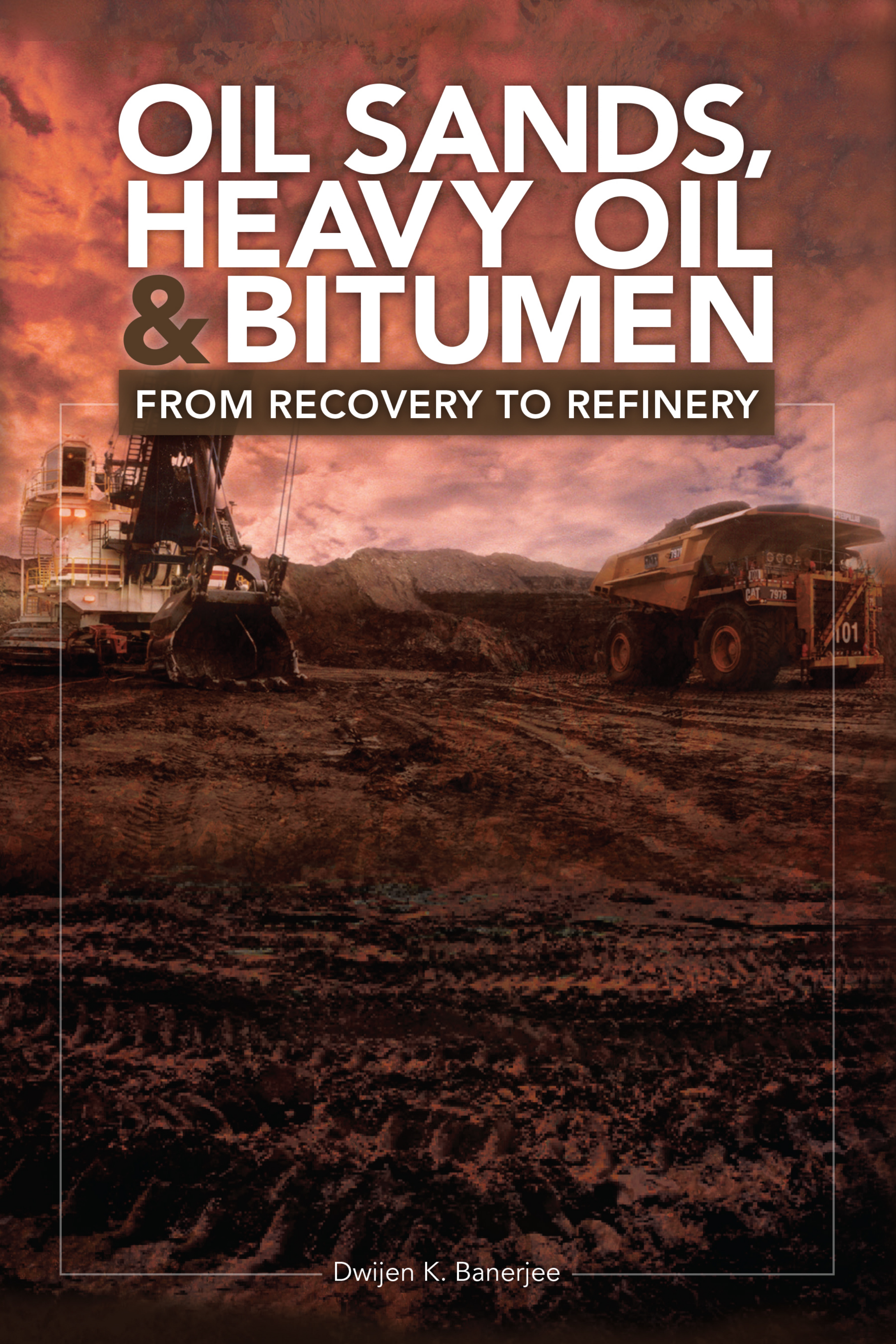
OIL SANDS, HEAVY OIL & BITUMEN

FROM RECOVERY TO REFINERY



Dwijen K. Banerjee

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Preface

During the late 1970s, when I was a graduate student just stepping into the petroleum arena and working toward my doctorate, the biggest fear in this field was the Organization of Petroleum Exporting Countries (OPEC). At that time, OPEC had an extraordinary influence over world oil industries. Baby boomers will remember the notorious “OPEC shock” of the ’70s, which caused panic in this country and had an immediate economic impact all over the world. More than a quarter-century later, that worry has diminished. OPEC’s ability to control the industry has immensely decreased, mostly because of the increasing availability of *unconventional* resources around the world. The vast oil sands deposits found in Canada—which are the second largest reserve, after the *conventional* resources in Saudi Arabia—changed everything. Few would disagree that the balance of power has shifted from the Middle East to the West. Canadian oil sands have become the focal point and comprise a major future energy source for the entire world—and will remain such as long as the price of conventional oil remains high.

At present, increasing concern for the environment marks a new age in the energy industry, with the move toward alternative clean and renewable energy. Such energy sources will have a considerable impact, reducing our dependence on hydrocarbon resources; nevertheless, this shift certainly will not reverse the demand for oil. The world is highly dependent on hydrocarbon resources and will remain so; hence, Canadian oil sands will remain a major source of energy for a long time. Keep in mind, though, to switch to the new energy system, we will need a new breed of professionals, skilled in the emerging technologies. This will take extensive research, millions of dollars in investments, and a huge infrastructure. Finally, reliable, robust technologies at affordable cost to the consumers will need to be developed, and this will take time.

Any visitor to northern Alberta can see the vast black land buried under the boreal forest across the Athabasca River. Further, visitors may notice busy mining operations that resemble other surface mining, as for precious metals. Those 400-ton monster-looking trucks are digging out black-oil sands with their shovels and are loading the sands into the back of another immense truck. The sands are then transported for the next step, which is the extraction of the black oil from the oil sands. This black oil is commonly known as *bitumen.*

There was a resemblance of Alberta in 2008, when the oil price was skyrocketing toward $150 a barrel, to the Gold Rush of the 1850s in California. In the past decade, the heavy oil business became so profitable that almost every energy company in the world rushed toward one town: Fort McMurray, in northern Alberta. As San Francisco did during the Gold Rush, Fort McMurray is becoming a boomtown. Consequently, the United States is the biggest importer of oil from Canada, at about a million barrels of bitumen per day, and this number may still be on the rise.

This book outlines the fundamental aspects of oil sands, heavy oil, and bitumen for the benefit of scientists, engineers, and graduate students interested in learning about the booming unconventional hydrocarbon resources. This book can also help junior- and senior-level managers whose experience is in conventional petroleum industries but not yet in oil sands and heavy oil crudes, so that they can deal with heavier and heavier crudes in the future. Further, it is my hope that this text will be used to complement advanced courses in petroleum engineering. (Those readers with no prior knowledge of conventional petroleum and refining industries, however, may first refer to *Petroleum Refining in Nontechnical Language,* by William Leffler; this is included along with other references of general interest to readers in appendix B.)

