8789	0.93
Freezing point, °C	33	30	26	26
Wax content, % w/w	20.2	13.2	5.9	10
Resid, % w/w	0.85	1.54	0.9	5
Distillation range, °C				
Initial boiling point	216	214	173	211
10% @	264	259	221	258
20% @	293	283	250	284
30% @	318	306	278	311
40% @	343	330	301	334
50% @	362	3540	331	366
Elemental composition, % w/w				
Carbon	85.39	84.82	85.17	84.84
Hydrogen	12.1	11.4	12.2	11.1
Sulfur	0.54	0.48	0.42	0.7
Nitrogen	1.27	1.1	0.75	0.97
Oxygen	0.71	2.2	1.43	2.4

instability and propensity to form sediment formation. In addition to the olefin derivatives and diolefin derivatives, shale oil may also contain appreciable amounts of aromatic hydrocarbon derivatives, polar aromatic derivative (often referred to as resins), and pentane or heptane insoluble materials constituents (the asphaltene fraction that should be referred to either as pentane-asphaltenes or heptane-asphaltenes according to the hydrocarbon used for the separation of this fraction).

The distribution of compound types as a function of distillation range shows that the concentration of polar aromatic derivatives and asphaltene constituents insolubles occur in the higher boiling fractions which parallels the nitrogen concentration in these fractions. The oxygen content of raw shale oil is higher than the oxygen content of crude oil but lower than the oxygen content of liquids derived from coal (Scouten, 1990; Lee, 1991; Speight, 2013, 2014). The sulfur content of shale oil varies widely but is generally lower than the sulfur content of high-sulfur crude oil, heavy oil, and extra heavy oil, as well as tar sand bitumen (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). Also, crude shale oils contains appreciable amounts of soluble arsenic, iron, and nickel derivatives that cannot be removed by filtration (Scouten, 1990).

The high pour point and also high viscosity of the raw shale oil and of the hydrotreated shale oil are a cause for concern. It appears that both the raw shale oil with its high nitrogen content, its high pour point and high viscosity and the hydrotreated shale oil with its high pour point may not be suitable for undedicated (to such oils) pipelines. In the absence of dedicated pipelines, conversion to pipeline-acceptable products (such as gasoline, diesel fuel, and jet fuel) at or near the retorting site is one alternative. Another is to subject the raw shale to a coking operation which lowers the pour point and, when followed by hydrotreating, gives a low-sulfur, low-nitrogen product with a pour point on the order of 7 °C (45 °F).

Depending on the process, some oil-shale distillates have a much higher concentration of higher boiling-point compounds that would favor production of middle-distillates (such as diesel and jet fuels) rather than naphtha (Hunt, 1983; Scouten, 1990). Above-ground retorting processes tended to yield lower API gravity oil than the in situ processes due to the residence time in the underground retort which encourages further cracking of the primary products. Thus, additional processing equivalent to hydrocracking would be required to convert oil-shale distillates to a lighter range hydrocarbon (gasoline). Removal of sulfur and nitrogen would, however, require hydrotreating.

However, on the positive side, oil shale retorting processes produce oil with none-to-very-little high-boiling residuum (Scouten, 1990). With upgrading, shale oil can be a low-boiling boiling premium product that has the potential to be at least as valuable as conventional crude oil (Scouten, 1990; Lee, 1991; Lee et al., 2007; Speight, 2014, 2017, 2019a). However, the properties of shale oil vary as a function of the production (retorting) process. Fine mineral matter carried over from the retorting process and the high viscosity and instability of shale oil produced by present retorting processes have necessitated upgrading of the shale oil before transport to a refinery.

After fines removal the shale oil is hydrotreated to reduce nitrogen, sulfur, and arsenic content and improve stability; the cetane index of the diesel and heater oil portion is also improved. The hydrotreating step is generally accomplished in fixed catalyst bed processes under high hydrogen pressures, and hydrotreating conditions are slightly more severe than for comparable boiling range crude oil stocks, because of the higher nitrogen content of shale oil.

However, catalytic hydrodesulfurization processes are not always the best solution for the removal of sulfur constituents from gasoline when high proportions of unsaturated constituents are present. A significant amount of the hydrogen would be used for hydrogenation of the unsaturated components. On the other hand, however, when hydrogenation of the unsaturated hydrocarbon derivatives is desirable, catalytic hydrogenation processes would be effective.

2. Shale oil properties

First and foremost, shale oil is not a naturally-occurring material and it is not the same (or even remotely similar) as oil from tight formation (tight oil). Shale oil (also known as kerogen-derived oil) is a synthetic crude oil produced by retorting oil shale. The physical and chemical properties of crude shale oil are affected by (i) the shale from which the oil was produced as well as (ii) the reaction parameters that were operative at the time of production of the oil.

Even though the shale oil never reached the maximum potential, upgrading shale oil to a finished suite of products is not unknown. The difference between the various operations lies in the nature of the desired final product. While some crude shale oils have pour points and viscosities that make transporting them difficult and expensive there were attempts to partially refine (upgrade) the shale oil at or near the retorting site to improve the transportation characteristics. In other instances, there was the desire to obtain a complete array of finished fuels from an integrated processing facility located near to the mine site. In such a case, a total-refining facility would be considered rather than a more simple upgrading plant.

Shale oil has a rather high specific gravity, approximately 0.9−1.0, owing to the presence of nitrogen-, sulfur-, and oxygen-containing compounds. Also, high pour points are observed and small quantities of arsenic and iron are present. The nitrogen compounds are the most deleterious components of shale oil, since they are well-known catalytic poisons in various refining processes, such as fluid catalytic cracking, catalytic reforming, and catalytic hydrotreating (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). These compounds can give rise to stability (and incompatibility) problems in naphtha (and, hence if not removed during refining, in finished products such as gasoline) as well as in kerosene (and, hence if not removed during refining, in finished products such as jet fuel and diesel fuel), and produce emissions of nitrogen oxide (NO_x) in burners.

Compared to tight oil (or for that matter, compared to any conventional light crude oil), shale oil is relatively viscous and is high in nitrogen and oxygen compounds. The low molecular oxygen compounds are predominantly phenol derivatives but carboxylic acid derivatives and non-acidic oxygen compounds such as ketone derivatives are also present in the oil. The basic nitrogen compounds in shale oils are pyridine, quinoline, acridine, amine and their alkyl substituted derivatives, the weakly basic ones are pyrrole, indole, carbazole and their derivatives, and the nitrile and amide homologues are the non-basic constituents. Sulfur compounds in the shale oils include thiol derivatives, sulfide derivatives, thiophene derivatives, as well as miscellaneous sulfur compounds. Elemental sulfur may occur in some shale oils but it is not a typical constituent.

Crude shale oil (also called raw shale oil, retort oil, or simply shale oil) is the liquid oil product recovered directly from the offgas stream of an oil shale retort. Synthetic crude oil (syncrude) results when crude shale oil is hydrogenated. In general, crude shale oil resembles conventional crude oil in that it is composed primarily of long-chain hydrocarbon derivatives with boiling points that span roughly the same range as those of typical crude oils. However, the three principal differences between crude shale oil and conventional crude are (i) a higher olefin content in shale oil because of the high temperatures used in the production processes, (ii) higher concentrations of oxygen and nitrogen derivatives that are produced from the oil shale kerogen, and, in many cases, (iii) a higher pour point and viscosity of shale oil.

The physical and chemical properties of crude shale oil are affected by the conditions under which the oil was produced. Some retorting processes subject it to relatively high temperatures, which may cause thermal cracking and thus produce an oil with a lower average molecular weight. In other processes (such as directly heated retorting) some of the lower-boiling constituents of the shale oil are incinerated during retorting − the result is a higher molecular weight (higher-boiling) final product. Other processes may produce lower-boiling products because of refluxing (cyclic vaporization and condensation) of the oil within the retort. One of the most important factors is the condensing temperature within the retorting system − this is the temperature at which the oil product is separated from the gaseous products of the retorting process. The lower this temperature, the higher the concentration of low molecular weight compounds in the product oil.

The properties of the oil produced by different above-ground retorting processes vary widely, but the differences between these oils and the in situ oils are much more significant. In situ oils are generally much lighter, as indicated by the higher yields of material with relatively low boiling points, and would produce more of a lower-boiling product (such as naphtha) and less of a higher-boiling product (such as resid). In general, the low yields of residuum make shale oils attractive as refinery feedstocks in comparison with many of the heavy conventional crude oils.

As a side note, coal-derived liquids (Speight, 2013) are often regarded as alternatives to shale oil feedstocks. However, synthetic crude oils from coal have a much higher yield of naphtha and low-boiling distillates than shale oil, with little or no material boiling at temperatures above 455−535 °C (850−1000 °F). The coal-derived liquids would be well-suited for gasoline blend stock or even gasoline production because of the higher concentrations of lower boiling constituents and, when refined, would yield the desired low-boiling naphtha fraction. On the other hand, shale oil has a much higher concentration of high-boiling compounds, and would favor production of middle distillate fractions (such as kerosene and fuel oil) rather than naphtha. Shale oil-derived synthetic crude oil and coal-derived synthetic crude oils should, therefore, be regarded not as a competitive or substitutable feedstocks but rather as complementary feedstocks, with each yielding a different major fuel product from an equivalent amount of refining.

Among the negative characteristics of most crude shale oils are high pour point, high viscosity, and high concentrations of arsenic and other heavy metals and of nitrogen. The pour point and viscosity are of economic importance because transporting viscous oil that has a high pour point is difficult and, thus suggesting the need for pretreatment prior to marketing. High concentrations of arsenic and other metals are a disadvantage because they poison refining catalysts, especially in hydrogenation units (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). These constituents must be removed prior to catalytic processing. It should be noted that the concentrations of heavy metals in crude shale oil will vary with the location of the deposit from which the oil is recovered. Shale oil produced from oil shales from different formation (or sites) may be relatively free of such contaminants.

Other characteristic properties of shale oils are: (i) high levels of olefin derivatives and diolefin derivatives which are not present in tight crude oil or in crude oil in general and require special care during processing due to their tendency to polymerize and form gums, (ii) high levels of aromatic compounds, which are deleterious to diesel fuel, (iii) high carbon/hydrogen ratio, (iv) low sulfur levels, compared with most crudes available in the world, although for some shale oils from the retorting of marine oil shale, relatively high concentrations sulfur compounds may be present, (v) suspended solids (finely divided rock) which cause process problems chiefly if a first step of processing is hydrotreating, and (vi) moderately high levels of metals. Because of these particular characteristics, further processes, such as upgrading and refining, are needed to improve the properties of shale oil products.

Some retorting processes subject it to relatively high temperatures, which may cause thermal cracking and thus produce an oil with a lower average molecular weight. In other processes (such as directly heated retorting) some of the lower molecular weight components of the oil are incinerated during retorting. The result is a higher molecular weight (higher density, more viscous) final product. Other retorting process may produce lower molecular weight products because of refluxing (cyclic vaporization and condensation) of the oil within the retort. One of the most important factors is the condensing temperature within the retorting system – the condensing temperature is the temperature at which the shale oil product is separated from the retort gases. The lower this temperature, the higher the concentration of low molecular weight compounds in the product oil.

Thus, among the negative characteristics of most crude shale oils are high pour point, high viscosity, and high concentrations of arsenic and other heavy metals and of nitrogen. The pour point and viscosity are of economic importance because transporting viscous oil that has a high pour point is difficult and costly, thus suggesting the need for pretreatment prior to marketing. However, shale oil produced by an in situ process with a relatively low pour point and viscosity could be marketed without pretreatment but they would retain their high nitrogen content. This would reduce their value as refinery feedstocks and boiler fuels.

A high concentration of arsenic and other metals are a disadvantage because these metals poison refining catalysts, especially in hydrogenation units and must be removed prior to catalytic processing – a variety of physical and chemical methods have been developed for this purpose (Scouten, 1990; Speight, 2014). It should be noted that the concentration of heavy metals in crude shale oil will vary with the location of the deposit from which the oil is recovered.

Shale oil is a synthetic crude oil produced by retorting oil shale and is the pyrolysis product of the organic matter (kerogen) contained in oil shale. The raw shale oil produced from retorting oil shale can vary in properties and composition (Scouten, 1990; Lee, 1991; US DOE, 2004a,b,c; Speight, 2019a). The two most significant characteristics of US western oil shales are the high hydrogen content, derived primarily from high concentrations of paraffins (waxes), and the high concentration of nitrogen, derived from high concentrations of pyridines and pyrroles.

Synthetic crude oil (syncrude) is the product that results when crude shale oil is refined (i.e., hydrogenated). In general, crude shale oil resembles conventional crude oil insofar as it is composed primarily of hydrocarbon derivatives and has a boiling range that is approximately the same range as the boiling range of typical of a typical crude oil. However, there are three principal differences between crude shale oil and conventional crude oil which are (i) crude shale oil has a higher olefin content a higher olefin content because of the high temperatures used in oil retorting, (ii) crude shale oil has a higher concentration of organic oxygen derivatives and organic nitrogen derivatives which are derived from the kerogen, (iii) in many cases, crude shale oil has a higher pour point and a higher viscosity than conventional crude oil, as well as (iv) crude shale oil with has a higher density (specific gravity of the crude oil – on the order of 0.9–1.0 owing to the presence of higher molecular weight nitrogen-, sulfur-, and oxygen-containing compounds). Shale oil also has small quantities of arsenic and iron are present.

A typical shale oil produced from the Green River formation in Colorado contains approximately 40% w/w hydrocarbon derivatives consists of saturated hydrocarbon derivatives, olefin hydrocarbon derivatives, and aromatic hydrocarbon derivatives (Table 16.2) and approximately 60% w/w heteroatomic organic compounds, which contain nitrogen, sulfur, and oxygen derivatives. The nitrogen occurs in ring compounds with nitrogen in the ring, such as in pyridine derivatives and pyrrole derivatives as well as in nitrile derivatives – the nitrogen derivatives comprise approximately 60% w/w of the non-hydrocarbon components of the oil. Another 10% w/w of the heteroatomic components of the oil are sulfur compounds, which exist as thiophene derivatives along with varying amounts of sulfide derivatives and disulfide derivatives. The remaining 30% w/w is made up of oxygen compounds, which occur as phenol derivatives and carboxylic acid derivatives.

Although the content of asphaltene constituents and resin constituents in shale oil may be low, it is responsible for the dark color as well as the viscosity. The presence of asphaltene constituents in shale oil is not necessarily unique since it is high in nitrogen content and, consequently, high in ash content as well – polar nitrogen species are typically insoluble in n-heptane. The solvent used to separate the asphaltene fraction for crude oil and even low molecular weight species would appear as (or in) an asphaltene fraction from shale oil (Speight, 2014). The polarity of the nitrogen-containing polycyclic derivatives may also explain the specific properties of emulsification of water and metal complexes.

The presence of the polar constituents in crude shale oil which contain nitrogen and oxygen functions, sulfur compounds are less of a problem because of the hydrotreating option when the shale oil is refined. However, shale oil can be notoriously incompatible with conventional crude oil feedstocks and with crude oil-derived products (Chapter 17) (Mushrush and Speight, 1995; Speight, 2014, 2017). As a result, particular care must be taken to ensure that all of the functions that cause such incompatibility are removed from the shale oil before it is blended with a conventional crude oil or crude oil product – the same rationale applied to blending shale oil with tight oil or tight oil products.

2.1 Hydrocarbons

The fundamental structure of the organic matter in oil shale gives rise to significant quantities of waxes consisting of long normal alkane derivatives and the alkane derivatives are distributed throughout the raw shale oil. However, the composition of shale oil depends on the shale from which it was obtained as well as on the retorting method by which it was produced (Table 16.3) (Scouten, 1990; Lee, 1991; Speight, 2019a). As compared with crude oil crude, shale oil is heavy, viscous, and is high in nitrogen and oxygen compounds.

Of the possible variables that can affect the quality of shale oil the retorting method is by far the most significant. The major difference in shale oils that are produced by different processing methods is in boiling-point distribution. Rate of heating as well as temperature level and duration of product exposure to high temperature affect product type and yield.

Retorting processes, which use flash pyrolysis, produce more fragments containing the high-molecular weight, multi-ring aromatic structures. Processes that use slower heating conditions, with greater reaction times at low temperature 300–400 °C (570–750 °F), tend to produce higher concentrations of n-alkane derivatives. Naphthene-aromatic compounds of intermediate boiling range (such as 200–400 °C, 390–750 °F) also tend to be formed with the slower heating processes.

Saturated hydrocarbon derivatives in the shale oil include n-alkane derivatives, iso-alkane derivatives, and cycloalkane derivatives, and the alkene derivatives consist of n-alkene derivatives, iso-alkene derivatives, and cycloalkene derivatives, while the main components of aromatic derivatives are monocyclic, bicyclic, and tricyclic aromatic derivatives and their alkyl substituted homologues. There is a variation of the distribution of saturated hydrocarbon derivatives, alkene derivatives, and aromatic derivatives in the different boiling ranges of the shale oil product. Saturated hydrocarbon derivatives in the shale oil increase and the aromatic derivatives increase slightly with a rise in boiling range, while alkene derivatives decrease with a rise in boiling range.

TABLE 16.3 Major compound types in shale oil.

Saturates	Heteroatom systems
Paraffin derivatives	Benzothiophene derivatives
Cycloparaffin derivatives	Dibenzothiophene derivatives
Olefin derivatives	Phenol derivatives
Aromatic derivatives	Carbazole derivatives
Benzene derivatives	Pyridine derivatives
Indan derivatives	Quinoline derivatives
Tetralin derivatives	Nitrile derivatives
Naphthalene derivatives	Ketone derivatives
Biphenyl derivatives	Pyrrole derivatives
Phenanthrene derivatives	
Chrysene derivatives	

TABLE 16.4 Challenges for oil shale processing.

Particulates	Plugging on processing
	Product quality
Arsenic content	Toxicity
	Catalyst poison
High pour point	Oil does not meet pipeline specifications
Nitrogen content	Catalyst poison
	Contributes to instability
	Toxicity
Diolefins	Contributes to instability
	Plugging on processing

Shale oil contains a large variety of hydrocarbon compounds (Table 16.3) but also has high nitrogen content compared to a nitrogen content of 0.2–0.3% w/w for a typical crude oil (Scouten, 1990; Speight, 2014, 2017, 2019a). In addition, shale oil also has a high olefin and di-olefin content – constituents, which are not present in crude oil and which require attention during processing due to their tendency to polymerize and form gums and sediments (fuel line deposits). It is the presence of these olefins and diolefins, in conjunction with high nitrogen content, which gives shale oil the characteristic difficulty as a refinery feedstock (Table 16.4). Crude shale oil also contains appreciable amounts of arsenic, iron and nickel that interfere with refining.

Other characteristic properties of shale oils are: (i) high levels of aromatic compounds, deleterious to kerosene and diesel fractions, (ii) low hydrogen-to-carbon ratio, (iii) low sulfur levels, compared with most crudes available in the world (though for some shale oils from the retorting of marine oil shale, high sulfur compounds are present), (iv) suspended solids (finely divided rock) typically die to entrainment of the rock in the oil vapor during retorting, and (v) low-to-moderate levels of metals.

Because of the characteristics of shale oil, further processes are needed to improve the properties of shale oil products. The basic unit operations in the oil refining are distillation, coking, catalytic hydrotreating, catalytic cracking, and reforming. The process selected will largely depend on the availability of equipment and the individual economics of the particular refinery.

Although the content of asphaltene constituents and/or resin constituents in shale oil is low – shale oil being a distillate – asphaltene constituents in shale oil may be unique since, in shale oil, it is high heteroatomic content that causes precipitation as an asphaltene fraction rather than high molecular weight – for example the hydroxy-pyridine derivatives are insoluble in low molecular weight alkane solvents. The polarity of the nitrogen polycyclic aromatic constituents may also explain the specific properties of emulsification of water and metal complexes.

2.2 Nitrogen-containing compounds

Nitrogen compounds in shale oil render technological difficulties in the downstream processing of shale oil, in particular, poisoning of the refining catalysts. Such nitrogen compounds are all originated from the oil shale and the amount and types depend heavily on the geochemistry of oil shale deposits. Since direct analysis and determination of molecular forms of nitrogen containing compounds in oil shale rock is very difficult, the analysis of shale oil that is extracted by retorting processes provides valuable information regarding the organo-nitrogen species in the oil shale.

The nitrogen content in the shale oil is relatively higher than in natural crude oil (Hunt, 1983; Scouten, 1990; Lee, 1991; Guo and Qin, 1993; Speight, 2014, 2017, 2019a). The nitrogen-containing compounds identified in shale oils can be classified as basic, weakly basic, and non-basic. The basic nitrogen compounds in shale oils are pyridine, quinoline, acridine, amine and their alkyl substituted derivatives, the weakly basic ones are pyrrole, indole, carbazole and their derivatives, and the nitrile and amide homologues are the non-basic constituents. Most of these compounds are useful chemicals (Scouten, 1990; Lee, 1991), although some of them are believed to affect the stability of shale oil. Generally, basic nitrogen accounts for approximately one-half of the total nitrogen, and is evenly distributed in the different boiling point fractions. Nitrogen compounds occur throughout the boiling ranges of the shale oil, but have a decided tendency to exist in high boiling point fractions. Pyrrole-type nitrogen increases with a rise in the boiling point of the shale oil fractions. Porphyrins may occur in the high boiling point fraction of the shale oil.

Of the nitrogen-containing compounds in the <350 °C (<660 °F) light shale oil fraction, the majority contain one nitrogen atom. Benzoquinoline derivatives, principally acridine and alkyl-substituted homologues, could not be present significantly in the lower-boiling shale oil fractions because the boiling point of benzoquinoline and its alkyl-substituted homologues is higher than 350 °C (660 °F).

Organic nitrogen-containing compounds in the shale oil poison the catalysts in different catalytic processes. They also contribute to stability problems during storage of shale oil products since they induce polymerization processes, which cause an increase in the viscosity and give rise to the odor and color of the shale oil product. The high nitrogen content of shale oil could contribute to the surface and colloidal nature of shale oil, which forms emulsions with water.

2.3 Oxygen-containing compounds

The oxygen content of shale oil is much higher than in natural crude oil (Scouten, 1990; Lee, 1991). Low molecular weight oxygen compounds in shale oil are mainly phenolic constituents — carboxylic acids and non-acidic oxygen compounds such as ketones are also present. Low molecular phenolic compounds are the main acidic oxygen-containing compounds in the light fraction of the shale oil and are usually derivatives of phenol, such as cresol and poly-methylated phenol derivatives. The oxygen content of crude oil is typically on the order of 0.1–1.0% w/w whereas the oxygen contents in shale oils are much higher and vary with different shale oil (Scouten, 1990; Lee, 1991; Speight, 2014, 2017). In addition, the oxygen content varies in different boiling point fractions of the shale oil. In general, it increases as the boiling point increases, and most of the oxygen atoms are concentrated in the high boiling point fraction.

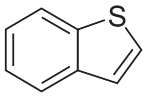
Low molecular weight phenolic compounds are the main acidic oxygen-containing compounds in the low-boiling fraction of the shale oil. For example, typically a high proportion of the phenol derivatives in shale oil concentrated in the <225 °C (<435 °F) fraction. Such phenolic compounds are phenol, cresol, dimethyl-phenol derivatives, ethyl phenol derivatives, trimethyl phenol derivatives, and tetramethyl phenol derivatives. Substituted phenol derivatives account for most of the volatile components of the acid fraction.

Other oxygen-containing constituents of shale oil include small amounts of carboxylic acids and non-acidic oxygen-containing compounds with a carbonyl functional group such as ketones, aldehydes, esters, and amides are also present in the <350 °C (<660 °F) fraction of shale oil. Ketones in the shale oil mainly exist as 2- and 3-alkyl ketone derivatives. Other oxygen-containing compounds in the low-boiling (<350 °C, <660 °F) fraction include alcohol derivatives, naphthol derivatives, and various ether derivatives (Scouten, 1990; Lee, 1991).

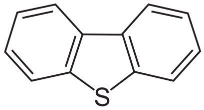
2.4 Sulfur compounds

Sulfur compounds in the shale oils include thiols, sulfides, thiophenes and other miscellaneous sulfur compounds. Elemental sulfur is found in some crude shale oil but is absent in others.

Generally, the sulfur content of oil-shale distillates is comparable in weight percentage to crude oil (Scouten, 1990; Lee, 1991; Lee et al., 2007; Speight, 2014, 2017, 2019a). Refiners will able to meet the current 500 ppm requirement by increasing the existing capacity of their hydrotreatment units and adding new units. However, refineries may face difficulty in treating diesel to below 500 ppm. The remaining sulfur is bound in multi-ring thiophene-type compounds that prove difficult to hydrotreat because of the presence of ring structure that are attached through the sulfur atom and as carbon-carbon bonds:



Benzothiophene



Dibenzothiophene

Also, if alkyl groups are present, the can (depending upon the position of the groups on the adjacent ring systems) provide steric protection for the sulfur atom. Although these compounds occur throughout the range of crude oil distillates, they are more concentrated in the residuum.

3. Shale oil upgrading

A conventional refinery distills crude oil into various fractions, according to the boiling point range, before further processing (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). The distilled fractions are - in order of the increasing boiling range and density, the distilled fractions are fuel gases, light and heavy straight-run naphtha (32−200 °C, 90-390 °F), kerosene (200−270 °C, 390-520 °F), gas-oil (270−565 °C, 520−1,050 °F), and residuum (>565 °C, >1,050 °F). The molecular range for naphtha (a gasoline blend stock) is typically C_5 to C_{10}; middle-distillate fuels (kerosene, jet, and diesel) range C_{11} to C_{18}. Conventional crude oil may contain varying amounts of naphtha − heavy crude oil contains much less naphtha than conventional crude oil (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017) − and early refineries directly distilled a straight-run naphtha (low-boiling naphtha that was used unchanged as gasoline) of low-octane rating. A hypothetical refinery may crack a barrel of crude oil into naphtha and kerosene with the amounts of each depending on the refinery configuration, the slate of crude oils refined, and the seasonal product demands of the market.

In order to convert shale oil to the analogous distillate produces, there have been several evaluations the expected performance of three types of options for upgrading shale oil and these are (i) thermal processes, (ii) catalytic processes, and (iii) additive processes in which the shale oil is blended with crude oil products.

Thermal processes include visbreaking (a relatively mild thermal treatment) and coking (a severe thermal treatment). Mild thermal treatment will reduce pour point and viscosity, but the oil will retain its initial amounts of nitrogen and sulfur. In contrast, severe thermal treatment reduces the pour point, viscosity, and sulfur content and also causes the nitrogen compounds to concentrate in the higher-boiling products. The properties of the lower-boiling products will thus be considerably improved.

In catalytic processes, the shale oil is reacted with hydrogen in the presence of a catalyst. Viscosity is reduced, and the nitrogen and sulfur are converted to ammonia and hydrogen sulfide gases that can be recovered as byproducts. In additive processes, such as hydrotreating, hydrogen is added to the feedstock ro remove obnoxious compounds such as the compounds containing nitrogen or oxygen, or sulfur. Blending agents are added that reduce the pour point and allow the crude to be transported by pipeline. Such pour point depressants have been added in several instances with success, but the technique is not yet highly developed. Providing compatibility of the blends can be avoided (Chapter 17), there is also the potential for blending shale moil with conventional crude oil or with conventional crude oil products (Mushrush and Speight, 1995; Speight, 2014).

Total refining studies have focused either on the needs of existing refineries that would have to be modified for processing shale oil, or on those of newly built facilities that could be designed specifically for shale oil feedstocks. These studies differ in their approach to the analysis of refining requirements. For example, upgrading shale oil in existing refineries must consider the equipment that is in place, and must allow for the limited flexibility of this equipment for processing a feedstock that is different from the one for which the refinery was designed. Upgrading shale oil in specially-built refineries, in contrast, need not be biased in this manner, and can draw upon any processing technique that is available within the refining industry. However, both types of studies must make assumptions about feedstock characteristics and desired product mixes. These will vary with the location of the refinery, the nature of the market it serves, and the type of retorting facility that supplies the feedstocks.

Shale oil-shale distillate has been considered a synthetic substitute for crude oil but the performance of shale oil in a modern is somewhat limited because the shale oil lacks the full range of hydrocarbon derivatives used by refineries in maximizing naphtha (thence gasoline) and kerosene (thence diesel) production. Also, because of technology limitations, only hydrocarbon derivatives in the range of middle distillates (kerosene and low-boiling gas oil) appear to be extractable in the refinery. In general, shale oil has a much higher concentration of high boiling-point compounds that would favor production of middle-distillates (such as diesel and jet fuels) rather than naphtha. In addtion, above-ground retorting processes have tended to yield a lower API gravity oil than the in situ processes (a 25° API gravity was the highest produced). Additional processing equivalent to hydrocracking would be required to convert oil-shale distillates to a lighter range hydrocarbon product (naphtha).

As a comparison, of shale oil with crude oil, a typical 35° API-gravity crude oil may be composed of up to 50% of gasoline and middle-distillate range hydrocarbon derivatives. West Texas Intermediate crude (a benchmark crude for trade in the commodity futures market) has a 0.3% sulfur content, and Alaska North Slope crude has a 1.1% sulfur content. The New York Mercantile Exchange (NYMEX) specifications for light "sweet" crude limits sulfur content to 0.42% or less (A.S.T.M. Standard D-4294) and an API gravity between 37 and 42° (A.S.T.M. Standard D-287). Shale oil also contains a large variety of hydrocarbon derivatives but also has a high nitrogen content compared to a nitrogen content of 0.2−0.3% w/w for a typical crude oil (Speight, 2014, 2017).

In addition, shale oil also has a high olefin and diolefin content. It is the presence of these olefins and diolefins, in conjunction with high nitrogen content, that gives shale oil the characteristic difficulty in refining and the tendency to form insoluble sediment. Crude shale oil also contains appreciable amounts of arsenic, iron and nickel that interfere with refining. Furthermore, blending shale oil products with corresponding crude oil products, using shale oil fractions obtained from shale oil can lead to incompatibility issues (Chapter 17). Hydroprocessing shale oil products, either alone or in a blend with the corresponding crude oil fractions, is therefore necessary. The severity of the hydroprocessing has to be adjusted according to the particular properties of the feed and the required level of the stability of the product.

In general, oil-shale distillates have a much higher concentration of high boiling-point compounds that would favor production of middle-distillates (such as diesel and jet fuels) rather than naphtha. Oil-shale distillates also had a higher content of olefins, oxygen, and nitrogen than crude oil, as well as higher pour points and viscosities. Above-ground retorting processes tended to yield a lower API gravity oil than the in situ processes (a 25° API gravity was the highest produced). 20 Additional processing equivalent to hydrocracking would be required to convert oil-shale distillates to a lighter range hydrocarbon (gasoline). Removal of sulfur and nitrogen would, however, require hydrotreating. By comparison, a typical 35° API-gravity crude oil may be composed of up to 50% of gasoline and middle-distillate range hydrocarbon derivatives. West Texas Intermediate crude benchmark crude for trade in the commodity futures market has 0.3% by weight sulfur, and Alaska North Slope crude has

1.1% by weight sulfur. The New York Mercantile Exchange (NYMEX) specifications for light sweet crude oil limits sulfur content to 0.42% w/w or less (ASTM D4294) and an API gravity on the order of 37°−42° (ASTM D287).

Thus, shale oil is different from conventional crude oils, and several refining technologies have been developed to deal with this. The primary problems identified in the past were arsenic, nitrogen, and the waxy nature of the crude. Nitrogen and wax problems were solved using hydroprocessing approaches, essentially classical hydrocracking and the production of t making high quality lube stocks, which require that waxy materials be removed or isomerized. However, the arsenic problem remains.

Shale oil is often (and more correctly) referred to as a synthetic crude oil and thus closely associated with synthetic fuel production. However, the recovered hydrocarbon derivatives from oil shale are not yet economically competitive against the crude oil crude produced. Furthermore, the value of hydrocarbon derivatives recovered from oil shale is diminished because of the presence of undesirable contaminants, such as are sulfur-containing, nitrogen-containing, and metal-containing (organometallic) compounds, which cause detrimental effects to various catalysts used in the subsequent refining processes (Speight, 2014, 2017). These contaminants are also undesirable because of their disagreeable odor, corrosive characteristics, and combustion products that further cause environmental problems.

Accordingly, there is great interest in developing more efficient methods for converting the heavier hydrocarbon fractions obtained in a form of shale oil into lighter-molecular-weight hydrocarbon derivatives. The conventional processes include catalytic cracking, thermal cracking, and coking. It is known that heavier hydrocarbon fractions and refractory materials can be converted to lighter materials by hydrocracking. These processes are most commonly used on liquefied coals or heavy residual or distillate oils for the production of substantial yields of low-boiling saturated products, and to some extent on intermediates that are used as domestic fuels, and still heavier cuts that are used as lubricants. These destructive hydrogenation or hydrocracking processes may be operated on a strictly thermal basis or in the presence of a catalyst.

Upgrading crude shale oil is necessary to reduce sulfur and nitrogen levels and contamination by mineral particulates. Since large portions of nitrogen and sulfur species in shale oil are present in forms of hetero-aromatic constituents, there is the need for selective removal of hetero-aromatic derivatives, final product quality control, and molecular weight reduction. Raw shale oil has relatively high pour point of 24−27 °C (75−80 °F), compared with −24 °C (−30 °F) for Arabian light crude oil. Olefins and diolefins may account for as much as one-half of the low-boiling fraction of 315 °C (600 °F) or lower, and lead to the formation of gums.

A conventional refinery distills crude oil into various fractions, according to boiling point range, before further processing. In order of their increasing boiling range and density, the distilled fractions are fuel gases, light and heavy straight-run naphtha (90−380 °F), kerosene (380−520 °F), gas-oil (520−1050 °F), and residuum (1050 °F +) (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). Crude oil may contain 10−40% v/v naphtha (a gasoline precursor), and early refineries directly distilled a low-boing naphtha low-octane rating which was sold as (straight-run) gasoline. A hypothetical refinery may crack a barrel of crude oil into two-thirds naphtha and one-third distillate fuel (kerosene, jet, and diesel), depending on (i) the configuration of the refinery, (ii) the slate of crude oils accepted by the refinery, and (iii) the seasonal product demands of the market.

The three primary factors that affect the design of a refining system for crude shale oil are: (i) the characteristics of the crude shale oil feedstock, (ii) the desired mix of finished products; and (iii) the constraints imposed by the equipment and operating practices of the proposed refinery.

The first factor probably will have the lowest effect because, except for the higher nitrogen and arsenic contents, the characteristics of crude shale oil are not widely different from those of conventional crude oil. The second factor (the product mix) is much more significant because of the changes that have occurred in the proposed configurations of shale oil refineries since the 1950s. The earlier studies placed much more emphasis on naphtha (or gasoline) production. The third factor (i.e., equipment and operating constraints) has become increasingly important. The modifications to convert a conventional refinery to shale oil feedstocks might not be economically justifiable unless the refiner could be assured of an adequate supply of shale oil. The economic desirability of building a refinery specifically for shale oil would be thoroughly scrutinized.

Upgrading, or partial refining, to improve the properties of a crude shale oil may be carried out with different objectives, depending on the intended use for the product. Complete refining of the crude shale oil or selected fractions to produce finished end products (e.g., gasoline, diesel, jet fuel). However, it is difficult to generalize regarding shale oil processing – not only do the shale oil properties vary; refineries vary widely (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). In addtion, upgrading activities are also dictated by factors such as the initial composition of the oil shale, the compositions of retorting products, the composition and quality of desired crude oil feedstocks or crude oil end products of market quality, and the business decision to develop other by-products such as sulfur and ammonia into saleable products. Product variety and quality issues aside, there are other logistical factors that determine the extent to which upgrading activities are conducted at the mine site. Most prominent among these factors is the ready availability of electric power and process water. In especially remote locations, factors such as these represent the most significant parameters for mine site upgrading decisions.

The initial composition of the crude shale oil produced in the retorting step is the primary influence in the design of the subsequent upgrading operation. In particular, nitrogen compounds, sulfur compounds, and organometallic compounds dictate the upgrading process that is selected. In general, crude shale oil typically contains nitrogen compounds (throughout the total boiling range of shale oil) in concentrations that are 10–20 times the amounts found in typical crude oils. Removal of the nitrogen-bearing compounds is an essential requirement of the upgrading effort, since nitrogen is poisonous to most catalysts used in subsequent refining steps and creates unacceptable amounts of NOx pollutants when nitrogen-containing fuels are burned.

Sulfur, also a poison to refinery catalysts, is typically present in much lower proportions as organic sulfides and sulfates. With respect to sulfur, crude shale oil compares favorably with most low-sulfur crude oils, which are preferred feedstocks for low-sulfur fuels that are often required by local air pollution regulations. Hydrotreating to the extent necessary to convert nitrogen compounds to ammonia is sufficient in most instances to simultaneously convert sulfur to hydrogen sulfide. Crude shale oil additionally contains much higher amounts of organometallic compounds than conventional crude oils. The presence of these organometallic compounds complicates the mine site upgrading, since they can readily foul the catalysts used in hydrotreating, causing interruptions in production and increased volumes of solid wastes requiring disposal, sometimes even requiring specialized disposal as hazardous wastes because of the presence of spoiled heavy-metal catalysts.

Desired end products for mine site upgrading are typically limited to mixtures of organic compounds that are acceptable for use as conventional refinery feedstock; however, it is possible to produce feedstocks that are of higher quality and value to refineries than even crude oils having the most desirable properties. Since crude shale oils are typically more viscous than conventional crude oils, their yields of lighter distillate fractions such as gasoline, kerosene, jet fuel, and diesel fuel are typically low. However, additional hydrotreating can markedly increase the typical yields of these distillate fractions.

Raw shale oil typically contains 1.5–2.0% w/w nitrogen, 0.5–1.0% w/w oxygen, and 0.1–1.0% w/w sulfur. Sulfur and nitrogen removal is necessary and must be complete, since these compounds poison most of the catalysts used in refining, and the sulfur oxides (SO_x) and nitrogen oxides (NO_x) are highly publicized air pollutants. Since raw shale oil is a condensed overhead product of pyrolysis, it does not contain the same kinds of macromolecules found in crude oil residua and coal tar or pitch (Speight, 2013, 2014, 2017). Conventional catalytic cracking, however, is an efficient technique for molecular weight reduction. It is crucially important to develop a new cracking catalyst that is more resistant to basic poisons (nitrogen and sulfur compounds) (Kundu et al., 2006). At the same time, the research should also focus on reduction of molecular weight of shale oil crude with low consumption of hydrogen.

Upgrading technologies are classified as primary, secondary or enhanced. Primary upgrading is mainly a molecular weight reduction process (especially in the case of tar sand bitumen) (Speight, 2014, 2017, 2019a), while secondary upgrading involves removal of impurities from the feed (which is more pertinent to upgrading synthetic crude oil from oil shale). The primary upgrading processes may or may not use a catalyst, while the secondary processes are catalytic.

Lower quality synthetic crude oil, such as shale oil from surface retorts produce lower quantities of conventional refinery products than light crude oils. As a result, the value of these oils is less than that of many higher API crude oils. Upgrading is the process of converting these lower value oils products more suitable for conventional refinery feedstocks. Partial upgrading reduces the amount of heteroatoms and other refinery-objectionable constituents to render the shale oil suitable for transportation to a refinery (Scouten, 1990; Lee et al., 2007). In contrast, the ICP process produces a refinery-ready shale oil that will not require partial upgrading prior to transportation to a refinery. The most common international standard for upgrading is the conversion of the vacuum residue to lower boiling point fractions.

Before II World War an industrial process for shale oil upgrading was worked out – retorting of oil shale was conjunct with cracking of shale oil in vapor phase. Furthermore, it was established that cracking of shale oil in presence of lime (as well as shale ash containing lime and aluminosilicates) results in increase of the yield of gasoline whereas a lot of phenolic oxygen is bound into carbonic acid and so great deal of hydrogen is released to form gasoline. Also resin donors are stabilized and H_2S is formed at 400–500 C (750–930 °F).

One significant difference among the various configurations described in the literature is the relative arrangement of distillation and thermal or catalytic treatment. Two general approaches have been investigated: (i) distillation of the whole crude into its components, then catalytic or thermal treatment, or (ii) catalytic or thermal treatment of the whole crude, then distillation. In the first approach the properties of the finished products are better controlled. In the second approach, the net load on successive processing units is reduced, and, in general, the overall yield of high-value hydrocarbon products is increased.