This will be the first book to cover a wide variety of subjects: the upstream, midstream, and downstream aspects of heavy oil industry—in other words, unconventional resources from recovery to refinery. This book describes the fundamental physical and chemical properties of heavy oil and bitumen, and it outlines analytical techniques that will be of use to analytical chemists working in heavy oil laboratories. It also discusses the various types of crude blends used for pipeline transportation.

Bitumen is an extremely poor-quality oil. It is a hydrogen-deficient resource and requires several energy-intensive and expensive steps to recover and upgrade. Several chapters in this book are devoted to those techniques. In northern Alberta, bitumen is mined from the earth because it so thick, heavy, and viscous that it can hardly move by itself and thus is removed only when it is shallow enough to make mining economical; otherwise, other techniques have to be utilized, such as steam injection.

One such process is in situ recovery, which requires a large amount of natural gas to generate steam for the production of bitumen. In my opinion, a much cleaner energy source, such as natural gas, should not be used for the recovery of the much dirtier, environmentally unfriendly bitumen (see chap. 11). A new, integrated concept for the production and upgrading of bitumen (clean-bitumen process) is discussed in chapter 9; in this process, natural gas is replaced by the heaviest part of the bitumen itself.

Being in the heavy oil research and development field for more than 25 years, I have been involved in characterizing and processing heavy oil, as well as in various emerging upgrading projects in several countries. However, to avoid reference to any confidential data of emerging or semicommercial upgrading technologies, detailed process data on individual technologies are not discussed in this book. I also do not endorse any particular emerging upgrading process; it has been my intent merely to discuss them.

It is true that our knowledge of conventional hydrocarbons is still maturing. For example, analytical techniques and computer models are being devised for the prediction of their properties and process design. However, the molecular composition of the new, unconventional resources—heavy oil and bitumen—are too complex for reliable analytical techniques to be developed. Although some experts in conventional resources use computer models for predicting the properties and process data of unconventional resources, acquisition of accurate results remains a great challenge. Therefore, readers should be extremely careful when using data without full knowledge of their source.

On one hand, the global supply of crude oil is getting heavier and heavier, and the quality of the oil is becoming poorer and poorer; on the other hand, the expectation of the quality of the refined product is increasing because of stringent environmental regulations. Engineers and scientists are struggling to find ways to meet the cost of converting poor-quality feedstocks into high-quality transportation fuel. At every step in the chain of production, recovery, transportation, upgrading, and refining, the oil industry is looking for innovative technologies to handle unconventional crudes in environmentally challenged cost-effective ways. However, cost-effectiveness of any project is highly dependent on the energy efficiency of the steps leading to the final product. Nevertheless, as always, economics beats technology.

I am confident that this book will serve as a reference for researchers. Moreover, I have cited several books and articles on heavy oil, which will be valuable sources of more-detailed information, for interested readers.

Virtually every explanation in this book is simplified and expressed in figures, which will be of particular value to readers for whom English is not their primary language. Most of the work in this arena is done by Canadian and Venezuelan researchers. I hope that this book summarizes the available knowledge base in regard to oil sands, heavy oil, and bitumen and will add to the momentum that is driving continued research in this area. Although this book mostly deals with the commercial aspects of the oil sands business and less with the academic aspects, a great amount of research and development activities remains to be performed.

Acknowledgments

I extend my thanks to my specific collaborators with whom I have been privileged to work at various stages of my research career (from my doctorate degree onward), listed in appendix C. Additionally, I thank my numerous past colleagues and the researchers around the world who have devoted their careers to this most difficult field of heavy oil.

In addition, I am indebted to Steve Hill, of PennWell, for his helpful suggestions on the structure of the manuscript. Further, I would like to acknowledge the major contribution made by my son Christopher, a medical student at the University of Miami, who tirelessly edited the manuscript and provided constructive suggestions. Finally, my heartiest appreciation and thanks go to my wife Anca for her constant support and encouragement during the many months I devoted to writing this manuscript.

INTRODUCTION 1

Definitions of Oil Sands, Heavy Oil, and Bitumen

People all over the world are familiar with the terms *petroleum* and *crude oil*. These are referred to in the industry as *conventional oil,* which is available in almost every part of the world. The main characteristics of this oil are that it is light and that its viscosity is low enough that it can be recovered from the subsurface by conventional means. In some places, simply digging a well is sufficient to recover the crude oil. We should remember the tension of summer 2010, when the offshore accident happened in the Macondo field in the Gulf of Mexico—the crude gushing out through the broken rig at the bottom of the ocean, polluting the water, and eventually reaching the Gulf Coast of the United States. Had that oil been heavy oil, it would have remained on the ocean floor, being heavier and much more viscous than the water. Because of these properties, heavy oil cannot be recovered by conventional means, and it is thus called *unconventional oil*.

The international definition of heavy oil was first discussed at the World Petroleum Congress in 1980, and the U.S. Department of Energy (DOE) continued the work through UNITAR (an international group of the United Nations). The body ultimately came out with the following definition: heavy crude oil is described as *dead oil* (gas-free oil) when its density is below 21°API and its viscosity is between 100 and 10,000 centipoise (cP) at original reservoir temperature. Dead oil was chosen because it is easily handled and because standardized analytical techniques were available to measure the properties. By contrast, a representative sample of *live oil* (actual core sample from the reservoir) is difficult to obtain, handle, and analyze.

The World Petroleum Congress later adopted UNITAR's definition, in 1987, with minor modifications. Later, Venezuela added its own definition of extraheavy oil, as a crude that is less than 10°API, with viscosity less than 10,000 cP. By contrast, Canadian heavy oil, which is obtained from the oil sands or carbonates, has an API gravity less than

10° and a viscosity above 10,000 cP at reservoir conditions. It is the most viscous hydrocarbon and is practically a solid at room temperature, now recognized all over the world as bitumen.

When the definition of heavy oil (API gravity <21°) was adopted, conventional oil of viscosity below 1,000 cP still dominated in the world market. As the demand for unconventional crude increases, the definition should change to match the need. Low-viscosity (below 1,000 cP) crude of API gravity from 10° to 21° should be called *conventional heavy oil*, to distinguish it from the real *unconventional heavy oil* of API gravity below 10° and viscosity of at least 1,000 cP.

In support of this statement, the argument can be made that bitumen producers in Alberta spend millions of dollars to upgrade the bitumen (API gravity <10°) to API gravity about 20° and viscosity below 1,000 cP to make it pipeline transportable. Although this is technically no longer a heavy oil, it still falls under the present definition of heavy oil.

Definitions of heavy oil and bitumen are shown graphically in figure 1–1. The value of 10°API, which is equivalent to that of water, provides a clear border between (unconventional) extraheavy oil and conventional heavy oil. However, it is more accurate to define heavy oil in terms of viscosity, rather than API gravity. Crude below 10°API with viscosity of 1,000–10,000 cP is considered as extraheavy oil, and that with viscosity above 10,000 cP is considered as bitumen.

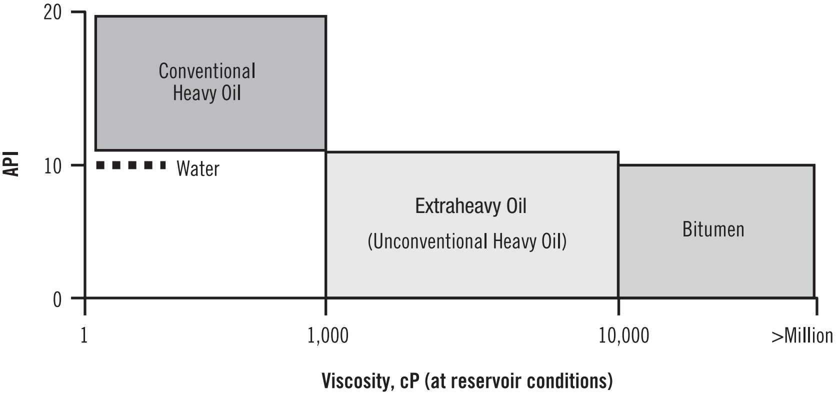

Fig. 1–1. Definition of heavy oil and bitumen

It is easier to remember bitumen as the crude obtained from oil sands in Canada. Note that oil sands are incorrectly also called *tar sands*. This terminology should be avoided because oil sands are neither tar nor sand. Tar is not a raw material; instead, it is a residual product that remains after severe thermal cracking of heavy oil. Also note that *asphalt* and *pitch* are actually the residual products obtained after the processing of heavy oil or bitumen and should not be confused with bitumen itself.

Almost all of the properties (except viscosity), process conditions, and upgrading technologies are the same for extraheavy oil and bitumen. Thus, for simplicity, the term *bitumen* will be used throughout this book, to avoid repetition. Only when a distinction is being made between the extraheavy oil and the bitumen will they be mentioned separately.

History of Oil Sands and Bitumen

The story of the oil sands and bitumen starts in Canada—in particular, in northeastern Alberta. Bitumen is so heavy, thick, and viscous that it is virtually immobile at normal conditions. The formation started before the time of the dinosaurs, in the Devonian period. One of the most widely accepted hypotheses is that bitumen was formed because of *biodegradation* of conventional oil that migrated across a distance, carried by marine waters. The degree of biodegradation varies considerably across the length and depth of the deposits. In support of this hypothesis, scientific evidence has shown that the extent of biodegradation in bitumen is directly related to the amount of remaining hydrocarbons of molecular range less than C_{20} *n*-alkanes and mono-aromatic hydrocarbons present. Undegraded oil in the same region found to have higher percentage of *n*-alkanes as compared to degraded oil. Scientists usually measure biodegradation by measuring the concentration of below C_{20} *n*-alkanes. Cyclic saturated hydrocarbons are not affected by biodegradation.[1]

Figure 1–2 shows the trend of relative percentages of C_{17}–C_{18} as biomarkers, used by the scientists, to determine the degree of biodegradation. The concentrations of C_{17}–C_{18} are highest in conventional heavy oil, as compared to unconventional heavy oil (extraheavy oil), and are lowest in bitumen. So far, the common belief is that biodegradation is mostly responsible for the heterogeneity of the subsurface formation because biotransformation reactions are highly dependent on the environment.

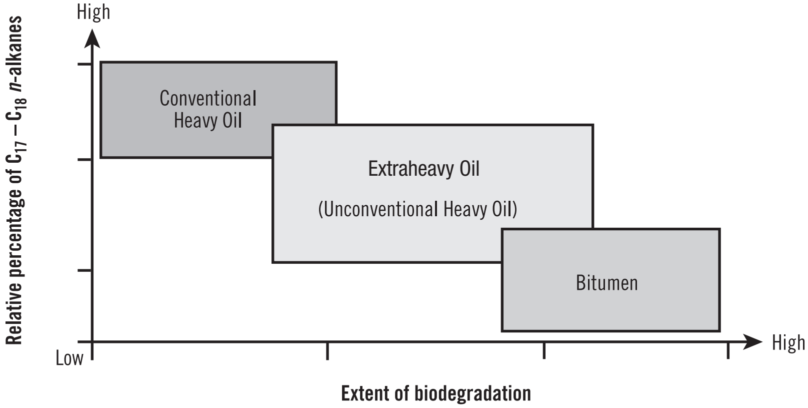

Fig. 1–2. Trend in the extent of biodegradation of heavy oil and bitumen

Note that there is an increase in relative concentrations of polynuclear aromatics and sulfur components with the increase in biodegradation. The cause of the relative increase of those species, however, is not their absolute increase in concentration but the decrease in the lower hydrocarbons below C_{20} *n*-alkane moiety as compared to the undegraded heavy oil. An alternative hypothesis, that bitumen formation occurred because of thermal degradation of the side chains of conventional oil, is no longer accepted.

Another explanation of why the degradation of side chains produces the heavier aromatic characteristics of bitumen is the theory of *water washing*. This theory posits that during marine transportation, the side chains of the lower hydrocarbon family ($<C_{20}$ *n*-alkanes) were broken and either evaporated or were flushed out by water; thus, the lighter fractions were removed, and the heavier residue remained inside the reservoir.

The uncertainty of the bitumen structure mostly arises because the structure contains a significant portion of very large molecules, called the *resid fraction*, that remain after the loss of low-molecular-weight fractions. In the case of oil sands, the migration of oil is always subject to some type of natural partitioning. Similar phenomena take place during separation through column chromatography, where bigger molecules are retained over lighter ones or aromatics are retained over aliphatics.

In summary, Alberta reservoirs are highly heterogeneous in nature owing to the variation in the environmental deposition of sand and bitumen, as well as the chemistry of the bitumen. Understanding the heterogeneity of the reservoirs is essential, because this property makes the process of recovery and production extremely challenging. Heterogeneity of the subsurface reservoir hinders the steam chamber's operation (discussed in chap. 5), because the viscosity and density differences within the reservoir destabilize the fluid flow. However, detailed discussion of the reservoir characteristics is beyond the scope of this book.

Deposits and Reserves of Extraheavy Oil and Bitumen

Various types and sizes of heavy oil deposits are found in the world. Among them, those in Alberta (in Canada), Alaska (in the United States), and the Orinoco belt (in Venezuela) are the most explored and biggest reserves. Unlike the deposits in Alaska and the Orinoco belt, which by definition fall into the extraheavy oil group, Alberta's deposits are made of oil sands containing very highly viscous hydrocarbons that fall in the category of bitumen.

Alberta

Almost all of the oil sands deposits in Canada lie in northeastern Alberta, over a surface area of 50,000 square kilometers. The API gravities of the oil sands vary from 8° to 12°, and the oil sands' viscosity is more than 1 million millipascal-seconds (mPa·s) or centipoises (i.e., >1,000,000 cP) at reservoir conditions, where the average reservoir temperature is 10–12°C (50–52°F).

Figure 1–3 shows the major bitumen deposits in Alberta. More precisely, Alberta has four main deposits. In the northeastern part, the largest one is Athabasca, and the second largest is Cold Lake, south of Athabasca. Two much smaller deposits are located on the western part of the Athabasca area: Peace River and Wabasca.