It is known that heavier hydrocarbon fractions and refractory materials can be converted to lighter materials by hydrocracking. Hydrocracking processes are most commonly used on liquefied coals or heavy residual or distillate oils for the production of substantial yields of low boiling saturated products and to some extent of intermediates which are used as domestic fuels and still heavier cuts which find uses as lubricants. These destructive hydrogenation processes or hydrocracking processes may be operated on a strictly thermal basis or in the presence of a catalyst. Thermodynamically speaking, larger hydrocarbon molecules are broken into lighter species when subjected to heat. The hydrogen-to-carbon (H/C) ratio of such molecules is lower than that of saturated hydrocarbon derivatives and abundantly supplied hydrogen improves this ratio by saturating reactions, thus producing liquid species. These two steps may occur simultaneously.

However, the application of the hydrocracking process has been hampered by the presence of certain contaminants in such hydrocarbon derivatives. The presence of sulfur and nitrogen containing compounds along with organometallics in crude shale oils and various refined crude oil products has long been considered undesirable. Desulfurization and denitrification processes have been developed for this purpose.

A preferred way of treating the shale oil involves using a moving bed reactor followed by a fractionation step to divide the wide-boiling-range crude oil produced from the shale oil into two separate fractions. The lower-boiling fraction is hydrotreated for the removal of residual metals, sulfur, and nitrogen, whereas the heavier fraction is cracked in a second fixed bed reactor normally operated under high-severity conditions.

The fluidized bed hydroretort process (Chapter 14) eliminates the retorting stage of conventional shale upgrading, by directly subjecting crushed oil shale to a hydroretorting treatment in an upflow, fluidized bed reactor such as that used for the hydrocracking of heavy crude oil residues (Scouten, 1990; Lee, 1991). This process is a *single stage retorting and upgrading* process. Therefore, the process involves: (i) crushing oil shale, (ii) mixing the crushed oil shale with a hydrocarbon liquid to provide a pumpable slurry, (iii) introducing the slurry along with a hydrogen-containing gas into an upflow, fluidized bed reactor at a superficial fluid velocity sufficient to move the mixture upwardly through the reactor, (iv) hydroretorting the oil shale, (v) removing the reaction mixture from the reactor, and (vi) separating the reactor effluent into several components.

The mineral carbonate decomposition is minimized, as the process operating temperature is lower than that used in retorting. Therefore, the gaseous product of this process has a greater heating value than that of other conventional methods. In addition, owing to the exothermic nature of the hydroretorting reactions, less energy input is required per barrel of product obtained. Furthermore, there is practically no upper or lower limit on the grade of oil shale that can be treated.

Upgrading, or partial refining, to improve the properties of a crude shale oil may be carried out using different options (US DOE, 2004a,b,c; Lee et al., 2007; Speight, 2019a). In conventional processing, Unocal catalytically hydrocracked raw kerogen oil. The process was both severe and costly, but resulted in a premium refinery feedstock. In the value-enhancement process, the raffinate, which has had its most problematic nitrogen removed, is hydrotreated under mild (approximately 300 °C, 570 °F), and low-cost conditions. This yields a refinery feedstock nearly as good as the Unocal feedstock. A comparison with the Shell ICP oil shows the premium quality of this in-situ oil, which is almost entirely atmospheric distillate. In general, oil from Green River oil shale is high in hydrogen and exhibits excellent properties for manufacturing aviation turbine fuel and diesel fuel.

Gasoline from shale oil usually contains a high percentage of aromatic and naphthenic compounds that are not affected by the various treatment processes. The olefin content, although reduced in most cases by refining processes, will still remain significant. It is assumed that diolefins and the higher unsaturated constituents will be removed from the gasoline product by appropriate treatment processes. The same should be true, although to a lesser extent, for nitrogen- and sulfur-containing constituents.

The sulfur content of raw shale oil gasoline may be rather high due to the high sulfur content of the shale oil itself and the frequently even distribution of the sulfur compounds in the various shale oil fractions. Not only the concentration but also the type of the sulfur compounds is of an importance when studying their effect on the gum formation tendency of the gasoline containing them.

Sulfides (R-S-R), disulfides (R-S-S-R), and mercaptans (R-SH) are, among the other sulfur compounds, the major contributors to the gum formation in gasoline. Sweetening processes for converting mercaptans to disulfides should therefore not be used for shale oil gasoline; sulfur extraction processes are preferred.

Gasoline derived from shale oil contains varying amounts of oxygen compounds. The presence of oxygen in a product, in which free radicals form easily, is a cause for concern. Free hydroxy radicals are generated and the polymerization chain reaction is quickly brought to its propagation stage. Unless effective means are provided for the termination of the polymerization process, the propagation stage may well lead to an uncontrollable generation of oxygen bearing free radicals leading to gum and other polymeric products.

Diesel fuel derived from oil shale is also subject to the degree of unsaturation, the effect of diolefins, the effect of aromatic derivatives, and to the effect of nitrogen and sulfur compounds. On the other hand, jet fuel produced from shale oil would have to be subjected to suitable refining treatments and special processes. The resulting product must be identical in its properties to corresponding products obtained from conventional crude oil. This can be achieved by subjecting the shale oil product to severe catalytic hydrogenation process with a subsequent addition of additives to ensure resistance to oxidation.

If antioxidants are used for a temporary reduction of shale oil instability, they should be injected into the shale oil (or its products) as soon as possible after production of the shale oil. The antioxidant types and their concentrations should be determined for each particular case separately. The antioxidants combine with the free radicals or supply available hydrogen atoms to mitigate the progress of the propagation and branching processes. When added to the freshly produced unstable product, the antioxidants may be able to fulfill this purpose. However, when added after some delay, i.e., after the propagation and the branching processes have advanced beyond controllable limits, the antioxidants would not be able to prevent formation of degradation products.

By comparison, a typical 35° API-gravity crude oil may be composed of up to 50% of gasoline and middle-distillate range hydrocarbon derivatives. West Texas Intermediate crude benchmark crude for trade in the commodity futures market has 0.3% by weight sulfur, and Alaska North Slope crude has 1.1% w/w sulfur. The New York Mercantile Exchange (NYMEX) specifications for light sweet crude limits sulfur content to 0.42% or less (ASTM D4294) and an API gravity between 37 and 42° (ASTM D287).

The first step is to prepare the crude shale oil for refining. As the oil exits the retort is it by no means a pure distillate. Crude shale oil usually contains emulsified water and suspended solids. Therefore, the first step in up grading is usually dewatering and desalting.

Furthermore, if not removed, the arsenic and iron in shale oil would poison and foul the supported catalysts used in hydrotreating. Because these materials are soluble, they cannot be removed by filtration. Several methods have been used specifically to remove arsenic and iron. Other methods involve hydrotreating; these also lower sulfur, olefin, and diolefin contents and thereby make the upgraded product less prone to gum formation. After these steps the shale oil may be suitable for admittance to typical refinery processing.

A conventional refinery distills crude oil into various fractions according to boiling point range, before further processing (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). In order of their increasing boiling range and density, the distilled fractions are fuel gases, light and heavy straight-run naphtha (32–200 °C; 90–390 °F), kerosene (200–270 °C; 390–520 °F), gas-oil (270–565 °C; 520–1050 °F), and residuum (565 °C+; 1050 °F+) (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). Crude oil may contain 10%–40% naphtha, and early refineries directly distilled a low-boiling naphtha (which is still incorrectly referred to as straight-run *gasoline*) of low-octane rating. A typical *cracking refinery* may convert a barrel of crude oil into high yields of naphtha (from which gasoline is produced) and lower yields of other distillate fuels such as kerosene from which jet fuel, and diesel fuel are produced, depending on the refinery configuration, the slate of crude oils refined, and the seasonal product demands of the market.

By way of recall, shale oil is different from conventional crude oils, and several refining technologies have been developed to deal with this. The primary problems identified in the past were arsenic, nitrogen, and the waxy nature of the crude. Nitrogen and wax problems were solved using hydroprocessing approaches, essentially classical hydrocracking and the production of t making high quality lube stocks, which require that waxy materials be removed or isomerized. However, the arsenic problem remains.

One significant difference among the various refinery options for upgrading shale oil a reflection of the early tar sand bitumen upgrading scheme (Speight, 2014, 2017, 2019c) and is the relative arrangement of distillation and subsequent catalytic treatment. Two general approaches are possible: (i) distillation of the whole shale oil into the component fractions followed by catalytic hydrotreatment of the fractions, each under process parameters that are suitable for the fraction (Fig. 16.1) and (ii) or catalytic hydrotreatment of the whole shale oil followed by distillation of the product into the component fractions (Speight, 2014, 2017, 2019c). In the first option, the properties of the finished products are subject to a higher degree of control. In the second option, the reliance on successive processing units is reduced, and, in general, the overall yield of high-value hydrocarbon products may be increased.

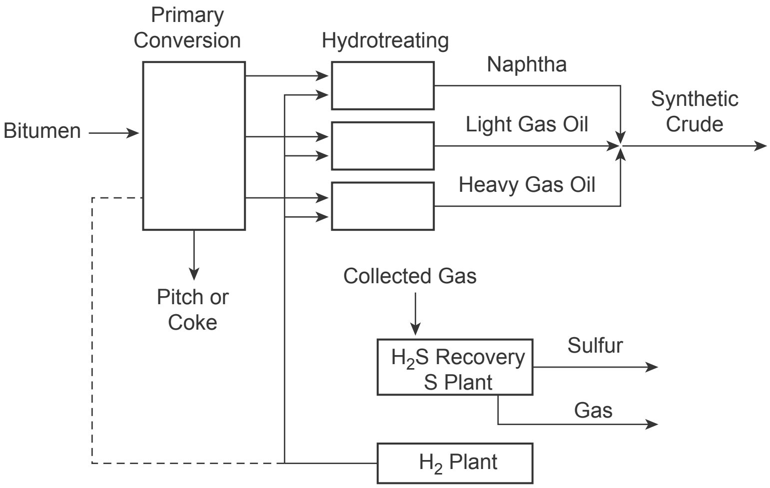


FIG. 16.1 Examples of sub-dividing a synthetic crude oil before hydrotreating – in this case, the example is Athabasca tar sand bitumen.

3.1 Visbreaking

Visbreaking (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017) is a mild thermal treatment insofar as the thermal reactions are no allowed to proceed to completion. This technique involves heating the crude shale oil to approximately 480°–525 °C (900°–980 °F) and holding the feedstock at this temperature range for from several seconds to several minutes. The product is then quenched (cooled), and the gases evolved during the heating are removed. There is little reduction in the content of nitrogen, sulfur, and oxygen and the principal improvements are reduction in pour point and reduction in the viscosity feedstock acceptable e to pipeline operators.

In the case of using raw shale oil as the feedstock, the process also causes the precipitation of arsenic but does little to reduce the contents of nitrogen, sulfur, or olefin derivatives unless the process is allowed to proceed to partial completion with the formation of low yield of coke at which time a high proportion of the nitrogen and sulfur derivatives will appear in the coke (Speight, 2014).

In the process, the feedstock is to a temperature on the order of 480–525 °C (900–980 °F) and holding it at this temperature range for from several seconds to several minutes, sometime under an atmosphere of hydrogen. Depending upon the residence time at the chosen temperature, some of the feedstock is cracked to gas but the majority of the product is a cracked liquid. The principal improvements, unless the process is carried out under hydrogen (hydrovisbreaking), are reductions in the pour point and a reduction in the viscosity.

The thermal cracking process is directed toward the recovery of gaseous olefins as the primarily desired cracked product, in preference to naphtha-range liquids. By this process, it is claimed that at least 15%–20% of the feed shale oil is converted to ethylene, which is the most common gaseous product. Most of the shale oil feedstock is converted to other gaseous and liquid products. Other important gaseous products are propylene, 1,3-butadiene, ethane, and butanes. Hydrogen is also recovered as a valuable nonhydrocarbon gaseous product. Liquid products can comprise 40–50% w/w or more of the total product. Recovered liquid products include benzene, toluene, xylene, gasoline-boiling-range liquids, and light and heavy oils. The thermal cracking reactor does not require a gaseous hydrogen feed. In the reactor, entrained solids flow concurrently through the thermal riser at an average riser temperature of 700–1400 °C (1290–2550 °F).

Coke is a solid product of the process and is produced by polymerization of unsaturated materials. Coke is typically formed in an oxygen-deficient environment via dehydrogenation and aromatization. Most of the formed coke is removed from the process as a deposit on the entrained inert heat carrier solids.

3.2 Coking

Delayed coking has been selected by many refiners as their preferred choice for bottom of the barrel upgrading, because of the ability of the process to conveniently handle even the heaviest of residues (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). The process is a semi-continuous (semi-batch) process in which the heated charge is transferred to large soaking (or coking) drums, which provide the long residence time needed to allow the cracking reactions to proceed to completion. The process provides essentially complete rejection of metals and precursors to term coke (precursors to Conradson carbon) while providing partial or complete conversion to naphtha and diesel.

In the past many delayed coking units were designed to provide complete conversion of atmospheric residue to diesel and lighter, and several coking units still operate in this mode (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). However, most recent cokers have been designed to minimize coke and produce heavy coker gas oil (HCGO) that is catalytically upgraded. The economics of delayed coking are driven by the differential between transportation fuels and high-sulfur residual fuel oil. The yield slate for a delayed coker can be varied to meet the objectives set by the refinery through the selection of operating parameters. Coke yield and the conversion of heavy coker gas oil are reduced, as the operating pressure and recycle are reduced and to a lesser extent as temperature is increased.

For treatment of raw shale oil, the delayed coking process involves heating the oil to approximately 480–525 °C (900–980 °F) and then charging it into a vessel in which thermal decomposition occurs. If the vessel is a coke drum, the process is called delayed coking and the coke (the solid product from thermal decomposition) is allowed to accumulate until it fills approximately two-thirds of the volume of the drum. The feed is then switched to another drum while the coke is cleaned out of the first one.

Fluid coking is a continuous process that uses the fluidized solids technique to convert residua, including vacuum residua and cracked residua, to more valuable products (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). In the process, hot feedstock is charged into a vessel that contains a fluidized bed of coke particles. This permits the coking reactions to be conducted at higher temperatures and shorter contact times than can be employed in delayed coking. Moreover, these conditions result in decreased yields of coke; greater quantities of more valuable liquid product are recovered in the fluid coking process. The particles become coated with oil, which then decomposes to yield gases and another layer of coke. The gases are withdrawn from the vessel. The coke is also withdrawn continuously, at a rate sufficient to maintain an active stock of coke within the bed. The yield of distillates from coking can be improved by reducing the residence time of the cracked vapors. In order to simplify handling of the coke product, and enhance product yields, fluidized-bed coking, or fluid coking, was developed in the mid-1950s.

Fluid coking uses two vessels, a reactor and a burner; coke particles are circulated between these to transfer heat (generated by burning a portion of the coke) to the reactor (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). The reactor holds a bed of fluidized coke particles, and steam is introduced at the bottom of the reactor to fluidize the bed. The feed coming from the bottom of a vacuum tower at, for example, 260−370 °C (500−700 °F), is injected directly into the reactor. The temperature in the coking vessel ranges from 480 to 565 °C (900−1050 °F), and the pressure is substantially atmospheric so the incoming feed is partly vaporized and partly deposited on the fluidized coke particles. The material on the particle surface then cracks and vaporizes, leaving a residue that dries to form coke. The vapor products pass through cyclones that remove most of the entrained coke.

The vapor is discharged into the bottom of a scrubber, where the products are cooled to condense a heavy tar containing the remaining coke dust, which is recycled to the coking reactor. The upper part of the scrubber tower is a fractionating zone from which coker gas oil is withdrawn and then fed to a catalytic cracking unit; naphtha and gas are taken overhead to condensers.

In the reactor, the coke particles flow down through the vessel into a stripping zone at the bottom. Steam displaces the product vapors between the particles, and the coke then flows into a riser that leads to the burner. Steam is added to the riser to reduce the solids loading and to induce upward flow. The average bed temperature in the burner is 590−650 °C (1095−1200 °F), and air is added as needed to maintain the temperature by burning part of the product coke. The pressure in the burner may range from 5 to 25 psi. Flue gases from the burner bed pass through cyclones and discharge to the stack. Hot coke from the bed is returned to the reactor through a second riser assembly.

Coke is one of the products of the process, and it must be withdrawn from the system to keep the solids inventory from increasing. The net coke produced is removed from the burner bed through a quench elutriator drum, where water is added for cooling and cooled coke is withdrawn and sent to storage. During the course of the coking reaction the particles tend to grow in size. The size of the coke particles remaining in the system is controlled by a grinding system within the reactor.

The yields of products are determined by the feed properties, the temperature of the fluid bed, and the residence time in the bed. The use of a fluidized bed reduces the residence time of the vapor-phase products in comparison to delayed coking, which in turn reduces cracking reactions. The yield of coke is thereby reduced, and the yield of gas oil and olefins increased. An increase of 5 °C (9 °F) in the operating temperature of the fluid-bed reactor typically increases gas yield by 1% by weight and naphtha by about 1% by weight. The lower limit on operating temperature is set by the behavior of the fluidized coke particles. If the conversion to coke and light ends is too slow, the coke particles agglomerate in the reactor, a condition known as *bogging*.

The disadvantage of burning the coke to generate process heat is that sulfur from the coke is liberated as sulfur dioxide. The gas stream from the coke burner also contains carbon monoxide (CO), carbon dioxide (CO_2), and nitrogen (N_2). An alternate approach is to use a coke gasifier to convert the carbonaceous solids to a mixture of carbon monoxide (CO), carbon dioxide (CO_2), and hydrogen (H_2).

The flexicoking process combines conventional fluid coking with gasification of the product coke. The advantage is that energy is recovered from the coke. The process is used in the refining industry but there is little evidence to show that the process be suitable for crude shale oil.

3.3 Hydrotreating

Hydrotreating (variously referred to as *hydroprocessing* to avoid any confusion with those processes that are referred to as *hydrotreating processes*) — sometime referred to as an additive process insofar as hydrogen is added to the feedstock — is a refining process in which the feedstock is treated with hydrogen at temperature and under pressure in which hydrocracking (thermal decomposition in the presence of hydrogen) is minimized. The usual goal of hydrotreating is to hydrogenate olefins and to remove heteroatoms, such as sulfur, and to saturate aromatic compounds and olefin derivatives (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). On the other hand, *hydrocracking* is a process in which thermal decomposition is extensive and the hydrogen assists in the removal of the heteroatoms as well as mitigating the coke formation that usually accompanies thermal cracking of high molecular weight polar constituents.

Hydrotreating is the option of choice to produce a stable product that is comparable to benchmark crude oils (Andrews, 2006; Speight, 2014, 2017, 2019a). In terms of refining and catalyst activity, the nitrogen content of shale oil is a disadvantage. But, in terms of the use of shale oil residua as a modifier for asphalt, where nitrogen species can enhance binding with the inorganic aggregate, the nitrogen content can be beneficial. If not removed, the arsenic and iron in shale oil would poison and foul the supported catalysts used in hydrotreating (Speight, 2014, 2017).

Catalytic processes which consume hydrogen are used to saturate olefins, to eliminate heterocyclic compounds (containing atoms of O, N, S), and stabilize oils to reduce tendency for oxidation and gum formation as a result of exposure to air and temperatures. Schemes know in petro-chemistry to get motor fuels of high quality from crude oil could not be used in case of shale oils due to the wide boiling range of heteroatomic compounds present not only in heavy fractions but also in lighter ones.

In these processes, the crude shale oil is reacted with hydrogen in the presence of a catalyst. The sulfur in the oil is converted to hydrogen sulfide, the nitrogen to ammonia, the oxygen to water, the olefin hydrocarbon derivatives to their paraffin equivalents. The hydrogenation reactions can take place in a fixed-bed reactor through which a mixture of oil vapors and hydrogen is passed, in a fluidized-bed reactor, or in an ebullating-bed reactor. Catalytic hydrogenation produces upgraded products of the highest quality, but it is relatively expensive. The use of fixed-bed reactors would probably be confined to the treatment of streams from an initial fractionation step; fluid-bed or ebullating-bed processes could be used for either fractionator products or for the whole shale oil.

The moving-bed hydroprocessing reactor is used to produce crude oil from oil shale containing large amounts of highly abrasive particulate matter, such as rock dust and ash.

The hydroprocessing takes place in a dual-function moving bed reactor, which simultaneously removes particulate matter by the filter action of the catalyst bed. The effluent from the moving bed reactor is then separated and further hydroprocessed in fixed bed reactors with fresh hydrogen added to the heavier hydrocarbon fraction to promote desulfurization.

Clay-based catalysts metallic catalysts help transform complex hydrocarbon derivatives to lighter molecular chains in modern refining processes. The *catalytic-cracking* process developed during the World War II era enabled refineries to produce high-octane gasoline needed for the war effort. *Hydrocracking*, which entered commercial operation in 1958, improved on catalytic-cracking by adding hydrogen to convert residuum into high-quality motor gasoline and naphtha-based jet fuel. Many refineries rely heavily on *hydroprocessing* to convert low-value gas oils residuum to high-value transportation fuel demanded by the market.

Middle-distillate range fuels (diesel and jet) can be blended from a variety of refinery processing streams. To blend jet fuel, refineries use desulfurized straight-run kerosene, kerosene boiling range hydrocarbon derivatives from a hydrocracking unit, and light coker gas-oil (cracked residuum). Diesel fuel can be blended from naphtha, kerosene, and light cracked-oils from coker and fluid catalytic cracking units. From the standard 42-gallon barrel of crude oil, United States refineries may actually produce more than 44 gallons of refined products through the catalytic reaction with hydrogen.

In general, oil-shale distillates have a much higher concentration of high boiling-point compounds that would favor production of middle-distillates (such as diesel and jet fuels) rather than naphtha. Oil-shale distillates also had a higher content of olefins, oxygen, and nitrogen than crude oil, as well as higher pour points and viscosities. Above-ground retorting processes tended to yield a lower API gravity oil than the in situ processes (a 25° API gravity was the highest produced).20 Additional processing equivalent to hydrocracking would be required to convert oil-shale distillates to a lighter range hydrocarbon (gasoline). Removal of sulfur and nitrogen would, however, require hydrotreating.

Arsenic removed from the oil by hydrotreating remains on the catalyst, generating a material that is a carcinogen, an acute poison, and a chronic poison. The catalyst must be removed and replaced when its capacity to hold arsenic is reached. Unocal found that its disposal options were limited.

3.4 Upgrading at the mine site

Upgrading crude shale oil at the mine site might consist of all of the above steps, although hydrogen-addition reactions generally predominate, and reactions to produce specialty chemicals are not likely to occur at all. In fact, it is at the mine site that partial upgrading through the use of visbreaking might be a good processing option.

Upgrading is typically directed only at the gaseous and liquid fractions of the retorting products and is rarely applied to the solid char that remains with the inorganic fraction of the oil shale, although coking of that solid fraction is possible. The most likely end products will be refinery feedstocks suitable for the production of middle distillates (kerosene, diesel fuel, jet fuel, No. 2 fuel oil), although lighter weight fuel components such as gasoline can also be produced. In general, hydrotreating followed by hydrocracking will produce jet fuel feedstocks, hydrotreating followed by fluid catalytic cracking is performed for production of gasoline feedstocks, and coking followed by hydrotreating is performed with the intention of producing diesel fuel feedstocks.

Similar to the preliminary steps taken at refineries, prior to or coincident with crude shale oil upgrading reactions, there are also activities to separate water from both the gas and liquid fractions, to separate oily mists from the gaseous fraction, and to separate and further treat gases evolved during retorting to remove impurities and entrained solids and improve their combustion quality. Actions to remove heavy metals and inorganic impurities from crude shale oils also take place.

3.5 Use of additives

Chemicals may also be added to crude shale oil to improve the transportation properties. Pour point depressants have been successful in some instances, but this does not mean that they would always work. However, a chemical that is suitable for one type of oil may not work at all with oil from another retorting process. Furthermore, pour point depressants are disadvantageous because they only change the physical characteristics of the oil and not the chemical properties. Thus, the cost of additives can be offset only if save transportation costs are reduced.

Conventional crude oils or crude oil products are other potential blending agents and the possibility exists (if the shale oil is produced in a crude oil recovery area) that conventional light crude oil could be mixed with crude shale oil to form a transportable blend. The feasibility of this concept is unclear because not only because the blend may not be as valuable as a refinery feedstock on a per-unit basis as would the crude oil alone but also because of the potential for incompatibility of the crude shale oil with the conventional crude oil (Chapter 17) (Mushrush and Speight, 1995; Speight, 2014).

4. The future

Projections that peak crude oil production may occur in the coming decades, along with increasing global demand, underscore the United States' dependence on imported crude oil. After Hurricanes Katrina and Rita, the spike in crude oil price and the temporary shutdown of some Gulf Coast refineries exacerbated that dependency. With imports making up 65% of the United States' crude oil supply and the expectation that the percentage will rise, proponents of greater energy independence see the huge but undeveloped oil shale resources of the United States as one of several promising alternatives (Speight, 2011, 2013, 2014, 2017).

However, oil shale is the least understood of the fossil fuel resources examined but new technologies, still in the research and development phase, have the potential to drastically alter the economics of oil shale production. Despite a long history of activity in the oil shale industry, there is not a large body of industrial knowledge based on successful operations from which to draw, so published costs for oil shale production have ranged from $10 to $95 per barrel.

Thus it is not surprising that the failure of oil shale has been tied to the variable price (especially the lower price) of crude oil, a much less risky conventional resource. Proponents of renewing commercial oil shale development might also weigh whether other factors detract from the potential of the resource. Refining industry profitability is overwhelmingly driven by light passenger vehicle demand for motor gasoline, and oil-shale distillate does not make ideal feedstock for gasoline production. Policies that discourage the wider use of middle distillates as transportation fuels indirectly discourage oil shale development. Because the largest oil shale resources reside on federal lands, the federal government would have a direct interest and role in the development of this resource.

Opponents of federal subsidies for oil shale argue that the price and demand for crude oil should act as sufficient incentives to stimulate development. Projections of increased demand and peaking crude oil production in the coming decades tend to support the price-and-supply incentive argument in the long term.

Nevertheless, oil shale still has a future and remains a viable option for the production of liquid fuels. Many of the companies involved in earlier oil shale projects still hold their oil shale technology and resource assets. The body of knowledge and understanding established by these past efforts provides the foundation for ongoing advances in shale oil production, mining, retorting, and processing technology and supports the growing worldwide interest and activity in oil shale development. In fact, in many cases, the technologies developed to produce and process kerogen oil from shale have not been abandoned, but rather *mothballed* for adaptation and application at a future date when market demand would increase and major capital investments for oil shale projects could be justified.

4.1 Processing options

The fundamental problem with all oil shale technologies is the need to provide large amounts of heat energy to decompose the kerogen to liquid and gas products. More than one ton of shale must be heated to temperatures in the range 850 and 1000 °F (425–525 °C) for each barrel of oil generated, and the heat supplied must be of relatively high quality to reach retorting temperature. Once the reaction is complete, recovering sensible heat from the hot rock is very desirable for optimum process economics. This leads to three areas where new technology could improve the economics of oil recovery: (i) recovering heat from the spent shale, (ii) disposal of spent shale, especially if the shale is discharged at temperatures where the char can catch fire in the air, and (iii) concurrent generation of large volumes of carbon dioxide.

The heat recovery from hot solids is generally not efficient, unless it is in the area of fluidized bed technology. However, to apply fluidized bed technology to oil shale would require grinding the shale to sizes less than approximately 1 mm, an energy intensive task that would result in an expensive disposal problem. However, such fine particles might be used in a lower temperature process for sequestering carbon dioxide.

Disposal of spent shale is also a problem that must be solved in economic fashion for the large-scale development of oil shale to proceed. Retorted shale contains carbon as char, representing more than half of the original carbon values in the shale. The char is potentially pyrophoric and can burn if dumped into the open air while hot. The heating process results in a solid that occupies more volume than the fresh shale because of the problems of packing random particles. A shale oil industry producing 100,000 barrels per day, which is approximately the minimum for a world-scale operation, would process more than 100,000 tons of shale (density approximately 3 g/cc) and result in more than 35 m^3 of spent shale; this is equivalent to a block more than 100 feet on a side (assuming some effort at packing to conserve volume). The Unocal 25,000 bpd project of the 1980s filled an entire canyon with spent shale over several years of operation. Part of the spent shale could be returned to the mined-out areas for remediation, and some can potentially be used as feed for cement kilns.

In situ processes such as the Shell ICP process (Chapter 15) avoid the spent shale disposal problems because the spent shale remains where it is created (Fletcher, 2005a,b,c). In addition, ICP avoids carbon dioxide decomposition by operating at temperatures below approximately 350 °C (650 °F). On the other hand, the spent shale will contain uncollected liquids that can leach into groundwater, and vapors produced during retorting can potentially escape to the aquifer. Shell has gone to great efforts to design barrier methods for isolating its retorts to avoid these problems (Mut, 2005). Control of in-situ operation is a challenge that Shell claims to have solved in its work (Mut, 2005; Karanikas et al., 2005).

Shale (such as the Colorado shale) that contains a high proportion of dolomitic limestone (a mixture of calcium and magnesium carbonates) thermally deposes under the conditions of retorting and releases large volumes of carbon dioxide. This consumes energy and leads to the additional problem of sequestering the carbon dioxide to meet global climate change concerns.

In addition, there are also issues with the produced shale oil that also need resolution. Shale oil is different from conventional crude oils, and several technologies have been developed to deal with this. The primary problems identified were arsenic, nitrogen, and the waxy nature of the crude. Nitrogen and wax problems were solved by Unocal and other companies using hydroprocessing approaches, essentially classical hydrocracking. Since that time, Chevron and ExxonMobil have developed technologies aimed at making high quality lube stocks, which require that waxy materials be removed or isomerized. These technologies are well adapted for shale oils. However, the arsenic problem remains (DOE, 2004b).

Unocal found that the produced shale oil contained several ppm of arsenic. It developed a specialty hydrotreating catalyst and process, called SOAR (shale oil arsenic removal). This process was demonstrated successfully in the 1980s and is now owned by UOP as part of the hydroprocessing package purchased from Unocal in the early 1990s. Unocal also patented other arsenic removal methods. Arsenic removed from the oil by hydrotreating remains on the catalyst, generating a material that is a carcinogen, an acute poison, and a chronic poison. The catalyst must be removed and replaced when its capacity to hold arsenic is reached. Unocal found that its disposal options were limited. Today, regulations require precautions to be taken when a reactor is opened to remove a catalyst. Opportunities for circumventing the arsenic problem include development of an in-reactor process for regenerating the catalyst, collecting arsenic in a safe form away from the catalyst, and development of a catalyst or process where the removed arsenic exits the reactor in the gas or liquid phase to be scrubbed and confined elsewhere.

Thus several issues need to be resolved before an oil shale industry can be a viable option. These issues are not insurmountable but require the search for viable alternatives. For example, an alternative not much explored involves chemical treatment of shale to avoid the high-temperature process. The analogy with coal liquefaction here is striking: liquids can be generated from coal in two distinct ways: (i) by pyrolysis, creating a char co-product, or (ii) by dissolving the coal in a solvent in the presence of hydrogen. However, no similar *dissolution approach* to oil shale conversion is known, because the chemistry of kerogen is markedly different from the chemistry of coal.

As a first step in developing a direct route, some attempts were made in the 1970s to isolate kerogen from the oil shale by dissolving away the minerals. Acid treatment to dissolve the mineral carbonate followed by fluoride treatment to remove the aluminosilicate minerals might be considered. Such a scheme will only work if the kerogen is not chemically bonded to the inorganic matrix. However, if the kerogen is bonded to the inorganic matrix, the bonding arrangement must be defined for the scheme to be successful.

Shale oil produced by both above-ground and in situ techniques in the 1970s and 1980s were rich in organic nitrogen. Nitrogen compounds are catalyst poisons in many common refinery processes such as fluid catalytic cracking, hydrocracking, isomerization, naphtha reforming, and alkylation. The standard method for handling nitrogen poisoning is hydrodenitrogenation (HDN). Hydrodenitrogenation is a well-established high-pressure technology using nickel molybdenum catalysts. It can consume prodigious amounts of hydrogen, typically made by steam reforming of natural gas, with carbon dioxide as a byproduct.

Thus, after a decline of production since 1980 and the current scenarios that face a crude oil-based economy, the perspectives for oil shale can be viewed with a moderately positive outlook. This perspective is prompted by the rising demand for liquid fuels, the rising demand for electricity, as well as the change of price relationships between oil shale and conventional hydrocarbon derivatives. Experience in Estonia, Brazil, China, Israel, Australia, and Germany has already demonstrated that fuels and a variety of other products can be produced from oil shale at reasonable, if not competitive, cost. New technologies can raise efficiencies and reduce air and water pollution to sustainable levels and if innovative approaches are applied to waste remediation and carbon sequestration, oil shale technology take on a whole new perspective.

In terms of innovative technologies, both conventional and in-situ retorting processes result in inefficiencies that reduce the volume and quality of the produced shale oil. Depending on the efficiency of the process, a portion of the kerogen that does not yield liquid is either deposited as coke on the host mineral matter, or is converted to hydrocarbon gases. For the purpose of producing shale oil, the optimal process is one that minimizes the regressive thermal and chemical reactions that form coke and hydrocarbon gases and maximizes the production of shale oil. Novel and advanced retorting and upgrading processes seek to modify the processing chemistry to improve recovery and/or create high-value by-products. Novel processes are being researched and tested in lab-scale environments. Some of these approaches include: Lower heating temperatures; higher heating rates; shorter residence time durations; introducing scavengers such as hydrogen (or hydrogen transfer/donor agents); and introducing solvents (Baldwin, 2002).

Finally, the development of western oil shale resources will require (i) water for plant operations, (ii) the supporting infrastructure, (iii) the environmental aspects of the development, and (iv) the associated economic growth in the region (Chapter 18). While some oil shale technologies may require reduced process water requirements, stable and secure sources of significant volumes of water may still be required for large-scale oil shale development. The largest demands for water are expected to be for land reclamation and to support the population and economic growth associated with oil shale activity.

Nevertheless, if a technology can be developed to economically recover oil from oil shale, the potential is enormous. If the kerogen could be converted to oil, the quantities would be far beyond all known conventional oil reserves. Unfortunately, the prospects for oil shale development are uncertain (Bartis et al., 2005). The estimated cost of surface retorting remains high and many consider it unwise to move toward near-term commercial efforts.

However, advances in thermally conductive in-situ conversion may cause shale-derived oil to be competitive with current high crude oil. If this becomes the case, oil shale development could soon occupy a very prominent position in the national energy agenda. Only when it is clear that at least one major private firm is willing to devote, without appreciable government subsidy, technical, management, and financial resources to oil shale development, will government decision-makers address the policy issues related to oil shale development.

In 2005, Congress conducted hearings on oil shale to discuss opportunities for advancing technology that would facilitate *environmentally friendly* development of oil shale and oil sands resources (US Congress, 2005). The hearings also addressed legislative and administrative actions necessary to provide incentives for industry investment, as well as exploring concerns and experiences of other governments and organizations and the interests of industry. The Energy Policy Act of 2005 included provisions under Section 369 (Oil Shale, Tar Sands, and Other Strategic Unconventional Fuels) that direct the Secretary of the Interior to begin leasing oil shale tracts on public lands and to cooperate with the Secretary of Defense in developing a program to commercially develop oil shale, among other strategic unconventional fuels.

4.2 Constraints

The types and amounts of water contaminants that are likely to be produced by major kinds of oil shale facilities The following subsections summarize the major sources of each class of waterborne contaminants found in oil shale facilities.

4.2.1 Suspended solids

Suspended solids will occur primarily in water from the dust-control systems used in shale mining and crushing operations. Mine drainage water will also contain suspended solids, as will a retort condensate stream that picks up fine shale particles as it trickles down through the broken shale. In aboveground retorts, some fine shale may be entrained in the retort gas and captured in the gas condensate, but levels should be low, thus should not be a problem to treat, Cooling water will pick up dust from the atmosphere, particularly if the cooling tower is near a shale crushing or disposal site. Precipitated salts and biological matter may also be present in the cooling tower blowdown.

4.2.2 Oil and grease

Oil and grease will be present in the retort condensate water that is removed from the in situ retort together with the product oil. Some oil remains in the water after product recovery and must be removed prior to further treatment. Part of the oil forms an emulsion in the water and its removal may be difficult. Volatile hydrocarbon derivatives leave with the retort offgas and condense in the gas condensate water. Tests indicate that the oil in the gas condensate occurs in well-defined droplets that can be separated without difficulty.

Oils in the coker and hydrotreater condensates are expected to be similar to those in the gas condensate.

4.2.3 Dissolved inorganics

Dissolved inorganic will be found in mine drainage water and retort condensates because these streams leach sodium, potassium, sulfate, bicarbonate, chloride, calcium, and magnesium ions from the shale that they contact. In addition, some inorganic volatilize and may be captured from the gas phase in the retort, Of the heavy metals present in raw oil shale, cadmium and mercury (probably as their respective sulfides) are expected to be present in the gas condensate in low concentrations. An analysis of TOSCO II gas condensate water showed the presence of cyanide, sodium, calcium, magnesium, silica, and iron ions, with only trace amounts of some of the heavy metal elements.

Trace elements and metals are not expected to occur in large concentrations in the major waste streams except those streams dis-cussed under dissolved inorganics.

Chromium was used for corrosion control in older cooling-water systems but other agents are now available and should be used to avoid the problem of chromium contamination of blowdown streams. If trace element and metal removal is required, chemical treatment, specific ion exchange, and membrane processes are available.

Dissolved inorganic gases include all of the NH_3 and some of the CO_2 and H_2S formed in the retorting process. These gases dissolve in the retort and gas condensates. Any NH_3 and H_2S that are formed during upgrading will appear in the hydrotreater condensates.

4.2.4 Dissolved organics and trace organics

Dissolved organics arise largely from the organic compounds in the raw oil shale, which may be altered during pyrolysis and end up in the retort, gas, or hydrotreater condensates. The types of organics in each condensate will probably depend on the volatility and volubility of the organics and the temperature at which the wastewater is condensed. A wide range of compounds, particularly carboxylic acids and neutral compounds, can be expected.

Many of the individual compounds should be biodegradable, but studies have shown that less than 50% of the organic matter can be removed by conventional biological oxidation. This poor performance is attributed to the effect of toxic compounds on waste-treatment bacteria. Both inorganic and organic toxic substances may be responsible. The specific types of toxic pollutants will differ with the retorting process and with raw shale composition.

Trace organics are toxic or hazardous organic compounds present in low concentrations. They may occur in the retort and gas condensate streams and in the wastewater stream from the upgrading section. These constituents can generally be removed together with other dissolved organics by ultrafiltration with carbon adsorption for final cleaning (“polishing”).

4.2.5 Toxics

Toxics, including carcinogens, mutagens, priority pollutants, and other hazardous-substances, have been reported for various types of oil shale processing wastes. Any toxic substances present in the wastewater streams will be removed along with the trace organics or inorganic substances. It is not expected that thermal oxidation, which is often employed to destroy hazardous organic compounds, will be required for the wastewater streams, although it may be considered for concentrates or sludges. However, the presence of toxic substances may interfere with biological oxidation processes used for bulk organic removal. If this is a problem, the substances could be removed in any of several conventional pretreatment steps.

4.2.6 Other constraints

In the commercial exploitation of shale oils, there are various constraints that represent possible deterring factors which can arise from a variety of sources, such as (i) technological, including the availability of water for the various processes, (ii) economic, (iii) institutional, (iv) environmental, (v) socioeconomic, and (vi) political, especially geopolitical where the oil-producing countries could maintain the price of oil at a level that would make a synthetic fuels (oil shale) industry well outside of the limits of economic balance and water availability constraints.

Since an oil shale plant of a significant capacity is quite costly to build, the product oil will have to be competitive for the current and future energy price structure. The world crude oil prices have been fluctuating for the past four decades. The crude oil price has been sharply rising in the early part of the 21st century. However, the long-term profitability of the industry could be impeded by future pricing strategies of competing fuels, which are normally uncontrollable from the standpoint of the oil shale industry. This concern makes the risk level of an oil shale industry somewhat higher. Considering the shortage of clean liquid fuel sources in the world energy market and the general trend of its price in an increasing slope, the marketability of oil shale in the future is getting better and better. This may be especially true in countries that do not produce sufficient crude oil and do possess vast deposits of oil shale.

In this regard, there are three issues possibly in the picture: (i) the involvement of government can make the economic picture much brighter by providing the industry incentives and credits in a variety of forms and/or tying the industry with the economic development of a region, (ii) the specialization of products and diversification of byproducts can contribute to the profitability of the industry, and (iii) securing the captive use of shale oil in strategically developed energy-intensive industries also can contribute to the stability of the industry.

The oil shale deposits found in the Green River Formation in the states of Colorado, Wyoming, and Utah are the largest in terms of the size of deposit and most studied in the United States. The oil contained in these deposits is estimated at to be on the order of 2 trillion barrels (2×10^{12} bbls) of recoverable shale oil. Due to the vast resources and the high oil content of shales, this region has long been the most attractive to oil shale industries. However, the technology used in mining and processing of oil shale must answer to a list of questions regarding environmental and ecological impacts (Chapter 18). The Devonian-Mississippian Eastern black shale deposits are widely distributed between Appalachian and Rocky Mountains. Even though these oil shales also represent a vast resource of fossil fuel, they are generally lower in grade (oil content per unit mass of shale rock) than Green River Formation oil shales.

A rate-limiting factor in further development of the area is the availability of water, which may not be a problem in other regions. Water of the Colorado River could be made available for depletion by oil shale. An important factor that must be taken into consideration in any water-use plan is the potential salt loading of the Colorado River. With oil shale development near the river, the average annual salinity is anticipated to increase, unless some prevention or treatment is implemented. The economic damages associated with these higher salinity levels could be significant and have been the subject of extensive economic studies.

The above constraints (of which only three are presented above) that are judged to be *moderate* will hamper but not necessarily preclude development; those constraints judged to be *critical* (such as environmental issues) could become more severe barriers. *Possible* are those constraints where it is inconclusive whether or to what extent certain factors would impede development.

5. Chemicals from shale oil

Compared to conventional crude oil, shale oil that is obtained by retorting oil shale (Chapters 14 and 15) are characterized by wide boiling range and by large concentrations of heteroelements and also by high content of oxygen-, nitrogen-, or sulfur-containing compounds. The chemical potential of oil shale as retort fuel to produce shale oil and from that liquid fuel and specialty chemicals has been used so far to a relatively small extent. While the majority of countries are discovering the real practical value of shale oil, in Estonia retorting of its national resource kukersite oil obtained for production of a variety of products is in use for 75 years. Using stepwise cracking motor fuels have been produced and even exported before World War II. At the same time, shale oils possess molecular structures of interest to the specialty chemicals industry and also a number of non-fuel specialty products have been marketed based on functional group, broad range concentrate, or even pure compound values.

Crude shale oil has three major potential uses: (i) as a boiler fuel, (ii) as a refinery feedstock, and (iii) as a feedstock for producing petrochemicals. The output from a mature oil shale industry will probably (more than likely) probably be used for all three purposes. However, the relative importance of the three markets will change with time as the industry develops. When shale oil first becomes available in significant amounts, its most likely use will be as boiler fuel, with some quantity directed to nearby refineries (depending upon the availability of conventional refinery feedstocks) that could be modified to accommodate the feedstock without large capital expenditures. At a later date, shale oil could begin to be used for petrochemical production (Scouten, 1990; Lee, 1991; Ogunsola, 2006; Speight, 2019b). In spite of the potential for added-value products, most oil shale companies have tended to concentrate on producing a single product stream. In short, there has been the tendency to compete with crude oil by producing a crude oil substitute. Unfortunately, whenever a shale oil industry was established strictly to compete head to head with crude oil, the industry became susceptible to the periodic downward fluctuations in crude oil prices.

The petrochemical industry had its modern origins in the later years of the 19th Century. However, the production of products from naturally-occurring bitumen is a much older industry. There is evidence that the ancient bronze-age towns of Tuttul (Syria) and Hit (also spelled Heet, Iraq) used bitumen from seepages as a caulking material and mastic. Also, Arabian scientists knew that attempts to distill the bitumen caused it to decompose into a variety of products. By the time that the 19th Century had dawned, it was known that kerosene, a fuel for heating and cooking, was the primary product of the crude oil industry in the 1800s. Rockefeller and other refinery owners considered gasoline a useless by product of the distillation process. But all of that changed around 1900 when electric lights began to replace kerosene lamps, and automobiles came on the scene. New crude oil-based fuels were also needed to power the ships and airplanes used in World War I. After the war, an increasing number of farmers began to operate tractors and other equipment powered by oil. The growing demand for petrochemicals and the availability of natural gas and crude oil caused the industry to quickly expand in the 1920s and 1930s. During World War II, vast amounts of oil were produced and made into fuels and lubricants. The United States supplied more than 80% of the aviation gasoline used by the Allies during the war. American oil refineries also manufactured synthetic rubber, toluene (an ingredient in TNT), medicinal oils, and other key military supplies.

The term *petrochemicals* represents a large group of chemicals manufactured from natural gas and crude oil as distinct from fuels and other products that are also derived from natural gas and crude oil by a variety of processes and used for a variety of commercial purposes. Petrochemical products include such items as plastics, soaps and detergents, solvents, drugs, fertilizers, pesticides, explosives, synthetic fibers and rubbers, paints, epoxy resins, and flooring and insulating materials. Petrochemicals are found in products as diverse as aspirin, luggage, boats, automobiles, aircraft, polyester clothes, and recording discs and tapes. It is the changes in product demand that have been largely responsible for the evolution of the crude oil industry from the demand for asphalt mastic used in ancient times to the current high demand for gasoline, other liquid fuels an products as well increasing demand for as a wide variety of petrochemicals.

As a result, the petrochemical industry is a huge field that encompasses many commercial chemicals and polymers. The organic chemicals produced in the largest volumes are methanol, ethylene, propylene, butadiene, benzene, toluene, and xylenes. Ethylene, propylene, and butadiene, along with butylenes, are collectively called olefins, which belong to a class of unsaturated aliphatic hydrocarbon derivatives having the general formula C_nH_{2n}. Olefins contain one or more double bonds, which make them chemically reactive. Benzene, toluene, and xylenes, commonly referred to as aromatics, are unsaturated cyclic hydrocarbon derivatives containing one or more rings. Olefins, aromatics, and methanol are precursors to a variety of chemical products and are generally referred to as primary petrochemicals. Given the number of organic chemicals and the variety and multitude of ways by which they are converted to consumer and industrial products. Furthermore, because ethylene and propylene are the major building blocks for petrochemicals, alternative ways for their production have always been sought. The main route for producing ethylene and propylene is steam cracking, which is an energy extensive process. Fluid catalytic cracking (FCC) is also used to supplement the demand for these low molecular weight olefins.

Basic chemicals and plastics are the key building blocks for manufacture of a wide variety of durable and nondurable consumer goods. Considering the items we encounter every day − the clothes we wear, construction materials used to build our homes and offices, a variety of household appliances and electronic equipment, food and beverage packaging, and many products used in various modes of transportation − chemical and plastic materials provide the fundamental building blocks that enable the manufacture of the vast majority of these goods. Demand for chemicals and plastics is driven by global economic conditions, which are directly linked to demand for consumer goods.

The search for alternative ways to produce monomers and chemicals from sources other than crude oil. In fact, Fisher Tropsch technology, which produces in addition to fuels, low molecular weight olefins, could enable to non-crude oil feedstocks (such as, such as heavy oil, extra heavy oil, tar and bitumen, coal, oil shale, and biomass) to be used as feedstocks for petrochemicals.

In addition to shale oil being a potential source of hydrocarbon products (Scouten, 1990; Lee, 1991), the oil can also be regarded as a source of other products (Table 16.5). However, the concentration of the individual constituents can vary substantially depending upon (i) the source of the shale oil, (ii) the type of kerogen in the shale from which the oil is produced, and (iii) the retorting process employed to obtain the shale oil. In general, the higher the temperature of the retort, the higher the amount of aromatic derivatives in the shale oil and the

TABLE 16.5 Examples of compound types in shale oil.

Hydrocarbons		Heteroatom compounds	
Saturates	n-Paraffins	Sulfur compounds	Benzothiophenes
	Iso-paraffins		Dibenzothiophenes
	Cycloparaffins	Nitrogen compounds	
Olefins	1-Olefins		Carbazoles
			Pyrroles
	Internal olefins		Aliphatic nitriles
Aromatics	Benzenes		Pyridines
			Quinolines
	Biphenyls		Tetrahydroquinolines
	Indans		Tetrahyrocarbazoles
	Tetralins	Oxygen compounds	
	Naphthalenes		2-Ketones
	Acenaphthenes		Benzofurans
	Fluorenes		Phenols
	Phenanthrenes		Hydroxyindans
	Pyrenes		Hydroxytetralins
	Chrysenes		
	Benzanthracenes		

lower the concentration of the paraffin derivatives and olefin derivatives (Scouten, 1990; Lee, 1991). In most cases, the predominant member of the series in the shale oil is the simplest (lowest molecular weight) member of the series. However, when a sufficient amount of a compound types is present, separation and isolation of the compound (or compound types) may be an economically viable option.

Because shale oil is produced by pyrolysis, its olefin content is approximately 12% v/v, which is appreciably higher than conventional crude oil. Together with its fairly high hydrogen content, these characteristics make shale oil, and its hydrogenated derivatives, appropriate feedstocks for petrochemical production. Steam pyrolysis has been used to process crude shale oil, and the yields of olefin products have been comparable with those from many conventional crude oil. Synthetic crude oil from shale oil, with even higher olefin yields, is considered to be a premium petrochemical feedstock.

Also, high yields of carboxylic acids can be obtained by supercritical fluid extraction of oil shale with carbon monoxide and water, methanol and water, or toluene. Total yield of organic liquids with this procedure was higher than is obtained by retorting and yields of as much as 90% w/w of the organic matter were obtained (Scouten, 1990). Whereas the normal alkane derivatives recovered showed odd-even predominance in carbon numbers, the normal carboxylic acids showed even-odd predominance.

To accomplish the isolation of the acids, oil shale is treated with methanol and water at 400 °C (750 °F) for 1 h, and then extracted with common solvents such as methylene chloride. At higher temperatures, pyrolysis reactions increase and the product composition changes dramatically. The products obtained in the first 15 min were almost entirely carboxylic acids amounting to about 25% w/w of the total organic matter in the oil shale. It should be noted that retorted oil shale contains only trace amounts of dicarboxylic acids in the 370−535 °C (700−995 °F) distillate, where they may be found in crude oil in either large or small quantities depending on the geologic history of the crude oil. The carboxylic acids decarboxylate during the retorting processes used to produce shale oil.

Historically, the primary feedstock for petrochemical plants has been natural gas liquids from the Gulf Coast. Because crude shale oil is quite different from these liquids (Chapter 17), it would be difficult to switch traditionally designed petrochemical plants to shale oil. Also, the availability of naphtha has been affected by a growing demand for use as a gasoline blending agent in response to the phasing out of tetraethyl lead. Gas oils are also being used more frequently for home heating fuels, which causes seasonal variations in their availability. Because of these supply uncertainties, new petrochemical plants are being designed to be highly flexible with respect to feedstocks. As the use of heavier feedstocks becomes more common in the industry, shale oil may become a highly regarded raw material. However,

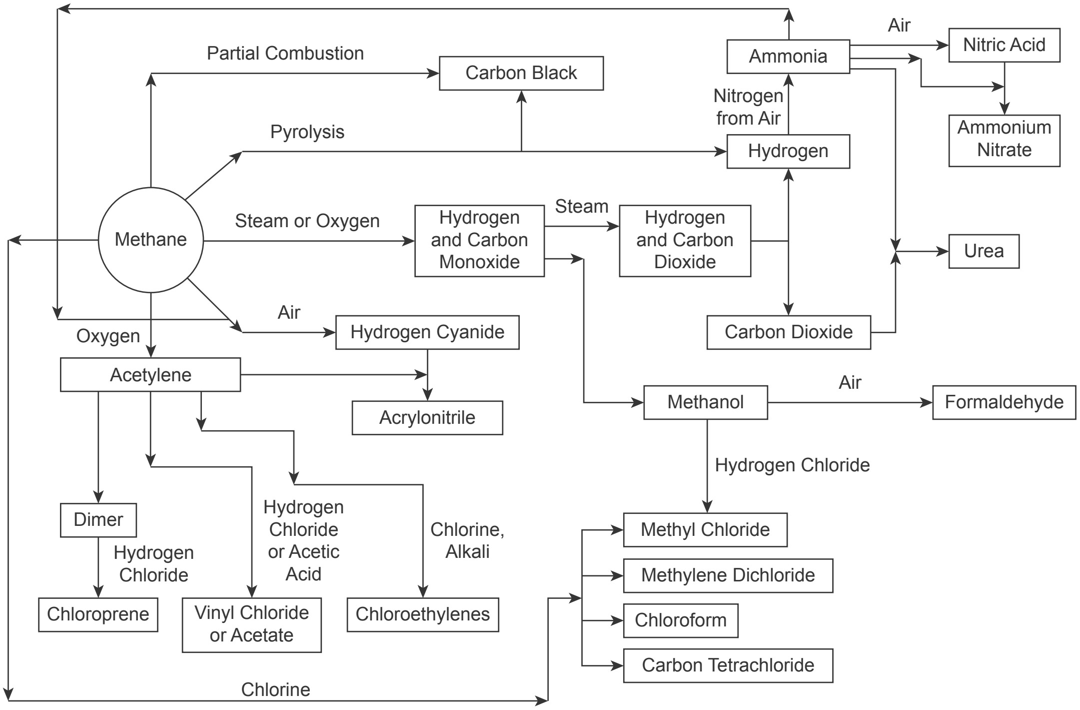


FIG. 16.2 Chemicals from methane.

the use of shale oil for petrochemical production is hampered by the distance between the oil shale region and the petrochemical plants. While refineries and oil-fired boilers are distributed fairly uniformly across the United States, the petrochemical industry is concentrated on the Gulf Coast.

As examples, shale oil can be future processed through steam cracking to produce methane (Fig. 16.2), naphtha, including benzene, toluene, and the xylene isomers (Fig. 16.3) and refinery gases which contain olefin derivatives such as ethylene (Fig. 16.4), propylene (Fig. 16.5), and, potentially, all of the potential isomers of butylene, (Fig. 16.6) (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017).

In summary, crude shale oil and its derivatives could be used to produce petrochemicals. In fact, the chemical potential of oil shales as retort fuel to produce shale oil and from that

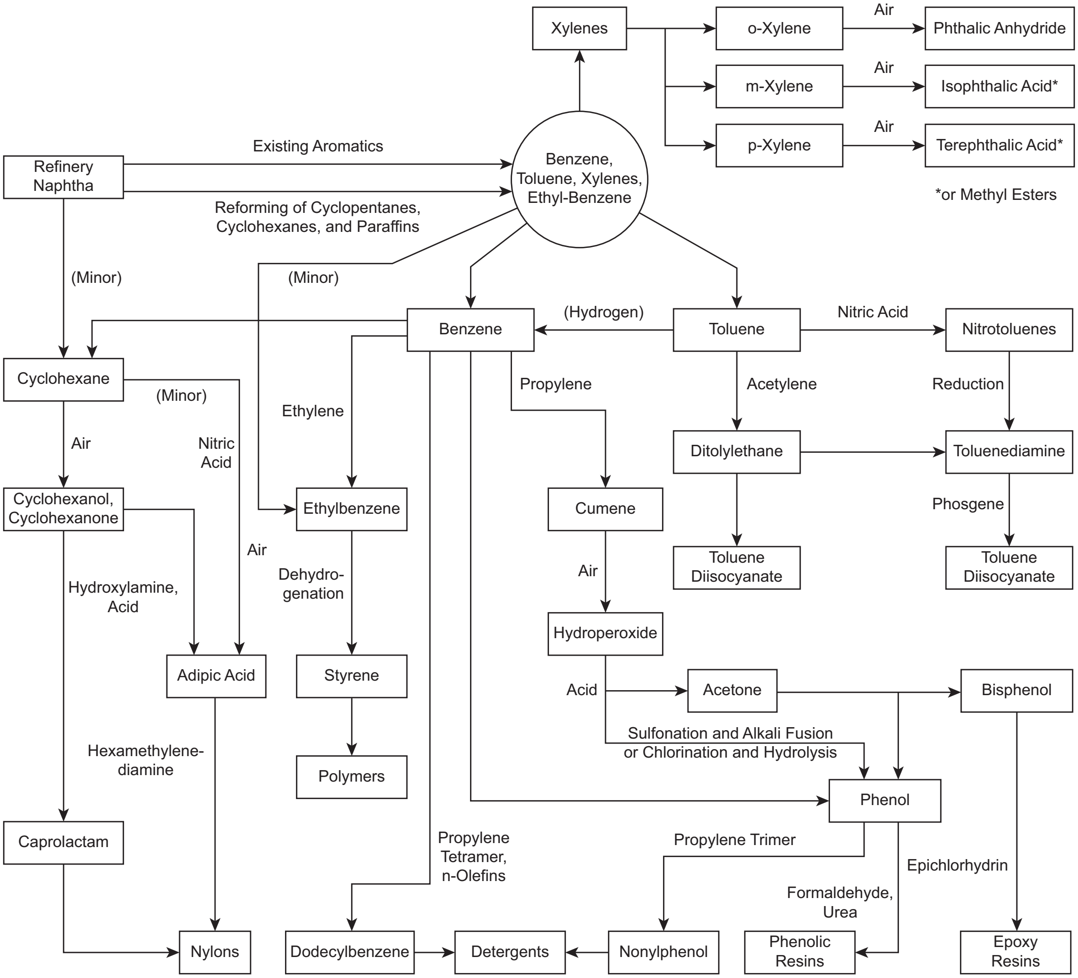


FIG. 16.3 Chemicals from benzene, toluene, and the xylene isomers.

liquid fuel and specialty chemicals has been used so far to a relatively small extent. However, shale oil possesses molecular constituents that are of interest to the specialty chemicals industry. Based on the amounts of oxygen-containing compounds in the high-boiling fraction of the shale oil, a variety of chemical are produced that would be of value to markets such as asphalt blending material and anticorrosion oils. In addtion, benzene and toluene for the production of benzoic acid as well as solvent mixtures on pyrolysis of the lower-boiling fractions of shale oil are produced. Water soluble phenol derivatives can be selectively extracted from

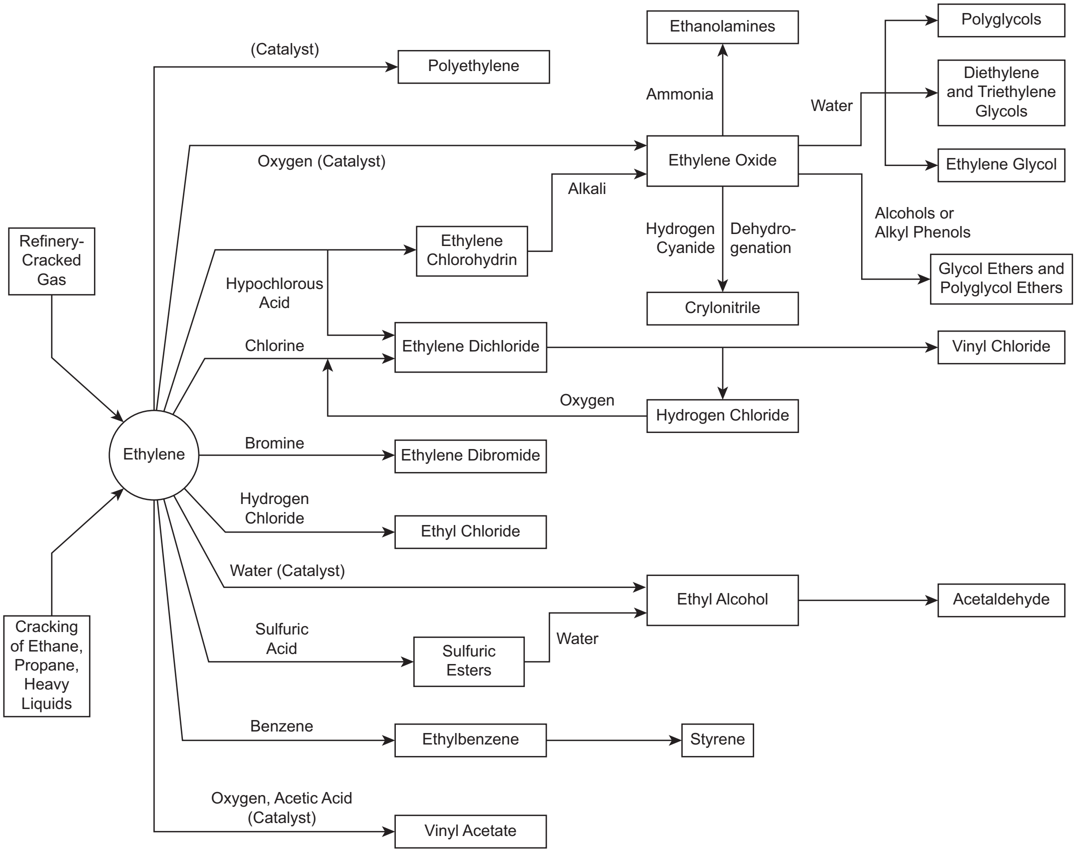


FIG. 16.4 Chemicals from ethylene.

shale oil, fractionated and crystallized for production of pure 5-methyl resorcinol and other alkyl resorcinol derivatives as well as high value intermediates to produce tanning agents, epoxy resins and adhesives, diphenyl ketone and phenol-formaldehyde adhesive resins, rubber modifiers, chemicals, and pesticides. Some conventional products such as coke and distillate boiler fuels are produced from shale oil as by-products. New market opportunities for shale oil and its fractions may be found improving the oil conversion and separation techniques.

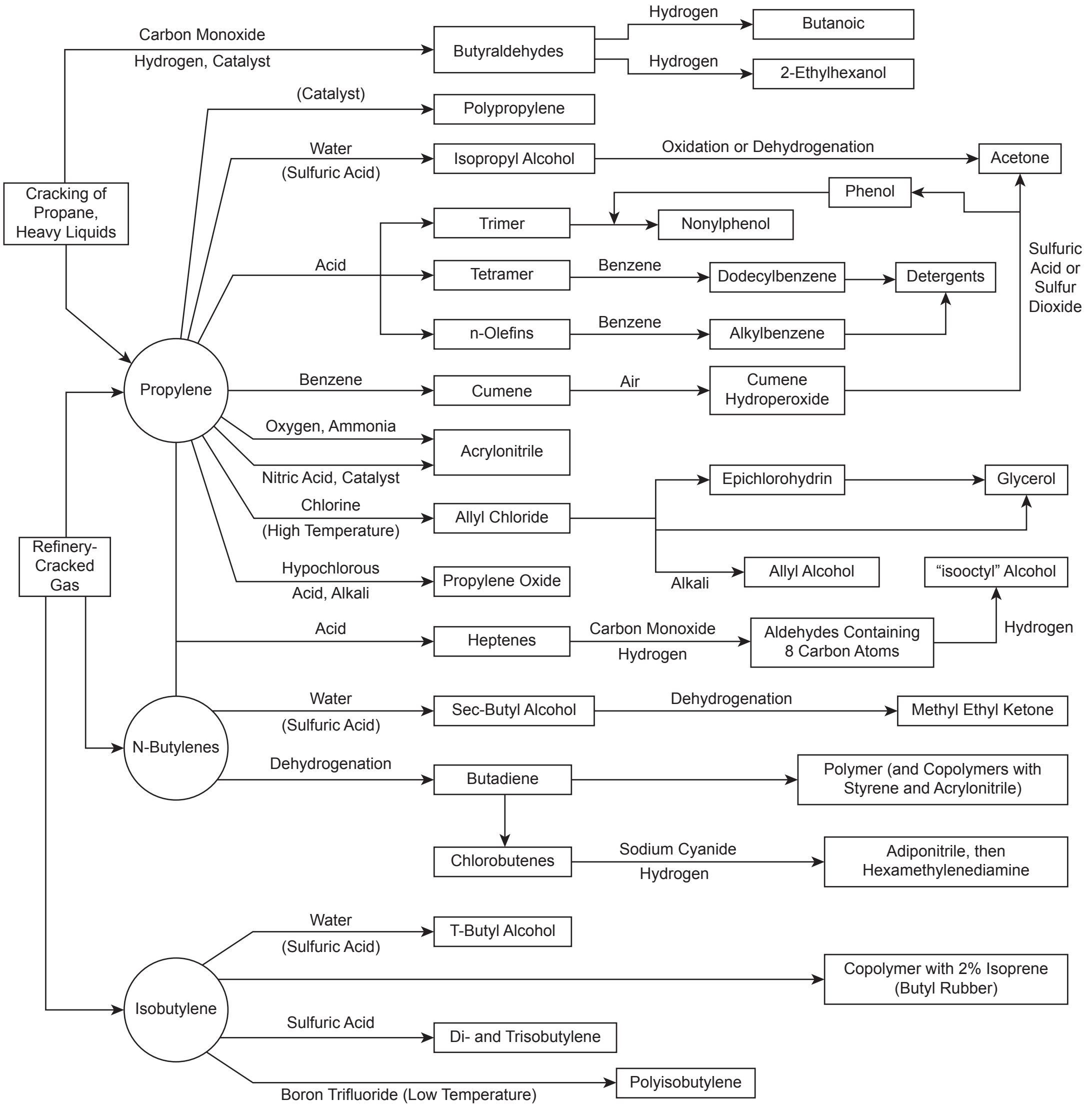


FIG. 16.5 Chemicals from propylene and butylene.

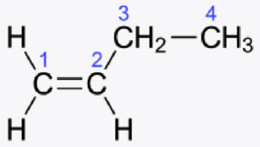
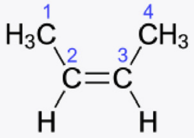
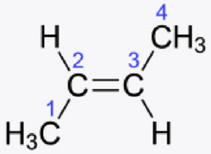
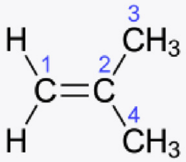
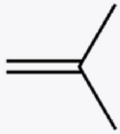
IUPAC name	Other names	Structure	Skeletal formula
But-1-ene	1-Butylene Butene-1		
cis-But-2-ene	*cis*-2-Butylene *cis*-Butene-2		
trans-But-2-ene	*trans*-3-Butylene *trans*-Butene-2		
2-Methyl prop-1-ene	Isobutylene 2-Methyl propene-1		

FIG. 16.6 Representation of the various isomers of butylene (C_4H_8).

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CHAPTER

17

Instability and incompatibility of tight oil and shale oil

1. Introduction

The study of the properties of tight oil and shale oil would not be complete without some attention to the phenomena of instability and incompatibility. Both result in formation of degradation products and other undesirable changes in the original properties of tight oil and shale oil products. And it is the analytical methods that provide the data that point to the reason for problems in the refinery or for the failure of products to meet specifications and to perform as desired.

While tight oil has been assessed as a light conventional crude oil and is, therefore, not assessed as a new commodity shale oil also is not a new commodity and the use of oil shale can be traced back to ancient times and has a long history (Chapter 11). In fact, humans have used oil shale as a fuel since prehistoric times, since it generally burns without any processing. It was also used for decorative purposes and construction. In Iron Age Britain (c.800 BCE to AD 100), oil shale was used to polish and form oil shale into ornaments. Oil shale was also used as a decorative material during the Greek period (c.800−400 BCE), the Roman period (c.700 BCE to AD 400), the Umayyad period (c.AD 660−750), and the Abbasid period (c.AD 750−1250) to decorate mosaics and floors of the palaces, churches and mosques. The use of oil shale was recorded in Austria in 1350. By the seventeenth century, oil shale was being exploited in several countries. As early as 1637, alum shale was roasted over wood fires to extract potassium aluminum sulfate, a salt used in tanning leather and for fixing colors in fabrics.

The use of shale oil continued until the 1980s when the shale oil production was considered as counter measure to the geopolitics of oil production and supply (Speight, 2011). With the varying price of crude oil, shale oil became a very expensive commodity and efforts to produce shale oil as a substitute for conventional crude oil were terminated. Nevertheless, the current lull in development activity offers a golden opportunity for scientific research to attack the many chemical, physical and material problems that were uncovered or brought into sharper focus during the late period of activity.

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Current refineries are a complex series of manufacturing plants that can be sub-divided into (i) separation processes, (ii) conversion processes, and (iii) finishing processes (Speight, 2014). Incompatibility can occur many of these processes and the product can also exhibit incompatibility and instability. Furthermore, there are a myriad of other products that have evolved through the life of the crude oil industry and the complexities of product composition have matched the evolution of the products (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). In fact, it is the complexity of product composition that has served the industry well and, at the same time, had an adverse effect on product use.

Product complexity and the means by which the product is evaluated (ASTM, 2019) have made the industry unique among industries. But product complexity has also brought to the fore issues such as *instability* and *incompatibility*. Product complexity becomes even more disadvantageous when various fractions from different types of crude oil are blended or are allowed to remain under conditions of storage (prior to use) and a distinct phase separates from the bulk product. The adverse implications of this for refining the fractions to salable products increase (Batts and Fathoni, 1991; Por, 1992; Mushrush and Speight, 1995).

Therefore, it is appropriate here to define some of the terms that are used in the liquid fuels field so that their use later in the text will be more apparent and will also alleviate some potential for misunderstanding. The general scientific areas of *instability* and *incompatibility* are complex and have been considered to be nothing better than a black art because not all of the reactions that contribute to instability and incompatibility have been defined (Wallace, 1964). Nevertheless, recent studies over the past three decades have made valuable contributions to our understanding of instability and incompatibility in fuels. But, for the most part, gaps remain in our knowledge of the chemistry and physics of instability and incompatibility.

Briefly, the term *incompatibility* refers to the formation of a *precipitate* (or *sediment*) or *separate phase* when two liquids are mixed. The term *instability* is often used in reference the formation of color, sediment, or gum in the liquid over a period of time and is usually due to chemical reactions, such as oxidation, and is chemical rather than physical. This term may be used to contrast the formation of a precipitate in the near term (almost immediately). The phenomenon of *instability* is often referred to as *incompatibility*, and more commonly known as *sludge formation*, and *sediment formation*, or *deposit formation*. In crude oil and its products and in the current context, *instability* often manifests itself in various ways (Table 17.1) (Stavinoha and Henry, 1981; Hardy and Wechter, 1990; Power and Mathys, 1992; Speight, 2014). Hence, there are different ways of defining each of these terms but the terms are often used interchangeably.

Gum formation (ASTM D525, IP 40) alludes to the formation of soluble organic material whereas *sediment* is the insoluble organic material. *Storage stability* (or *storage instability*) (ASTM D381, ASTM D4625, IP 131, IP 378) is a term used to describe the ability of the liquid to remain in storage over extended periods of time without appreciable deterioration as measured by gum formation and/or the formation sediment. *Thermal stability* is also defined as the ability of the liquid to withstand relatively high temperatures for short periods of time without the formation of sediment (i.e., carbonaceous deposits and/or coke). *Thermal oxidative stability* is the ability of the liquid to withstand relatively high temperatures for short periods of time in the presence of oxidation and without the formation of sediment or deterioration of properties (ASTM D3241) and there is standard equipment for various oxidation tests (ASTM D4871). *Stability* is also as the ability of the liquid to withstand long periods at

TABLE 17.1 Examples of properties related to instability in petroleum and petroleum products.

Property	Comments
Asphaltene constituents	Influence oil-rock interactions
	Separates from oil when gases are dissolved
	Thermal alteration can cause phase separation
Heteroatom constituents	Provide polarity to oil
	Preferential reaction with oxygen
	Preferential thermal alteration
Aromatic constituents	May be incompatible with paraffinic medium
	Phase separation of paraffinic constituents
Non-asphaltene constituents	Thermal alteration causes changes in polarity
	Phase separation of polar species

temperatures up to 100 °C (212 °F) without degradation. Determination of the *reaction threshold temperature* for various liquid and solid materials might be beneficial (ASTM D2883).

Existent-gum is the name given to the non-volatile residue present in the fuel as received for test (ASTM D381, IP 131). In this test, the sample is evaporated from a beaker maintained at a temperature of 160−166 °C (320−331 °F) with the aid of a similarly heated jet of air. This material is distinguished from the *potential gum* that is obtained by aging the sample at an elevated temperature.

Thus, *potential gum* is determined by the *accelerated gum test* (ASTM D873, IP 138) that is used as a safeguard of storage stability and can be used to predict the potential for gum formation during prolonged storage. In this test, the fuel is heated for 16 h with oxygen under pressure in a bomb at 100 °C (212 °F). After this time, both the gum content and the solids precipitate are measured. A similar test, using an accelerated oxidation procedure is also in use for determining the oxidative stability of diesel fuel (ASTM D2274), steam turbine oil (ASTM D2272), distillate fuel oil (ASTM D2274) and lubricating grease (ASTM D942).

Dry sludge is defined as the material separated from crude oil and crude oil products by filtration and which is insoluble in heptane. *Existent dry sludge* is the dry sludge in the original sample as received and is distinguished from the accelerated dry sludge obtained after aging the sample by chemical addition or heat. The *existent dry sludge* is distinguished from the *potential dry sludge* that is obtained by aging the sample at an elevated temperature. The *existent dry sludge* is operationally defined as the material separated from the bulk of a crude oil or crude oil product by filtration and which is insoluble in heptane. The test is used as an indicator of process operability and as a measure of potential downstream fouling.

An analogous test, the *thin film oven test* (*TFOT*) (ASTM D1754) and an aging test (IP 390) are used to indicate the rate of change of various physical properties such as penetration (ASTM D5), viscosity (ASTM D2170), and ductility (ASTM D113) after a film of asphalt or bitumen has been heated in an oven for 5 h at l63 °C (325 °F) on a rotating plate. A similar test is available for the stability of engine oil by thin film oxygen uptake (*TFOUT*) (ASTM D4742).

This test establishes the effects of heat and air based on changes incurred n the above physical properties measured before and after the oven test. The allowed rate of changes in the relevant bitumen properties after the exposure of the tested sample to the oven test, are specified in the relevant specifications (ASTM D3381).

Attractive as they may be, any tests that involve *accelerated oxidation of* the sample must be used with caution and consideration of the chemistry. Depending on the constituents of the sample, it is quite possible that the higher temperature and extreme conditions (oxygen under pressure) may not be truly representative of the deterioration of the sample under storage conditions. The higher temperature and the oxygen under pressure might change the chemistry of the system and produce products that would not be produced under ambient storage conditions. An assessment of the composition of the fuel prior to storage and application of the test will assist in this determination.

In general, *fuel instability* and *fuel incompatibility* can be related to the heteroatom-containing compounds (i.e., nitrogen-, oxygen-, and sulfur-containing compounds) that are present. The degree of unsaturation of the fuel (i.e., the level of olefinic species) also plays a role in determining instability/incompatibility. And, recent investigations have also implicated catalytic levels of various oxidized intermediates and acids as especially deleterious for middle distillate fuels.

Fuel *incompatibility* can have many meanings. The most obvious example of incompatibility (*non-miscible*) is the inability of a hydrocarbon fuels and water to mix. In the present context, incompatibility usually refers to the presence of various polar functions (i.e., heteroatom function groups containing nitrogen, or oxygen, or sulfur, and even various combinations of the heteroatoms) in the tight oil or, more particularly, in the shale oil.

Instability reactions are usually defined in terms of the formation of filterable and non-filterable sludge (sediments, deposits, and gums), an increased peroxide level, and the formation of color bodies. Color bodies in and of themselves do not predict instability. However the reactions that initiate color body formation can be closely linked to heteroatom-containing (i.e., nitrogen-, oxygen-, and sulfur-containing) functional group chemistry.

Thus, the constituents of shale oil are *incompatible* when sludge, semi-solid, or solid particles (for convenience here, these are termed *secondary products* to distinguish them from the actual oil product) are formed during and after blending. This phenomenon usually occurs prior to use. If the secondary products are marginally soluble in the blend, use might detract from solubility of the secondary products and they will appear as sludge or sediment that can be separated by filtration or by extraction (ASTM D4310). When the secondary products are truly insoluble, they separate and settle out as a semi-solid or solid phase floating in the fuel or are deposited on the walls and floors of containers. In addition, secondary products usually increase the viscosity of the product. Standing at low temperatures will also cause a viscosity change in certain fuels and lubricants (ASTM D2532). Usually the viscosity change might be due to separation of paraffins as might occur when diesel fuel and similar, engines are allowed to cool and stand unused overnight in low temperature climates.

The most significant and undesirable instability change in fuel liquids is the formation of solids, termed *filterable sediment*. Filterable sediments can plug nozzles, filters, coke heat exchanger surfaces and otherwise degrade engine performance. These solids are the result of free radical autoxidation reactions. Although slight thermal degradation occurs in non-oxidizing atmospheres, the presence of oxygen or active oxygen species, such as hydroperoxides, will greatly accelerate oxidative degradation as well as significantly lower the temperature at which undesirable products are formed. Solid deposits that form as the result of short-term high temperature reactions share many similar chemical characteristics with filterable sediment that form in storage.

The soluble sludge/sediment precursors that form during processing or use may have a molecular mass in the several hundred range. For this soluble precursor to reach a molecular weight sufficient to precipitate (or to phase-separate), one of two additional reactions must occur. Either the molecular weight must increase drastically as a result of condensation reactions leading to the higher molecular weight species. Or the polarity of the precursor must increase (without necessarily increasing the molecular weight) by incorporation of additional oxygen, sulfur, or nitrogen functional groups. Additionally, the polarity may increase because of the removal of non-polar hydrocarbon moieties from the polar core, as occurs during cracking reactions. In all three cases, insoluble material will form and separate from the liquid medium.

Additives are chemical compounds intended to improve some specific properties of fuels or other crude oil products. Different additives, even when added for identical purposes, may be incompatible with each other, for example react and form new compounds. Consequently, a blend of two or more fuels, containing different additives, may form a system in which the additives react with each other and so deprive the blend of their beneficial effect.

The chemistry and physics of incompatibility can, to some extent, be elucidated (Wallace, 1969; Por, 1992; Power and Mathys, 1992; Mushrush and Speight, 1995) but many unknowns remain. In addition to the chemical aspects, there are also aspects such as the attractive force differences, such as: (i) specific interactions between like/unlike molecules, such as hydrogen bonding and electron donor-acceptor phenomena, (ii) interactions such as dispersion forces and dipole-dipole interactions, and (iii) any effects imposed on the system by the size and shape of the interacting molecular species.

Such interactions are not always easy to define and, thus, the measurement of instability and incompatibility has involved visual observations, solubility tests hot filtration sediment (HFS), and gum formation. However, such methods are often considered to be *after-the-fact methods* insofar as they did not offer much in the way of predictability. In refinery processes (Chapter 15), predictability is not just a luxury, it is a necessity. The same principle must be applied to the measurement of instability and incompatibility. Therefore methods are continually being sought to aid in achieving this goal.

In addition to the gravimetric methods, there have also been many attempts to use crude oil and/or product characteristics and their relation to the sludge and deposit formation tendencies. In some cases, a modicum of predictability is the outcome but, in many cases, the data appear as *preferred ranges* and are subject to personal interpretation. Therefore, caution is advised.

It is the purpose of this chapter to document some of the more prominent methods used for determining instability and incompatibility. No preference will be shown, and none will be given to any individual methods. It is the choice of the individual experimentalist to choose the method on the basis of the type of the initial indications of the constituents of the shale oil that can influence incompatibility and/or instability and the projected utilization of the test data. As elsewhere, it the use of the data that often detracts from an otherwise sound method.

2. Composition of tight oil and shale oil

In the current context, the meaning of the term *incompatibility* is found when it is applied to shale oil recovery but more specifically to shale oil transportation and shale oil refining. The application occurs when a product is formed in the formation or well pipe (recovery) or in a reactor (refining) and the product is incompatible with (immiscible with or insoluble in) the original shale oil or its products. Such an example is the formation and deposition of wax and other solids during recovery or the formation of coke precursors and even of coke during many thermal and catalytic operations. Coke formation is considered to be an initial *phase-separation* of an insoluble, solid, coke precursor prior to coke formation proper. In the case of tight oil and shale oil, *sediments* and *deposits* are closely related to *sludge*, at least as far as compositions are concerned. The major difference appears to be in the character of the material. Another example is when tight oil or shale oil is blended with conventional crude oil and/or conventional crude oil products.

There is also the suggestion (often, but not always, real) in that the sediments and deposits originate from the inorganic constituents of tight oil or shale oil. They may be formed from the inherent components of the tight oil or shale oil (i.e., such as the organo-metallic constituents of the oil) or from the ingestion of contaminants by the oil during the initial processing operations. For example, tight oil and shale oil are known to bring insoluble mineral matter as they emerge from the formation or as a result (in the case of ex situ shale oil) of the retorting process. In addtion, other metal contaminants in both oils may arise as a result of contact with pipelines and pumps.