According to the Energy Resource Conservation Board (ERCB), the latest 2010 estimate of bitumen deposits in Alberta is about 1.8 trillion barrels (bbl), or 280×10^9 cubic meters (m^3); however, established reserves comprise 177 billion bbl (the amount recoverable by known technologies).[2] About 20% of the total reserves are recoverable by surface mining (discussed in chap. 5), and the remaining 80% of the reserves are recoverable by in situ technologies (discussed in chap. 5).

Athabasca has the largest bitumen deposit. Its 2009 production was 825,000 bbl/day (BPD) by mining and 300,000 BPD by in situ production. Cold Lake produced 318,000 BPD, and Peace River produced 46,000 BPD—both by in situ operations.

A freehand sketch of the cross-sectional view of an oil sands deposit in Alberta is shown in figure 1–4.

Fig. 1–3. Map showing oil sands deposits in Alberta

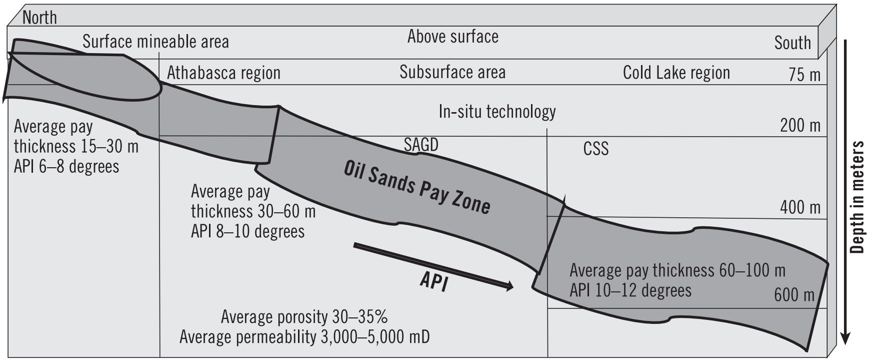

Fig. 1–4. Cross-sectional view of oil sands deposit in Alberta (not to scale)

The depth of the oil sands deposit increases from level with the surface in the northern part to more than 600 m deep in the southern part of Alberta. At the same time, the pay-zone thickness also increases from a few meters in the north, on the surface, to about 65 m to 100 m in the south. API gravity of the bitumen also increases from 6° to 12° from north to south, respectively. The northernmost part of Alberta is the Athabasca area, where surface mining to around 75 m deep is done to recover the bitumen. There are open-pit mines on the surface, where trucks and shovels are used for the recovery of bitumen (for detailed discussion, see chap. 5). Surface mining covers about 20% of the total Athabasca deposit, which comprises about 30–35 billion barrels of bitumen. Further south, where the Athabasca's depth exceeds 75 m, surface mining is not possible. Thereafter, the in situ recovery process is applied. Different in situ technologies are applied as the depth of the deposit increases; for example, steam-assisted gravity drainage (SAGD) technology and cyclic steam stimulation (CSS) technology (for details of SAGD and CSS, see chap. 5) are used. Farther south, toward the Cold Lake area, the depth of the deposits varies in the range of 300–600 m (1,000–2,000 ft).

Surface mining was the first technology to recover bitumen, and it still exceeds other technologies. According to ERCB, the 2009 production by mining was greater than that by in situ operations. However, they are projecting that in situ production will surpass mining by 2015. In situ deposits are highly heterogeneous, and recovery is done by steam injection only.

As shown in figure 1–4, the bitumen gets lighter with the increase in depth from north to south. The average porosity varies from 30% to 35% throughout the region, whereas the average permeability varies from about 3,000 to 5,000 millidarcies (mD). Permeability is a measure of flow of liquid through the oil sands particles in the reservoir. (The unit of permeability is the darcy [D].) According to ERCB, in 2009, the United States imported about 1 million barrels of bitumen per day from Canada.[3]

Venezuela

Figure 1–5 shows four major extraheavy oil deposits in Venezuela. These deposits lie parallel to the northern bank of the Orinoco River and extend from east to west along the Orinoco petroleum belt. The length of the deposit from east to west is 500–600 km, and the depth varies in the range of 350–1,000 m (1,150–3,280 ft).

Fig. 1–5. Venezuela's major extraheavy oil deposits

Those four deposits, from east to west, are

- Cerro Negro
- Hamaca
- Zuata
- Machete

It is estimated that about 1.2 trillion barrels of extraheavy oil are located in those deposits, across a surface area of 55,000 square kilometers. According to the United States Geological Survey (USGS), about 513 billion barrels of the extraheavy oil are recoverable by today's technology.[4] As mentioned before, Venezuela's heavy oil is categorized as extraheavy oil (an unconventional heavy oil). The API gravity of the heavy oil varies from 8–12°, and its viscosity is 1,000–5,000 cP. Although the API gravities are in the same range, the viscosity is much lower than that of Alberta's bitumen. However, the Venezuelan deposit is much deeper than Alberta's—hence, surface mining is not carried out in Venezuela. The temperature of the reservoirs is high enough, in the range of 55–60°C (130–140°F), to keep the heavy oil mobile. Average oil saturation in that region is about 70%; porosity is 30%–35%; and permeability varies from 2–3 D.

Alaska

The majority of the unconventional oil deposits in the United States are in Alaska, although there are also some in California. The biggest deposit in Alaska is the North Slope (ANS), and this reservoir is much deeper, with more than 3,000 ft of permafrost, making recovery an extremely challenging task. According to a 2005 DOE report, it is estimated that about 20–25 billion bbl of heavy oil exists in ANS alone, and it is the most underdeveloped reservoir in North America.[5]

As shown in figure 1–6, ANS consists primarily of three subdeposits: West Sak, Ugnu, and Milne Point. Even though ANS has the largest reserves in Alaska, heavy oil production there is greatly limited by the harsh conditions and technological challenges. However, at present, energy companies are focusing on the nearby Prudhoe Bay reservoirs, where the oil is less viscous and is easily transportable through the Trans-Alaska Pipeline System to the southern United States.

The characteristics of West Sak heavy oils resemble those of conventional heavy oils, with viscosities below 3,000 cP and API gravity of 12–22°. However, because of its deep location, just below permafrost, the oil is not recoverable by conventional production techniques.