Thus, sediments can also be formed from organic materials but the usual inference is that these materials are usually formed from inorganic materials. The inorganic materials can be salt, sand, rust and other contaminants that are insoluble in the oil and which settle to the bottom of the storage vessel. For example, *gum* typically forms by way of a hydroperoxide intermediate that induces polymerization of olefin derivatives. The intermediates are usually soluble in the liquid medium. However, gum that has undergone extensive oxidation reactions tends to be higher in molecular weight and much less soluble. In fact, the high molecular weight sediments that form in fuels are usually the direct result of *autoxidation* reactions. Active oxygen species involved include both molecular oxygen and hydroperoxides. These reaction proceed by a free radical mechanism and the solids produced tend to have increased incorporation of heteroatom and are thus also more polar so increasingly less soluble in the fuel (Mushrush and Speight, 1995; Speight, 2014).

2.1 Tight oil

The crude oils found in reservoirs classed as tight reservoirs are typically light sweet crude oils (high API gravity) with a low sulfur content and a relatively high proportion of lower molecular weight volatile constituents (Chapter 10). In fact, crude oils from tight formation are highly variable in their respective properties. For example, density and other properties can show wide variation, even within the same field. However, as an illustration of all things not being equal, the low-density tight oils from the two different formations have different properties although sharing a common crude oil production technique.

The American Petroleum Institute (API) gravity is a specific gravity scale developed by the oil industry to identify crude oils and other crude oil liquids based on the relative density. It is expressed in degrees (°API), and is an inverse measure of the relative density of a crude oil product and the density of water. Thus, the lower the API gravity, the heavier (higher density) the oil. Arbitrary numbers have been assigned to identify the various crude oils but these numbers should not be used to classify crude oils (Speight, 2014, 2015). For example, light crude oil has an API gravity higher than 30° while a medium crude oil falls in the API range 20−30° API and heavy crude oil is assigned an API gravity below 20° API. Sweet crude oils contain less than 0.5% w/w sulfur (sour crudes contain more than that). Crude oils from tight formations are typically light (low density) and sweet (low sulfur) with an API gravity on the order of 40−50° API.

Typical of the crude oil from tight formations (*tight oil, tight light oil, and tight shale oil* have been suggested as alternate terms, although the term *shale oil* is incorrect and adds confusion to the nomenclature) (Chapter 1) is the Bakken crude oil which is a light sweet highly volatile crude oil with an API gravity on the order of 40−43° API and a sulfur content on the order of 0.2% w/w, or less (Chapter 10). The relatively high quality of Bakken crude oil high quality is an advantage insofar as these properties make the oil easier to refine into commercial products but is also a disadvantage insofar as unless the oil is stabilized by removal of the light ends (low-boiling hydrocarbon gases), it is highly flammable when compared to many conventional crude oils. The *flash point* − the lowest temperature at which ignition can occur − is lower for Bakken crude oil than it is for many conventional crude oils, which should be (must be) interpreted as the Bakken crude oil is particularly flammable (in fact, it is highly flammable) and, moreover, when flammable gases (methane and the low-boiling hydrocarbon derivatives) are dissolved in oil, the oil should be stabilized (*degasified*) before transportation.

Unlike most conventional light crude oils, tight oils are light sweet oils, with a high paraffin content and low acidity. They also have minimal asphaltenic content and varying content of filterable solids, hydrogen sulfide (H_2S), and mercaptan derivatives. There are significant differences in the sulfur content and amount of the filterable solids. In addition, the streams from a tight oil production region can have significant variability, with colors ranging from pale amber to black.

Tight oils are, in general, light crude oils and the feed API derived from these oils are higher than API of feeds from conventional gas oils and typically have a lower amount of contaminants than conventional crude oils. However, the properties of tight oils are significantly different than typical crude oils and, as a result, a series of challenges exists that need to be solved to ensure uninterrupted transportation and refining of the tight oils to contend with and mitigate the potential disadvantages of the tight crude oils (Table 10.2).

On a comparative basis, tight oils typically have a higher API gravity than traditional crude oils, as well as much different properties. For example, Bakken crude oil and Eagle Ford crude oil have an API gravity on the order of 42−46° whereas Louisiana light sweet crude oil (a light sweet crude oil from the United States) and Brent crude oil (and international crude oil from the North Sea) have an API gravity on the order of 36−39°. In keeping with the higher API gravity, Bakken crude oil and Eagle Ford crude oil give a higher yield of light ends (low-boiling hydrocarbon gases) and naphtha than Louisiana light sweet crude oil or Brent (North Sea) crude oil as well as a lower yield of residuum (Table 10.3) (Olsen, 2015).

In addition, the crude oil assay reflects the yield pattern of distillates and is key information for determining the refinery products (Table 10.4). Thus, the tight formation crude oils (such as Bakken crude oil, Eagle Ford crude oil, and Utica crude oil) typically have a lower boiling range with a higher API gravities, and have predominantly higher gas constituents, naphtha with less high-boiling vacuum gas oil vacuum residue materials. Furthermore, the API gravity of crude oil can be used to approximate key properties, such as distillate yields, contaminants and paraffin concentration — there is a general trend of increasing lower-boiling constituents with increasing API (Speight, 2014, 2015). Consequently, Eagle Ford oil with an API on the order of 48° has would be expected to have a higher yield of naphtha (boiling range: 50—200 °C (120—390 °F)) than Bakken crude oil with an API on the order of 40—43°. Contaminant levels also trend with gravity. For example, sulfur and nitrogen concentrations are generally lower for the light sweet crude oils produced from tight oil plays and higher for lower-gravity crude oils. However, higher-API gravity crudes typically have higher paraffin (wax) concentrations.

However, although tight oil is considered sweet (i.e., low sulfur content in the crude oil itself), hydrogen sulfide gas comes out of the ground with the crude oil. This gas is flammable (producing the noxious sulfur dioxide during combustion) and poisonous.

$$H_2S + O_2 \rightarrow SO_2 + H_2O$$

Therefore, the presence of hydrogen sulfide must be monitored at the drilling site and during loading at the wellhead, transportation, and offloading of the crude oil at the refinery. Prior to transportation, amine-based scavengers should be added to the crude oil prior to transport to refineries. These scavengers react with the hydrogen sulfide to produce non-volatile products:

$$H_2S + RNH_2 \rightarrow RNH_3^+ \, HS^-$$

However, mixing in the railcar due to movement, along with a change in temperature that raises the vapor pressure of the crude oil (an easily achievable event considering the volatility of the crude oil, Tables 10.1 and 10.3), can cause the release of hydrogen sulfide during off-loading thereby creating a safety issues, especially when the crude oil is handled in warmer climates.

Thus, while tight oil is currently more readily available for refiners in North America, there are numerous issues that arise from working with this type of oil which often place category known as *opportunity crude oils* (Chapter 1). Tight oils typically pose unique challenges in the context of incompatibility and instability because they: (i) contain entrained hydrogen sulfide which requires the addition of amine-based hydrogen sulfide scavengers in the pipeline, truck, or railcar prior to transport, (ii) are contaminated with paraffin wax constituent that cause fouling in piping, tank walls, and crude preheat exchangers, (iii) contain large amounts of filterable solids, and (iv) may be incompatible with other types of crude oils used for blending.

2.2 Shale oil

First and foremost, shale oil is not a naturally-occurring material and it is not the same as (or even remotely similar to) the crude oil that is recovered from tight formations (tight oil). Shale oil (also known as kerogen-derived oil) is a synthetic crude oil produced by retorting oil shale. The physical and chemical properties of crude shale oil are affected by (i) the shale from which the oil was produced as well as (ii) the reaction parameters that were operative at the time of production of the oil.

Shale oil has a rather high specific gravity, approximately 0.9—1.0, owing to the presence of nitrogen-, sulfur-, and oxygen-containing compounds. Also, high pour points are observed and small quantities of arsenic and iron are present. The nitrogen compounds are the most deleterious components of shale oil, since they are well-known catalytic poisons in various refining processes, such as fluid catalytic cracking, catalytic reforming, and catalytic hydrotreating (Speight, 2014. These compounds can give rise to stability (and incompatibility) problems in naphtha (and, hence if not removed during refining, in finished products such as gasoline) as well as in kerosene (and, hence if not removed during refining, in finished products such as jet fuel and diesel fuel), and produce emissions of nitrogen oxide (NOx) in burners.

Compared to tight oil (or for that matter, compared to any conventional light crude oil), shale oil is relatively viscous and is high in nitrogen and oxygen compounds. The low molecular oxygen compounds are predominantly phenol derivatives but carboxylic acid derivatives and non-acidic oxygen compounds such as ketone derivatives are also present in the oil. The basic nitrogen compounds in shale oils are pyridine, quinoline, acridine, amine and their alkyl substituted derivatives, the weakly basic ones are pyrrole, indole, carbazole and their derivatives, and the nitrile and amide homologues are the non-basic constituents. Sulfur compounds in the shale oils include thiol derivatives, sulfide derivatives, thiophene derivatives, as well as miscellaneous sulfur compounds. Elemental sulfur may occur in some shale oils but it is not a typical constituent.

Crude shale oil (also called raw shale oil, retort oil, or simply shale oil) is the liquid oil product recovered directly from the offgas stream of an oil shale retort. Synthetic crude oil (syncrude) results when crude shale oil is hydrogenated. In general, crude shale oil resembles conventional crude oil in that it is composed primarily of long-chain hydrocarbon derivatives with boiling points that span roughly the same range as those of typical crude oils. However, the three principal differences between crude shale oil and conventional crude are (i) a higher olefin content in shale oil because of the high temperatures used in the production processes, (ii) higher concentrations of oxygen and nitrogen derivatives that are produced from the oil shale kerogen, and, in many cases, (iii) a higher pour point and viscosity of shale oil.

The physical and chemical properties of crude shale oil are affected by the conditions under which the oil was produced. Some retorting processes subject it to relatively high temperatures, which may cause thermal cracking and thus produce an oil with a lower average molecular weight. In other processes (such as directly heated retorting) some of the lower-boiling constituents of the shale oil are incinerated during retorting — the result is a higher molecular weight (higher-boiling) final product. Other processes may produce lower-boiling products because of refluxing (cyclic vaporization and condensation) of the oil within the retort. One of the most important factors is the condensing temperature within the retorting system — this is the temperature at which the oil product is separated from the gaseous products of the retorting process. The lower this temperature, the higher the concentration of low molecular weight compounds in the product oil.

The properties of the oil produced by different above-ground retorting processes vary widely, but the differences between these oils and the in situ oils are much more significant. In situ oils are generally much lighter, as indicated by the higher yields of material with relatively low boiling points, and would produce more of a lower-boiling product (such as naphtha) and less of a higher-boiling product (such as resid). In general, the low yields of residuum make shale oils attractive as refinery feedstocks in comparison with many of the heavy conventional crude oils.

Among the negative characteristics of most crude shale oils are high pour point, high viscosity, and high concentrations of arsenic and other heavy metals and of nitrogen. The pour point and viscosity are of economic importance because transporting viscous oil that has a high pour point is difficult and, thus suggesting the need for pretreatment prior to marketing. High concentrations of arsenic and other metals are a disadvantage because they poison refining catalysts, especially in hydrogenation units (Speight, 2014). These constituents must be removed prior to catalytic processing. It should be noted that the concentrations of heavy metals in crude shale oil will vary with the location of the deposit from which the oil is recovered. Shale oil produced from oil shales from different formation (or sites) may be relatively free of such contaminants.

Other characteristic properties of shale oils are: (i) high levels of olefin derivatives and diolefin derivatives which are not present in tight crude oil or in crude oil in general and require special care during processing due to their tendency to polymerize and form gums, (ii) high levels of aromatic compounds, which are deleterious to diesel fuel, (iii) high carbon/hydrogen ratio, (iv) low sulfur levels, compared with most crude oils that available throughout the world, although for some shale oils from the retorting of marine oil shale, relatively high concentrations sulfur compounds may be present, (v) suspended solids (finely divided rock) which cause process problems chiefly if a first step of processing is hydrotreating, and (vi) moderately high levels of metals. Because of these particular characteristics, further processes, such as upgrading and refining, are needed to improve the properties of shale oil products.

Some retorting processes subject it to relatively high temperatures, which may cause thermal cracking and thus produce an oil with a lower average molecular weight. In other processes (such as directly heated retorting) some of the lower molecular weight components of the oil are incinerated during retorting. The result is a higher molecular weight (higher density, more viscous) final product. Other retorting process may produce lower molecular weight products because of refluxing (cyclic vaporization and condensation) of the oil within the retort. One of the most important factors is the condensing temperature within the retorting system – the condensing temperature is the temperature at which the shale oil product is separated from the retort gases. The lower this temperature, the higher the concentration of low molecular weight compounds in the product oil.

Thus, among the negative characteristics of most crude shale oils are high pour point, high viscosity, and high concentrations of arsenic and other heavy metals and of nitrogen. The pour point and viscosity are of economic importance because transporting viscous oil that has a high pour point is difficult and costly, thus suggesting the need for pretreatment prior to marketing. However, shale oil produced by an in situ process with a relatively low pour point and viscosity could be marketed without pretreatment but they would retain their high nitrogen content. This would reduce their value as refinery feedstocks and boiler fuels.

A high concentration of arsenic and other metals are a disadvantage because these metals poison refining catalysts, especially in hydrogenation units and must be removed prior to catalytic processing – a variety of physical and chemical methods have been developed for this purpose (Speight, 2014). It should be noted that the concentration of heavy metals in crude shale oil will vary with the location of the deposit from which the oil is recovered.

Shale oil is a synthetic crude oil produced by retorting oil shale and is the pyrolysis product of the organic matter (kerogen) contained in oil shale. The raw shale oil produced from retorting oil shale can vary in properties and composition. The two most significant characteristics of US western oil shales are the high hydrogen content, derived primarily from high concentrations of paraffins (waxes), and the high concentration of nitrogen, derived from high concentrations of pyridines and pyrroles.

Synthetic crude oil (syncrude) is the product that results when crude shale oil is refined (i.e., hydrogenated). In general, crude shale oil resembles conventional crude oil insofar as it is composed primarily of hydrocarbon derivatives and has a boiling range that is approximately the same range as the boiling range of typical of a typical crude oil. However, there are three principal differences between crude shale oil and conventional crude oil which are (i) crude shale oil has a higher olefin content a higher olefin content because of the high temperatures used in oil retorting, (ii) crude shale oil has a higher concentration of organic oxygen derivatives and organic nitrogen derivatives which are derived from the kerogen, (iii) in many cases, crude shale oil has a higher pour point and a higher viscosity than conventional crude oil, as well as (iv) crude shale oil with has a higher density (specific gravity the crude oil – on the order of 0.9–1.0 owing to the presence of higher molecular weight nitrogen-, sulfur-, and oxygen-containing compounds). Shale oil also has small quantities of arsenic and iron are present.

A typical shale oil produced from the Green River formation in Colorado contains approximately 40% w/w hydrocarbon derivatives consists of saturated hydrocarbon derivatives, olefin hydrocarbon derivatives, and aromatic hydrocarbon derivatives (Table 16.1) and approximately 60% w/w heteroatomic organic compounds, which contain nitrogen, sulfur, and oxygen derivatives. The nitrogen occurs in ring compounds with nitrogen in the ring, such as in pyridine derivatives and pyrrole derivatives as well as in nitrile derivatives – the nitrogen derivatives comprise approximately 60% w/w of the non-hydrocarbon components of the oil. Another 10% w/w of the heteroatomic components of the oil are sulfur compounds, which exist as thiophene derivatives along with varying amounts of sulfide derivatives and disulfide derivatives. The remaining 30% w/w is made up of oxygen compounds, which occur as phenol derivatives and carboxylic acid derivatives.

Although the content of asphaltene constituents and resin constituents in shale oil may be low, these constituents can be responsible for the dark color as well as the viscosity. The presence of asphaltene constituents in shale oil is not necessarily unique since it is high in nitrogen content and, consequently, high in ash content as well – polar nitrogen species are typically insoluble in n-heptane (the solvent used to separate the asphaltene fraction for crude oil and even low molecular weight species would appear as (or in) an asphaltene fraction from shale oil) (Speight, 2014). The polarity of the nitrogen-containing polycyclic derivatives may also explain the specific properties of emulsification of water and metal complexes.

It must also be taken into consideration when planning to blend shale oil with other liquid hydrocarbon products, or even with whole crude oil prior to refining, that there are no guarantees of complete compatibility of the constituents of the blend or stability of the blend. The origin and chemical composition of the kerogen is not well known and largely speculative and the composition of the produced shale oil is also subject to change, depending upon the origin of the oil shale. Thus, the problems of incompatibility must be recognized when using the shale oil for blending with hydrocarbon products. Also, in the initial stages after blending, compatibility and blend stability may appear to be in order but there may be an induction period after which instability and incompatibility are manifested by the appearance of separate phases in the blend. Oil shales range widely in composition as does the kerogen and it must, therefore, be anticipated that the thermally produced shale oil will also vary in composition. Thus, the suitability of one particular shale oil for a blending operation may be denied when a different shale oil is added to the mix!

The presence of the polar constituents in crude shale oil which contain nitrogen and oxygen functions, sulfur compounds are less of a problem because of the hydrotreating option when the shale oil is refined. However, shale oil can be notoriously incompatible with conventional crude oil feedstocks and with crude oil-derived products (Mushrush and Speight, 1995; Speight, 2014). As a result, particular care must be taken to ensure that all of the functions that cause such incompatibility are removed from the shale oil before it is blended with a conventional crude oil or crude oil product – the same rationale applied to blending shale oil with tight oil or tight oil products.

3. Instability and incompatibility

The instability/incompatibility of tight oil, shale oil, and their respective products is a precursor to either the formation of degradation products or the occurrence of undesirable changes in the properties of the fuel. Individually, the components of a product may be stable and in compliance with specifications, but their blend may exhibit poor stability properties, making them unfit for use.

The problem of instability in tight oil, shale oil and their respective products may manifest itself in changes to the liquid such as: (i) asphaltene separation that occurs when the paraffinic nature of the liquid medium increases – as is often the case in residual fuel oil, (ii) wax separation that occurs when there is a drop in temperature or the aromaticity of the liquid medium increases, as may be the case in lubricating oil, (iii) sludge/sediment formation in fuel products that occurs because of the interplay of several chemical and physical factors (Mushrush and Speight, 1995; Speight, 2000, 2001, 2014). In addition to the phase-separation phenomenon, there may also be a general darkening of the color of the liquid product (ASTM D1500).

Asphaltene-type deposition may, however, result from the mixing of feedstocks of different origin and treatment, each of which may be perfectly satisfactory when used alone. For example, straight run products (i.e., distillates) from the same oil are typically normally stable and mutually compatible whereas fuel oils produced from thermal cracking and visbreaking operations that may be stable but can be unstable or incompatible if blended with straight run fuels and vice versa.

This may not be the case with shale oil where oxidation of the heteroatom-containing constituents (i.e., the constituents containing nitrogen, or oxygen, or sulfur). In fact, problems related to instability and incompatibility in oils are associated with those fuels used in oil fired naval or marine vessels-where the oil is usually passed through a preheater before being fed to the burner system. In earlier days this preheating, with some fuels, could result in the deposition of asphaltic matter culminating, in the extreme case, in blockage of preheaters, pipelines and even complete combustion failure. In addtion, paraffin precipitation and deposition in oil pipelines is an issue that decreases the cross-sectional area of the pipeline thereby restricting operating capacities, and places additional strain on pumping equipment. On the other hand, asphaltene deposition can lead to fouling of preheaters on heating the fuel to elevated temperatures (Mushrush and Speight, 1995; Speight, 2014).

In order to assess the possibility of gum formation of product during storage, in other words, the gum stability of the gasoline, a test (ASTM D525) is employed which determines, in a pressure vessel, the *induction period* or time of heating at 100 °C (212 °F) with oxygen at an initial pressure of 100 pounds per square inch, which elapses before the oxygen pressure begins to fall, due to the oxidation of the sample and the formation of gum therein indicates the onset of oxidative instability (ASTM D2893, ASTM D4636, ASTM D5483). The data for oxidation stability, or *break-down time* as it is sometimes called, is thus regarded as a measure of the stability of the fuel.

However, due to the multiplicity of types and conditions of storage, it is impossible to equate induction-period with safe storage time, but it has been found by long experience that a minimum of 240 min induction-period usually ensures a satisfactory level of gum stability for most normal marketing and distributing purposes. Induction period is also a useful control test for determining the amount of gum inhibitor to be added to gasoline, provided that the storage stability of the combination of the gasoline and inhibitor has been established by practical storage experiments.

Sludge (or sediment) formation takes one of the following forms: (i) material dissolved in the liquid; (ii) precipitated material; and (iii) material emulsified in the liquid. Under favorable conditions, sludge or sediment will dissolve in the raw oil or the oil product with the potential of increasing the viscosity. Sludge or sediment, which is not soluble in the oil (ASTM D473, ASTM D1796, ASTM D2273, ASTM D4007, ASTM D4807, ASTM D4870), may either settle at the bottom of the storage tanks or remain in the oil as an emulsion. In most of the cases the smaller part of the sludge/sediment will settle satisfactorily, the larger part will remain in the oil as an emulsion. In any case there is a need of breaking the emulsion, whether it is a water-in-oil emulsion or whether it is the sludge itself, which has to be separated into the oily phase and the aqueous phase. The oily phase can be then processed with the oil and the aqueous phase can be drained out of the system.

Emulsion breaking, whether the emulsion are due to oil-sludge emulsions, oil-water emulsions or breaking of the sludge themselves into their oily and inorganic components, are of a major importance form operational as well as commercial aspects. With some high-boiling fuel oil products and heavy crude oils, phase separation difficulties often arise (Mushrush and Speight, 1995). Also, some oil emulsions may be stabilized by naturally occurring substances in the oil. Many of these polar particles accumulate at the oil-water interface, with the polar groups directed toward the water and the hydrocarbon groups toward the oil. A stable interfacial skin may be so formed; particles of clay or similar impurities, as well as wax crystals present in the oil may be embedded in this skin and make the emulsion very difficult to break (Schramm, 1992).

Chemical and electrical methods for sludge removal and for water removal, often combined with chemical additives, have to be used for breaking such emulsions. Each emulsion has its own structure and characteristics: water-in-oil emulsions where the oil is the major component or oil in water emulsions where the water is the major component. The chemical and physical nature of the components of the emulsion play a major role in their susceptibility to the various surface active agents used for breaking them.

Therefore, appropriate emulsion breaking agents have to be chosen very carefully, usually with help of previous laboratory evaluations. Water or oil soluble demulsifiers, the latter being often non-ionic surface active alkylene oxide adducts, are used for this purpose. But, as had been said in the foregoing, the most suitable demulsifier has to be chosen for each case from a large number of such substances in the market, by a prior laboratory evaluation.

In addition to stability of the tight oil or shale oil system, there are many oil products that are unstable under service conditions. For example, many products are manufactured by cracking processes contains unsaturated components that may oxidize during storage and form undesirable oxidation products. If storage for considerable time before use is anticipated, it is essential that the product should not undergo any deleterious change under storage conditions and should remain stable.

Heteroatoms (particularly nitrogen, sulfur, and trace metals) are present in shale oil and might be also expected to be present in liquid fuels and other products from the shale oil (Speight, 2014). And, indeed, this is often the case, although there may have been some skeletal changes induced by the refining process(es). However, it must be stressed that instability/incompatibility is not directly related to the total nitrogen, oxygen, or sulfur content. The formation of color/sludge/sediment is a result of several factors. Perhaps the main factor is the location and nature of the heteroatom that, in turn, determines reactivity (Mushrush and Speight, 1995).

Compatibility in distillate products is important to commercial and consumers as well as to the producer. Distillate products that are made from the refining process based on straight-run distillation show very little incompatibility problems. However at present and in the future, problems for refiners will continue to increase as the quality of the available conventional crude oil decreases world-wide. This decrease coupled with the inevitable future use of liquid fuels from bio-sources, coal, and shale sources will exacerbate the present problems for the producers.

When various stocks are blended at the refinery, incompatibility can be explained by the onset of acid-base catalyzed condensation reactions of the various organo-nitrogen compounds in the individual blending stock themselves. These are usually very rapid reactions with practically no observed induction time period (Mushrush and Speight, 1995).

When the product is transferred to a storage tank or some other holding tank incompatibility can occur the free-radical hydroperoxide induced polymerization of active olefins. This is a relatively slow reaction, because the observed increase in hydroperoxide concentration is dependent on the dissolved oxygen content (Mayo and Lan, 1987). Another incompatibility mechanism involves degradation when the product is stored for prolonged periods, as might occur during stockpiling of fuel for military use (Goetzinger et al., 1983; Hazlett and Hall, 1985; Stavinoha and Westbrook, 1980). This incompatibility process involves (i) the buildup of hydroperoxide moieties after the gum reactions; (ii) a free-radical reaction with the various organo-sulfur compounds present (such as mercaptan sulfur, R-SH) (ASTM D3227, ASTM D5305), that can be oxidized to sulfonic acids; and

(iii) reactions such as condensations between organo-sulfur and nitrogen compounds and esterification reactions.

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Incompatibility in crude oil products can be linked to the presence of several different deleterious heteroatomic compound classes (Mushrush and Speight, 1995; Speight, 2014). The incompatibility observed in a fuel is dependent on the blending stocks employed in its production. The low-boiling cycle oils produced during catalytic process contain the unstable heteroatomic species that are responsible for the observed deterioration in fuel. The solution is to use straight-run distillate product but a deficiency in supply and an option is to use chemical additives that overcome the incompatibilities of the variant chemical composition of the low-boiling cycle oil.

In general, the reaction sequence for sediment formation can be envisaged as being dependent upon the most reactive of the various heteroatomic species that are present in fuels (Pedley et al., 1986, 1988, 1989). The worst-case scenario would consist of a high olefin fuel with both high indole concentration and a catalytic trace of sulfonic acid species. This reaction matrix would lead to rapid degradation. However, just as there is no *one* specific distillate product, there is also no *one* mechanism of degradation. In fact, the mechanism and the functional groups involved will give a general but not specific mode of incompatibility (Hiley and Pedley, 1986, 1987; Mushrush et al., 1990, 1991). The key reaction in many incompatibility processes is the generation of the hydroperoxide species from dissolved oxygen. Once the hydroperoxide concentration starts to increase, macromolecular incompatibility precursors form in the fuel. Acid or base catalyzed condensation reactions then rapidly increase both the polarity, incorporation of heteroatoms, and the molecular weight.

When various feedstocks are blended at the refinery, incompatibility can be explained by the onset of acid-base catalyzed condensation reactions of the various organo-nitrogen compounds in the individual blending stocks. These are usually very rapid reactions with practically no observed induction time period. When the product is transferred to a storage tank or some other holding tank incompatibility can occur by the free-radical hydroperoxide induced polymerization of active olefins. This is a relatively slow reaction, because the observed increase in hydroperoxide concentration is dependent on the dissolved oxygen content (Mayo and Lan, 1987; Mushrush and Speight, 1995).

The third incompatibility mechanism involves degradation when the product is stored for prolonged periods, as might occur during stockpiling of fuel for military use (Goetzinger et al., 1983; Hazlett and Hall, 1985; Stavinoha and Westbrook, 1980). This incompatibility process involves (i) the buildup of hydroperoxide moieties after the gum reactions, (ii) a free-radical reaction with the various organo-sulfur compounds present that can be oxidized to sulfonic acid derivatives, and (iii) reactions such as condensations between organo-sulfur and nitrogen compounds and esterification reactions.

Incompatibility during refining can occur in a variety of processes, either by intent (such as in the deasphalting process) or inadvertently when the separation is detrimental to the process. Thus, separation of solids occurs whenever the solvent characteristics of the liquid phase are no longer adequate to maintain polar and/or high molecular weight material in solution. Examples of such occurrences are: (i) the separation of asphaltene constituents, which occurs when the paraffinic nature of the liquid medium increases (Mushrush and Speight, 1995; Speight, 2014), (ii) wax separation, which occurs when there is a drop in temperature or the aromaticity of the liquid medium increases (Mushrush and Speight, 1995; Speight, 2014), (iii) sludge/sediment formation in a reactor which occurs when the solvent characteristics of the liquid medium change so that asphaltic or wax materials separate, coke formation which occurs at high temperatures and commences when the solvent power of the liquid phase is not sufficient to maintain the coke precursors in solution (Speight, 2014), and sludge/sediment formation in fuel products which occurs because of the interplay of several chemical and physical factors (Mushrush and Speight, 1995; Speight, 2014).

The instability/incompatibility of crude oil and of crude oil products is manifested in the formation of sludge, sediment, and general darkening in color of the liquid (ASTM D1500). Phase separation can be accomplished by either the use of suitable surface active agents allowing for sufficient settling time, or by use of a high voltage electric field for breaking such emulsions after admixing water at a rate of about 5% and at a temperature of about 100 °C (212 °F).

Emulsion breaking, whether the emulsion is due to crude oil-sludge emulsions, crude oil-water emulsions or breaking the sludge themselves into organic (oily) and inorganic components are of a major importance form operational as well as commercial aspects. With some high-boiling fuel oil products and heavy crude oils phase separation difficulties often arise (Por, 1992; Mushrush and Speight, 1995). Also, some crude oil emulsions may be stabilized by naturally occurring substances in the crude oil. Many of these polar particles accumulate at the oil-water interface, with the polar groups directed toward the water and the hydrocarbon groups toward the oil. A stable interfacial skin may be so formed; particles of clay or similar impurities, as well as wax crystals present in the oil may be embedded in this skin and make the emulsion very difficult to break (Schramm, 1992).

Chemical and electrical methods for sludge removal and for water removal, often combined with chemical additives, have to be used for breaking such emulsions. Each emulsion has its own structure and characteristics: water-in-oil emulsions where the oil is the major component or oil in water emulsions where the water is the major component. The chemical and physical nature of the components of the emulsion plays a major role in their susceptibility to the various surface-active agents used for breaking them.

Therefore, appropriate emulsion breaking agents have to be chosen very carefully, usually with help of previous laboratory evaluations. Water or oil soluble demulsifiers, the latter being often non-ionic surface-active alkylene oxide adducts, are used for this purpose. But, as had been said in the foregoing, the most suitable demulsifier has to be chosen for each case from a large number of such substances in the market, by a prior laboratory evaluation.

The focus of incompatibility studies has usually been on the whole crude oil and specifically on the asphaltene fraction. As already stated (Chapters 12 and 13), the asphaltene constituents are the highest molecular weight and most polar fractions found in crude oil. The characteristics of the asphaltene constituents and the amount in crude oil depend to a greater or lesser extent on the crude oil source. During refining of crude oil, asphaltene constituents will end up in a high percentage in the residual fuels as the light fractions (naphtha, kerosene, and fuel oil) are removed from the oil through cracking and visbreaking.

The problems with the asphaltene constituents have increased due to the need to extract even the heaviest crude oils as well as the trend to extract large amounts of low-boiling fractions out of crude oil by among other methods cracking and visbreaking. The deposition of asphaltene constituents is the consequence of instability of the crude oil or the crude oil product (Table 17.2). The asphaltene constituents are stabilized by resin constituents (Speight, 2014) and maintained in the crude oil due to this stabilization. Asphaltene dispersants are substitutes for the natural resin constituents and are able to keep the asphaltene constituents dispersed to prevent flocculation/aggregation and phase separation (Speight, 1994; Browarzik et al., 1999). Dispersants will also clean up sludge in the fuel system and they have the ability to adhere to surface of materials that are insoluble in the oil and convert them into stable colloidal suspensions.

At the other end of the molecular weight scale and refining, the heteroatoms (particularly nitrogen, sulfur, and trace metals) (Chapter 8) that are present in crude oil and might be also expected to be present in liquid fuels and other products from crude oil. And, indeed, this is often the case, although there may have been some skeletal changes induced by the refining process(es). Oxygen is much more difficult to define in crude oil and liquid fuels. However, it must be stressed that instability/incompatibility is not directly related to the total nitrogen, oxygen, or sulfur content. The formation of color/sludge/sediment is a result of several factors. Perhaps the main factor is the location and nature of the heteroatom which, in turn, determines reactivity (Por, 1992; Mushrush and Speight, 1995).

Thus, although tight oil is considered sweet (i.e., low sulfur content in the crude oil itself), hydrogen sulfide gas comes out of the ground with the crude oil. ~S is flammable and poisonous, and therefore must be monitored at the drilling site and during loading, transport,

TABLE 17.2 Example of problems due to flocculation and/or sedimentation of asphaltene constituents and reacted asphaltene constituents.

Process	Outcome
Oil recovery	Wellbore plugging and pipeline deposition.
Visbreaking	Degraded asphaltene constituents are more aromatic and less soluble.
Emulsion formation	A high degree of water contamination can result in emulsion formation.
	Asphaltene constituents are highly polar and surface active.
	Asphaltene constituents are responsible for the undesired stabilization of emulsions, since.
Preheating	Preheating can encourage precipitation of the reacted asphaltene constituents leading to coking.
Blending	The change of medium during mixing can cause destabilization of asphaltene and reacted asphaltene constituents.
Storage	Sedimentation and plugging can occur due to oxidation of the asphaltene constituents.
	Increased polarity can cause asphaltene aggregation and sludge/sediment formation.

and off-loading of the tight oil. Amine-based ∼S scavengers are added to the crude oil prior to transport to refineries. However, mixing in the railcar due to movement, along with a change in temperature that raises the oil's vapor pressure, can cause the release of entrained hydrogen sulfide during off-loading - creating a safety hazard. For example, crude from the Bakken shale play in North Dakota that is loaded on railcars in winter and then trans-ported to a warmer climate becomes hazardous due to the higher vapor pressure.

4. Factors influencing instability and incompatibility

Some refiners blend two or more crudes to achieve the right balance of feedstock qualities which may cause problems if the crude oils being mixed are incompatible. When crude oils are incompatible, increased asphaltene precipitation accelerates fouling in the heat exchanger train downstream of the crude desalter. Accelerated fouling increases the amount of energy that must be supplied by the crude fired heater, which limits throughput when the fired heater reaches its maximum duty. It may also necessitate an earlier shutdown for cleaning. This sequence of events increases operating costs and negatively impacts the profit-ability of the refinery. Manual monitoring of heat exchanger fouling often fails to detect crude blends that are incompatible, so the same incompatible crudes might be blended in the future.

Some refiners that tried to run with a high percentage of light tight oil found that the preheat exchangers did not have sufficient heat-transfer capability, which created an energy imbalance across the preheat train and fired heater. The side streams from the atmospheric distillation unit fractionator provide a large amount of heat to the preheat exchangers. When the flowrates of these side cut streams are low (due to the lack of heavy components in tight oil), there is an energy imbalance in the preheat exchangers.

With very little gas oil and residuum (i.e., the heaviest materials in a crude oil, also referred to as the bottom-of-the- barrel components) in tight oil, the amount of heat available in the crude preheat exchangers upstream of the crude fired heater is insufficient, which increases the crude fired heater's fuel consumption. Some refiners experienced fired heater limitations and reduced throughput, as well. Energy imbalances are one of the main reasons crude blending is more common with tight oils than other crudes.

A number of experimental methods are available for estimation of the factors that influence instability/incompatibility. These factors which can related to chemical properties or physical properties are presented below in alphabetical order rather than by any order related to the extent of effects of the incompatibility. Also, it should be no surprise that some of the properties are strongly related to the inducement of incompatibility.

4.1 Acidity

The acidity of crude oil or crude oil products is usually measured in terms of the *acid number* which is defined as the number of milli-equivalents per gram of alkali required to neutralize the acidity of the crude oil sample (ASTM D664, ASTM D974, ASTM D3242).

Acidity due to the presence of inorganic constituents is not expected to be present in crude oils, but organic acidity might be found. Acidic character is composed of contributions from strong organic acids and other organic acids. Values above 0.15 mg potassium hydroxide per gram are considered to be significantly high. Crude oils of higher acidities may exhibit a tendency of instability.

The acid imparting agents in crude oils are naphthenic acids and hydrosulfides (thiols, mercaptans, R-SH). These are sometimes present in the crude oil originally in small and varying concentrations. Normally, the total acidity of crude oils is in the range of 0.1—0.5 mg potassium hydroxide per gram, although higher values are not exceptional.

Free hydrogen sulfide is often present in crude oils, a concentration of up to 10 ppm being acceptable in spite of its toxic nature. However higher hydrogen sulfide concentrations are sometimes present, 20 ppm posing serious safety hazards. Additional amounts of hydrogen sulfide can form during the crude oil processing, when hydrogen reacts with some organic sulfur compounds converting them to hydrogen sulfide. In this case it is referred to as potential hydrogen sulfide, contrary to free hydrogen sulfide.

Acidity can also form by bacterial action insofar as some species of aerobic bacteria can produce organic acids from organic nutrients. On the other hand, anaerobic sulfate-reducing bacteria can generate hydrogen sulfide, which, in turn, can be converted to sulfuric acid (by bacterial action).

4.2 Asphaltene content

The asphaltene fraction is separated as a dark brown to black friable solids that have no definite melting point and usually intumesce on heating with decomposition to leave a carbonaceous residue. They are obtained from crude oil by the addition of a non-polar solvent (such as a liquid hydrocarbon). Liquids used for this purpose are *n*-pentane and *n*-heptane (Table 17.3) (Chapters 9, 10, and 12) (Speight, 1994). Usually, the Asphaltene fraction is removed by filtration through paper but more recently a membrane method has come into use (ASTM D4055). Liquid propane is used commercially in processing crude oil residua (Chapter 20) — the asphaltene constituents are soluble in liquids such as benzene, toluene, pyridine, carbon disulfide, and carbon tetrachloride.

The asphaltene fraction of feedstocks is particularly important because as the proportion of this fraction increases, there is (a) concomitant increase in thermal coke yield and an increase in hydrogen demand as well as catalyst deactivation. The constituents of the asphaltene fraction form coke quite readily which is of particular interest in terms of the compatibility/incompatibility of the coke precursors (Speight, 1994).

The asphaltene constituents do not dissolve in crude oil, but exist as a colloidal suspension (Mushrush and Speight, 1995; Speight, 2014). They are soluble in aromatic compounds, such as xylene, but precipitate in the presence of light paraffinic compounds, such as pentane. Mixing stable crude blends with asphaltic and paraffinic oils creates the potential for precipitating the unstable asphaltenes. The high naphtha content of tight oils also creates favorable conditions for asphaltenes to more readily precipitate. It should be noted that the ratio of crudes in a blend may have an impact on crude incompatibilities. For example, 20 tight oil in an 80—20 blend might not cause accelerated fouling, whereas a 70—30 blend may be unstable and cause more rapid fouling.

TABLE 17.3 Standard methods for asphaltene precipitation.

Method	Precipitant	Volume precipitant per g of sample (mL)
ASTM D893	*n*-pentane	10
ASTM D2006	*n*-pentane	50
ASTM D2007	*n*-pentane	10
ASTM D3279	*n*-heptane	100
ASTM D4124	*n*-heptane	100
IP 143	*n*-heptane	30

ASTM Annual Book of Standards, 1980–2012.

The effect of asphaltene constituents and the micelle structure, the state of dispersion also merit some attention. The degree of dispersion of asphaltene constituents is higher in the more naphthenic/aromatic crude oils because of higher solvency of naphthenes and aromatics over paraffinic constituents. This phenomenon also acts in favor of the dissolution of any sludge that may form thereby tending to decrease sludge deposition. However, an increase in crude oil often accompanies sludge dissolution.

The higher the asphaltene content, the greater the tendency of the crude oil to form sludge, especially when blended with other non-compatible stocks.

4.3 Composition

Tight oil tends to have a higher API gravity than traditional crude oils, as well as much different properties. For example, Eagle Ford tight oil can have twice as much naphtha as Light Louisiana Sweet, a typical light United States crude oil. Also, Eagle Ford tight oil has an average API gravity in the range of 40–45° API, whereas Light Louisiana Sweet has an API gravity of approximately 35° API. To best utilize existing downstream units, tight oils must be blended with heavier crudes, because a more-consistent.

4.4 Density and specific gravity

In the earlier years of the crude oil industry, density and specific gravity (with the API gravity) were the principal specifications for feedstocks and refinery products (Chapters 10, 24, and 26). They were used to give an estimate of the most desirable product, i.e., kerosene, in crude oil. At the present time, a series of standard tests exists for determining density and specific gravity (Chapter 10) (Speight, 2001, 2014, 2015).