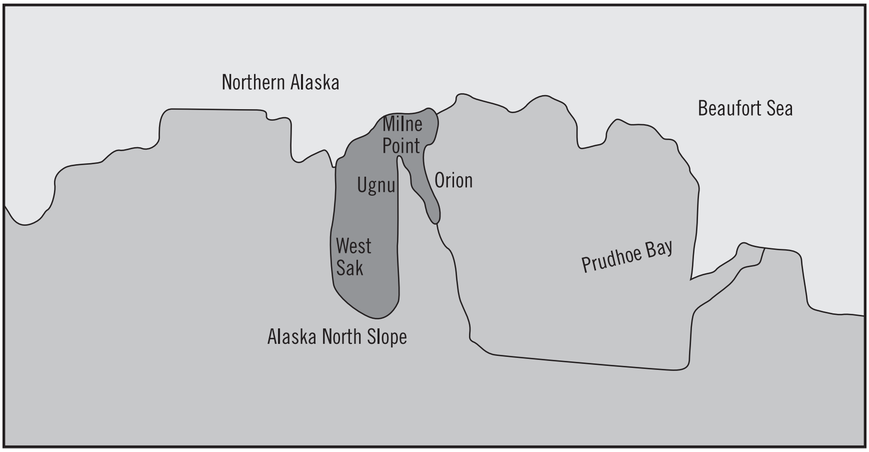

Fig. 1–6. Map showing heavy oil deposits in northern Alaska (not to scale)

By contrast, the Ugnu heavy oil deposit resembles those of unconventional (extra) heavy oil of much higher viscosity with API gravity of 6–16°. The viscosity varies as a function of depth and temperature, from 2,500 cP to greater than 500,000 cP from the eastern to the western parts of Ugnu. Therefore, several different processes need to be applied for the recovery of heavy oil in ANS, depending on the characteristics of the region. New technologies are still under pilot testing in this area. Hence, the future production of heavy oil in Alaska may well depend on the success of these emerging technologies.

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5 U.S. Department of Energy report on Fossil Energy Techline, issued May 12, 2005. Heavy oil potential key to Alaskan North Slope Oil future. http://www.fossil.energy.gov/news/techlines/2005/tl_alaska_oil.html.

THE CHEMISTRY OF BITUMEN 2

Composition of Oil Sands and Bitumen

Bitumen comprises part of the oil sands—namely, the organic content in the oil sands after recovery. As shown in figure 2–1, oil sands are basically a mixture of quartz/clay particles, water, and bitumen.

There is a thin layer of water, around 10 microns across, between the quartz and the bitumen. This layer, which makes the oil sands *water-wet*, plays an important role in the separation of bitumen from the quartz by use of a hot-water extraction technique. In contrast, shale oil, which has no water layer between the clay and the oil, is called *oil-wet* and cannot undergo hot-water extraction. Because of this key difference between oil sands and shale oil, there are two different techniques to recover oil from the respective solid particles. Therefore, wettability of the reservoir is determined before a process is in place.

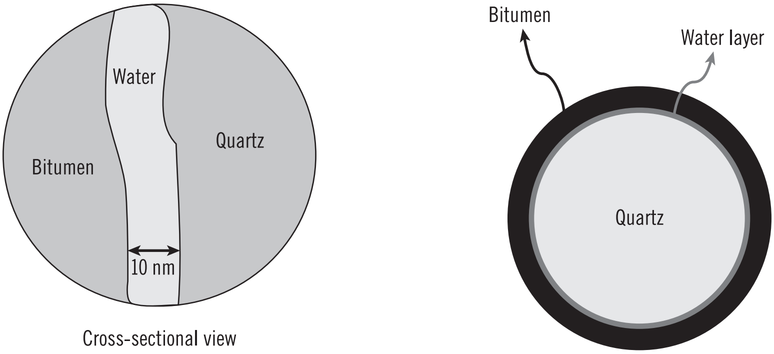

Fig. 2–1. Composition of oil sands bitumen

Bitumen content in the oil sands in Alberta varies with the types of deposits. It may vary from 0 to 15 weight percent (wt%), depending on the location. Oil sands are usually divided into three main classes, depending on the concentration of bitumen, as follows:

- Low-grade oil sands—bitumen content 6–8 wt%
- Medium-grade oil sands—bitumen content 8–10 wt%
- Rich oil sands—bitumen content >10 wt%

Mined oil sands in the northern part of Alberta fall in the category of rich oil sands.

The total percentage of bitumen plus water in the oil sands remains almost constant at 15 wt%. The remaining 85 wt% is made of quartz and clay. As the bitumen content increases, the water content decreases by the same ratio.

Even though Canadian researchers have been working on various aspects of bitumen for more than four decades, much remains to be discovered. Most of the data presented in this chapter are derived from the author's research on various projects in Canada. Other data are collected from the various books and reports, which are cited where appropriate; interested readers are also referred to the additional reading presented in appendix B.

Properties of bitumen

For the benefit of the readers and for simplicity, instead of providing exact values, which may vary depending on the reservoir location (Athabasca, Cold Lake, or Peace River), a typical expected range of composition and properties of Alberta bitumen is provided here. The exact value may also vary from laboratory to laboratory, because the results are exquisitely sensitive to the sampling technique and analytical protocol used by the laboratory.

As shown in figure 2–2, the bottom half of a barrel of typical bitumen consists of undistillable *resid* (boiling point >535°C), and the top half is distillable *gas oil product* (boiling point <535°C)—that is, distilled under a vacuum at atmospheric equivalent temperature of 535°C (1,000°F). About one-fifth of the barrel contains *asphaltenes*, which are part of the resid itself.

Of the distillable fraction, about one-third is recovered under atmospheric pressure at a temperature below 350°C; this fraction is called *distillate* or *atmospheric gas oil* (AGO), with a temperature range from the initial boiling point (IBP) to 350°C. The other two-thirds is distillable under vacuum, of boiling range 350—535°C, and is called *vacuum gas oil* (VGO).

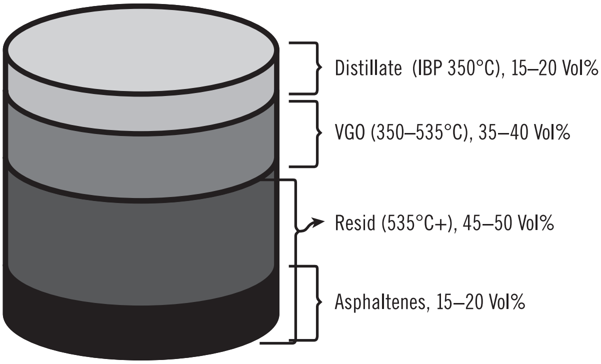

Fig. 2–2. Typical composition of Alberta bitumen

The analysis of detailed properties of bitumen is very complex, expensive, and time consuming. Therefore, to simplify the characterization process, one need concentrate only on the key properties of bitumen required for a specific evaluation. For example, some of the most important characteristics of the Alberta bitumen are summarized in table 2–1 (details of each property are discussed below).

The region holds bitumen of average API gravity of 8° (ranges from 6° to 10°) with average sulfur content of 5.0 wt% and nitrogen content of 4,000 parts per million (ppm). Bitumen is a high-acid crude of average TAN value (total acid number) of 2.5 mg KOH/gram of sample. Concentrations of asphaltene and *Conradson carbon residue* (CCR) in the bitumen are 15.0 wt% and 13.5 wt%, respectively.

Table 2–1. Typical properties of Athabasca bitumen

Properties	Average value
API	8.0°API
Sulfur	5.0 wt%
Nitrogen	4,000 ppm
TAN	2.5 mg KOH / g
Ni / V	80 / 220 ppm
CCR	13.5 wt%
Viscosity @100°F	20,000 cSt
n-C_5-asphaltenes	15.0 wt%

Nickel and vanadium are the two major elements present in bitumen. Usually, the nickel concentration (80 parts per million [ppm]) is less than half the vanadium concentration (220 ppm). In addition, viscosity is an important property because it represents the fluid characteristic of bitumen. Viscosity varies over a wide range with temperature. Because bitumen is a highly viscous liquid, it is extremely difficult to measure the viscosity at room temperature. The kinematic viscosity of Athabasca bitumen at 38°C (100°F) is around 20,000 centistokes (for definition, see chap. 3).