There is no direct relation between the density and specific gravity of crude oils to their sludge forming tendencies, but crude oil having a higher density (thus, a lower API gravity) is generally more susceptible to sludge formation, presumably because of the higher content of the polar/asphaltic constituents.

4.5 Elemental analysis

The ultimate analysis (elemental composition) of crude oil and its products is not reported to the same extent as for coal (Speight, 2013). Nevertheless, there are ASTM procedures (ASTM, 2019) for the ultimate analysis of crude oil and crude oil products (Chapter 10) but many such methods may have been designed for other materials.

Of the data that are available, the proportions of the elements in crude oil vary only slightly over narrow limits: carbon 83.0–87.0% w/w, hydrogen 10.0–14.0% w/w, nitrogen 0.10–2.0% w/w, oxygen 0.05–1.5% w/w, sulfur 0.05–6.0% w/w (Chapters 8 and 10). And yet, there is a wide variation in physical properties from the lighter more mobile crude oils at one extreme to the extra heavy crude oil at the other extreme (Chapter 1). In terms of the instability and incompatibility of crude oil and crude oil products, the heteroatom content appears to represent the greatest influence. In fact, it is not only the sulfur and nitrogen content of crude oil are important parameters in respect of the processing methods which have to be used in order to produce fuels of specification sulfur concentrations but also the type of sulfur and nitrogen species in the oil. There could well be a relation between nitrogen and sulfur content and crude oil (or product) stability; higher nitrogen and sulfur crude oils are suspect of higher sludge forming tendencies.

4.6 Filterable solids

Filterable solids also contribute to fouling in the crude preheat exchangers. A tight crude can contain over seven times more filterable solids than a traditional crude. Refiners have reported filterable solids in excess of 200 lbs per thousand barrels of tight oil. For a refinery that processes 100,000 barrels per day, this translates to more than 10 ton of solids per day entering the refinery with the crude.

To mitigate filter plugging, the filters at the entrance of the refinery require automated monitoring because they need to capture large volumes of solids. In addition, wetting agents are added to the desalter to help capture excess solids in the water, rather than allowing the undesired solids to travel further downstream into the process.

4.7 Metals content

The majority of crude oils contain metallic constituents that are often determined as combustion ash (ASTM D482). This is particularly so for the heavier feedstocks. These constituents, of which nickel and vanadium are the principal metals, are very influential in regard to feedstock behavior in processing operations.

The metal (inorganic) constituents of crude oil or a liquid fuel arise from either the inorganic constituents present in the crude oil originally or those picked up by the crude oil during storage. The former are mostly metallic substances like vanadium, nickel, sodium, iron, silica etc.; the latter may be contaminants such as sand, dust, and corrosion products.

Incompatibility, leading to deposition of the metals (in any form) on to the catalyst leads to catalyst deactivation whether it is by physical blockage of the pores or destruction of reactive sites. In the present context, the metals must first be removed if erroneously high carbon residue data are to be avoided. Alternatively, they can be estimated as ash by complete burning of the coke after carbon residue determination.

Metals content above 200 ppm are considered to be significant, but the variations are very large. The higher the ash content the higher is the tendency of the crude oil to form sludge or sediment.

4.8 Pour point

The *pour point* (Chapter 10) defines the cold properties of crude oils and crude oil and crude oil products, i.e., the minimal temperature at which they still retain their fluidity (ASTM D97). Therefore, pour point also indicates also the characteristics of crude oils: the higher the pour point, the more paraffinic is the oil and vice versa. Higher pour point crude oils are waxy and therefore they tend to form wax-like materials that enhance sludge formation.

To determine the *pour point* (ASTM D97, ASTM D5853) the sample is contained in a glass test tube fitted with a thermometer and immersed in one of three baths containing coolants. The sample is dehydrated and filtered at a temperature 25 °C (45 °F) higher than the above the anticipated cloud point. It is then placed in a test tube and cooled progressively in coolants held at −1 to +2 °C (30–35 °F), −18 to −20 °C (−4 to 0 °F) and −32 to −35 °C (−26 to −31 °F), respectively. The sample is inspected for cloudiness at temperature intervals of 1 °C (2 °F). If conditions or oil properties are such that reduced temperatures are required to determine the pour point, alternate tests are available that accommodate the various types of samples.

4.9 Viscosity

The viscosity of a feedstock varies with the origin and type of the crude oil and also with the properties of the chemical constituents, particularly the polar functions where intermolecular interactions can occur. For example, there is a gradation of viscosity between conventional crude oil, heavy oil, and bitumen (Chapter 10).

Viscosity is a measure of fluidity properties and consistencies at given temperatures (Chapter 10). Heavier crude oil, i.e., crude oil having lower API gravity, typically have higher viscosity. Increases of viscosity during storage indicate either an evaporation of volatile components or formation of degradation products dissolving in the crude oil.

4.10 Volatility

Crude oil can be subdivided by distillation into a variety of fractions of different *boiling ranges* or *cut points* (Chapters 10 and 17). In fact distillation was, and still is, the method for feedstock evaluation for various refinery options. Indeed, volatility is one of the major tests for crude oil products and it is inevitable that the majority of all products will, at some stage of their history, be tested for volatility characteristics (Chapter 10).

As an early part of characterization studies, a correlation was observed between the quality of crude oil fractions and their heteroatom content since gasoline, kerosene, diesel fuel, and lubricating oil are made up of hydrocarbon constituents containing high proportions of hydrogen. Thus, it is not surprising that test to determine the volatility of crude oil and crude oil products were among the first to be defined.

The very nature of the distillation process by which residua are produced (Chapter 16), i.e., removal of distillate without thermal decomposition, dictates that the majority of the heteroatoms which are predominantly in the higher molecular weight fractions, will be concentrated in the higher boiling products and the residuum (Chapter 9; see also *Asphalt*, Chapter 26) (Speight, 2000). Thus, the inherent nature of the crude oil and the means by which it is refined can seriously influence the stability and incompatibility of the products.

Heavier crude oils, yielding higher amounts of residua, tend to form more sludge during storage compared to light crude oils.

4.11 Water content, salt content, and bottom sediment/water

Water content (ASTM D4006, ASTM D4007, ASTM D4377, ASTM D4928) salt content (ASTM D3230), and bottom sediment/water (BS&W) (ASTM D96, ASTM D1796, ASTM D4007) indicate the concentrations of aqueous contaminants, present in the crude either originally or picked up by the crude during handling and storage. Water and salt content of crude oils produced at the field can be very high, forming sometimes its major part. The salty water is usually separated at the field, usually by settling and draining, surface-active agents electrical emulsion breakers (desalters) are sometimes employed. The water and salt contents of crude oil supplied to the buyers is function of the production field. Water content below 0.5%, salt content up to 20 pounds per 1000 barrels, and bottom sediment and water up to 0.5% are considered to be satisfactory.

Although the centrifuge methods are still employed (ASTM D96, ASTM D1796, ASTM D2709 and ASTM D4007), many laboratories prefer the Dean and Stark adaptor (ASTM D95). The apparatus consists of a round-bottom flask of capacity 50 mL connected to a Liebig condenser by a receiving tube of capacity 25 mL, graduated in 0.1 mL. A weighed amount, corresponding to approximately 100 mL of oil, is placed in the flask with 25 nil of dry toluene. The flask is heated gently until the 25 mL of toluene have distilled into the graduated tube. The water distilled with the toluene, separates to the bottom of the tube where the volume is recorded as ml, or the weight as mg, or percent.

To determine the sediment in crude oil or in a crude oil product, the method involves solvent extraction using a Soxhlet extractor.

The Karl Fischer titration method (ASTM D1744), the Karl Fischer titration method (ASTM D377), and the colorimetric Karl Fischer titration method (ASTM D4298) still find wide application in many laboratories for the determination of water in liquid fuels, specifically the water content of aviation fuels.

The higher the bottom sediment and water content, the higher sludge and deposit formation rates can be expected in the stored crude oil.

4.12 Wax deposition

Paraffin waxes contaminate tight oils and remain on the walls of railcars, crude oil tank walls, and piping. They are also known to foul the preheat sections of crude heat exchangers (before they are removed in the crude desalter). Paraffin waxes that stick to piping and vessel walls can trap amines against the walls, which can create localized corrosion.

The severe fouling in heat exchangers upstream of the desalter was initially a surprise to many refiners - fouling is typically worse in the hotter exchangers that are downstream of the desalter. Refiners now monitor the crude preheat exchangers more closely, and are working with both automation and chemical companies to counter this fouling and corrosion potential.

5. Methods for determining instability and incompatibility

Stability/instability and compatibility/incompatibility can be estimated using several tests. These tests are:

1. Compatibility spot tests (ASTM D2781, ASTM D4740).
2. Thermal stability test data (ASTM D873, ASTM D3241).
3. Existent and potential sludge formation (hot filtration test) (ASTM D4870).
4. Asphaltene content (ASTM D3729).
5. The rate of viscosity increase (ASTM D445) of stored residual fuel oil samples at various temperatures with and without exposure to air.
6. Color (ASTM D1500).

In addition to the test for the stability and compatibility of residual fuels (ASTM D4740), the other most frequently stability test used is the existent and accelerated dry sludge content determination of residual fuels (the hot filtration test). Hot filtration test results of up to 0.2% w/w are considered to be satisfactory, results above 0.4% w/w. Indicate a poor stability, but differing values might be required, depending on the intended use of the product.

One test, or property, that is somewhat abstract in its application but which is becoming more meaningful popular is the *solubility parameter* (Chapters 12 and 13), which allows estimations to be made of the ability of liquids to become miscible on the basis of miscibility of model compound types where the solubility parameter can be measured or calculated.

Although the solubility parameter is often difficult to define when complex mixtures are involved, there has been some progress. For example, crude oil fractions have been assigned a similar solubility parameter to that of the solvent used in the separation. However, there is also the concept (Speight, 1992) that the solubility parameter of crude oil fractions may be defined somewhat differently insofar as they can be estimated from data such as the atomic hydrogen-to-carbon ratios. Whichever method is the best estimate may be immaterial as long as the data are used to the most appropriate benefit and allow some measure of predictability.

Bottle tests constitute the predominant test method and the test conditions have varied in volume, type of glass or metal, vented and unvented containers, type of bottle closure. Other procedures have involved stirred reactor vessels under both air pressure or under oxygen pressure, and small volumes of fuel employing a cover slip for solid deposition (ASTM D4625). All of these procedures are gravimetric in nature.

There are several *accelerated fuel stability tests* that can be represented as a time-temperature matrix (Goetzinger et al., 1983; Hazlett, 1992). A graphical representation shows that the majority of the stability tests depicted fall close to the solid line, which represents a doubling of test time for each 10 °C (18 °F) change in temperature. The line extrapolates to approximately one year of storage under ambient conditions. Temperatures at 100 °C (212 °F) or higher present special chemical problems.

The heteroatom content of the deposits formed in stability studies varied as the source or type of dopant and fuel liquid source varied. This would be an anticipated result. The color changes of both the fuel and the deposits formed are more difficult to interpret.

It is also worthy of note that *fractionation* of crude oil and its products may also give some indication of instability. There are many schemes by which crude oil and related materials might be fractionated (Chapter 9). It is not the intent to repeat the details of these in this chapter. However, a brief overview is necessary since fractional composition can play a role in stability and incompatibility phenomena.

Crude oil can be fractionated into four broad fractions by a variety of techniques (Chapters 9 and 10) although the most common procedure involves precipitation of the asphaltene fraction and the use of adsorbents to fractionate the deasphalted (deasphaltened) oil. The fractions are named for convenience and the assumption that fractionation occurs by specific compound type is not quite true.

In general terms, studies of the composition of the incompatible materials often involves determination of the distribution of the organic functional groups by *selective fractionation* that is analogous to the deasphalting procedure and subsequent fractionation of the maltene constituents (Mushrush and Speight, 1995; Speight, 2014): (i) heptane soluble materials: often called maltene fraction (maltenes) or petrolene fraction, (ii) heptane-insoluble material, benzene (or toluene) soluble material, often referred to as asphaltene constituents, (iii) toluene insoluble material, which is referred to as carbenes and carboids and occur especially when the fraction is a thermal product – there is little or no such material in untreated tight oil. Pyridine, carbon disulfide and tetrahydrofuran have been used in place of toluene.

Whichever solvent separation scheme is employed, there should be ample description of the procedure so that the work can be repeated not only in the same laboratory by a different researcher but also in different laboratories by various researchers. Thus, for any particular feedstock and solvent separation scheme, the work should repeatable and reproducible within the limits of experimental error.

Fractionation procedures allow a before-and-after inspection of any feedstock or product and can give an indication of the means by which refining or use changes the composition of the feedstock. In addition, fractionation also allows studies to be made of the interrelations between the various fractions. For example, the most interesting phenomenon (in the present context) to evolve from the fractionation studies is the relationship between the asphaltene constituents and the resin constituents.

In crude oil, the asphaltene constituents and resin constituents have strong interactions to the extent that the asphaltene constituents are immiscible (insoluble/incompatible) with the remaining constituents in the absence of the resin constituents (Koots and Speight, 1975). And there appears to be points of structural similarity (for a crude oil) between the asphaltene and the resin constituents thereby setting the stage for *a more-than-is-generally-appreciated* complex relationship but confirming the hypothesis that crude oil is a continuum of chemical species, including the asphaltene constituents (Chapter 12).

This sets the stage for the incompatibility of the asphaltene constituents in any operation in which the asphaltene or resin constituents are physically or chemically altered. Disturbance of the asphaltene-resin relationships can be the stimulation by which, for example, some or all of the asphaltene constituents form a separate *insoluble* phase leading to such phenomena as coke formation (in thermal processes) or asphalt instability during use.

There is a series of characterization indices that an also present indications of whether or not a crude oil product is stable or unstable. For example, the *characterization factor* indicates the chemical character of the crude oil and has been used to indicate whether a crude oil was paraffinic in nature or whether it was a naphthenic/aromatic crude oil.

The *characterization factor* (sometimes referred to as the *Watson characterization factor*) (Chapter 10) is a relationship between boiling point and specific gravity:

$$K = T_b^{1/3}/d$$

T_b is the cubic average boiling point, degrees Rankine (°F + 460) and d is the specific gravity at 15.6 °C (60 °F).

The characterization factor was originally devised to illustrate the characteristics of various feedstocks. Highly paraffinic oils have $K = 12.5-13.0$ while naphthenic oils have $K = 10.5-12.5$. In addition, if the characterization factor is above 12, the liquid fuel or product might, because of its paraffinic nature, be expected to form waxy deposits during storage.

The *viscosity-gravity constant* (*vgc*) was one of the early indices proposed to classify crude oil on the basis of composition. It is particularly valuable for indicating a predominantly paraffinic or naphthenic composition. The constant is based on the differences between the density and specific gravity for the various hydrocarbon species:

Where d is the specific gravity and v is the Saybolt viscosity at 38 °C (100 °F). For viscous crude oils (and viscous products) where the viscosity is difficult to measure at low temperature, the viscosity at 991 °C (2101 °F) can be used:

$$\text{vgc} = [d - 0.24 - 0.022 \log(v - 35.5)]/0.755$$

In both cases, the lower the index number is indicative of a more paraffinic sample. For example, a paraffinic sample may have a vgc on the order of 0.840 while the corresponding naphthenic sample may have an index on the order of 0.876.

The obvious disadvantage is the closeness of the indices, almost analogous to comparing crude oil character by specific gravity only where most crude oils fall into the range $d = 0.800-1.000$. The API gravity expanded this scale from 5 to 60 thereby adding more meaning to the use of specific gravity data.

In a similar manner, the *correlation index* which is based on a plot of the specific gravity (d) versus the reciprocal of the boiling point (K) in °K (°K = degrees Kelvin = °C + 273) for pure hydrocarbon derivatives adds another dimension to the numbers:

$$\text{Correlation Index (CI)} = 473.7d - 456.8 + 48640/K$$

In the case of a crude oil fraction, K is the average boiling point determined by the standard distillation method.

The line described by the constants of the individual members of the normal paraffin series is given a value of CI = 0 and a parallel line passing through the point for benzene is given a value of CI = 100 (Chapter 10). Values between 0 and 15 indicate a predominance of paraffin hydrocarbon derivatives in the sample and values from 15 to 20 indicate predominance either of naphthenes or of mixtures of paraffins/naphthenes/aromatics; an Index value above 50 indicates a predominance of aromatics in the fraction.

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CHAPTER

18

Environmental aspects

1. Introduction

Natural gas and crude oil production from hydrocarbon rich tight formation (such as shale, sandstone, and carbonate formations) (Chapter 1) is one of the most rapidly expanding trends in domestic natural gas and crude natural gas and crude oil exploration and production. Moreover, this type of resource development is spreading to other countries and regions of the world (Chapter 2). In some areas, this has included bringing drilling and production to regions and countries that have seen little or no activity of these technologies in the past. New natural gas and crude oil developments bring change to the environmental and socio-economic landscape, particularly in those areas where natural gas and crude oil development is a relatively new activity, especially in terms of the development of these unconventional natural gas and crude oil resources (Table 18.1) (Reig et al., 2014).

With these changes have come questions related to the nature of tight gas and tight oil development, the potential environmental impacts, and the ability of the current regulatory structure to deal with this development. Regulators, policy makers, and the public need an objective source of information on which to base answers to these questions and decisions related to how to manage the challenges that may accompany development. In fact, environmental impacts associated with shale gas development occur at the global and local levels. These include impacts to climate change (Shine, 2009; Schrag, 2012), local air quality, water availability, water quality, seismicity, and local communities (Clark et al., 2012).

The widespread adoption of hydraulic fracturing (fracking) and horizontal drilling in the United States to extract oil and natural gas from previously inaccessible shale formations has caused some concerns related to the effect on the environment. The environmental, health, and quality of life impacts of shale development have stoked controversy across the country. In contrast, the expectation of long-term domestic natural gas abundance has been widely reported and little questioned, despite the myriad economic and policy consequences. There is no question that the development of shale gas has created a surge in production. However, a look at the fundamentals of shale plays reveals that they come with serious drawbacks, both in terms of environmental impact and the sustainability of long term production.

Most crude oil or gas-bearing tight formation in the United States tend to be at least 4600 feet below the surface, whereas aquifers are generally no more than 1550 feet below the surface. Given the thickness of rock separating target tight formation formations from overlying aquifers,

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TABLE 18.1 Environmental impacts from deep tight formation development.

Site preparation
Land clearing and infrastructure construction
Storm water flows
Habitat fragmentation and disruption
Effect on surface water quality
Drilling
Venting of methane – air quality
Casing and cementing – casing accidents and cementing accidents
Drilling fluids/cuttings
Fracturing fluids
Flowback and produced water
Effect on groundwater quality
Fracturing and completion
Freshwater withdrawals
Surface water and groundwater availability
Storage of fracturing fluids
Effect on surface water quality
Venting of methane and air quality
Storage/disposal of fracturing fluids and flowback water
Fracturing fluids, flowback water, and produced water
On-site pit/pond storage
Effect on surface water quality and groundwater quality
Water treatment by municipal wastewater treatment plants
Water treatment by industrial wastewater treatment plants

and the extremely low permeability of tight formation formations themselves, and also assuming the implementation of good oilfield practices (such as casing and cementing), it is considered by the industry that the risk of contamination of overlying aquifers as a result of hydraulic fracturing operations is remote. Instances where contamination of aquifers has been alleged are generally believed to have involved poor drilling practices, in particular poor casing and cementing of a well or poor construction of surface storage facilities.

The rapid expansion in shale gas production has given rise to concerns related to the impact of operations in areas such as water, road, air quality, seismic and greenhouse gas emissions (GHG) (Howarth et al., 2011a, 2011b; Stephenson et al., 2011; O'Sullivan and Paltsev, 2012).

The process of hydraulic fracturing (fracking) in a shale gas well requires significant volumes of water and causes additional greenhouse gas emissions compared to conventional gas wells (Spellman, 2013). There is already significant resistance to shale gas development due to these water and emission concerns in many parts of the United States and Western Europe, with some countries imposing a nationwide moratorium on shale gas production through fracking. The regulation of shale gas is an evolving issue as the industry has developed so rapidly that it has often outpaced the availability of information for regulators to develop specific guidance (Clark et al., 2012).

Development of these resources (and the resources related to kerogen-containing formations) has generated concern and debate over potential environmental risks and the risks to human health risks. Concerns include potential impacts to groundwater and surface water resources from well development and stimulation operations and wastewater management, as well as air quality impacts from emissions of air pollutants, including methane. These concerns have drawn scrutiny of regulatory regimes governing this industry and have led to calls for greater federal oversight of the development. A growing concern is that the deep-well disposal of oil and gas production wastewater may be responsible for increasing rates of seismic activity in certain areas. Although primary regulatory authority over oil and natural gas exploration and production on state and private lands generally rests with the states, provisions of several federal environmental laws currently apply to certain activities associated with oil and natural gas exploration and production. Moreover, that United States Environmental Protection Agency has been reviewing other statutory authorities and pursuing new regulatory initiatives, and the United States Bureau of Land Management is continually planning further revisions to the oil and gas rules to address venting and flaring of natural gas on federal and Native American lands.

A broader concern among some is that the low price of natural gas is having negative consequences for the development and growth in energy efficiency, renewable energy sources, and nuclear power, potentially resulting in another generation of greenhouse-gas-producing energy sources. The importance of tight oil and shale gas resources to the energy policy of the United States and regional economies is likely to keep issues surrounding their development on the future agenda of future sessions of the United States Congress.

Thus, there are environmental concerns with the specialized techniques used to exploit shale gas (Arthur et al., 2008, 2009; GAO, 2012). There is potential for a heavy draw on freshwater resources because of the large quantities required for hydraulic fracturing fluid. The land-use footprint of shale gas development is not expected to be much more than the footprint of conventional operations, despite higher well densities, because advances in horizontal drilling technology allow for up to ten or more wells to be drilled and produced from the same well site. Finally, there is potential for a high carbon footprint through emissions of carbon dioxide (CO_2), a natural impurity in some shale gas. In fact, environmental concerns related to shale gas exploitation have received significant attention (US GAO, 2012). The issues raised are fresh water usage in competition with other uses such as farming, improper disposal of produced water and contamination of fresh water aquifers.

Although shale gas wells use up to 6 million gallons (6×10^6 gallons) of water per well, the water volume used per unit of energy produced is small compared to a number of alternatives. Although this usage is relatively low compared to alternatives, any usage of water may appear to be in competition with other uses, especially in draught years. To address this situation, salt water might be used in place of fresh water. Recent advances in fracturing permit this with small modifications to the needed chemicals.

Improper discharge of produced water is an issue. It is best addressed by simply recycling. However, since the produced water has salinity from 6000 to 300,000 ppm, this can be costly. The ability to tolerate salinity mentioned above can be a huge cost saving. Technology to clean up the other constituents exists and can be expected to be affordable. There are two potential ways in which shale gas operations could contaminate aquifers. One is through leakage of the chemicals used in fracturing. These then would be liquid contaminants. The second is the infiltration of aquifers by produced methane. It is a gaseous contaminant, albeit it gets dissolved in the water. Also, if methane is present, a portion may be released as a gas. The distinction between potential liquid and gaseous contamination is important because the hazards are different, as are the remedies and safeguards. Also, because well water could not naturally have the liquid contaminants, their presence is evidence of a man made source. Therefore, simple testing of wells proximal to drilling operations is sufficient, with the only possible complication being the influence from some source other than drilling, such as agricultural runoff, for example. This is easily resolved because of the specificity in the chemicals used for fracturing.

Methane leakage can happen because of possible combination of not locating cement in the right places and of a poor cement job. Many wells will have intervals above the producing zone that are charged with gas, usually small quantities in coal bodies and the like. If these are not sealed off with cement some gas will intrude into the well bore. This will still be contained unless the cement up near the fresh water aquifers has poor integrity. In that case the gas will leak. Wells constructed to specification will not leak.

Extracting natural gas or crude oil from tight formations poses a number of risks to the environment and requires large quantities of nearby water (Muresan and Ivan, 2015). Much of this water is needed for fracturing the tight formation to allow the gas and/or oil to flow to the surface. Environmental impacts associated with natural gas and crude oil development occur at the global and local levels since resources in tight formations are not always located where water is abundant — for example, China, India, South Africa, and Mexico have large quantities of natural gas and crude oil but limited supplies of freshwater for use in recovery operations (Reig et al., 2014).

In fact, at least one-third of the area where resources in tight formations are located is arid or under significant water stress (water availability issues). These factors pose significant social, environmental, and financial challenges to accessing water and could limit tight formation development. Thus, as countries escalate the exploration of gas and oil resources in tight formations, limited availability of freshwater could become a stumbling block. Extracting resources from tight formations requires large amounts of water for drilling and hydraulic fracturing (Chapter 5). In most cases, the demands for water are met by freshwater sources, making companies developing tight formation significant users and managers of water at local and regional levels often, unfortunately, in competition with ranches, farms, households, and other water-dependent industries.

A typical hydraulic fracturing fluid is more than 98% v/v water and sand. The other 2% consists of additives which may vary depending on the particular well and operator. Typically, additives include many substances that are commonly found in small measure in various household products. During a typical hydraulic fracturing process, the fracking fluid is transmitted down a cased well-bore to the target zones and then forced deep into the targeted natural gas and crude oil formations. In order to minimize the risk of any groundwater contamination, good drilling practice normally requires that one or more strings of steel casing are inserted into the well and cemented into place so as to ensure that the entire wellbore, other than the production zone, is completely isolated from the surrounding formations including aquifers. Thus, the focus of the environmental impact has tended to be on hydraulic fracturing fluids and to some extent, the impact of the resource development on climate change (Shine, 2009; Schrag, 2012), local air quality, water availability, water quality, seismicity, and local communities (Brown, 2007; WHO, 2011; Clark et al., 2012). A number of suspected groundwater contamination due to hydraulic fracturing has been documented but in some cases the direct link between hydraulic fracturing and groundwater contamination is has not been clearly established (Mall, 2011). In addition, there are also pertinent questions related to the reliability the sampling techniques and the analytic technique that have been used to implicate the effects of anthropogenic activities on climate change (Islam and Speight, 2016).

Rapid development of tight formation resources through horizontal drilling and hydraulic fracturing is significantly increasing the contribution of natural gas, natural gas liquids, and crude oil to the global energy supply mix (BP, 2015). Continued growth could transform the global energy market. While profitable production has yet to spread outside the United States and Canada, governments, investors, and companies have begun to explore the commercial potential of tight formation resources throughout the world (Chapter 2). However, it is not sufficient to understand the potential benefits of resources in tight formations relative to other energy sources; it is also necessary to know if the natural gas or crude oil can actually be extracted from the formation. This depends on several factors, including but not limited to: (i) the amount of resource in the reservoir, (ii) the mineralogy of the reservoir, (iii) the pore size distribution in the reservoir rock, (iv) processes that contribute to diagenesis, (v) the texture of the reservoir rock as well as (vi) the reservoir pressure and the reservoir temperature (Bustin et al., 2008).

Generally, the rapid expansion in natural gas and crude oil production from tight formations has given rise to concerns related to the impact of operations in areas such as water, road, air quality, seismic and greenhouse gas emissions (Howarth et al., 2011a, 2011b; Stephenson et al., 2011; O’Sullivan and Paltsev, 2012). However, the differences between the tight formations and the differences even within a tight formation add a degree of complicity to the development of such resources, especially when environmental management is taken into consideration. For example, the process of horizontal drilling and hydraulic fracturing (Chapter 5) to recover natural gas and crude oil tight reservoir requires significant volumes of water (which differs according to the reservoir character) and can cause carrying amounts of greenhouse gas emissions compared to conventional gas wells (Spellman, 2013). There is already significant resistance to natural gas and crude oil development due to the water use and water disposal (Chapter 5) and emission concerns in many parts of the United States and Western Europe, with some countries imposing a nationwide moratorium on natural gas and crude oil production because of the environmental disturbances caused by the hydraulic fracturing technology. In fact, the regulation of natural gas and crude oil extraction from tight formations is an evolving issue because the rate of the rapid development of the industry that has often outpaced the rate of availability of information that regulators need to develop specific guidance and policies (Clark et al., 2012).

Nevertheless, there are justifiable environmental concerns because of the specialized techniques that are used to exploit natural gas and crude oil resources in tight formations (Arthur et al., 2008, 2009; GAO, 2012). There is potential for a heavy draw on freshwater resources because of the large quantities required for hydraulic fracturing fluids (Chapter 5). However, the land-use footprint of this type of natural gas and crude oil development is not expected to be much more than the environmental footprint of conventional natural gas and crude oil recovery operations, despite higher well densities, because advances in horizontal drilling technology allow for up to ten or more wells to be drilled and produced from the same well site. Finally, there is, however, the potential for a high carbon footprint because of the emissions of carbon dioxide (CO_2), which is a natural impurity in some natural gas and crude oil reservoirs.

In fact, estimates of resource productivity and their implications for the environmental footprint of unconventional natural gas and crude oil development are, of necessity, ongoing. However, a more comprehensive approach is needed to understand how much energy will ultimately be extracted vis-à-vis the environmental costs. In this respect, important issues include: (i) the reservoir characteristics and fluid-transport mechanisms that govern resource storage and production in tight formation and other low-permeability formations, (ii) the types of estimation techniques can provide the most accurate estimated ultimate recovery for the unconventional natural gas and crude oil resources, (iii) the technical pathways toward improving recovery strategies and well completion to enhance short- and long-term well productivity, (iv) the effectiveness of stimulation methods, such as hydraulic fracturing, at enhancing well productivity, and (v) maximizing ultimate recovery of the resource.

Furthermore, public concerns related to the environmental impacts of hydraulic fracturing have accompanied the rapid growth in energy production. These concerns include (i) the potential for groundwater and surface-water pollution, (ii) the potential for a decrease in the air quality, (iii) the potential for fugitive greenhouse gas emissions, (iv) the disturbance to the ecosystem, and (v) the potential for induced seismic events. Many of these issues are not unique to unconventional natural gas and crude oil production. However, the scale of hydraulic fracturing operations is much larger than for conventional exploration. Moreover, particularly worthy of note and giving rise to concern by local communities, is the fact that extensive industrial development and high-density drilling are occurring in areas where there has been little or no previous natural gas and crude oil production activities.

In order to mitigate such concerns, it is vital that resource development companies assist local communities to understand these issues so that the residents can obtain a clearer picture of the productive capacity of unconventional resources and how intensive its development will be over the coming decades, particularly as unconventional natural gas and crude oil are promoted as a bridge the gap between current energy generation and use and the real, potential for lower-carbon based energy future.

In terms of the development of unconventional natural gas and crude oil, if the correct approaches are not taken with regulatory agencies and with local communities, regulatory constraints related to environmental concerns could hinder (perhaps even terminate) developments, but if handled correctly the potential economic and energy security benefits from the development of unconventional natural gas and crude oil could result in significantly higher growth of the production natural gas and crude oil.

In summary, one tight reservoir is not necessarily the same as the next tight reservoir and there is even variability within a specific reservoir. Furthermore, the economic viability of the resources, that is, the cost and feasibility of extraction, as well as on the onsite environmental and social considerations must also be given consideration. For natural gas and crude oil to be extracted successfully from tight reservoirs, governments and the developing companies must cooperate to overcome a series of technical, environmental, legal, and social challenges. Without good management, these challenges will, without doubt, impede development.

Thus, it is the purpose of this chapter to introduce the reader to the various aspects of natural gas and crude oil production that can cause pollution and to review that various regulations that apply to natural gas and crude oil production.

1.1 Environmental regulations

The condition of the environment is important to floral and faunal life on Earth and any disadvantageous disturbance of the environment can have serious consequences for continuation of this life. The regulation of natural gas and crude oil production has traditionally occurred primarily at the state level with most states that produce natural gas and crude oil issuing more rigorous standards that take primacy over federal regulations, as well as additional regulations that control areas not covered at the federal level, such as hydraulic fracturing. Within states, regulation is carried out by a range of agencies.

Regulation of oil and gas production has traditionally occurred primarily at the state level, which is currently also the case for shale gas, with most shale gas-producing states issuing more rigorous standards that take primacy over federal regulations, as well as additional regulations that control areas not covered at the federal level, such as hydraulic fracturing. Within states, regulation is carried out by a range of agencies.

Energy or natural resource-focused departments generally set requirements for site permits, drilling, completion and extraction, while environmental or water departments regulate water, emissions and waste management. The specific regulations vary considerably among states, such as different depths for well casing, levels of disclosure on drilling and fracturing fluids, or requirements for water storage. The majority of states in shale gas-producing regions now have varying hydraulic fracturing regulations on their books, specifically for disclosure of fracking fluids, proper casing of wells to prevent aquifer contamination and management of wastewater from flow-back and produced water. Disposal of wastewater by underground injection has emerged as a point of concern for state regulators due to large inter-state flows of wastewater to states with suitable geology for and reports of seismic activity near some well sites.

However, the specific regulations vary considerably among states, such as different depths for well casing, levels of disclosure on drilling and fracturing fluids, or requirements for water storage. Currently, the majority of states that produce natural gas and crude oil have varying hydraulic fracturing regulations, specifically regulations related to (i) the disclosure of the components of hydraulic fracturing fluids, (ii) the proper casing of wells to prevent aquifer contamination, and (iii) management of wastewater from flow-back and produced water. The disposal of wastewater by underground injection has emerged as a concern for state regulators due to large interstate flows of wastewater to states with suitable geology for the water disposal as well as the potential for seismic activity near some well sites.

A series of federal laws govern most environmental aspects of shale gas development. For example, the *Clean Water Act* regulates surface discharges of water associated with shale gas drilling and production, as well as storm water runoff from production sites. The *Safe Drinking Water Act* directs the underground injection of fluids from shale gas activities. The *Clean Air Act* limits air emissions from engines, gas processing equipment, and other sources associated with drilling and production. The *National Environmental Policy Act* (NEPA) requires that exploration and production on federal lands be thoroughly analyzed for environmental impacts.

However, federal agencies do not have the resources to administer all of these environmental programs for all the oil and gas sites throughout the country. In addition, federal regulations may not always be the most effective way of assuring the desired level of environmental protection. Therefore, most of these federal laws have provisions for granting primacy to the states, which have usually developed their own sets of regulations. By statute, states may adopt these standards of their own, but they must be at least as protective as the federal principles they replace – they may actually be more protective in order to address local conditions.

Once these programs are approved by the relevant federal agency (usually the United States Environmental Protection Agency), the state then has primacy jurisdiction. State regulation of the environmental practices related to shale gas development can more easily address the regional and state-specific character of the activities, compared to one-size-fits-all management at the federal level. Some of these factors include geology, hydrology, climate, topography, industry characteristics, development history, state legal structures, population density, and local economics.

Thus, the regulation of shale gas drilling and production is a cradle-to-grave approach, and states have many tools at their disposal to assure that shale gas operations do not adversely impact the environment. They have broad powers to regulate, permit, and enforce all activities – from drilling and fracturing of the well, to production operations, to managing and disposing of wastes, to abandoning and plugging the production well(s).

Different states take different approaches to this regulation and enforcement, but their laws generally give the state oil and gas director or the agency the discretion to require whatever is necessary to protect the human health and the environment. In addition, most have a general prohibition against pollution from oil and gas drilling and production. A majority of the state requirements are written into rules or regulations; however some are added to permits on a case-by-case basis as a result of environmental review, on-the-ground inspections, public comments, or commission hearings.

Finally, the organization of regulatory agencies within the different oil and gas producing states varies considerably. Some states have several agencies that may oversee some facet of oil and gas operations, particularly environmental requirements. In different states, these agencies may be located in sundry departments or divisions within their respective governments. These various approaches have developed over time within each state, and each state tries to create a structure that best serves its citizenry and all of the industries that it must oversee. The one constant is that each oil and gas producing state has one agency with primary responsibility for permitting wells and overseeing general operations. While these agencies may work with other agencies in the regulatory process, they serve as a central organizing body and a useful source of information related to the various agencies that may have jurisdiction over oil and gas activities (Arthur et al., 2008).

In terms of the development of unconventional natural gas and crude oil resources, a major environmental concern is the potential contamination of water courses. Apart from water, which makes up 99.5% v/v of the hydraulic fracturing fluid, the fluid also contains chemical additives to improve the process performance. The additives are varied and can include acid, friction reducer, surfactant, gelling agent and scale inhibitor (Table 18.2) (API, 2010). The composition of the fracturing fluid is tailored to differing geologies and reservoir characteristics in order to address particular challenges including scale build-up, bacterial growth, and proppant transport.

TABLE 18.2 Additives used in the hydraulic fracturing process.

		Water and sand: Approximately 98% v/v	
Water	Expand the fracture and delivers sand	Some stays in the formation while the remainder returns with natural formation water as produced water (actual amounts returned vary from well to well)	Landscaping and manufacturing
Sand (proppant)	Allows the fractures to remain open so that the oil and natural gas can escape	Stays in the formation, embedded in the fractures (used to “prop” fractures open)	Drinking water filtration, play sand, concrete and brick mortar
		Other additives: ∼2%	
Acid	Helps dissolve minerals and initiate cracks in the rock	Reacts with the minerals present in the formation to create salts, water and carbon dioxide (neutralized)	Swimming pool chemicals and cleaners
Anti-bacterial agent	Eliminates bacteria in the water that produces corrosive by-products	Reacts with micro-organisms that may be present in the treatment fluid and formation; these micro-organisms break down the product with a small amount returning to the surface in the produced water	Disinfectant; sterilizer for medical and dental equipment
Breaker	Allows a delayed breakdown of the gel	Reacts with the crosslinker and gel in the formation making it easier for the fluid to flow to the borehole; this reaction produces ammonia and sulfate salts, which are returned to the surface in the produced water	Hair colorings, as a disinfectant and in the manufacture of common household plastics

(*Continued*)

TABLE 18.2 Additives used in the hydraulic fracturing process.—cont'd

		Water and sand: **Approximately 98% v/v**	
Clay stabilizer	Prevents formation clays from swelling	Reacts with clays in the formation through a sodium−potassium ion exchange; this reaction results in sodium chlorine (table salt), which is returned to the surface in the produced water	Low-sodium table salt substitutes, medicines, and IV fluids
Corrosion inhibitor	Prevents corrosion of the pipe	Bonds to the metal surfaces, such as pipe, downhole; any remaining product that is not bonded is broken down by micro-organisms and consumed or returned to the surface in the produced water	Pharmaceuticals, acrylic fibers and plastics
Crosslinker	Maintains fluid viscosity as temperature increases	Combines with the “breaker” in the formation to create salts that are returned to the surface in produced water	Laundry detergents, hand soaps and cosmetics
Friction reducer	Minimizes friction	Remains in the formation where temperature and exposure to the breaker allows it to be broken down and consumed by naturally occurring micro-organisms; a small amount returns to the surface with the produced water	Cosmetics including hair, make-up, nail and skin products
Gelling agent	Thickens the water to suspend the sand	Combines with the breaker in the formation making it easier for the fluid to flow to the borehole and return to the surface in the produced water	Cosmetics, baked goods, ice cream, toothpastes, sauces and salad dressings
Iron control	Prevents precipitation of metal in pipe	Reacts with minerals in the formation to create simple salts, carbon dioxide and water, all of which are returned to the surface in the produced water	Food additives; food and beverages; lemon juice
Non-emulsifier	Breaks or separates oil/water mixtures (emulsions)	Generally, returns to the surface with produced water, but in some formations it may enter the gas stream and return to the surface in the produced oil and natural gas	Food and beverage processing, pharmaceuticals, and wastewater treatment
pH adjusting agent	Maintains the effectiveness of other components, such as crosslinkers	Reacts with acidic agents in the treatment fluid to maintain a neutral (non-acidic, non-alkaline) pH; this reaction results in mineral salts, water and carbon dioxide − a portion of each is returned to the surface in the produced water	Laundry detergents, soap, water softeners and dish washer detergents

Unfortunately, in the past many of the chemical compounds used in the hydraulic fracturing process lacked scientifically based maximum contaminant levels, making it more difficult to quantify their risk to the environment (Colborn et al., 2011). Moreover, uncertainty related to the chemical makeup of fracturing fluids persists because of the limitations on required chemical disclosure (Centner, 2013; Centner and O’Connell, 2014; Maule et al., 2013).

The measures required by state and federal regulatory agencies in the exploration and production of natural gas and crude oil from deep tight formations have been very effective, for example, in protecting drinking water aquifers from contamination. In fact, a series of federal laws govern most environmental aspects of natural gas and crude oil development (Table 18.3). However, federal regulation may not always be the most effective way of assuring the desired level of environmental protection. Therefore, most of these federal laws have provisions for granting primacy to the state governments, which have usually developed their own sets of regulations. By statute, the different states may adopt these standards of their own, but they must be at least as protective as the federal principles they replace and, as a result, may be more protective in order to address local conditions.

State regulation of the environmental practices related to natural gas and crude oil development can more easily address the regional and state-specific character of the activities,

TABLE 18.3 Examples of federal laws in the United States to monitor hydraulic fracturing projects.

Act	Purpose
Clean air Act	Limits air emissions from engines, gas processing equipment, and other sources associated with drilling and production.
Clean water Act	Regulation of surface discharges of water associated with natural gas and crude oil drilling and production, as well as storm water runoff from production sites.
Energy policy Act	Exempted hydraulic fracturing companies from some regulations; may disclose chemicals through a report submitted to the regulatory authority but in some instances, chemical information may be exempt from disclosure to the public as trade secrets.
NEPA[a]	Requires that exploration and production on federal lands be thoroughly analyzed for environmental impacts.
NPDES[b]	Requires tracking of any toxic chemicals used in fracturing fluids.
Oil pollution Act	Regulation of ground pollution risks relating to spills of materials or hydrocarbon derivatives into the water table; also regulated under the hazardous materials transport Act.
Safe drinking water Act	Directs the underground injection of fluids from natural gas and crude oil activities; disclosure of chemical content for underground injections; after 2005, see energy policy Act.
TSCA[c]	Suggestion that this act be used to regulate the reporting of hydraulic fracturing fluid information.

Note: The laws are (listed alphabetically and not by any order of importance or preference.

NB: The Fracturing Responsibility and Awareness of Chemicals Act (the FRAC Act) was an attempt to define hydraulic fracturing as a federally regulated activity under the Safe Drinking Water Act. https://www.congress.gov/bill/114th-congress/senate-bill/785/text.

[a] *National Environmental Policy Act.*

[b] *National Pollutant Discharge Elimination System.*

[c] *TSCA: Toxic Substance Control Act.*

compared to a one-size-fits-all management by the federal level. Some of these factors include geology, hydrology, climate, topography, industry characteristics, development history, state legal structures, population density, and local economics and, thus, the regulation of natural gas and crude oil production is a detailed monitoring of each stage of the development through the many controls at the state level. Each state has the necessary powers to regulate, permit, and enforce all activities − from drilling and fracturing of the well, to production operations, to managing and disposing of wastes, to abandoning and plugging the production well(s). These powers are a means of assuring that natural gas and crude oil operations do not have an adverse impact on the environment.

Moreover, because of the regulatory make-up of each state − which can vary from state-to-state − different states take different approaches to the regulation and enforcement of resource development but the laws of each state generally give the state agency responsible for natural gas and crude oil development the discretion to require whatever is necessary to protect the environment, including human health. In addition, most have a general prohibition against pollution from natural gas and crude oil production. A majority of the state requirements are written into rules or regulations but some of the regulations may be added to permits on a case-by-case basis as a result of (i) environmental review, (ii) on-site inspections, (iii) commission hearings, and (iv) public comments.

Finally, the organization of regulatory agencies within the different states where natural gas and crude oil is produced varies considerably. Some states have several agencies that oversee different aspects (with some inevitable overlap powers) of natural gas and crude oil operations, particularly the requirements that protect the environment. In different states, the various approaches have developed over time to create a structure that best serves its citizenry and all of the industries that it must oversee. The one constant is that each in each state where natural gas and crude oil is produced, there is one agency that has the responsibility for issuing permits for gas and oil development projects. The permitting agencies work with other agencies in the regulatory process and often serve as a central organizing body and a useful source of information related to activities related to natural gas and crude production (Arthur et al., 2008).

1.2 General aspects

The productivity of an unconventional well is typically estimated using two factors: (i) the initial production rate after well completion and (ii) the production decline curve. The initial production (IP) rate quantifies the maximum production of natural gas or crude oil from a well, which is usually a calculated averaged of production over the first month. The decline curve describes the rate of decline of natural gas or crude oil production from which an estimate of the number of years that production can be expected from that well in addition to any potential environmental impacts will be. The variables that determine initial production rate and decline curves are complex and include geological factors, such as: (i) the inorganic sedimentary composition of the formation, (ii) the organic composition of the formation, (iii) the burial history, (iv) the natural fracturing patterns, (v) various petrophysical factors, such as formation porosity and formation permeability, and (vi) other factors such as the level of induced fracturing during well completion (Lash and Engelder, 2009; Miller et al., 2011; Clarkson et al., 2012).

A number of federal laws direct natural gas and crude oil development (Table 18.3) (US EPA, 2012; Spellman, 2013). These regulations affect water management and disposal, as well as air quality (Gaudlip et al., 2008; Veil, 2010). In addition, current regulations require within 30 days of completing the last stage of a hydraulic fracturing operation, the responsible development company must disclose the type and amount of the chemicals used in the hydraulic fracturing process (i.e. in the fracturing fluid) for each well as well as submittal of a report which details the handling and disposal of recovered fluids to the relevant regulation authority.

Although hydraulic fracturing is not directly regulated by federal standards, a number of federal laws still direct oil and gas development, including shale gas (US EPA, 2012; Spellman, 2013). These regulations affect water management and disposal, as well as air quality and activities on federal land (Gaudlip et al., 2008; Veil, 2010). The Clean Water Act is focused on surface waters and regulates disposal of wastewater and also includes authorizing the National Pollutant Discharge Elimination System (NPDES) permit program, as well as requiring tracking of any toxic chemicals used in fracturing fluids. The Hazardous Materials Transport Act and the Oil Pollution Act both regulate ground pollution risks relating to spills of materials or hydrocarbon derivatives into the water table.

The disclosure of chemicals used in hydraulic fracturing operations is predominately a state issue. In some instances, chemical information may be exempt from disclosure to the public as trade secrets (Centner, 2013; Centner and O'Connell, 2014; Maule et al., 2013; Shonkoff et al., 2014). However, a company seeking such as an exemption will have to submit an affidavit and, if requested by the regularity authority, the chemical information for evaluation. If the regulatory authority determines that the information is not exempt from disclosure, the authority will notify the company prior to releasing any information related to the chemical content of the fracturing fluid to allow the company to seek a court order preventing release of the information.

1.3 New regulations

Hydraulic fracturing techniques have grown to be carefully engineered processes employed to generate a more extensive network of fractures and thereby produce a larger portion of the in-place natural gas. This innovation has transformed shale gas into a bona fide economic resource play and has led to the drilling of many more shale gas wells and to increased attention on potential environmental effects.

Briefly and historically, hydraulic fracturing of gas wells began in 1949; however, it remained largely unregulated until significant unconventional gas production began at the beginning of the 21st Century with the commercial development of coalbed methane. As production grew, reports of drinking water contamination raised concerns, leading the US Environmental Protection Agency to commission a study into the risks of hydraulic fracturing to drinking water. In 2004, this study found that hydraulic fracturing of coal-bed methane posed minimal threat to underground sources of drinking water, which was a significant finding in support of the industry. In 2005, the federal Energy Policy Act granted hydraulic fracturing a specific exemption from the Safe Drinking Water Act (SDWA), which regulates all underground injection.

Since the Energy Policy Act passed in 2005, natural gas and crude oil production in the United States has grown significantly and this rapid growth − along with continued reports of environmental effects − has led to renewed calls for the federal government to provide increased regulation or guidance. This pressure led to the introduction to Congress in 2009 of the Fracturing Responsibility and Awareness of Chemicals Act (the FRAC Act) to define hydraulic fracturing as a federally regulated activity under the Safe Drinking Water Act (Table 18.3). The proposed requires the energy industry to disclose the chemical additives used in the hydraulic fracturing fluid. The Act went did not receive any action, was reintroduced in 2011, and appears to have been held in limbo since that time.

In the absence of new federal regulations, the various states that produce natural gas and crude oil by hydraulic fracturing have continued to use existing natural gas and crude oil and environmental regulations to manage natural gas and crude oil development, as well as introducing individual state regulations for hydraulic fracturing (Table 18.3). In fact, the current regulations are comprised of an overlapping collection of federal, state, and local regulations and permitting systems and these regulations cover different aspects of the development and production of a natural gas and crude oil with the intention that the regulations combine to manage any potential impact on the surrounding environment, including any effects on water management. However, the hydraulic fracturing process that has not previously been regulated under current laws and, therefore, in terms of water management, emissions management, and site activity, the existing regulations are being (must be) reassessed for suitability for application to the hydraulic fracturing process. In the meantime, many states (including Wyoming, Arkansas and Texas) have already implemented regulations requiring disclosure of the materials used in hydraulic fracturing fluids and the United States Department of the Interior has indicated an interest in requiring similar disclosure for sites on federal lands.

The Bureau of Land Management (BLM) of the United States Department of the Interior has proposed draft rules for natural gas and crude oil production on public lands and these proposals would require disclosure of the chemical components used in hydraulic fracturing fluids. The proposed rule requires that an operations plan should be submit to the relevant authority − prior to initiation of the hydraulic fracturing project − that would allow the Bureau of Land Management to evaluate groundwater protection designs based on (i) a review of the local geology, (ii) a review of any anticipated surface disturbance, and (iii) a review of the proposed management and disposal of project-related fluids. In addition, the Bureau of Land Management would require submittal of the information necessary to confirm wellbore integrity before, during, and at the conclusion of the stimulation operation. Furthermore, before hydraulic fracturing commenced, the company would have to certify that the fluids comply with all applicable Federal, state, and local laws, rules, and regulations. After the conclusion of the hydraulic fracturing stage of the project, a follow-up report would be required in which the actual events that occurred during fracturing activities would be summarized and this report would have to include the specific chemical makeup of the hydraulic fracturing fluid.

On April 17, 2012, the United States Environmental Protection Agency released new performance standards and national emissions standards for hazardous air pollutants in the natural gas and crude oil industries. These rules include the first federal air standards for hydraulically fractured gas wells, along with requirements for other sources of pollution in the natural gas and crude oil industry that currently are not regulated at the federal level. These standards require either flaring or *green completion* on all natural gas wells developed prior to January 1, 2015, with only green completions allowed for wells developed on and after that date.

Briefly, *green completion* requires natural gas companies capture the gas at the wellhead immediately after well completion instead of releasing it into the atmosphere or flaring the gas. Thus, the green completion systems are systems to reduce methane losses during well completion. After a new well completion or workover, the well bore and formation must be cleaned of debris and fracturing fluid. Conventional methods for doing this include producing the well into an open pit or tank to collect sand, cuttings and reservoir fluids for disposal. Typically, the natural gas that is produced is vented or flared and the large volume of natural gas that is lost may not only affect regional air quality. When using green completion systems, gas and hydrocarbon liquids are physically separated from other fluids (a form of wellhead gas processing) (Mokhatab et al., 2006; Speight, 2014a, 2019) — there is no venting or flaring of the gas — and delivered directly into equipment that holds or transports the hydrocarbon derivatives for productive use. Furthermore, by using portable equipment to process natural gas and natural gas condensate, the recovered gas can be directed to a pipeline as sales gas. The use of truck-mounted or trailer-mounted portable systems can typically recover more than half of the total gas produced.

Since the Energy Policy Act passed in 2005, shale gas production in the United States has grown significantly, from less than one trillion cubic feet (1.0×10^{12} ft^3) in 2005 to more than three trillion cubic feet (3.0×10^{12} ft^3) in 2009. Such rapid growth, along with continued reports of environmental effects, has led to renewed calls for the federal government to provide increased regulation or guidance. This pressure led to the introduction to Congress in 2009 of the Fracturing Responsibility and Awareness of Chemicals Act (the FRAC Act) to define hydraulic fracturing as a federally regulated activity under the Safe Drinking water Act. The proposed requires the energy industry to disclose the chemical additives used in the hydraulic fracturing fluid. The Act went did not receive any action, was reintroduced in 2011, and appears to have been a non-issue since that time.

In the absence of new federal regulation, states have continued to use existing oil and gas and environmental regulations to manage shale gas development, as well as introducing individual state regulations for hydraulic fracturing. In fact, the current regulations is a comprised of an overlapping collection of federal, state and local regulations and permitting systems, implemented by oil and gas, natural resources and environmental agencies.

These regulations cover different aspects of the development and production of a shale gas well, with the intention that they combine to manage any potential impact on the surrounding environment and water supplies. These combinations of regulations have long served to regulate oil and gas development in numerous states. However, the new process of hydraulic fracturing is something that has not previously been managed by these regulations. Therefore, the related intensity in terms of water, emissions and site activity mean existing regulations are being reassessed for their suitability for this new production method.

In the meantime, many states (including Wyoming, Arkansas and Texas) have already implemented regulations requiring disclosure of the materials used in fracking fluids and the United States Department of the Interior has indicated an interest in requiring similar disclosure for sites on federal lands. The Bureau of Land Management (BLM) of the

Department of the Interior proposed draft rules for oil and gas production on public lands require disclosure of the chemical components used in hydraulic fracturing fluids, among other groundwater protections. The proposed rule requires the operator to submit an operation plan prior to hydraulic fracturing that would allow the Bureau of Land Management to evaluate groundwater protection designs based on the local geology, review anticipated surface disturbance, and approve proposed management and disposal of recovered fluids. In addition, operators would provide to the Bureau of Land Management the information necessary to confirm wellbore integrity before, during, and at the conclusion of the stimulation operation. Before hydraulic fracturing begins, operators would have to self-certify that the fluids comply with all applicable Federal, state, and local laws, rules, and regulations. After the conclusion of hydraulic fracturing, a follow-up report would summarize what actually occurred during fracturing activities, including the specific chemical makeup of the hydraulic fracturing fluid.

In addition to the United States Environmetnal Protection Agency which has regulatory authority under the *Safe Drinking Water Act*, the Agency is exploring the possibility of developing rules under the *Toxic Substances Control Act* (TSCA) to regulate the reporting of hydraulic fracturing fluid information. The EPA also has authority under the *Clean Air Act* to regulate hazardous air emissions from hydraulic fracturing operations.

On April 17, 2012, EPA released new source performance standards and national emissions standards for hazardous air pollutants in the oil and natural gas sector. The final rules include the first Federal air standards for hydraulically fractured gas wells, along with requirements for other sources of pollution in the oil and gas industry that currently are not regulated at the Federal level. These standards require either flaring or green completions on all feasible natural gas wells developed prior to January 1, 2015, with only green completions allowed for wells developed on and after that date. These rules are expected to reduce emissions of volatile organic compounds from applicable hydraulically fractured wells by approximately 95%, while reducing the emissions of volatile organic compounds, hazardous air pollutants, and methane by approximately 10%.

2. Environmental impact − gas and oil from tight formations

The emergence of natural gas and crude oil from tight formations has quickly changed the landscape of opportunities for energy provision and security in different regions of the world. Difficulties in assessing the actual quantity of existing global shale hydrocarbon reserves and some nations − such as the United States − have already started the exploitation of this comparatively cheap energy resource, providing new and favorable conditions for domestic energy supplies. Extraction of the natural gas and crude oil is often accomplished through hydraulic fracturing (fracking) and evidence of the impacts is emerging in places where intense, unregulated fracking takes place. Many of these impacts make themselves felt in water resources.

Fracking is a water-intensive activity and, as the reserves are often found in dry areas, extraction poses additional challenges in what are often already water-stressed environments. The vast water quantities needed over the life span of a shale gas well, where water is used to fracture rock under high pressure, pile further stress on local fresh water sources which are already needed for many different purposes. At times when water supplies are running short in a specific area it has to be transported to the fracking site from afar.

Water quality is also under threat from hydraulic fracturing as well as the quantity available. Many chemicals used in the fracturing fluid (the composition of which is often protected for commercial confidentiality reasons) have increasingly been found to be harmful both to the environment and to human health, yet poor regulations and legislation governing fracking often allow accidents which contaminate surrounding water sources. Moreover, there is a need for greater responsibility, through developing codes of conduct and regulatory systems governing fracking so as to protect water resources and the environment. It should be adopted by all nations currently exploiting or liable to exploit shale resources as part of their energy supply.

Thus, it is important to recognize the ever-present environmental risks of natural gas and crude oil recovery from tight formations and the damage that can be caused (Muresan and Ivan, 2015). Particular attention should be given to those areas of the region or state which have not been accustomed to natural gas and crude oil development, and where all of the necessary regulatory and physical infrastructure may not yet be in place (Arthur et al., 2008; Hoffman et al., 2014).

The fracturing process (Chapter 5) entails pumping the fracturing fluid, primarily water with sand proppant and chemical additives, at sufficiently high pressure to overcome the compressive stresses within the tight target formation for the duration of the fracturing procedure. In the process, formation pressure is increased to exceed the critical fracture pressure which creates narrow fractures in the formation. A proppant (typically sand) is then pumped into these fractures to maintain a permeable pathway for fluid flow after the fracture fluid is withdrawn and the operation is completed. While there are several environment-related issues that must receive attention, the major focus has been on the fracturing process, which poses risk to the shallow groundwater zones that may exist above or near to the gas-bearing formation or the oil-bearing formation.

The primary risks are (i) contamination of groundwater aquifers with drilling fluids or natural gas while drilling and setting casing through the shallow zones, (ii) on-site surface spills of drilling fluids, fracture fluids and wastewater from fracture flowbacks, (iii) contamination as a result of inappropriate off-site wastewater disposal, (iv) excessive water withdrawals for use in high-volume fracturing, and (v) excessive road traffic and impact on air quality.

As described previously (Chapter 5), multiple layers of cement and casing are put in place to protect the freshwater zones as the fracture fluid is pumped from the surface down into the tight formation. This protection is tested at high pressures before the fracturing fluids are pumped downhole. Once the fracturing process is underway, the large vertical separation between the tight formation sections being fractured and the shallow zones prevents the growth of fractures from the tight formation into shallow groundwater zones. It should be noted here that only shallow zones contain potable water because the salinity of the groundwater increase with depth to the point where the water is too saline to be of any use.

After the hydraulic fracturing treatment, the water pressure in the well is reduced to allow the fracturing fluid to flow back out of the well followed by the natural gas and crude oil. As the fluid flows back to the surface, a process commonly referred to as flowback, the sand and other proppants pumped into the formation are left behind to prop open the new and enlarged cracks. As flowback continues, the composition of the fluid carries higher and higher proportions of hydrocarbon derivatives. Within the first few weeks of flowback, some or most of the fracturing fluid returns to the surface as wastewater. In North America, estimates of the volume of flowback vary between 10% and 75% v/v of the fracturing fluid originally injected. Because of its chemical content, this wastewater is recycled and treated for reuse, placed into disposal wells, or treated and discharged into surface waters. If not managed properly, flowback water and other wastewater from hydraulic fracturing operations can cause significant degradation to surface water and groundwater that could pose serious risks to the ecosystems and communities that depend on them.

Moreover, anywhere from 5% to 20% of the original volume of the fluid will return to the surface within the first 10 days as flowback water. An additional volume of water, equivalent to anywhere from 10% to almost 300% of the injected volume, will return to the surface as produced water over the life of the well. It should be noted that there is no clear distinction between so-called flowback water and produced water, with the terms typically being defined by operators based upon the timing, flow rate, or sometimes composition of the water produced.

The rate at which water returns to the surface is highly dependent upon the geology of the formation. In the Marcellus play, operators recycle 95% of the flowback, whereas in the Barnett and Fayetteville plays, operators typically recycle 20% of the flowback. Water management and reuse are local issues and often depend upon the quality and quantity of water and the availability and affordability of management options (Veil, 2010). Over a 30-year life cycle, assuming a typical well is hydraulically fractured three times during that time period, construction and production of natural gas and crude oil typically consumes between 7,090,000 and 16, 810, 000 gallons of water per well.

Thus, the primary risks to the environment are (i) air pollution, (ii) water pollution, and (iii) surface effects.

2.1 Air pollution

Any oil and gas drilling operation impacts air quality. Dust and engine exhaust from truck traffic and emissions from diesel-powered pumps are health hazards. These emissions include primarily ozone precursors such as nitrogen oxides (like NOx), non-methane volatile organic compounds (VOC), and particulate matter. In some cases extremely high ozone levels have been reported, comparable to major cities in their worst conditions (Hoffman et al., 2014).

Air quality is also influenced by methane emissions during the well completion process when wells are flowed back or tested. This can include emissions from flares used to burn off excess natural gas. Another source of air pollution is non-combustion particulates, both from gravel roads constructed for drill pad access as well as from silica dust from proppant handling during hydraulic fracturing. The silica sand can lodge in lungs and cause silicosis. Equipment used during the gas and liquids production process can also create harmful emissions, including inadvertent methane releases from valves, compressor blowdown, and volatile organic compounds such as benzene, toluene, ethylbenzene and xylene isomers (collectively known as BTEX) that escape from condensate or oil tanks (Hoffman et al., 2014).

Thus, during the process, gas escape or escape of volatile hydrocarbon derivatives can have an impact on air quality while contamination of groundwater aquifers with drilling fluids or natural gas while drilling and setting casing through the shallow zones can also occur. There is also the potential for on-site surface spills of drilling fluids, fracture fluids and wastewater from fracture flowback. Shale gas production activities can produce significant amounts of air pollution that could impact local air quality in areas of concentrated development. In addition to greenhouse gas emissions, fugitive emissions of natural gas can release volatile organic compounds (VOCs) and hazardous air pollutants (HAPs), such as benzene. Nitrogen oxides (NOx) are another pollutant of concern, as drilling, hydraulic fracturing, and compression equipment—typically powered by large internal combustion engines—produce these emissions.

Several state emission inventories have shown that oil and natural gas operations are significant sources of local air pollution. However, uncertainty related to the impacts of these emissions exists, as air quality is highly dependent on local conditions. For example, in some areas emissions of volatile organic compounds will not be the primary driver of ozone formation; therefore, detailed modeling is required to understand the impact of emissions on local air quality. In addition, while elevated levels of benzene emissions have been found near production sites, concentrations have been below health-based screening levels, and with little data on how the emissions of hazardous air pollutants impact human health, further examination is needed.

Greenhouse gas emissions and other air emissions from shale well sites are also a key environmental concern. Greenhouse gas emissions are generated in shale gas operations from exploration through processing to transmission and distribution. The United States Environmental Protection Agency has finalized regulations for reporting of greenhouse gas emissions from many of these emissions sources under the Mandatory Reporting of Greenhouse Gases Rule. Additional air emissions regulations on a state and federal level impact many of these operations as well.

Most natural gas production requires processing to remove traces of other hydrocarbon derivatives and impurities from the natural gas stream. The recovery of natural gas liquids such as propane, butane, pentanes and higher molecular weight hydrocarbon derivatives other condensate is a value-adding process throughout much of the gas processing industry. Other trace products such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2) are referred to as acid gas and must be removed from the gas stream to prevent corrosion of pipelines and equipment for safety reasons.

Air pollutant emission sources from the development of tight formations can be grouped into two main (i) emissions from drilling, processing, well completions, servicing, and other gas-producing activities, and (ii) emissions from transportation of water, sand, chemicals, and equipment to and from the well pad. Thus, natural gas and crude oil production activities from tight formations can produce significant amounts of air pollution that can have an impact on air quality in areas surrounding the reservoir development program. In addition to greenhouse gas emissions, fugitive emissions of natural gas can release volatile organic compounds (VOCs) and hazardous air pollutants (HAPs), such as benzene into the air. Nitrogen oxides (NOx) are also pollutants of concern since drilling, hydraulic fracturing, and compression equipment — typically powered by large internal combustion engines — produce these emissions.

However, uncertainty related to the impacts of these emissions may exist, since air quality is highly dependent on local conditions. For example, in some areas emissions of volatile organic compounds will not be the primary source of organic emissions and, in such cases, there is the necessity to understand the impact of these emissions on local air quality. In addition, while elevated levels of benzene emissions have been found near production sites, concentrations are variable — some are below health-based screening levels — and with little data on how the emissions of hazardous air pollutants behave in such circumstances, further examination is needed.

Greenhouse gas emissions and other air emissions from tight formation well sites are also a key environmental concern. These emissions are generated though the whole gamut of natural gas and crude oil operations from exploration through recovery, wellhead processing, transportation, and distribution. The United States Environmental Protection Agency has finalized greenhouse gas emissions reporting regulations from many of these emissions sources under the Mandatory Reporting of Greenhouse Gases Rule (US EPA, 2015). Additional air emissions regulations on a state and federal level impact many of these operations as well.

Gaseous emissions such as hydrogen sulfide (H_2S), ammonia (NH_3), carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen oxides (NO_x), and trace metals are sources for air pollution. Such emissions are at least conceivable in oil tight formation processing operations and the lifetime of these species in the atmosphere is relatively short and if they were distributed evenly their harmful effects would be minimal. Unfortunately, these man-made effluents are usually concentrated in localized areas and their dispersion is limited by both meteorological and topographical factors. Furthermore, synergistic effects mean that the pollutants interact with each other: in the presence of sunlight, carbon monoxide, nitrogen oxide(s), and unburned hydrocarbon derivatives lead to photochemical smog, while when sulfur dioxide concentrations become appreciable, sulfur oxide-based smog is formed.

Natural gas has been referred to as a low-carbon fuel, as its combustion produces significantly less carbon dioxide emissions than coal and crude oil-based fuels. However, to understand the implications for climate change, one must look at not only the greenhouse gas emissions from combustion in a vehicle or power plant but also those from production activities. For natural gas, the primary concern is leakage and venting throughout the supply chain, as methane (CH_4), a potent greenhouse gas, is its primary constituent.

The leakage of methane, the main component of natural gas, into the atmosphere also raises environmental concerns. The Energy Information Administration says that methane emissions from all sources account for approximately 1% of total US greenhouse gas emissions, but approximately 9% of the "greenhouse gas emissions based on global warming potential. Methane can leak at any stage of the entire process leading to consumption.

Normally, field production, gathering and cleaning, separation of water or oil from associated gas, and the extraction of natural gas liquids reduce gross natural gas production by approximately 6%–10%. In addition, transmission and distribution consume another 3% to 8%, further reducing the gross natural gas volume. As a result, only approximately 85%–90% of the gross production in the United States reaches end users. However, whether the natural gas flows from a vertical well or from a horizontal well, the process leading to consumption does not vary.

A further examination of the carbon footprint on a *per-well* basis may generate an apparent contradictory result. The carbon footprint of a horizontal well far exceeds that of a typical vertical well since the drilling process, the completion process, and the production stimulation process (hydraulic fracturing) require more carbon-based fuels, more drilling mud, and more water. Further, running the required equipment and pumps produces more emissions.

It is worth remembering that even the non-toxic, but non-life supporting and suffocating, carbon dioxide may have an important effect on the environment. The surface of the earth emits infrared radiation with a peak of energy distribution in the region where carbon dioxide is a strong absorber. This results in the situation whereby this infrared radiation is trapped by the atmosphere and the temperature of the surface of the Earth is raised. As a result of the combustion of fossil fuels, the concentration of carbon dioxide in the atmosphere is increasing from its present level. Although many factors are involved, it does seem that an increase in the carbon dioxide concentration in the atmosphere would result in a temperature increase at the surface of the earth which could cause an appreciable reduction in the polar ice-caps and this in turn would result in further heating.

Acid gases (SOx and NO_x) emitted into the atmosphere during tight formation processing provide the essential components in the formation of acid rain. Sulfur is present in oil tight formation as both an organic and inorganic compounds. On processing, most of the sulfur is converted to sulfur dioxide with a small proportion remaining in the ash as sulfite:

$$S + O_2 \rightarrow SO_2$$

In the presence of excess air, some sulfur trioxide is also formed:

$$2SO_2 + O_2 \rightarrow 2SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

Only a small amount of sulfur trioxide can have an adverse effect as it causes the condensation of sulfuric acid and causes severe corrosion. Also, nitrogen inherent in the kerogen can be converted to nitrogen oxides during processing which also produce acidic products thereby contributing to the acid rain:

$$2\,N + O_2 \rightarrow 2NO$$
$$NO + H_2O \rightarrow HNO_3$$

Nitrous acid

$$2NO + O_2 \rightarrow 2NO_2$$
$$NO_2 + H_2O \rightarrow HNO_3$$

Nitric acid.

Most stack gas scrubbing processes are designed for sulfur dioxide removal; nitrogen oxides are controlled as far as possible by modification of combustion design and flame temperature regulation (Mokhatab et al., 2006; Speight, 2014a, 2019). However, processes for the removal of sulfur dioxide usually do remove some nitrogen oxides; particulate matter can be removed efficiently by commercially well-established electrostatic precipitators.

Most natural gas cleaning processes require removal of the traces of other hydrocarbon derivatives and impurities from the natural gas stream (Chapter 8) (Mokhatab et al., 2006; Speight, 2014a, 2019). The recovery of natural gas liquids such as propane, butane, pentanes and higher molecular weight hydrocarbon derivatives) other condensate is a value-adding process throughout much of the gas processing industry (Mokhatab et al., 2006; Speight, 2007, 2014). Other trace products such as hydrogen sulfide ($_{H2S}$) and carbon dioxide (CO_2) (the *acid gases*) must be removed from the gas stream to prevent corrosion of pipelines and equipment for safety reasons (Speight, 2014c).

Another local air pollutant of growing concern is crystalline silica dust, which can be generated from the sand proppant. Silica dust can be generated in the mining and transporting of sand to the well site and in the process of moving and mixing sand into the hydraulic fracturing fluid on the well pad. Crystalline silica dust within the respirable size range ($<4\ \mu$m) is considered a hazardous air pollutants and a carcinogen. In addition to an increased risk of lung cancer, exposure to crystalline silica can lead to a chronic, inflammatory lung disease called silicosis.

In 2011, the United States Environmental Protection Agency doubled its estimates of methane leakage for the US natural gas industry, in part because of the inclusion of emissions from shale gas production for the first time. One key activity that can produce significant methane emissions is shale gas well completions. When flowback water is removed from the well prior to the beginning of gas production, natural gas can be vented to the atmosphere over the course of several days. Periodically, a shale gas well may need a *workover* to improve gas flow, which can involve hydraulically fracturing the well again, and thus further methane emissions can occur if these operations are not controlled (Osborn et al., 2011).

In reality, natural gas operators often take steps to limit these emissions. The STAR program of the United States Environmental Protection Agency, an industry and government partnership to reduce methane emissions, has been reporting significant (approximately 50%) emission reductions through the use of flaring and *reduced emissions completions (RECs)*, which allow them to capture gas that otherwise would have been vented to the atmosphere (Burnham et al., 2012). However, the estimates of savings lack transparency, as they are highly aggregated to protect confidential business information. Another area of uncertainty when estimating the impacts of these emissions is projecting future well productivity, which is an important factor in life-cycle calculations (Berman, 2012; Branosky et al., 2012). Because shale gas production is so new, these projections range widely, and if wells are less productive than the industry projects, then the emissions impacts of well completions will be of greater importance.

Several studies have been released that have estimated the life-cycle Greenhouse gas emissions of shale gas; however, results have varied due to differences in methodology and data assumptions (Howarth et al., 2011a, 2011b; Burnham et al., 2012; Weber and Clavin, 2012). The EPA does not explicitly examine shale gas leakage, rather examines the entire natural gas industry; however, previous estimates by the United States Environmetnal Protection Agency for natural gas leakage prior to large-scale shale gas production were 1.4% for the life cycle and 0.4% for the production phase (Kirchgessner et al., 1997). While the estimated leakage rate has increased significantly from previous estimates for various activities associated with production, those for other stages such as transmission and distribution have declined due to replacement of older pipelines, thereby reducing the overall impact. On the other hand, Cornell researchers estimated a base case leakage rate for shale gas of 5.8% for the life cycle; however, they do not account for technologies that capture vented methane and include several data points that likely overestimate emissions.

Using current leakage estimates for large-scale production, natural gas methane emissions account for approximately 15% of the total life-cycle greenhouse gas emissions on a 100-year time scale and the relative benefits of natural gas depend on how it is ultimately used. For example, most studies show that natural gas power plants can provide approximately 30%–50% reduction in greenhouse gas emissions, depending on the plant efficiency, as compared to a typical coal plant (Burnham et al., 2012). For light-duty vehicles, use of compressed natural gas may provide nearly a 10% reduction in greenhouse gas emissions as compared to gasoline (Burnham et al., 2012). However, for heavy-duty natural gas vehicles using spark-ignited engines, such as a transit bus, there may be no greenhouse gas emissions benefit as compared to diesel vehicles, owing to the efficiency advantage of compression-ignition engines.

Another local air pollutant of growing concern is crystalline silica dust, which can be generated from the sand proppant. Silica dust can be generated in the mining and transporting of sand to the well site and in the process of moving and mixing sand into the hydraulic fracturing fluid on the well pad. Crystalline silica dust within the respirable size range ($<4\ \mu$m) is considered a hazardous air pollutants and a carcinogen. In addition to an increased risk of lung cancer, exposure to crystalline silica can lead to a chronic, inflammatory lung disease called silicosis.

Air emissions associated with unconventional oil and natural gas production have also raised public health concerns and have drawn regulatory scrutiny. Air pollutants can be released during various stages of oil and natural gas production. Emission sources include pad, road, and pipeline construction; well drilling and completion, and flowback activities and natural gas processing, storage, and transmission equipment. Key pollutants include methane (the main component of natural gas and a potent greenhouse gas), volatile organic compounds (VOCs), nitrogen oxides, sulfur dioxide, particulate matter, and various hazardous air pollutants. According to united States Environmental Protection Agency, the oil and gas industry is a significant source of methane and VOC emissions, which react with nitrogen oxides to form ozone (smog). EPA has identified hydraulically fractured gas wells during flowback as an additional source of these emissions in the natural gas industry.

Releases of methane and other pollutants can also occur where natural gas is produced in association with oil and natural gas gathering pipelines and other infrastructure are lacking. In such cases, the natural gas must generally be flared or vented. Flaring reduces VOC emissions compared to venting, but like venting, it contributes to greenhouse gas emissions without producing an economic value or displacing other fuel consumption. Natural gas flaring has become an issue with the rapid and intense development of tight oil from the Eagle Ford Formation in Texas and the Bakken Formation in North Dakota, which have significant amounts of associated gas. Other areas that have experienced large increases in tight oil production have also had increases in the amount of natural gas being flared.

2.2 Water pollution

In the United States, shale basins are found across most of the lower forty eight states (Chapter 2). A large volume of water is needed for the development of shale plays. Water is used for drilling, where it is mixed with clays to form drilling mud. This mud is used to cool and lubricate the drill-bit, provide well-bore stability and also carry rock cuttings to the surface. Water is also used in significant volumes in hydraulic fracturing – a typical fraccing fluid is more than 98% water and sand. The other 2% is made up of a number of additives which may vary depending on the particular well and operator. Typically additives include many substances that are commonly found in small measure in various household products. In addition to water and sand, a small concentration of other additives is added to the fluid to improve the efficiency of the hydraulic fracturing process (Chapter 5) (Speight, 2016). In the United States, the water is typically trucked to the drilling location or transported via temporary pipelines.

During a typical hydraulic fracturing process (Chapter 5) the fracturing fluid is transmitted down a cased well-bore to the target zones and then forced deep into the targeted shale gas formations (Speight, 2016). In order to minimize the risk of any groundwater contamination, good drilling practice normally requires that one or more strings of steel casing are inserted into the well and cemented into place so as to ensure that the entire wellbore, other than the production zone, is completely isolated from the surrounding formations including aquifers. Most oil or gas-bearing shales in the US tend to be at least 5000 feet below the surface, whereas aquifers are generally no more than 1700 feet below the surface. Given the thickness of rock separating target shale formations from overlying aquifers, and the extremely low permeability of shale formations themselves, and also assuming the implementation of good oilfield practices (such as casing and cementing), it is considered by the industry that the risk of contamination of overlying aquifers as a result of hydraulic fracturing operations is remote. Instances where contamination of aquifers has been alleged are generally believed to have involved poor drilling practices, in particular poor casing and cementing of a well or poor construction of surface storage facilities.

Currently, most of the flowback fluid from fraccing operations is either transported from well sites for disposal or is processed for re-use in further operations. Suspended solids must be removed from the water before re-use. The recycling of this water can be costly and is a major focal point of many environmental groups and environmental regulators. New, more efficient, technologies have been developed which allow frac fluid to be recycled on-site at reduced cost. Fluids other than water may be used in fraccing processes, including carbon dioxide, nitrogen or propane, although their use is currently much less widespread than water.

Currently, the most active shale basins in the United States are (alphabetically) the Antrim Shale, the Barnett Shale, the Fayetteville Shale, the Haynesville/Bossier Shale, the Marcellus Shale, and New Albany Shale, with other gas shale formation under serious investigation as gas producers (Chapter 2) (EIA, 2011a). The only commonality is the name *shale* and, as is the case with processing the natural gas, each gas shale basin presents its own unique set of challenges with respect to water resource management.

In terms of water resources, the issue is the application of hydraulic fracturing to release the gas form the shale formation – high-volume hydraulic fracturing to create fissures in the rock to release gas or oil trapped inside. Thus, water-related issues in shale drilling are leading to growing and complex policy and regulatory challenges and environmental compliance hurdles that could potentially challenge shale gas production expansion and increase operational costs.

Water that originates from hydraulic fracturing often contains chemical additives to help carry the proppant and may become enriched in salts after being injected into shale formations. Therefore, the water that is recovered during natural gas production must be either treated or disposed of in a safe manner – typically by injection into deep, highly saline formations through one or more wells drilled specifically for that purpose and by following clearly defined regulations. Flow-back water is infrequently reused in hydraulic fracturing because of the potential for corrosion or scaling, where the dissolved salts may precipitate out of the water and clog parts of the well or the formation.

In addition to fracturing fluid additives, wastewater from shale gas extraction may contain high levels of total dissolved solids (TDS) metals and naturally occurring radioactive materials. Furthermore, the amount of saline formation water produced from gas shale formations varies widely – from zero to several hundred barrels per day. The water comes from the gas shale itself or from adjacent formations that are connected through the fracture-induced fracture network. The water, like flow-back water, is normally highly saline and must be treated and/or disposed of, typically by injection into deep saline formations, which is also subject to clearly defined regulations. In fact, in some oil- and gas-producing states, regulatory agencies have implemented regulations regarding the disclosure of chemicals used in the process of hydraulic fracturing.

Well casing provides a protective barrier from potential contamination from hydraulic fracturing fluid, oil and natural gas flowing from the well. However some of the risks to water quality occur from ground and surface spills – such as shale gas drilling water contamination or other mishandling of wastewater, rather than from the hydraulic fracturing process itself (EIUT, 2012).

Nevertheless, the potential contamination of groundwater raises another environmental concern. The hydraulic fracturing process requires the use of hundreds of thousands of gallon of water treated with chemicals that facilitate both the suspension of the proppant (sand, most times) and the lubrication of the conveying mediums. In the development of an entire field, the amount of water injected into a shale formation could reach into the hundreds of millions of gallons. Although field operators retrieve most of the injected water upon completion of the hydraulic fracturing stimulation, a significant quantity of water and chemicals remain within the formation.

Development of several shale formations, for example, the Barnett near Fort Worth, Texas, is occurring near major population centers. As a result, some environmentalists claim that potential leakage of chemicals used in the hydraulic fracturing process pose a health and safety risk and are calling for stricter regulation. The natural gas industry responds to the concern by pointing out that “the chemical injections [into the shale formations] are happening thousands of feet below the surface, whereas groundwater is usually just hundreds of feet deep.

Some states, including New York, have issued regulatory requirements for *responsible development* of shale formations. These regulations include guidelines for the use and disposal of water, the protection of groundwater, and the use of chemicals. Further, the regulatory requirements include: (i) review of each drilling application for environmental compliance, (ii) complete environmental assessment of all proposed oil or gas well that is within 2000 feet of a municipal water well, (iii) strict review of the well design to ensure groundwater protection, (iv) on-site of inspection of drilling operations, and (v) enforcement of strict restoration rules when drilling ends.

In terms of waste water, a number of issues face the hydraulic fracturing industry and the main driver behind these issues is (i) the presence of chemical additives that are added to the water before the fracturing process begins and (ii) chemicals leached from the formation during the process and while the water returns to the surface. However, efforts by the industry are being continued to reduce and, if possible, eliminate completely any water contamination. In addition to monitoring organic compounds in the water, metals concentration must be continually monitored since heavy metals can be extremely hazardous when released to the environment.