Elemental composition. Bitumen is a complex mixture of hydrocarbons containing carbon, hydrogen, nitrogen, and sulfur (CHNS). Concentrations of CHNS in petroleum represent the real characteristics of a feedstock. A range of elemental composition of Alberta bitumen is shown in table 2–2. Heavy oil/bitumen falls in the category of hydrocarbon, because its major components are carbon and hydrogen; it consists of more than 80 wt% carbon and about 10 wt% hydrogen. The atomic ratio of hydrogen to carbon (H/C ratio) is frequently used to indicate the quality and value of a feedstock. The higher the H/C ratio is, the better will be the quality of the hydrocarbons. The H/C ratios of various types of bitumen remain almost constant, within 1.4–1.5, as compared to conventional light crude (1.7–1.8) and asphaltenes (1.2–1.3). There is more hydrogen in the distillate fraction than in the resid fraction.

Also, the content of sulfur and nitrogen plays an important role in how the feedstock should be processed at a refinery. For example, the high sulfur content of bitumen (about 4–6 wt%) poses a major expense in the hydrotreating process. Similarly, the high nitrogen content of bitumen (about 3,000–5,000 ppm) raises a major concern for catalyst activity and environmental emission.

Table 2–2. Expected ranges of elemental and metal composition of Alberta bitumen

Element	Range
Carbon	82.0–83.0 wt%
Hydrogen	10.1–10.2 wt%
Nitrogen	3,000–5,000 ppm
Sulfur	4.5–6.0 wt%
Oxygen	< 1.0 wt%
Vanadium	180–250 ppm
Nickel	60–90 ppm

Almost all heteroatoms and metals found in the bitumen are in the form of cyclic structures, as has been detailed by Speight[1] and Gray.[2] Most of the sulfur is in the form of thiophenes, benzothiophenes, or dibenzothiophenes, although a few are found as normal sulfides or disulfides. There are two major types of nitrogen:

- Pyroles and indoles in the nonbasic forms
- Pyridine and quiniline in the basic forms

Bitumen also contains less than 1 wt% oxygen in the form of cyclic, acidic, or ketonic structures.[3]

Metal content. Bitumen contains a large concentration of various metals, among which nickel and vanadium are present at highest concentrations (table 2–2). Its properties are not well defined or characterized. This is partly because of the lack of analytical techniques or protocols available. Venezuelan extraheavy crude contains almost double the amount of metals as Canadian bitumen does. High concentrations of metals have a detrimental effect on catalyst activity in hydroprocessing.

Distillation. In the oil industry, conventional crude is most frequently characterized by its boiling fractions (table 2–3). The first two refining steps of conventional crude are atmospheric distillation followed by vacuum distillation. By contrast, as shown in figure 2–2, in the case of bitumen, only about 50% of a barrel can be recovered by atmospheric and vacuum distillation combined, and the unrecovered material remains at the bottom of the vacuum tower as resid or residue. The resid fraction starts cracking before distillation at higher temperature, even under high vacuum. This is why not all of the bitumen can be recovered by distillation or characterized by a boiling-point distribution.

Table 2–3. Various fractions of petroleum crude oil

Fraction	Boiling range,[a] °C (°F)	Specific gravity	°API
Light naphtha	C5–90 (195)	0.68	76
Heavy naphtha	90–180 (195–355)	0.76	55
Jet fuel/kerosene	180–240 (355–465)	0.81	43
Diesel	240–320 (465–610)	0.85	35
AGO	320–350 (610–660)	0.92	22
VGO	350–535 (660–1,000)	0.95	17
Resid/residue	535+ (1,000+)	>1.00	<10

[a] Boiling points may vary by laboratory or by refinery.

Bitumen is better characterized into various classes on the basis of different solvent extraction techniques. The two most popular classifications are known by their acronyms:

- SARA (saturates, aromatics, resins, and asphaltenes)
- PONA (paraffins, olefins, naphthenes, and aromatics)

Asphaltenes and Their Role in Bitumen

Asphaltenes are the most poorly defined class of compounds in bitumen but play an important role in characterization and processing. By definition, asphaltenes are in the fraction of the bitumen that is insoluble in normal-paraffin solvent and soluble in benzene or toluene. They are usually named along with the solvent used for their precipitation, because every asphaltene is different in quality and quantity on the basis of the solvent used. For example, n-C_5-asphaletene or n-C_6-asphaltene means that the asphaltene was precipitated using normal pentane or normal hexane, respectively, as solvents. In a commercial process, lower hydrocarbons—such as propane, butane, or a mixture of the two—are used as solvents. Yields of asphaltenes depend on the solvent or mixture of solvents used, their solubility in that solvent, and the bitumen-to-solvent ratio. The term *asphaltene* does not imply any particular molecular structure or molecular weight. Rather, asphaltenes are a group of molecular species, whose exact molecular weight is still unknown and varies from 500 to 15,000 depending on the analytical technique used.

A typical molecular structure of an asphaltene is shown in figure 2–3. Note, however, that the structure can vary greatly.

Asphaltenes comprise a heterogeneous fraction consisting of largely polycondensed aromatic rings and cyclic naphthenes, containing most of the heteroatoms (S, N, and O) and metals of the bitumen. Almost all of the heteroatoms and the metals in the asphaltenes are present in five- or six-member ring structures, in a layer of blocks lying one after another. As the molecular weight of asphaltenes increases, the nonaromatic nature of their structure also increases.

Asphaltene molecules are grouped together in a layer of sheets that are dissolved in the *maltenes* fraction. If either the structure of the asphaltenes is disturbed or the maltenes are partially removed, then the asphaltenes start to agglomerate and settle as solid.

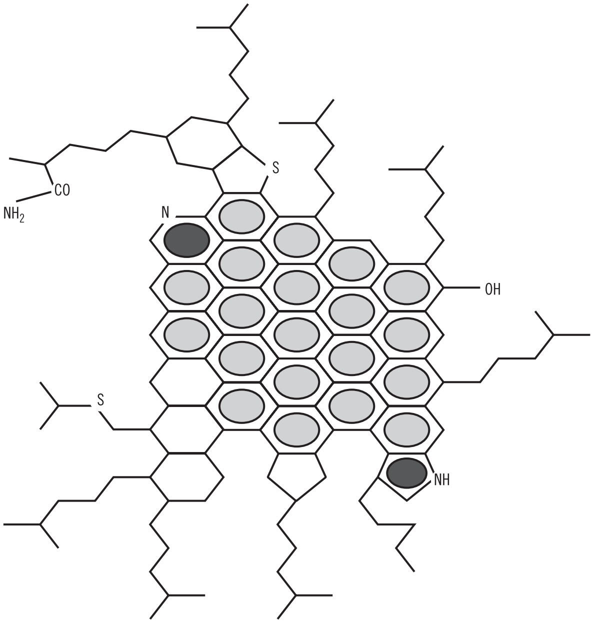

Fig. 2–3. Molecular structure of asphaltene proposed for residue of Venezuelan crude by L. Carbognani (*Source:* Intevep technical report, 1992)

The average asphaltene content in Alberta bitumen varies in the range of 15–20 wt%. It is aromatic in nature, with an average carbon content of about 80–82 wt% and hydrogen content of 8–9 wt%, with an H/C ratio of 1.22–1.24. It also contains about 7.0–8.0 wt% of sulfur and about 1.1–1.5 wt% of nitrogen.

All asphaltenes belong to the resid fraction of the bitumen (fig. 2–2); hence, no part of the asphaltene is distillable below 535°C (1,000°F). The asphaltenes comprise the heaviest part of the heavy oil resid and play a negative role in bitumen recovery, in transportation, and, most important, in the upgrading and refining processes. The concentration of asphaltenes in the resid fraction of the Canadian bitumen is much higher (30–35 wt%) than in the heavy oil resid of Venezuela or Mexico. (For example, Zuata or Cero Negro resid of Venezuela has an asphaltenes content of 15–18 wt%, and that of Mexico's Maya resid is 20–25 wt%.)

Asphaltene plays a threefold role in the fouling process:

- First and foremost, it has the tendency of precipitating out in the presence of lighter paraffinic hydrocarbon fractions, making the crude's mobility restricted. This creates fouling in the production well during the recovery process, as well as in the pipeline during the transportation of bitumen.

- Second, once the structure of the asphaltene is disturbed, the fouling tendency increases (e.g., thermally cracked asphaltenes foul at a higher rate than unprocessed asphaltenes).
- Finally, an increase in asphaltene concentration in the feedstock results in a high rate of fouling on furnace walls.

The high density and high viscosity of bitumen are also attributed to its asphaltene content. Asphaltenes are so complex that no single research group can complete a study or answer all the questions about them. Scientists are still debating the molecular weight of asphaltenes, which can vary from hundreds to millions in some cases. It is still debated whether the physical nature of asphaltenes presents as an aggregate, a colloid, or an association with resins. Asphaltenes are a contentious area among researchers, with long-standing battles still raging.[4]

Asphaltenes are very sensitive to atmospheric oxygen. It has been observed that just the handling of asphaltenes in the atmosphere oxidizes the sample rapidly enough that its characteristics change. Visually, one can observe the asphaltene color change rapidly with the time of exposure, and any chemical properties measured will be influenced by the length of time of exposure to air.

Pre-asphaltenes

A part of the asphaltene mixture is not soluble in toluene or benzene. This part is known as *pre-asphaltenes* or *toluene-insoluble material*. It is usually a carbon-like solid material, but it is not the same as coke, which is similarly defined as the toluene-insoluble material left after thermal cracking of bitumen. Pre-asphaltenes are solid but organic in nature, soluble in carbon disulfide (CS_2) or tetrahydrofuran (THF), whereas coke is a solid carbonaceous material that is insoluble in both CS_2 and THF.

SARA Classification of Bitumen

Bitumen is usually classified based on its four major fractions—namely, saturates, aromatics, resins, and asphaltenes. Together, these are commonly referred to by the acronym SARA.

Originally, the classifications were done by column chromatography, using different adsorbing materials and solvents. Results of SARA analysis of Alberta bitumen extracted by various solvents are shown in figure 2–4.

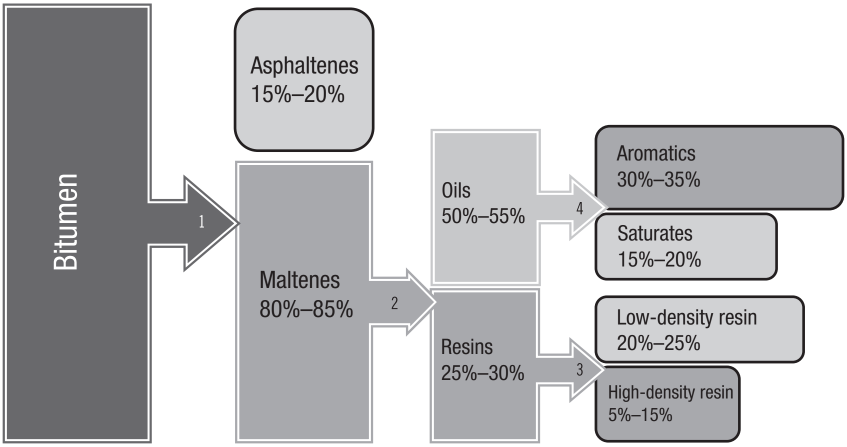

Fig. 2–4. SARA classification of bitumen based on solvent extraction and adsorption chromatography (percentages are weight % of bitumen in the sample) (*Sources:* Research studies by Banerjee et al. CANMET Project Report # 42105109, Ottawa, Ontario, 1985)

The technique used in SARA analysis is based on adsorbing the bitumen or its fractions in a column packed with an activated adsorbent and then eluting a particular fraction with a selective solvent in series. The fractions were then used for further chemical analysis. This will be discussed in further detail in chapter 3.

Asphaltenes

Alberta bitumen contains asphaltenes in the range of 15–20 wt%, depending on the reservoir and the type of solvent used. Asphaltene yield is the highest in case of *n*-pentane (15–18 wt%) and decreases with the increase in molecular weight of the hydrocarbon solvent. As shown in step 1 (fig. 2–4), the bitumen is separated into solid asphaltene, and the soluble portion of the *n*-paraffin solvent is considered as maltene.

Maltenes

The maltene fraction is further separated (step 2 [fig. 2–4]) by a clay-packed chromatography column, using pentane as solvent. The lower-molecular-weight (<800) fraction is eluted out from the maltene as the pentane-soluble portion, considered as oil, and the higher-molecular-weight (>800) fraction is retained in the column and is considered as resins. Almost a quarter of the maltene is resin, with the rest being oil.

Resins

The resin fraction retained in the column in step 2 is further separated in step 3 (fig. 2–4) into low-density and high-density resin fractions. Low-density resin is a dark-colored liquid (yield 75–80 wt% of the total resin), whereas the high-density resin (yield 20–25 wt% of the total resin) is obtained as a dark-colored crystalline semisolid.

Oil—saturates and aromatics

The oil fraction from step 2 is further separated in step 4 (fig. 2–4) into saturated and aromatic fractions. About 25–30 wt% of the oil fraction consists of colorless liquid that represents the saturated fraction, with the rest being the colored aromatic fraction.

Comparison of SARA

Comparative data on SARA fractions between Alberta resid and Venezuelan resid are shown in table 2–4. Variation in the results of the SARA fractions depends on many factors.