For the most part, aqueous wastes are regulated under the Safe Drinking Water Act (SDWA) which requires that the water be recycled through many stages during the purification process and passes through several treatment processes, including a wastewater treatment plant, before being released into surface waters. The wastes discharged into surface waters are subject to state discharge regulations and are regulated under the Clean Water Act (CWA). These discharge guidelines limit the amounts of sulfides, ammonia, suspended solids and other compounds that may be present in the wastewater. Although these guidelines are in place, contamination from past discharges may remain in surface water bodies.

At the surface facilities of the fracturing operation, the options for water treatment are: (i) solid settling and removal and (ii) the use of bacteria and aeration to enhance organic degradation, and (iii) filtration through activated carbon, applications of ozone, and chlorination. Thus, toxic constituents in the water must be identified and plans must be developed to alleviate any problems. In addition, regulators have established, and continue to establish, water-quality standards for priority toxic pollutants.

In addition, for deep formations, contamination may occur due to defects in the wellbore. When the annulus between the well casing and surrounding geology is not adequately sealed during well installation, methane can migrate from the tight formation resource up the outside of the wellbore to shallow aquifers where it could dissolve in the drinking water. Another possible pathway for contamination is a defect in the casing at a shallow depth, allowing gas to flow from inside the wellbore to the aquifer. Faulty well construction appears to have caused one of the largest documented instances of water contamination. In addition to faulty well construction, uncased, abandoned wells may also provide pathways for methane migration to occur (Osborn et al., 2011). The most obvious, and perhaps most easily prevented, pathway for contamination is intentional dumping or accidental spilling of flowback water on the surface. A common cause of accidental spillage is overflows from retention ponds during major rain events.

Water for tight formation energy projects is used most intensely in the fracturing portion of the life cycle of a project. Under current practices, fracturing – typically a water-dependent activity – may require up to ten million gallons of water for each horizontal well and the associated fractures. Production activities and management and treatment of the wastewater produced during natural gas or crude oil from tight formations (including flowback from fracturing and water produced from source formations) have raised concerns over the potential contamination of groundwater and surface water and also the potential for induced seismicity associated with wastewater injection wells.

In fact, constraints on the ability of the producer to use water resources may serious effect the future development of the production of natural gas and crude oil from formations that require horizontal drilling and hydraulic fracturing. The potential for such projects to cause adverse environmental effects – particularly effects associated with fluids management (Chapter 5) – have prompted the various regulatory actions to introduce and enforce regulations to protect water supplies. Future actions may influence development of tight formations that hold natural gas and crude oil reserves through additional regulatory oversight or other policy actions. At the same time, innovations and advances in the extraction of natural gas a crude oil from tight formations as well as innovations and improvements in water use and in wastewater management protocols may reduce some of the potentially adverse environmental development impacts (Tiemann et al., 2014). Furthermore, water management issues are relevant to the entire life cycle of energy development from tight formations because fluids will continue to be produced even after a well is drilled, hydraulically fractured, and produces natural gas and/or crude oil Furthermore, it must not be forgotten that in the United States, where tight formation basins are found across most of the contiguous forty-eight states (Chapter 2) (US EIA, 2011a), the only commonality is the use of the umbrella term *tight formation* and, as is the case with processing the natural gas (Chapter 78 and crude oil (Chapter 10) (Speight, 2014a), each tight formation presents an individual set of unique challenges with respect to water contamination and water resource management.

2.2.1 *Water consumption*

Water consumption for hydraulic fracturing occurs during: (i) drilling, (ii) extraction and processing of proppant sands, (iii) testing natural gas transportation pipelines, and (iv) gas processing plants. Typically, for most tight formation basins, water is acquired from local water supplies, including: (i) surface water bodies, such as rivers, lakes, and ponds, (ii) groundwater aquifers, (iii) municipal water supplies, (iv) treated wastewater from municipal and industrial treatment facilities, and (v) produced and/or flowback water that is recovered, treated, and reused (Chapter 5). Water contamination can occur because of the presence of (i) suspended solids, (ii) dissolved inorganic constituents, (iii) dissolved organic constituents, as well as (iv) a variety of other contaminants that will vary with the locale and the characteristics of the project, including the characteristics of the reservoir.

Although water is used in several stages of the shale gas life cycle, the majority of water is typically consumed during the production stage. This is primarily due to the large volumes of water (2.3–5.5 million gallons) required to hydraulically fracture a well (Clark et al., 2011). Water in amounts of 190,000–310,000 gallons is also used to drill and cement a shale gas well during construction (Clark et al., 2011). After fracturing a well, anywhere from 5% to 20% of the original volume of the fluid will return to the surface within the first 10 days as flowback water. An additional volume of water, equivalent to anywhere from 10% to almost 300% of the injected volume, will return to the surface as produced water over the life of the well. It should be noted that there is no clear distinction between so-called flowback water and produced water, with the terms typically being defined by operators based upon the timing, flow rate, or sometimes composition of the water produced.

The rate at which water returns to the surface is highly dependent upon the geology of the formation. In the Marcellus play, operators recycle 95% of the flowback, whereas in the Barnett and Fayetteville plays, operators typically recycle 20% of the flowback. Water management and reuse are local issues and often depend upon the quality and quantity of water and the availability and affordability of management options (Veil, 2010). Over a 30-year life cycle, assuming a typical well is hydraulically fractured three times during that time period, construction and production of shale gas typically consumes between 7,090,000 and 16, 810, 000 gallons of water per well.

Once the gas is produced, it is processed, transported and distributed, and ultimately used. Water consumption occurs in each of these stages as well, with the most significant non-production consumption potentially occurring during end use. Although natural gas can be combusted directly with no additional water consumption, if the end use of the gas is a vehicle tank, it might be compressed via an electric compressor. The electricity for compression is associated with water consumption of 0.6–0.8 gallon per gasoline gallon equivalent (GGE) (King and Webber, 2008), making the total consumption for the vehicle life cycle 1.0–2.5 gal/GGE depending upon location and the extent that flowback water is recycled. For comparison, vehicle life cycle water consumption associated with the use of conventional natural gas is between 0.9 and 1.1 gal/GGE, gasoline is between 2.6 and 6.6 gal/GGE, and corn ethanol is between 26 and 359 gal/GGE (Wu et al., 2011).

2.2.2 *Water quality*

Concerns over water quality focus on potential drinking water contamination by methane or fluids from hydraulic fracturing activities. The possible pathways for this contamination include underground leakage from the wellbore to drinking water aquifers and improper disposal or accidental leakage of hydraulic fracturing fluids to surface water bodies. Owing to the depth of most shale plays, it is unlikely that a credible pathway (independent of the wellbore) exists for fluids to flow from the fractures within the shale through thousands of feet of overlaying rock into a drinking water aquifer. However, shallower shale deposits may be vulnerable to this direct connection, as is suggested by ongoing groundwater investigation by the United States Protection Agency in Pavilion, Wyoming, whereas little as 400 feet separated gas deposits from drinking water resources.

For deep formations, contamination may occur due to defects in the wellbore. When the annulus between the well casing and surrounding geology is not adequately sealed during well installation, methane can migrate from the shale resource up the outside of the wellbore to shallow aquifers where it could dissolve in the drinking water. Another possible pathway for contamination is a defect in the casing at a shallow depth, allowing gas to flow from inside the wellbore to the aquifer. Faulty well construction appears to have caused one of the largest documented instances of water contamination, which occurred in Bradford County, Pennsylvania, after wells had been drilled but before any hydraulic fracturing took place. In addition to faulty well construction, uncased, abandoned wells may also provide pathways for methane migration to occur (Osborn et al., 2011). The most obvious, and perhaps most easily prevented, pathway for contamination is intentional dumping or accidental spilling of flowback water on the surface. A common cause of accidental spillage is overflows from retention ponds during major rain events.

Contaminants in flowback water from the mineral formation, such as NORM, or from additives to the hydraulic fracturing fluid can be a health concern when present in significant concentrations. The investigation by the United States Environmetnal Protection Agency into possible groundwater contamination at Dimock, Pennsylvania, was launched out of concern over such toxic substances. While there are no Federal drinking water standard limits for methane, it is nevertheless a hazard in water because at sufficient concentrations it can volatilize and collect in houses, which can lead to suffocation or serve as a fuel for fire and explosions.

Suspended solids will occur primarily in water from the dust-control systems used in tight formation as well as in site drainage water. In above-ground wellhead treating systems, some fine particulate matter may be entrained in the produced natural gas as well as in the gas condensate. A wellhead cooling tower that may be associated with, and necessary for, natural gas and crude oil treatment before transportation, may cause contamination of the water due to dust picked up from the atmosphere. Also, precipitated salts and biological matter may also be present in the cooling tower blowdown.

Dissolved inorganic constituents will occur in produced water, flowback water, and in site drainage water — these streams have a propensity to leach sodium, potassium, calcium, and magnesium ions from the tight formation. Anions such as sulfate $\left(SO_4{}^{2-}\right)$, bicarbonate $\left(HCO_3{}^{-}\right)$, and chloride (Cl^-) are associated with the cations (sodium, Na^+, potassium, K^+, calcium, Ca^{2+}, and magnesium, Mg^{2+}) may also be present depending upon the contact the water has made with the tight formation. The inorganic constituents that leached from the reservoir (assuming that the well bore and the fracturing operation has not allowed the water to have contact with other formations) include acidic materials, highly alkaline materials, and dilute concentrations of heavy metals. These materials can have an adverse effect on the indigenous flora and fauna by creating a hostile environment (often through poisoning the waterways) and, in some cases, cause the destruction of flora and fauna.

Dissolved organic constituents arise largely from the organic compounds in the natural gas, in the gas condensate, or in the crude oil. The types of organics in each condensate will probably depend on the solubility of the organic constituents and the reservoir temperature at which the gas and oil came into contact with the water. Water-soluble acidic compounds, that occur in some crude oils (Speight, 2014a, 2014b), accumulate in water that has been in contact with the crude oil-containing tight formation. Constituents of natural gas, such as hydrogen sulfide (H_2S) and thiols (RSH) also have a measurable solubility in water as do certain hydrocarbon species. In terms of soluble organic constituents, the general rule of thumb, is to assume that soluble organic constitunets will be also have an adverse effect on the indigenous flora and fauna by creating a hostile environment (often through poisoning the waterways) and, in some cases, cause the destruction of flora and fauna.

In addition to constituents solubilized in the water while in the reservoir, water that originates from hydraulic fracturing (flowback water and produced water) often contains chemical additives to help carry the proppant and may become enriched in salts after being injected into tight formation formations (Chapter 5). Some of the chemicals used in hydraulic fracturing are common and generally considered to be harmless, this is not true of all chemicals used in the process. In fact, consideration must be given to the injection of the so-called *harmless chemicals* into the formations and (since these chemicals are not indigenous to the formation) and the effect of these harmless but non-indigenous chemicals on the environment. Consideration must also be given to the injection of the so-called *harmless chemicals* into the formations and (even if the chemicals are identical to chemicals that are indigenous to the formation) and the effect of these indigenous chemicals on the environment. Within the local environment, these chemicals will be present in a measurable concentration but the flora and fauna present in that ecosystem may be fatally susceptible to such chemicals when they are present in a concentration that is above the indigenous concentration of the chemicals. Thus, it is essential that companies participating in the hydraulic fracturing process must be willing to provide to regulatory authorities the name of the ingredients that are used in the hydraulic fracturing fluid and there must also be a thorough understanding of the potential risks that these chemicals pose to the environment. Without knowing the identity of any proprietary components, regulators cannot test for their presence (in order to establish an ecosystem baseline) and this prevents government regulators from establishing baseline levels of the substances prior to a hydraulic fracturing project and changes in the levels of these chemicals cannot be documented, thereby making it more difficult to prove the effect (adverse or benign) that hydraulic fracturing has on the environment.

Until recently, the chemical composition of fracturing fluids was considered a trade secret and was not made public. This position has fallen increasingly out of step with public insistence that the community has the right to know what is being injected into the ground. Since 2010, voluntary disclosure has become the norm in most of the United States. The industry is also looking at ways to achieve the desired results without using potentially harmful chemicals. “Slick-water”, made up of water, proppant, simple drag reducing polymers and biocide, has become increasingly popular as a fracturing fluid in the United States, though it needs to be pumped at high rates and can carry only very fine proppant. Attention is also being focused on reducing accidental surface spills, which most experts regard as a more significant risk of contamination to groundwater.

Therefore, the water that is recovered during natural gas or crude oil production from tight formations must be either treated or disposed of in a safe manner — typically by injection into deep, highly saline formations through one or more wells drilled specifically for that purpose and by following clearly defined regulations. There has been a tendency of late to investigate (and advocate) further the use of flowback water for re-use in hydraulic fracturing project. In addition to the presence of what-might-be-termed dangerous chemicals (to the flora and fauna of the ecosystem) in the water. There are also additional effects that can cause dissolution of more chemicals into the water — the potential for corrosion or scaling (Speight, 2014c), where the dissolved salts may precipitate out of the water and clog parts of the well or the formation may become a reality thereby introducing more environmentally detrimental chemical species into the ecosystem.

In addition to the chemical additives in the hydraulic fracturing fluid, wastewater from natural gas and crude oil extraction from tight formations may contain high levels of total dissolved solids (TDS) metals and naturally occurring radioactive materials (NORM). Furthermore, the amount of saline formation water produced from tight formation formations varies widely — up to several hundred barrels of water per day deepening upon the formation. The water comes from either (i) the tight reservoir formation or from (ii) any adjacent formations that are connected through the fracture-induced fracture network. The water, like flowback water, is normally highly saline and must be treated and/or sent for disposal — typically by injection into deep saline formations, which are also protected and injection of non-indigenous fluids is also subject to clearly defined regulations. In fact, many states where natural gas and crude oil are produced, have (though the various state regulatory agencies) implemented regulations regarding the disclosure of chemicals used in the process of hydraulic fracturing. There are, however, agreement that protect the states from disclosure of the name of proprietary chemicals thereby protecting the intellectual property of the production company.

The well casing does, in general, provides a protective barrier from potential contamination from hydraulic fracturing fluid, oil and natural gas flowing from the well. Nevertheless, risks to water contamination (and thence, risks to water quality) occur from ground and surface spills. These spills include natural gas and crude oil drilling water contamination or other mishandling of wastewater, rather than from the hydraulic fracturing process itself (EIUT, 2012). Thus, the potential for contamination of the groundwater raises another environmental concern. The hydraulic fracturing process requires the use of copious quantities of water treated with chemicals that facilitate both the suspension of the proppant (such as sand) and the lubrication (for friction reduction) of the conveying medium (the hydraulic fracturing fluid) (Table 18.2). In the development of an entire field, the amount of water injected into a tight formation could potential be on the order of hundreds of millions of gallons. Although field operators retrieve most of the injected water upon completion of the hydraulic fracturing stimulation, a significant quantity of water and chemicals remain within the formation. As a result, there have been claims that the potential leakage of the chemicals used in the hydraulic fracturing process pose a risk to the flora and fauna of the local ecosystem (including a risk to human health and safety) and are calling for stricter regulation.

Thus, in order to protect water sources (including surface water and groundwater sources), existing regulations must (typically, the regulations do) require that natural gas and crude oil recovery projects must use cement well casings using cement of a certain quality and depth. Under any such rule, hydraulic fracturing operations will be required to follow any prevailing and new standards. In addition, the cement used for hydraulic fracturing operations must be adequately bonded and of a prescribed minimum depth. In certain instances, there may be the requirement for the project operator to submit cement evaluation data to demonstrate compliance to the regulations as well as test data to show the surface pressure of any casing or fracturing string prior to conducting fracking operations. In fact, some states have issued regulatory requirements for *responsible development* of tight formation formations and these regulations include guidelines for the use and disposal of water, the protection of groundwater, and the use of chemicals. Furthermore, the regulatory requirements include: (i) review of each drilling application for environmental compliance, (ii) complete environmental assessment of all proposed oil or gas well that is within a prescribed distance — usually a distance on the order of 2000 feet — of a municipal water well, (iii) strict review of the well design to ensure groundwater protection, (iv) on-site of inspection of drilling operations, and (v) enforcement of strict restoration rules when drilling ends. Improper discharge of produced water is an issue and is often best addressed by recycling but one of the limitations to recycling and reusing water is that the amount of flowback returned to the surface varies between and within tight formations (Reig et al., 2014).

Water quality issues have received much attention, and of these, the potential risks associated with well stimulation by hydraulic fracturing have been at the forefront. Complaints of contaminated well water have emerged in some areas where unconventional oil and gas development has occurred, although regulators have not reported a direct connection between hydraulic fracturing of shale formations at depth and groundwater contamination.

In shale formations, the vertical distance separating the target zone from useable aquifers generally is much greater than the length of the fractures induced during hydraulic fracturing. Thousands of feet of rock layers typically overlay the produced portion of shale, and these layers serve as barriers to flow. In these circumstances, geologists and state regulators generally view as remote the possibility of creating a fracture that could reach a potable aquifer. If the shallow portions of shale formations were developed, then the thickness of the overlying rocks would be less and the distance from the shale to potable aquifers would be shorter, posing more of a risk to groundwater. In contrast to shale, coalbed methane (CBM) basins often qualify as underground sources of drinking water. Injection of fracturing fluids directly into or adjacent to such sources of drinking water. Injection of fracturing fluids directly into or adjacent to such Water use issues include the impacts that large water withdrawals might have on groundwater resources, streams and aquatic life (particularly during low-flow periods), and other competing uses (e.g., municipal or agricultural uses). Such impacts may be regional or localized and can vary seasonally or with longer-term variations in precipitation.

The management of the large volumes of wastewater produced during natural gas production (including flowback from hydraulic fracturing operations and water produced from source formations) has emerged in many areas as a significant water quality issue as well as a cost issue for producers. In some areas, such as portions of the Marcellus Shale region, capacity is limited for wastewater disposal using underground injection wells (historically, the most common and preferred produced-water disposal practice in oil and natural gas fields), and surface discharge of wastewater is an increasingly restricted option. Such issues, as well as water-use concerns, are driving increased water recycling and reuse in the industry.

2.2.3 *Water treatment*

The treatment of waste water is a critical issue for unconventional gas production — especially in the case of the large amounts of water customarily used for hydraulic fracturing. After being injected into the well, part of the fracturing fluid (which is often almost entirely water) is returned as flow-back in the days and weeks that follow. The total amount of fluid returned depends on the geology; for shale it can run from 20% to 50% of the input, the rest remaining bound to the clays in the shale rock. Flow-back water contains some of the chemicals used in the hydraulic fracturing process, together with metals, minerals and hydrocarbon derivatives leached from the reservoir rock. High levels of salinity are quite common and, in some reservoirs, the leached minerals can be weakly radioactive, requiring specific precautions at the surface. Flow-back returns (like waste water from drilling) requires secure storage on site, preferably fully contained in stable, weather-proof storage facilities as they do pose a potential threat to the local environment unless handled properly.

Once separated out, there are different options available for dealing with waste water from hydraulic fracturing. The optimal solution is to recycle it for future use and technologies are available to do this, although they do not always provide water ready for re-use for hydraulic fracturing on a cost-effective basis. A second option is to treat waste water at local industrial waste facilities capable of extracting the water and bringing it to a sufficient standard to enable it to be either discharged into local rivers or used in agriculture. Alternatively, where suitable geology exists, waste water can be injected into deep rock layers.

2.2.4 Water recycling

The issue of shale gas regulation is dominated by hydraulic fracturing, the key feature of shale gas that separates it from well-regulated conventional gas production. However, existing regulations to protect water resources during oil and gas development are also affected by the greater intensity of water, energy and infrastructure used in shale gas operations.

This consequence is driving significant uncertainty in the United States, which is still adapting to the new industry. The speed of industry growth has outpaced the availability of rigorous data on its potential impact, which has hindered the ability of government to adequately assess and regulate operations. To resolve this issue, there has been renewed focus by the US federal government on establishing better understanding of the potential impacts of shale gas development, to most effectively regulate this critical new energy resource.

A large volume of water is needed for the development of shale gas plays. Water is used for drilling, where it is mixed with clay minerals to form drilling mud. This mud is used to cool and lubricate the drill-bit, provide well-bore stability and also carry rock cuttings to the surface.

Water is also used in significant volumes in hydraulic fracturing. In addition to water and sand, a small concentration of other additives is added to the fluid to improve fraccing efficiency. Chesapeake Energy cites a figure of 4.5 million gallons of fluid for the fracturing of a typical horizontal well. This significant volume of water needs a plentiful source. In the US, the water is typically trucked to the drilling location or transported via temporary pipelines.

A typical fraccing fluid is more than 98% v/v water and sand. The other 2% consists of additives which may vary depending on the particular well and operator. Typically additives include many substances that are commonly found in small measure in various household products.

During a typical hydraulic fracturing process the fracking fluid is transmitted down a cased well-bore to the target zones and then forced deep into the targeted shale gas formations. In order to minimize the risk of any groundwater contamination, good drilling practice normally requires that one or more strings of steel casing are inserted into the well and cemented into place so as to ensure that the entire wellbore, other than the production zone, is completely isolated from the surrounding formations including aquifers.

Most oil or gas-bearing shale in the United States tend to be at least 4600 feet below the surface, whereas aquifers are generally no more than 1550 feet below the surface. Given the thickness of rock separating target shale formations from overlying aquifers, and the extremely low permeability of shale formations themselves, and also assuming the implementation of good oilfield practices (such as casing and cementing), it is considered by the industry that the risk of contamination of overlying aquifers as a result of hydraulic fracturing operations is remote. Instances where contamination of aquifers has been alleged are generally believed to have involved poor drilling practices, in particular poor casing and cementing of a well or poor construction of surface storage facilities.

Currently, most of the flow-back fluid from fracking operations is either transported from well sites for disposal or is processed for re-use in further operations. Suspended solids must be removed from the water before re-use. Recycling this water can be costly and is a major focal point of many environmental groups and environmental regulators.

New, more efficient, technologies have been developed which allow fracking fluid to be recycled on-site at reduced cost.

However, hydraulic fracturing does not require water that is of potable (drinking water) quality. Recycling wastewater helps conserve water use and provide cost-saving opportunities. In gas recovery from the Marcellus shale, there are examples of companies reusing up to ninety six percent of the produced water. Other examples of recycling and reuse include (KPMG, 2012):

(i) The use of portable distilling plants to recycle water in the Barnett Shale, particularly in regions such as the Granite Wash field in North Texas, where water resources are more critical than in other shale basins in the United States.

(ii) A water purification treatment center can recycle several thousand barrels of flowback and prod"uced water per day generated from extracting oil and natural gas from a shale formation – this approach is being used in the Eagle Ford shale and in the Marcellus Shale.

(iii) The Marcellus Shale also employs vapor recompression technology to reduce the cost of recycling fracturing water by using waste heat. The unit produces water vapor and solid residue that is disposed of in a waste facility. In addition, to reduce contamination risks during shale operations, many gas companies in the Marcellus Shale are reducing the amount of chemical additives used in fracturing fluid while producing shale gas.

(iv) A wastewater treatment company specializing in the oil and gas industry has designed a mobile integrated treatment system for hydraulic fracturing that allows the reuse of water for future drilling. Using dissolved air flotation technology, the system can treat up to 900 gallons per minute of fracking flowback water. The accelerated water treatment reduces the equipment burdens and logistics of traditional treatment methods and could significantly reduce operational costs.

(v) Produced water can have high total dissolved solids (TDS) concentrations that can be difficult to treat. Thermal distillation, reverse osmosis (RO), and other membrane-based desalination technologies can be deployed to desalinate produced water to a level fit for purpose.

Fluids other than water may be used in fracking processes, including carbon dioxide, nitrogen, or propane, although their use is currently much less widespread than water.

2.2.5 Water disposal

When water returns to the surface from a shale drilling operation, it may be disposed of in a variety of ways, depending on the shale basin: (i) reused in a new well, with or without treatment, (ii) injected into on- or off-site disposal wells regulated by the United States Environmental Protection Agency, (iii) taken to a municipal wastewater treatment plant or a commercial industrial wastewater treatment facility – most wastewater treatment plants are not capable of treating the contaminants in shale gas wastewater, (iv) or discharged to a nearby surface water body.

In the Marcellus Shale, one of the largest shale basins in the United States located in Pennsylvania and New York state, a large proportion of the hydraulic fracturing fluid is usually recovered after drilling and stored on-site in evaporation pits. Recovered fluid may be trucked off-site for use in another fracking operation or for treatment and disposal in surface waters, underground reservoirs, or at a wastewater treatment facility. The remainder of the fluid remains underground (Veil, 2010). However, in the water-deprived shale basins of Texas (such as Eagle Ford), more of the hydraulic fracturing fluid may remain underground. This water is much harder to track than surface water, which may lead to increased short and long-term risks for shale gas companies.

2.3 Land pollution

2.3.1 Fluids management

A variety of waste fluids are generated on site at shale gas wells. During drilling, used mud and saturated cuttings are produced and must be managed. The volume of mud approximately correlates with the size of the well drilled, so a horizontal Marcellus well may generate twice as much drilling waste as a single vertical well; however, as discussed above, it will replace four such holes (Arthur et al., 2008). Drilling wastes can be managed onsite either in pits or in steel tanks. Each pit is designed to keep liquids from infiltrating vulnerable water resources. On-site pits are a standard in the oil and gas industry but are not appropriate everywhere; they can be large and they disturb the land for an extended period of time. Steel tanks may be required to store drilling mud in some environments to minimize the size of the well site *footprint* or to provide extra protection for a sensitive environment. Steel tanks are not, of course, appropriate in every setting either but in rural areas or pits or ponds, where space is available at the well site, steel tanks are usually not needed (Arthur et al., 2008).

Horizontal drilling development has the power to reduce the number of well sites and to group them so that management facilities such as storage ponds can be used for several wells. Make-up water is used throughout the development process to drill the well and to form the basis of the hydraulic fracturing fluid. Large volumes of water may be needed and are often stored at the well site in pits or tanks. For example, surface water can be piped into the pit during high-water runoff periods and used during the year for drilling and fracture treatments in nearby wells. Storage ponds are not suitable everywhere in the area of a shale gas resource – just as steel tanks are appropriate in some locations but not in others.

2.3.2 Induced seismic activity

Disposal of flowback water from hydraulic fracturing depends upon the availability of suitable injection wells. For example, the limited availability of suitable geology in Pennsylvania has led to hauling flowback water to Ohio for injection. The increased injection activity has been linked to *seismic events* or earthquakes. Additional studies have indicated that injection activities in Arkansas have been linked to nearby earthquakes (Horton, 2012).

A properly located injection well will not cause earthquakes. A number of factors must be present to induce seismic events at a disposal site. In order for earthquakes to occur, a fault must exist nearby and be in a near-failure state of stress. The injection well must have a path of communication to the fault, and the fluid flow rate in the well must be at a sufficient quantity and pressure for a long enough time to cause failure along the fault or system of faults. A recent National Research Council study concludes that the majority of disposal wells for hydraulic fracturing wastewater do not pose a hazard for induced seismicity. This report also concludes that the process of hydraulic fracturing itself does not pose a high risk for inducing felt seismic events (NRC, 2012).

Nevertheless, there have been instances of earthquakes associated with unconventional gas production, for example the case of the Cuadrilla shale gas operations near Blackpool in the United Kingdom, or a case near Youngstown, Ohio, in the United States, which has been provisionally linked to injection of waste water, an operation that is similar in some respects to hydraulic fracturing. The registered earthquakes were small, of a magnitude of approximately 2.0 two on the Richter scale, meaning they were discernible by humans but did not create any surface damage.

Because it creates cracks in rocks deep beneath the surface, hydraulic fracturing always generates small seismic events; these are actually used by petroleum engineers to monitor the process. In general, such events are several orders of magnitude too small to be detected at the surface: special observation wells and very sensitive instruments need to be used to monitor the process. Larger seismic events can be generated when the well or the fractures happen to intersect, and reactivate, an existing fault. This appears to be what happened in the Cuadrilla case.

Hydraulic fracturing is not the only anthropogenic process that can trigger small earthquakes. Any activity that creates underground stresses carries such a risk. Examples linked to construction of large buildings, or dams, have been reported. Geothermal wells in which cold water is circulated underground have been known to create enough thermally-induced stresses to generate earthquakes that can be sensed by humans (Cuenot et al., 2011) and the same applies to deep mining (Redmayne et al., 1998).

In order to circumvent any such issues arising from hydraulic fracturing, it is essential for unconventional gas development engineers to make a carful survey of the geology (with the geologists) of the area to assess whether deep faults or other geological features present an enhanced risk and to avoid such areas for fracturing. In any case, multi-disciplinary monitoring is necessary so that operations can be suspended and corrective actions taken if there are signs of increased seismic activity.

2.3.3 Aquifer protection

Environmental concerns related to natural gas and crude oil exploitation have received significant attention in the media. The issues raised are fresh water usage in competition with other uses such as farming, improper disposal of produced water and contamination of fresh water aquifers. Thus, concerns over water quality focus on potential drinking water contamination by methane or fluids from hydraulic fracturing activities (WHO, 2011). The possible pathways for this contamination include underground leakage from the wellbore to drinking water aquifers and improper disposal or accidental leakage of hydraulic fracturing fluids to surface water bodies. Owing to the depth of most tight formation plays, it is unlikely that a credible pathway (independent of the wellbore) exists for fluids to flow from the fractures within the tight formation through thousands of feet of overlaying rock into a drinking water aquifer. Although natural gas and crude oil wells use up to 6 million gallons (6×10^6 gallons) of water per well, the water volume used per unit of energy produced is small compared to a number of alternatives. Although this usage is relatively low compared to alternatives, any usage of water may appear to be in competition with other uses, especially in draught years. To address this situation, salt water might be used in place of fresh water. Recent advances in fracturing permit this with small modifications to the needed chemicals.

There are two potential ways in which natural gas and crude oil operations could contaminate aquifers. One is through leakage of the chemicals used in fracturing. These then would be liquid contaminants. The second is the infiltration of aquifers by produced methane. It is a gaseous contaminant, albeit it gets dissolved in the water. If methane is present, a portion may be released as a gas. The distinction between potential liquid and gaseous contamination is important because the hazards are different, as are the remedies and safeguards. Also, because well water could not naturally have the liquid contaminants, their presence is evidence of a man made source.

Therefore, simple testing of wells proximal to drilling operations is sufficient, with the only possible complication being the influence from some source other than drilling, such as agricultural runoff, for example. This is easily resolved because of the specificity in the chemicals used for fracturing.

Methane leakage can happen because of possible combination of not locating cement in the right places and of a poor cement job. Many wells will have intervals above the producing zone that are charged with gas, usually small quantities in coal bodies and the like. If these are not sealed off with cement some gas will intrude into the well bore. This will still be contained unless the cement up near the fresh water aquifers has poor integrity. In that case the gas will leak. Wells constructed to specification will not leak.

3. Environmental impact — oil shale

Oil shale will, unfortunately, contribute to environmental pollution, including acid rain, the greenhouse effect, and *allegedly* global warming (global climate change) (Speight, 2019). Whatever the effects, the risks attached to the oil shale fuel cycle could be minimized by the introduction of relevant technologies for the protection of the environment. Until the 1960s, a legacy of unchecked fossil fuel use had led to environmental damage which spurred the Congress of the United States to introduce federal regulations to limit impacts to the environment. This legacy includes physical disturbances to the landscape, subsidence and settlement above abandoned underground mines, flooding and increased sedimentation, polluted ground and surface-waters, unstable slopes, and public safety and land disturbance issues. In countries where such regulations do not exist, these issues will be a major concern for the development of oil shale resources.

Oil shale itself is considered to be harmless and presents no risk when it is in-situ where it was formed and deposited millions of years· ago. When involved in related activities, however, its environmental impacts are deleterious if the oil shale is utilized in the wrong place at the wrong time and in the wrong amounts. Thus, concerns related to the impacts of oil shale on the environment and human health are not new.

Oil shale in the ground does not generally pose an environmental threat although mineralogy can influence groundwater properties. However, oil shale production and use have diverse impacts on the surrounding earth and atmosphere, generating various. Irrespective of how it is extracted in mines and used in industry, oil shale produces three distinct types of pollutants: (i) gaseous, (ii) liquid, and (iii) solid substances, which generally demand quite different preventive or ameliorative measures. In this context, other impacts like noise, subsidence, waste disposal should also be classified as pollutants arising from oil shale use. Numerous methods have been devised to keep environmental standards at threshold limits and thus minimize pollution damage while at the same time improving worker productivity, oil shale quality and accident prevention schemes.

Oil shale mining, like coal mining, remains, a dangerous occupation (Speight, 2013). Mine atmospheres are hazardous in terms of the health and safety of miners and, although technological advancements and legislation have led to improvement in the environmental and safety aspects in mines, pollutants are still produced at significant levels from oil shale excavation in both surface and underground mines.

The production of airborne dust particles is a major problem in underground mines where dust explosions with or without explosions due to released gases, are the main concern. In addition, dust is not solely a localized problem since fine particles can be transported to contaminate areas far from their source.

Dust is a by-product of blasting and (in open pit mines) earth moving operations. The degree of risk is relative to the physical size of particulate matter, the humidity of air, and the velocity and direction of prevailing winds. Particle size and duration of exposure determine how far dust and droplets penetrate the respiratory tract. Inhaled fine dust remains in the alveoli, but all types of larger particles are removed by the filtering capacity of the respiratory system.

On the surface, water spraying, site selection and screening from winds are advantageous, while in underground working sites suppression by water, dilution and dispersion by ventilation and removal by filtration or electrostatic precipitation are advisable.

Significant volumes of earth must be displaced to mine oil shale and the resulting rock waste can disrupt the environment. Furthermore, waste material from deep mines derives from the sinking of shafts, roadways, and ventilation tunnels, and extraction of the oil shale sediment.

The enormous volumes of waste material, which are the by-product of both underground and surface excavation operations, are a major pollution issue and disposal of these solid wastes is the most controversial aspect of oil shale mining. The primary environmental damage of waste piles (mines tips) are not only noise and dust from moving vehicles but also groundwater contamination, leaching of toxic and acid pollutants, and loss of useable land (Golpour and Smith, 2017). Reclamation to some degree restores the land, but reduction in the fertility of the soil and diminished ecological habitat are slow to recover. In fact, old mine tips, inherited from unregulated past practices of dumping mine waste, are a danger to local drainage systems and may have toxic effects on human health.

Once the mine is worked out and oil shale recovery operations cease, mined out areas are to be converted into productive agricultural land or restored to their former natural beauty. Potential recovery work is comprised of top-soil and sub-soil replacement, compaction, regrading, re-vegetation of the land, and chemical treatment and management of contaminated water resources. Cultivation necessitates the enrichment of soil for seeding and planting. Generally, land restoration reduces the potential for land destruction and pollution hazards.

Furthermore, all approaches to oil shale exploitation – aboveground retorting, *in situ*, and modified *in situ* – must address substantial environmental and health and safety concerns. The regulatory structure is already in place, and the projects will have to comply with the Clean Water Act, the Clean Air Act, and the numerous other federal and state regulations that govern the adverse effects of industrial operations. Some research, development, and testing may be required to ensure compliance with the regulations, because no large-scale industry exists to provide a data base.

The most serious environmental concerns are associated with the management and disposal of solid waste, especially the rock that remains after shale oil has been extracted. In fact, both above-ground retorting processes *in situ* retorting processes have been plagued with technical and environmental problems. Above-ground retorting required underground or open-pit mining to excavate the shale first. While either mining method is well-practiced, the expended shale that remained after retorting presented a disposal problem, not to mention the overburden rock that had to be removed in the case of open-pit mining. Above-ground retorts also faced frequent problems from caked-up shale, which led them to shut down. Also, apart from the problem of sustaining controlled combustion underground, *in situ* retorting suffered from the environmental drawback of causing groundwater contamination.

Commercial-scale aboveground retorting operations will generate huge quantities of retorted and spent shale, which will contain soluble salts, organic compounds, and trace concentrations of numerous heavy metals. Regardless of where the wastes are disposed, they must be protected from leaching by snowmelt, rainfall, and groundwater, because leached salts and toxins could contaminate both aquifers and surface streams. Toxics, including carcinogens, mutagens, priority pollutants, and other hazardous-substances, have been reported for various types of oil shale processing wastes (Kahn, 1979).

Any toxic substances present in the wastewater streams will be removed along with the trace organics or inorganic substances. It is not expected that thermal oxidation, which is often employed to destroy hazardous organic compounds, will be required for the wastewater streams, although it may be considered for concentrates or sludges. However, the presence of toxic substances may interfere with biological oxidation processes used for bulk organic removal. If this is a problem, the substances could be removed in any of several conventional pretreatment steps.

In the case of *in situ* and modified *in situ* operations, the retorted shale will be left underground, out of sight and out of reach but potentially exposed to groundwater infiltration and leaching. If infiltration occurs, it could be very difficult to confine the contamination because there will be little access to the affected areas.

Air quality will also be threatened by fugitive dust, acidic gases, and combustion products from retorts, heaters, and electrical generators. This concern also affects all approaches to shale oil extraction, as does the potential for surface subsidence.

Interest in retorting oil from oil shale in order to produce a competitively priced synthetic fuel has been intensified since the oil embargo of the 1970s. The commercial interest, once very high in 1970s and 1980s, decreased substantially in the 1990s due to the fluctuation (words to low end of the scale) of oil prices. However, the interest in oil shale for clean liquid fuel source is being revitalized in the 21st century, mainly triggered by the tendency for the variable (typically an increase) in the price of crude oil as well as the shortage of oil in the global market.

With this renewed interest and stricter environmental regulations comes the higher interest in environmental issues that always accompany the development of any fossil fuel resource.

The technology that will be used to produce shale oil is dependent on depth, thickness, richness, and accessibility of the deposit. Deeper and thicker beds will likely be produced in-situ. A combination of approaches will likely be used in the western US basins. Various land impacts are associated with each type of oil shale processing. Open-Pit (surface) mining involves significant surface disturbance and can impact surface-water runoff patterns and subsurface water quality. Experience in coal mining and other mining industries has demonstrated that impacted lands can be very effectively reclaimed with minimal long-term effect (Speight, 2013).

Air and water quality, topography, wildlife, and the health and safety of the workers will be affected by the development of an oil shale industry. Many effects will be similar to those caused by any type of mineral development, but the scale of operations, their concentration in a relatively small geographic area, and the nature of the wastes will present some unique challenges. The environmental impacts will be regulated by State and Federal laws.

The potential leaching of waste disposal areas and *in situ* retorts after the plants are abandoned is a major concern. If it occurs, the leachates could degrade the water quality in any nearby water system. Such *nonpoint* wastewater discharges are neither well understood nor well regulated, although the Clean Water Act provides a regulatory framework. Techniques for preventing leaching need to be demonstrated on a commercial scale. It will be necessary to test a variety of development technologies to assure adequate control of a large industry.

The developers of oil shale leases would do well to look to Estonia to observe, and learn from, the development of the Estonian oil shale tracts. Canada, specifically Alberta, where development of tar sand (oil sand) leases has been commercial since 1967 can also give pointers in the protection of the environment.

This chapter focuses on the environmental and human health issues related to development of oil shale resources. Emphasis is placed on those issues that are related to the petrographic, chemical, and mineralogical composition of oil shale − recognizing that a balance must be struck between industrial development and the energy required in order to build self-contained national economies.

3.1 Air pollution

The Clean Air Act is the only existing environmental law that could prevent the creation of a large industry. The procedures for obtaining environmental permits can take several years, which should not preclude the establishment of an individual project, they must be factored into the overall project costs.

Oil shale is a carbonate rock that, when heated to 450−500° centigrade, creates kerogen oil and hydrocarbon gases along with a slate of other gases, that may include: (i) oxides of sulfur and nitrogen, (ii) carbon dioxide, (iii) particulate matter, and (iv) water vapor. Commercially available stack gas clean-up technologies that are currently in use in electric power generation and crude oil refining facilities have improved over the years and should be effective in controlling oxides and particulates emissions from oil shale projects.

3.1.1 Dust emissions and particulate matter

The production of airborne dust particles is a major problem in underground mines where dust explosions with or without explosions due to released gases, are the main concern. In addition, dust is not solely a localized problem since fine particles can be transported to contaminate areas far from their source.

Dust is a by-product of blasting and (in open pit mines) earth moving operations. The degree of risk is relative to the physical size of particulate matter, the humidity of air, and the velocity and direction of prevailing winds. Particle size and duration of exposure determine how far dust and droplets penetrate the respiratory tract. Inhaled fine dust remains in the alveoli, but all types of larger particles are removed by the filtering capacity of the respiratory system. The constituents of particulate matter (*particulates*) having a diameter less than 10 μm (particularly those in the range of 0.25—7 μm) may give rise to such respiratory diseases as chronic bronchitis and pneumoconiosis. If the dust contains silica particles, diseases such as silicosis (progressive nodular fibrosis) become a major threat to health.

Operations as crushing, sizing, transfer conveying, vehicular traffic, and wind erosion are typical sources of fugitive dust. Control of airborne particulate matters (PM) could pose a challenge. Compliance with the regulations regarding the particulate matter control must be factored in. On the surface, water spraying, site selection and screening from winds are advantageous, while in underground working sites suppression by water, dilution and dispersion by ventilation and removal by filtration or electrostatic precipitation are advisable. In addition to the economic and hazards to health, dust in a mine can present serious explosion hazards. Provision of efficient ventilation and restriction of electrical or thermal sources of ignition are required by regulation.

The main sources of dust emissions are crushers, breakers, de-dusters, dry screens, and transfer points between the units. The size of the oil shale particles that become airborne generally falls into the range 1—100 μm ($1-100 \times 10^{-6}$ m) and particles larger than this usually deposit close to the point of origin. It is the usual practice to extract the dust clouds from the various sources through ducts that exhaust to a central air cleaning unit, although some equipment may include integral dust suppression devices. Dust collection equipment includes (i) dry units such as cyclones, dynamic collectors, and baghouses (fabric filters), and (ii) wet units such as dynamic, impingement, or centrifugal devices; or gravity, disintegrator, or venturi scrubber systems.

Other sources of dust are windblown losses from storage piles and from railcars during loading and transportation. Various chemical treatments are available for stockpile sealing and are being used for spraying the tops of railcars; active stockpiles present an almost insurmountable problem.

3.1.2 Mine waste disposal

Like coal mining (Speight, 2013), significant volumes of earth must be displaced to mine oil shale and the resulting rock waste can disrupt the environment.

Waste material from deep mines derives from the sinking of shafts, roadways, and ventilation tunnels, and extraction of the oil shale. This is then hauled to the surface and dumped locally. However, the implementation of modern mechanical techniques, particularly with the introduction of rock cutting machines, has dramatically increased the proportion of waste material.

The enormous volumes of waste material, which are the by-product of both underground and surface excavation operations, are a major pollution issue and disposal of these solid wastes is the most controversial aspect of oil shale mining. The primary environmental damage of waste piles (mines tips) are not only noise and dust from moving vehicles but also groundwater contamination, leaching of toxic and acid pollutants, and loss of useable land. Reclamation to some degree will restore the land, but reduction in the fertility of the soil and diminished ecological habitat are slow to recover. In fact, old coal mine tips, inherited from unregulated past practices of dumping mine waste, point to a potential are a danger of oil shale tips to local drainage systems and may have toxic effects on human health.

Another issue related to waste disposal arose because of the oxidation of pyrite which produces acidic compounds which, with other toxic materials, can be leached into the local water supply. While pyrite is not as plentiful in oil shale as it is in coal, danger still exits from its presence. Simultaneously, heat produced from such chemical reactions led to spontaneous combustion of organic particles in the waste tips. The potential hazards from spontaneous combustion in the spoil heaps can be substantially reduced by controlled tipping, site selection, as well as compaction of waste.

Surface mining has a greater adverse effect on the surroundings than underground mining operations. For example in strip mining operations, the overburden is removed and the volume produced may be many times the volume of oil shale produced. . In addition, the mining operations (which use power shovels, draglines, and bucket-chain/bucket-wheel excavators) alter the topography of the surface and destroy all of the original vegetation and often lead to contamination of surface water and groundwater courses. Nevertheless, surface mining is not considered to be a major contributor to air pollution.

Rock waste, dumped indiscriminately during surface and underground mining processes, will weather rapidly, with the potential for producing *acid drainage*, which is a source of oxygen-containing sulfur-containing compounds that combine with water vapor to form acidic species. In the past, mine overburden or mine tipple was usually dumped into low-lying areas, often filling wetlands or other sources of water. This resulted in dissolution of heavy metals which seeped into both ground and surface water causing disruption to marine habitats and deteriorate drinking water sources. In addition, pyrite (FeS_2) can form sulfuric acid (H_2SO_4) and iron hydroxide [$Fe(OH)_2$]when exposed to air and water. When rainwater washes over these rocks, the runoff can become acidified affecting local soil environments, rivers, and streams (*acid mine drainage*) (Speight, 2013). The extent and toxicity of the waste streams depend on oil shale characteristics, local rainfall patterns, topography and site drainage features. Leaching of such waste could lead to an unacceptable level of contamination of surface and groundwater.

Area mining occurs on level ground, where workers use excavation equipment to dig a series of long parallel strips, or *cuts*, into the earth. The overburden is cleared from each cut, and the material (known as *spoil*) is stacked alongside the long trench. After the exposed mineral is retrieved from the cut, workers dump the spoil back into the trench to help reclaim the mined area.

Once the mine is worked out and recovery operations cease, mined out areas are to be converted into productive agricultural land or restored to their former natural beauty. Potential recovery work is comprised of top-soil and sub-soil replacement, compaction, regrading, re-vegetation of the land, and chemical treatment and management of contaminated water resources. Cultivation necessitates the enrichment of soil for seeding and planting. Generally, land restoration reduces the potential for land destruction and pollution hazards.

3.1.3 Hazardous air pollutants

Gaseous emissions such as hydrogen sulfide (H_2S), ammonia (NH_3), carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen oxides (NO_x), and trace metals are sources for air pollution. Such emissions are at least conceivable in oil shale processing operations. However, the level of severity is far less than that of other fossil fuel processing. The very same argument can be made for the emission of carbon dioxide, which is a major greenhouse gas.

The lifetime of these species in the atmosphere is relatively short and if they were distributed evenly their harmful effects would be minimal. Unfortunately these man-made effluents are usually concentrated in localized areas and their dispersion is limited by both meteorological and topographical factors. Furthermore, synergistic effects mean that the pollutants interact with each other: in the presence of sunlight, carbon monoxide, nitrogen oxide(s), and unburned hydrocarbon derivatives lead to photochemical smog, while when sulfur dioxide concentrations become appreciable, sulfur oxide-based smog is formed.

It is worth remembering that even the non-toxic, but non-life supporting and suffocating, carbon dioxide may have an important effect on the environment. The surface of the earth emits infrared radiation with a peak of energy distribution in the region where carbon dioxide is a strong absorber. This results in the situation whereby this infrared radiation is trapped by the atmosphere and the temperature of the surface of the Earth is raised. As a result of the combustion of fossil fuels, the concentration of carbon dioxide in the atmosphere is increasing from its present level. Although many factors are involved, it does seem that an increase in the carbon dioxide concentration in the atmosphere would result in a temperature increase at the surface of the earth which could cause an appreciable reduction in the polar ice-caps and this in turn would result in further heating.

Acid gases (SOx and NO_x) emitted into the atmosphere during shale processing provide the essential components in the formation of acid rain. Sulfur is present in oil shale as both an organic and inorganic compounds. On processing, most of the sulfur is converted to sulfur dioxide with a small proportion remaining in the ash as sulfite:

$$S + O_2 \rightarrow SO_2$$

In the presence of excess air, some sulfur trioxide is also formed:

$$2SO_2 + O_2 \rightarrow 2SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

Only a small amount of sulfur trioxide can have an adverse effect as it causes the condensation of sulfuric acid and causes severe corrosion.

Also, nitrogen inherent in the kerogen can be converted to nitrogen oxides during processing which also produce acidic products thereby contributing to the acid rain:

$$2\,N + O_2 \rightarrow 2NO$$

$$NO + H_2O \rightarrow \underset{\text{Nitrous acid}}{HNO_3}$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$NO_2 + H_2O \rightarrow \underset{\text{Nitric acid.}}{HNO_3}$$

Most stack gas scrubbing processes are designed for sulfur dioxide removal; nitrogen oxides are controlled as far as possible by modification of combustion design and flame temperature regulation (Speight, 2007, 2013). However, processes for the removal of sulfur dioxide usually do remove some nitrogen oxides; particulate matter can be removed efficiently by commercially well-established electrostatic precipitators.

3.2 Water pollution

Unconventional natural gas and crude oil resources offer an opportunity to access a relatively clean fossil fuels that could potentially lead to energy independence for some countries. Horizontal drilling and hydraulic fracturing make the extraction of tightly bound natural gas from shale formations economically feasible (Chapter 5). These technologies are not free from environmental risks, however, especially those related to regional water quality, such as gas migration, contaminant transport through induced and natural fractures, wastewater discharge, and accidental spills. Improved understanding of the fate and transport of contaminants of concern and increased long-term monitoring and data dissemination will help manage these water-quality risks today and in the future (Vidic et al., 2011).

Furthermore, chemical additives in the fluids used for hydraulic fracturing in the Marcellus Shale include friction reducers, scale inhibitors, and biocides (Table 18.2). Eight US states currently require that all chemicals that are not considered proprietary must be published online, whereas many companies are voluntarily disclosing this information in other states. However, many of the chemicals added for fracturing are not currently regulated by the US Safe Drinking Water Act, raising public concerns related water supply contamination.

From 2005 to 2009, approximately 750 chemicals and other components were used in hydraulic fracturing, ranging from harmless components, including coffee grounds or walnut hulls, to 29 components that may be hazardous if introduced into the water supply. An inorganic acid such as hydrochloric acid is often used to clean the wellbore area after perforation and to dissolve soluble minerals in the surrounding formation. Organic polymers or crude oil distillates are added to reduce friction between the fluid and the wellbore, lowering the pumping costs. *Anti*-scalants are added to the fracturing fluid so as to limit the precipitation of salts and metals in the formation and inside the well. Besides scaling, bacterial growth is a major concern for the productivity of a gas well (quantity and quality of produced gas). Glutaraldehyde is the most common antibacterial agent added, but other disinfectants [such as 2,2-dibromo-3-nitrilopropionamide (DBNPA) or chlorine dioxide] are often considered. Surfactants (alcohols such as methanol or isopropanol) may also be added to reduce the fluid surface tension to aid fluid recovery (Vidic et al., 2011).

3.2.1 Water quality

Suspended solids will occur primarily in water from the dust-control systems used in shale mining and crushing operations. Mine drainage water will also contain suspended solids, as will a retort condensate stream that picks up fine shale particles as it trickles down through the broken shale. In aboveground retorts, some fine shale may be entrained in the retort gas and captured in the gas condensate, but levels should be low, thus should not be a problem to treat. Cooling water will pick up dust from the atmosphere, particularly if the cooling tower is near a shale crushing or disposal site. Precipitated salts and biological matter may also be present in the cooling tower blowdown.

Dissolved inorganics will be found in mine drainage water and retort condensates because these streams leach sodium, potassium, sulfate, bicarbonate, chloride, calcium, and magnesium ions from the shale that they contact. In addition, some inorganic volatilize and may be captured from the gas phase in the retort, Of the heavy metals present in raw oil shale, cadmium and mercury (probably as their respective sulfides) are expected to be present in the gas condensate in low concentrations.

Dissolved organics arise largely from the organic compounds in the raw oil shale, which may be altered during pyrolysis and end up in the retort, gas, or hydrotreater condensates. The types of organics in each condensate will probably depend on the volatility and volubility of the organics and the temperature at which the wastewater is condensed.

Water-soluble phenols accumulate in water layers of the retorting-unit condensation systems and additional quantities are obtained by washing the shale oil fractions with water. These phenol waters are subjected to removal of the phenols – phenols constitute up to 2% of oil formed during oil shale retorting. (1/3 dissolved in the tar-water, 2/3 by supplementary washing of shale oil).

Toxic minerals and substances exposed during removal of the overburden include acidic materials, highly alkaline materials, and dilute concentrations of heavy metals. These materials can have an adverse effect on the indigenous wildlife by creating a hostile environment (often through poisoning the waterways) and, in some cases, destruction of species. Thus, mine design should include plans to accommodate potentially harmful substances which are generated by weathering of spoil piles.

Being predominantly in the western United States, oil shale development will most likely take place in areas of historic interest – and this may well be the case on other countries. Artifacts of historic sites will be destroyed unless they have been systematically investigated before being disturbed by mining. The mining plan should include the provision for systematic archaeological studies of the area to be mined. Such studies by the mining industry often benefit the community and create an appreciation for historic values.

Finally, aesthetic rehabilitation of mined lands should, and is, being done so that the land is aesthetically more pleasing after mining than before. The removal of overburden, however, is disruptive to the landscape and aesthetically repugnant for a temporary period until the lands are restored. From the community and regulatory viewpoint, it is beneficial if the mining company includes consideration of aesthetic values in the mining plan.

3.2.2 *Water requirements*

A rate-limiting factor in further development of the oil shale resources of the western United States is not only the effect of water quality but also the availability of water, which may not be a problem in other regions. Water of the Colorado River could be made available for depletion by oil shale. An important factor that must be taken into consideration in any water-use plan is the potential salt loading of the Colorado River. With oil shale development near the river, the average annual salinity is anticipated to increase, unless some prevention or treatment is implemented. The economic damages associated with these higher salinity levels could be significant and have been the subject of extensive economic studies.

The water required for oil shale retorting is estimated at one to three barrels of water per barrel of shale oil. Still, some processes may be net producers of water. For an oil shale industry producing 2.5 million barrels per day, this equates to between 105 and 315 million gallons of water per day. A 2.5 million barrel per day oil shale industry would require 0.18 million−0.42 million acre feet of water per year, depending on location and processes used.

In the Western United States, water will be drawn from local and regional sources. The major water source is the Colorado River Basin, including the Colorado, Green, and White Rivers. The Colorado River flows between 10 and 22 million acre feet per year. Water may also be purchased from other existing reservoirs. In addition, transfers may be possible from other water basins, including the Upper Missouri. Another water source will come from western oil shale itself, which has high water content.

Oil shale typically holds 2 to 5 gallons of water per ton, though some oil shale can contain as much as 30 to 40 gallons of water per ton. Much of this connate water can be recovered during processing and used to support mining, disposal, or reclamation operations. Though this produced water will contain organic and inorganic substances, the impurities can be removed with conventional water treatment technologies. Recycling and re-use of process water will help to reduce water requirements (US DOE, 2006). Produced water from other conventional and unconventional oil and gas operations may also provide a water source.

Development of oil shale resources in the western United States will require significant quantities of water for mine and plant operations, reclamation, supporting infrastructure, and associated economic growth. Initial process water requirement estimates of 2.1−5 barrels of water per barrel of oil, first developed in the 1970s, have declined. More current estimates based on updated oil shale industry water budgets suggest that requirements for new retorting methods will be 1 to 3 barrels of water per barrel of oil (US OTA, 1980). Some processes may be net producers.

For an oil shale industry producing 2,500,000 barrels per day, this equates to between 105 and 315 million gallons of water per day These numbers include water requirements for power generation for in-situ heating processes, retorting, refining, reclamation, dust control and on-site worker demands. Municipal and other water requirements related to population growth associated with industry development will require an additional 58 million gallons per day.

A 2,500,000 barrels oil shale industry would require 0.18−0.42 million acre feet of water per year, depending on location and processes used. Water supply issues will be less critical for eastern oil shales where water supply is ample. In the dry areas, such as the west United States, water will be drawn from local and regional sources. The major water source is the

Colorado River Basin, including the Colorado, Green, and White Rivers (Fig. 1)3. The Colorado flows between 10 and 22 million acre feet/yr. Water may also be purchased from other existing reservoirs. Transfers may be possible from other water basins, including the Upper Missouri.

Western oil shale has high water content. Some oil shale contains 30—40 gallons per ton of shale. More typically it holds 2—5 gallons of water per ton. Much of this water can be recovered during processing and used to support operations. Produced water will contain organic and in-organic substances that can be removed with conventional filtering technologies. Recycling and re-use of process water will help to reduce water requirements.

Water in the West is treated much the same as other commodities — it can be bought and sold in a competitive market. Interstate "compacts" control the amount of river water each state is entitled to use. They allocate 5.3—5.9 million acre feet to the states. States are expected to use approximately 4.8 million acre feet of their allocations by 2020. If all industry water were withdrawn from the river, oil shale development would increase withdrawals by 0.18—0.42 million acre feet/year. Use of connate water and water reuse could reduce this volume. A system of rights and seniority has been established that allocates expected resources. Many private companies previously engaged in oil shale development retain very senior rights they obtained during the 1970s. Because Federal lands and prospective future leases will not come with water rights, some lessees may need to negotiate water purchases to advance projects.

Initial estimates indicate that enough water will be available to support oil shale industry development in the Western states. However, variability of supply during low flow years may cause conflicts among water users. As the industry grows, additional water resources for human consumption and for oil shale processes will likely be required. The water consumption growth will slow as oil shale technologies become more efficient. For a mature industry, substantial water storage and water transfers may be required over time. The overall allocation of water today is governed by the Colorado River Compact, originally agreed to on November 24, 1922. Currently there is a mix of both absolute and conditional water rights.

Absolute rights are those that have been decreed by the state Water Court available for use. Conditional rights are rights that have not been through the Court process and therefore have not been decreed. They cannot be used until a decree has been granted and the rights have been determined to be absolute. Conditional rights only preserve the seniority of a holder in accordance with the doctrine of *first in time, first in right*. In addition, conditional rights must undergo a diligence test every six years to preserve the conditional right. An absolute right is still subject to being curtailed (a call) in the event the water balance is insufficient for all rights and a senior right holder is being injured. To help assure supply, it is customary to file an Augmentation Plan which may consist of a plan for reservoir storage and release or purchase of senior rights that can be provided to a senior right holder.

An agreement (signed in October 2003) between the State of California and the Upper Basin States returns approximately 0.8 million-acre feet per year to the Upper Basin States that was being over-used by the State of California. This 0.8 million acre-feet/year increment could help support an oil shale industry, if the water were largely allocated to this use (US DOE, 2004a, 2004b; 2004c).

Disposal of excess water is an integral and essential phase of mining operations because pollutants in the waterways result in the reduction of the oxygen content of water leading to devastation of the aquatic life. With modem mining practices for controlling water flow, sumps and pools are provided where drainage water accumulates and where suspended shale and clay particles can ultimately be removed. Sedimentation, with or without the use of flocculants, is applied to process water in lagoons. Occasionally, if geological conditions are favorable, an adequate thickness of strata is left as a wall-pillar between the aquifer and mine workings to prevent water flow into mines.

Remedies are mainly aimed at restricting water flows seeping through the porous structure, boreholes and fractures in the water bearing strata. This can be brought related to by sealing of boreholes, grouting of fracture zones, restricting free oxygen into the mine, caving-ins to fill the voids and diverting groundwater courses.

3.3 Land pollution

3.3.1 Subsidence

Subsidence is a costly economic impact of underground mining because it creates horizontal and vertical displacement of the surface, which generally causes structural damage to buildings, roads, and railroads as well as pipeline rupture.

The factors contributing to the ground movement and ultimate surface damage are thickness, dip and depth of the oil shale seam, angle of draw, the nature and thickness of the overburden, and the amount of support left in the *goaf* (*goff* or *gob* – that part of a mine from which the mineral has been partially or wholly removed). In addition, seepage of methane through the cracks into the houses has resulted in accumulation and gas explosions causing excessive damage to property.

A reduced likelihood of subsidence will occur if the dimensions of the working areas are limited and permanent support practices are applied in the part of a mine from which the mineral has been partially or wholly removed. Surface destruction may be scaled down by backfilling the abandoned workings with stowing material or solid mine waste. However, such preventive methods to reduce ground movement are only one aspect of the problem since it must be achieved without excess loss of oil shale in the pillars and with minimum interference to normal mining operations.

Underground mine planning and design has as its goal an integrated mine systems design, whereby a mineral is extracted and prepared at a desired market specification and at a minimum unit cost within acceptable social, legal, and regulatory constraints. A large number of individual engineering disciplines contribute to the mine planning and design process, such that it is a multi-disciplinary activity. Given the complexity of the mining system, planning assures the correct selection and coordinated operation of all subsystems, while design applies to the traditionally held engineering design of subsystems.

Planning must account for both environmental protection, beginning as early as the initial exploration, and for reclamation. It is critical that planning alleviate or mitigate potential impacts of mining for two key reasons: (i) the cost of environmental protection is minimized by incorporating it into the initial design, rather than performing remedial measures to compensate for design deficiencies, and (ii) negative publicity or poor public relations may have severe economic consequences. From the start of the planning process, adequate consideration must be given to regulatory affairs. The cost of compliance may be significantly reduced when taken into account in the design or planning process, in a proactive manner, rather than being addressed on an ad hoc basis as problems develop or enforcement actions occur.

From the beginning of the mine design planning stage, data gathering and permitting, environmental considerations are important, although benefits from a strictly economic sense may be intangible. From exploration, where core holes must be sealed and the site reclaimed, through plan development, the impacts on the environment must be considered. These impacts include aesthetics, noise, air quality (dust and pollutants), vibration, water discharge and runoff, subsidence, and process wastes – sources include the underground and surface mine infrastructure, mineral processing plant, access or haul roads, and remote facilities. If mining will cause quality deterioration of either surface water or groundwater, remedial and treatment measures must be developed to meet discharge standards. The mine plan must include all the technical measures necessary to handle all the environmental problems from initial data gathering to the mine closure and reclamation of the disturbed surface area.

Reclamation plans include many of the following concerns: drainage control, preservation of top soil, segregation of waste material, erosion and sediment control, solid waste disposal, control of fugitive dust, regrading, and restoration of waste and mine areas. The plan must also consider the effects of mine subsidence, vibration (induced by mining, processing, transport, or subsidence), and impact on surface water and groundwater. These environmental items often dictate the economics of a planned mining operation and determine its viability.

The environmental aspects of underground mining are different from those encountered in surface mining operations. They have been considered to be different, even to the point of being considered (erroneously) to be of lesser importance. But it cannot be denied that underground mining can disturb aquifers either in the construction of the shaft or as a result of other influences such as formation disturbance due to subsidence. Indeed, it is only in the last three decades that subsidence has been elevated to the role of a major environmental issue.

In addition, the transportation of spoil or tipple to the surface from an underground mine where it is then deposited in piles or rows offers a new environmental hazard. The potential for leaching materials from spoil/tipple offers a mode of environmental contamination not often recognized that is of at least equal importance to the potential contamination from surface mining operations. Similarly the discharge of gaseous and liquid effluents from underground mining operations should be of at least equal concern to those arising from surface mining operations. Thus the environmental issues related to oil shale mining, be they underground or surface, operations are multi-faceted.

Whether the objective is underground mining or surface mining, preparation of the site or stripping of the overburden from the oil shale formation is a trauma to the environment. Vegetation is removed, flora and microorganisms are disturbed and/or destroyed, soil and subsoil are removed, underlying strata are ruptured and displaced, hydrological systems may also suffer, and the surface is exposed to weathering (i.e. oxidation, which can result in chemical alteration of the mineral components), as well as other general topographic changes.

For example, there is the ever-present danger of waterways contamination during (and after mining operations). Materials in the overburden (such as heavy metals and/or minerals) can be leached from the overburden, usually after erosion by rain or by run-off water from snowfall, into a nearby waterway and due caution must be used in such enterprises. However, in a more positive aspect, mining can also be a benefit to the local hydrology; spoil piles may act as “sponges” absorbing large quantities of water for future plant growth and use, retarding and diminishing runoff, making good aquifers for supplying flow to nearby streams on a steady basis.

Mining can and does cause some long-lasting wildlife habitat impairment or changes of habitat. A few wildlife species may be unable to adjust to these changes, and they do not return to the restored lands but live elsewhere in the neighborhood. But it is more than likely that, given sufficient time after restoration of the mined lands, the long-term impact of mining is favorable for wildlife. Long-term impacts of surface mining on wildlife can be minimized by careful consideration of wildlife presence when making plans for mining.

Toxic minerals and substances exposed during removal of the overburden include acidic materials, highly alkaline materials, and dilute concentrations of heavy metals. These materials can have an adverse effect on the indigenous wildlife by creating a hostile environment (often through poisoning the waterways) and, in some cases, destruction of species. Thus, mine design should include plans to accommodate potentially harmful substances which are generated by weathering of spoil piles.

Finally, aesthetic rehabilitation of mined lands should, and is, being done so that the land is aesthetically more pleasing after mining than before. The removal of overburden, however, is disruptive to the landscape and aesthetically repugnant for a temporary period until the lands are restored. From the community and regulatory viewpoint, it is beneficial if the mining company includes consideration of aesthetic values in the mining plan.

3.3.2 Noise, vibration, and visibility

Noise from underground mining operations does not have a significant environmental impact on the population but can be hazardous to miners working in the underground caverns. However, residential communities in the locality of open-pit mines often find the quality of life diminished due to the effects of noise from mining operations, vibration from blasting, and continuous heavy traffic. Furthermore, clouds of dust may reduce visibility and increase haze promoting severe distress and annoyance.

These adverse conditions can be improved to a certain degree limiting excavation to one section of the mining area at any one time, siting of boundaries and screening banks, erection of barriers, and use of low-noise machinery fitted with effective exhaust silencers. The implementation of environmentally friendly techniques has served to establish better public relations between the mining companies and the local populace.

3.3.3 Reclamation

Surface and underground mining of oil shale can disrupt the pre-mining environment. Vegetative cover must often be removed. Geologic and soil profiles can be overturned so that rich soils are now buried and leachable, lifeless rock is on top. After mining is complete, reclamation of the land is necessary.

Thus, *reclamation*, as it applies to mining activities, means to rehabilitate the land to a condition where it can support *at least* the same land uses as it supported prior to the mining activity. In some countries, reclamation may not involve restoring the land to its exact condition prior to mining but only to a condition where it can support the same or other desired productive land use. This can involve re-establishment of the biological community (flora and fauna), or alternate biological community on the surface following mining. Reclamation can be done periodically or contemporaneously with mining operations.

Periodic reclamation may occur at area strip mines, where reclamation activities may follow the advancing strip pit by a specified distance. Alternatively, as may occur with a large open pit, reclamation may have to be deferred to the end of the mining operations where the pit expands with time or is needed to provide space for production and mining support traffic.

Much of the reclamation work is part of the overburden handling in the miningsequence, leaving little but final grading and planting operations for post-mining activities. With good reclamation planning, it is possible to have competitive, productive mining operations and unspoiled post-mining landscapes at the same time as well as town infrastructure.

Successful reclamation is generally defined by regulatory standard, private or community agreement, or the goals of the mining company. Surface mining requires handling the entire surface and overburden mass above the oil shale – reclaiming and restructuring this mass offers a greater opportunity to select and structure the land for the needs and purposes of the human and natural community than would be available in almost any other way. Selecting a post-mining land use must be based on cultural factors in the surrounding community, subject to the constraints of the environment that are beyond human control.

The *choice of post-mining land use* (including the type of land ownership) is often a significant factor in reclamation. Land leased from a farmer would often be reclaimed for agricultural use, while government held land in recent years has often been used for parks, recreation, or wildlife habitat. Surrounding land use should be considered since land may often be reclaimed to its former use or to the predominant land use in the immediate area.

3.4 Production of shale oil

After mining, the oil shale is transported to a facility for retorting after which the oil must be upgraded by further processing before it can be sent to a refinery, and the spent shale must be disposed of, often by putting it back into the mine. Eventually, the mined land is reclaimed. Both mining and processing of oil shale involve a variety of environmental impacts, such as global warming and greenhouse gas emissions, disturbance of mined land, disposal of spent shale, use of water resources, and impacts on air and water quality. The development of a commercial oil shale industry in the United States would also have significant social and economic impacts on local communities. Other impediments to development of the oil shale industry in the United States include the relatively high cost of producing oil from oil shale (currently greater than $60 per barrel), and the lack of regulations to lease oil shale.

The potential exists for generation of significant levels of atmospheric pollutants from every major operation in an oil shale retorting facility. These pollutants include coal dust, combustion products, fugitive organics, and fugitive gases. The fugitive organics and gases could include carcinogenic polynuclear organics, and toxic gases such as oxides of carbon, hydrogen sulfide, ammonia, sulfur oxides, and mercury.

Emissions from auxiliary processes include combustion products from onsite steam/electric power plant and volatile emissions from the waste water system, cooling towers, and fugitive emission sources. Volatile emissions from cooling towers, waste water systems, and fugitive emission sources possibly can include every chemical compound present in the retorting. Compounds that can be present include hazardous organics, metal carbonyls, trace elements such as mercury, and toxic gases such as carbon dioxide, hydrogen sulfide, hydrogen cyanide, ammonia, carbonyl sulfide, and carbon disulfide.

Environmental factors, including the potential quantity and the composition of the pollutants, in addition to those compounds in the fuel stream recognized as mutagens that are initially present in internal process and utility streams, are a necessary consideration in the operation of fossil fuel conversion plants.

In terms of innovative technologies that might be applied to cleaner production of shale oil, both conventional and in-situ retorting processes result in inefficiencies that reduce the volume and quality of the produced shale oil. Depending on the efficiency of the process, a portion of the kerogen that does not yield liquid is either deposited as coke on the host mineral matter, or is converted to hydrocarbon gases. For the purpose of producing shale oil, the optimal process is one that minimizes the regressive thermal and chemical reactions that form coke and hydrocarbon gases and maximizes the production of shale oil. Novel and advanced retorting and upgrading processes seek to modify the processing chemistry to improve recovery and/or create high-value by-products. Novel processes are being researched and tested in lab-scale environments. Some of these approaches (like those advocated for coal processing; Speight, 2013) include: Lower heating temperatures; higher heating rates; shorter residence time durations; introducing scavengers such as hydrogen (or hydrogen transfer/donor agents); and introducing solvents.

4. Remediation requirements

The occurrence and production of natural gas from fractured, organic-rich Paleozoic and Mesozoic shale formations in the United States may be better understood by considering source rock, reservoir, seal, trap, and generation-migration processes within the framework of a crude oil system. The system concept must be modified but inasmuch as organic shale formations are both source and reservoir rocks and, at times, seals. Additional consideration must be given to the origin of the gas, whether biogenic or thermogenic, in defining the critical moment in the evolution of potentially producible hydrocarbon derivatives. This emerging resource can be considered a technology driven play as achieving gas production out of otherwise unproductive rock requires technology-intensive processes. Maximizing gas recoveries requires far more wells than would be the case in conventional natural gas operations.

Remediation requirements become of greater importance as wells reach the end of their life cycles. More than half of the total production of a well is usually achieved in the first ten years of operative well life. When a well can no longer produce shale gas economically, it is plugged and abandoned according to the standards of each state. Disturbed areas, such as well sites and access roads, are reclaimed back to the native vegetation and contours, or to conditions specified by the landowner.

The issue of natural gas and crude oil regulation is dominated by hydraulic fracturing, the key feature of natural gas and crude oil that separates it from well-regulated conventional gas production. However, existing regulations to protect water resources during natural gas and crude oil development are also affected by the greater intensity of water, energy and infrastructure used in natural gas and crude oil operations.

This consequence is driving significant uncertainty in the United States, which is still adapting to the new industry. The speed of industry growth has outpaced the availability of rigorous data on its potential impact, which has hindered the ability of government to adequately assess and regulate operations. To resolve this issue, there has been renewed focus by the US federal government on establishing better understanding of the potential impacts of natural gas and crude oil development, to most effectively regulate this critical new energy resource.

A large volume of water is needed for the development of natural gas and crude oil plays. Water is used for drilling, where it is mixed with clay minerals to form drilling mud. This mud is used to cool and lubricate the drill-bit, provide well-bore stability and also carry rock cuttings to the surface.

The treatment of waste water is a critical issue for unconventional gas production – especially in the case of the large amounts of water customarily used for hydraulic fracturing. After being injected into the well, part of the fracturing fluid (which is often almost entirely water) is returned as flow-back in the days and weeks that follow. The total amount of fluid returned depends on the geology; for tight formation it can run from 20% to 50% of the input, the rest remaining bound to the clays in the tight formation rock. Flow-back water contains some of the chemicals used in the hydraulic fracturing process, together with metals, minerals and hydrocarbon derivatives leached from the reservoir rock. High levels of salinity are quite common and, in some reservoirs, the leached minerals can be weakly radioactive, requiring specific precautions at the surface. Flow-back returns (like waste water from drilling) requires secure storage on site, preferably fully contained in stable, weather-proof storage facilities as they do pose a potential threat to the local environment unless handled properly.

Once separated out, there are different options available for dealing with waste water from hydraulic fracturing. The optimal solution is to recycle it for future use and technologies are available to do this, although they do not always provide water ready for re-use for hydraulic fracturing on a cost-effective basis. A second option is to treat waste water at local industrial waste facilities capable of extracting the water and bringing it to a sufficient standard to enable it to be either discharged into local rivers or used in agriculture. Alternatively, where suitable geology exists, waste water can be injected into deep rock layers.

Most of the fluids used in hydraulic fracturing is water and chemicals (typically 1% v/v of the water). The formulas for fracturing fluids vary, partly depending on the composition of the gas-bearing or oil-bearing formations, remembering that all gas-bearing and oil-bearing formations are not the same even when the formations are composed of the same minerals (tight formation, sandstone, or carbonate). In addition, some of the chemical additives can be hazardous if not handled carefully (Table 5.3) and caution is advised since the amount of the chemical(s) must not exceed the amount specified in regulatory requirements related to handling hazardous materials. Even if the chemical is one that is indigenous to the subsurface (and supposedly benign because it is found naturally), the amount used must not exceed the indigenous amount – in some case, exceeding the indigenous amount of a chemical can cause environmental problems.

Safe handling of all water and other fluids on the site, including any added chemicals, must be a high priority and compliance with all regulations regarding containment, transport and spill handling is essential. When it comes to disposal of the fracturing fluid, there are options. For example, the fluid, when possible without causing adverse effects to the environment, can be reused for additional wells in a single field – this reduces the overall use of fresh water and reduces the amount of recovered water and chemicals that must be sent for disposal. However, in such cases, recognition of the geological or mineralogical similarities or difference within a site must have been determined to assure minimal environmental damage. In addition, tanks (or *lined* storage pits) for the storage of recovered water are also a necessity until the water can be sent for disposal of in a permitted saltwater injection disposal well or taken to a treatment plant for processing. The linings of such pits must be in accordance with local environmental regulations.

All injection wells must be designed to meet the regulations set by the national agency (for example, the United States Environmental Protection Agency) or any local agency to protect the groundwater. In addition, production zones should have that have multiple confining layers above the zone to keep the injected fluids within the target gas-bearing or oil-bearing formation. In addition, multiple layers of well casing and cement (similar to production wells) should be used with periodic mechanical integrity tests to verify that the casing and cement are holding the liquids. The amount and pressure of the injected fluid (specified in each well permit) should be monitored to maintain the fluids in the target zone and the pressure in the injection well and the spaces between the casing layers (also called the annuluses) should also be monitored check and verify the integrity of the injection well.

More particularly, the occurrence and production of natural gas from fractured, organic-rich Paleozoic and Mesozoic tight formation formations in the United States may be better understood by considering source rock, reservoir, seal, trap, and generation-migration processes within the framework of a crude oil system. The system concept must be modified. However, inasmuch as organic tight formation formations are both source and reservoir rocks and, at times, seals. Additional consideration must be given to the origin of the gas, whether biogenic or thermogenic, in defining the critical moment in the evolution of potentially producible hydrocarbon derivatives.

Remediation requirements become of greater importance as wells reach the end of their life cycles. More than half of the total production of a well is usually achieved in the first ten years of operative well life. When a well can no longer produce natural gas and crude oil economically, it is plugged and abandoned according to the standards of each state. Disturbed areas, such as well sites and access roads, are reclaimed back to the native vegetation and contours, or to conditions specified by the landowner.

Improperly closed or abandoned natural gas and crude oil wells may create human health and safety risks, as well as air pollution and surface and groundwater contamination risks. Most states require operators to post a bond or some form of financial security to ensure compliance, but also to ensure there are funds to properly plug the well once production ceases. However, the size of the bond may cover only a small fraction of the site reclamation costs.

The economics of natural gas and crude oil development encourages the transfer of assets from large entities to smaller ones. With the assets go the liabilities, but without a mechanism to prevent the new owners from assuming reclamation liabilities beyond their means, the economics favor default on well-plugging and site restoration obligations. In fact, a combination of improved technology and tight formation-specific experience has also led – and will continue to lead – to improvements in recovery factors and reductions in decline rates. It is now recognized that each gas tight formation resource requires a specific completion technique, which can be determined through careful analysis of rock properties. Continuing efforts to make the correct selection of well orientation, stimulation equipment, fracture size and fraccing fluids will serve to enhance the performance of a well and the overall recovery of natural gas or crude oil. Indeed, for developed tight formation formations in North America the combined benefits of improved technology and increased experience will continue to provide enhanced production over time. Both the expected ultimate recovery per well and the peak production per well will continue to increase as developed natural gas and crude oil formations move to maturity.

Following on from the advances in the extraction of natural gas and crude oil from tight formations in the United States, a number of natural gas and crude oil companies will be willing to apply the techniques developed in North America in new geological basins and markets outside North America. A considerable number of regions throughout the world have been the focus of interest for their tight formation potential – in fact forty-eight major tight formation basins are identified in thirty-two countries around the world that are prospects for development (US EIA, 2011b, 2011c; 2011d).

These prospects include a number of tight formation formations across Europe where organic-rich tight formation sediments are present, including: (i) Lower Paleozoic tight formation formations, which extend from Eastern Denmark and Southern Sweden to Northern and Eastern Poland, (ii) Carboniferous tight formation formations, which extend from North-West England through Netherlands and North-West Germany to South-West Poland, and (iii) Lower Jurassic bituminous tight formation formations, which extend from the South of England to the Paris Basin in France, the Netherlands, Northern Germany and Switzerland. Poland and France are identified (US EIA, 2011b) as countries with some of the largest estimated natural gas and crude oil technically recoverable resources in Europe – both countries are currently highly dependent on imported gas to meet domestic demand.

Furthermore, horizontal wells with horizontal legs up to one mile or more in length are widely used to access the reservoir to the greatest extent possible. Multi-stage hydraulic fracturing, where the tight formation is cracked under high pressures at several places along the horizontal section of the well, is used to create conduits through which gas can flow. Micro-seismic imaging allows operators to visualize where this fracture growth is occurring in the reservoir.

Although fracture and matrix permeability, enhanced by application of appropriate well stimulation treatments, are key to achieving economical gas flow rates, sufficient amounts of organic matter (either for generation of thermogenic gas or as a microbial feedstock) must initially have been present to have generated the reservoir gas. Therefore, deciphering the thermal history of the organic matter within the tight formations and analyzing the rock mechanics response of the tight formation matrix and organic matter to local and regional stresses are critical steps in establishing their complex relationship to gas producibility.

The poor quality of one factor (e.g., low adsorbed gas) may be compensated for by another factor (e.g., increased reservoir thickness); however, tight formation-gas production cannot always be achieved even where optimum combinations of geological and geochemical factors apparently are present.

However, as a technology-driven resource, the rate of development of natural gas and crude oil may become limited by the availability of required resources, such as fresh water, fracture proppant, or drilling rigs capable of drilling wells miles in length. Thus, to important challenges for developing the Natural gas and crude oil resources are (i) the significant depth and (ii) the lack of information for many of the resources.

In areas where the resources are present, companies must continue to focus on the careful environmental develop and companies before setting their sights on a deeper target with an uncertain payoff. On the other hand, in areas where the natural gas and crude oil development has already occurred and new resources are discovered and opened up to development, there may be an infrastructure advantage. Drilling pads, roadways, pipelines, gathering systems, surveying work, permit preparation data and landowner relationships might still be useful for developing future tight formation resources.

There are some environmental concerns with the specialized techniques used to exploit natural gas and crude oil that need to be continually addressed. There is potential for a heavy draw on freshwater resources because of the large quantities required for hydraulic fracturing fluid. The land-use footprint of natural gas and crude oil development is not expected to be much more than the footprint of conventional operations, despite higher well densities, because advances in horizontal drilling technology allow for up to ten or more wells to be drilled and produced from the same well site.

Finally, there is potential for a high carbon footprint through emissions of carbon dioxide (CO_2), a natural impurity in some natural gas and crude oil.

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About the Author

Dr. James G. Speight has doctorate degrees in Chemistry, Geological Sciences, and Petroleum Engineering and is the author of more than 80 books in petroleum science, petroleum engineering, biosciences, and environmental sciences as well as books relating to ethics and ethical issues. With over 50 years of experience in petrochemicals, refining and heavy oil, he has been awarded many accomplishments including the Scientists without Borders Medal of Honor and most recently the American Excellence Award for Excellence in Client Solutions from the United States Institute of Trade and Commerce.

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