As shown in table 2–4, on the one hand, Alberta resid has very low saturates (<2%), has very low aromatic fractions (<8%), and is very rich in resins (>50%). On the other hand, Venezuelan resid is very rich in aromatic fractions (almost 50%) at the expense of lower resin (about 25%) and asphaltenes (15%–18%). Although the differences between the two resids are significant, some of the differences noted above and in table 2–3 can be attributed to the different distillation methods and analytical protocols used by the two separate laboratories and to the boiling-point differences between the two samples. Note that Alberta vacuum resid represents a 525°C+ fraction, whereas Venezuelan vacuum resid represents a 500°C+ fraction. Comparison of the two resids clearly shows that the Venezuelan resid is of much better quality, containing higher concentrations of aromatics and less resin and asphaltenes. Thus, Venezuelan extraheavy oil is easier to recover, transport, and process as compared to Alberta bitumen.

Figure 2–5 represents the trend in the variation of the average molecular weight and density of the SARA fractions. The exact values of molecular weight are very sensitive to the way laboratory work is done—hence, they may vary widely between different samples. The average values for molecular weight were obtained using gel-permeation chromatography (GPC). Results indicate that both the density as well as the molecular weight of the fractions increases in the following order: saturates < aromatics < resins < asphaltenes.

Figure 2–5 illustrates that the average molecular weights of the saturate (200) and aromatic (500) fractions are less than that of the average molecular weight of the whole bitumen (approximately 700). Further, the molecular weight of the saturated molecules is less than half of the molecular weight of the aromatic molecules.

In general, the aromatic structure is denser than the corresponding hydrogenated (saturated) molecular structure. Thus, as expected, the average density of the saturates (about 800 kg/m^3) is less than that of the aromatics (about 900 kg /m^3), and both are less than the average density of the whole bitumen (>1,000 kg/m^3).

Due to the nature of the asphaltenes, which are made of polycondensed layers of aromatic structures, their average molecular weight and density are both expected to be the highest among all fractions. Clearly, asphaltenes comprise the heaviest (average molecular weight above 2,000) and the most dense (density above 1,200 kg/m^3) fraction and are mostly responsible for the increase in mass and density of the whole bitumen. Asphaltenes and resins both have molecular weights and densities higher than the average values of the whole bitumen.

Table 2–4. Comparison of trend of SARA composition of resids in Alberta bitumen and Venezuelan heavy oil

SARA	Alberta 525 C+ Vacuum Resid	Venezuela 500 C+ Vacuum Resid
Saturates, wt%	1–2	5–7
Aromatics, wt%	5–8	45–50
Resins, wt%	50–55	25–28
Asphaltenes, wt%	30–35	15–18

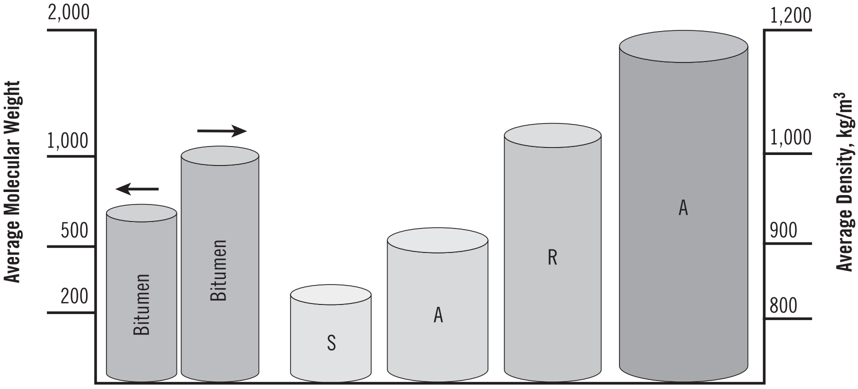

Fig. 2–5. Variation of average molecular weight and density of SARA fractions in bitumen

PONA characterization

Whereas SARA analysis is usually done on the resid fraction or the whole bitumen but not on the distillate fraction, PONA analysis is usually done on the distillate fraction of the bitumen by use of chromatographic techniques such as high-performance liquid chromatography. PONA should not be done on the resid fraction, because it will give erroneous results; thus, PONA analysis on the distillate fraction (350–535°C), and a typical PONA concentration may vary depending on the origin of the sample, as follows:

- Paraffins + olefins, <10 wt%
- Naphthenes, 20–30 wt%
- Aromatics, 60–70 wt%

The aromatic portion of the bitumen is further separated into mono-, di-, and polyaromatic fractions by chromatographic techniques. The concentrations of those subfractions with respect to the total aromatics are usually on the order of 20–25 wt% mono-, 30–35 wt% di-, and more than 50 wt% polyaromatic.

Thus, the above results indicate that the Alberta bitumen is highly aromatic in nature and mostly consists of polycondensed aromatic structures. As the boiling-point ranges of various fractions increase, the molecules become heavier and heavier, the relative concentrations of aromatics increase, and the relative concentrations of saturated hydrocarbons (e.g., naphthenes and paraffins) decrease.

The above results confirm the fact that bitumen is a poor-quality feedstock for the upgraders or refiners because of its large molecular structure, high aromaticity, high deficiency in hydrogen, and high concentrations of metals and heteroatoms. However, the high-aromatic asphaltene bitumen responds better to steam-injected thermal recovery processes than high-paraffinic crude does.

Distillation/Simulated Distillation

In the petroleum industry, fractionation by distillation is the most important single characteristic to evaluate a conventional crude oil feedstock and its processed product. Because not all the fractions are in the liquid phase, it is not possible to distill all of the raw bitumen. The temperature at which bitumen can be distilled depends on the vacuum applied and the maximum temperature that can be attained without cracking the bitumen.

The equivalent atmospheric temperature of distillation under vacuum varies by refinery and by laboratory, from 525°C to 545°C. For simplicity, this book will use 535°C (1,000°F) as the atmospheric equivalent cut-point temperature of the distillate and the residue.

Distillation

In a refinery, the distillate portion is first distilled under atmospheric pressure (i.e., at 760 millimeters of mercury [mm Hg]) in an atmospheric tower (or crude unit) at a temperature of about 350°C (660°F). The portion distilled is AGO, and the undistilled portion is known as *atmospheric residue*. Figure 2–2 shows that the amount of AGO varies in the range of 15–20 vol% in a typical Alberta bitumen. The remaining atmospheric resid is distilled under vacuum, and as the applied vacuum increases, the boiling point decreases. Usually, in a commercial process, the maximum vacuum achieved is below 1 mm Hg, which lowers the boiling point to about 325°C without cracking the resid. The equivalent atmospheric temperature attained is 525–545°C, depending on the vacuum applied. Bitumen usually contains about 35–40 vol% VGO. So, the total distillable amount (i.e., AGO + VGO) in the bitumen varies in the range of 50–55 vol%.

Simulated distillation

In a laboratory, gas chromatography (GC) is used as a quick method of determining the boiling-point distribution of a bitumen sample, on a micro scale, using an analytical technique widely known as simulated distillation (SimDist). The latest improvement in SimDist can achieve a recovery temperature as high as 650–700°C (1,200–1,300°F) in a high-temperature SimDist (HTSD) gas chromatograph.

The basic principal of GC is that a known amount of a crude sample, diluted in a solvent, is injected into the GC column, and then the column temperature is raised gradually, at a known rate. As the temperature of the column increases, a part of the hydrocarbon of the crude gradually vaporizes and elutes out of the GC column into the detector. Then, the GC detector records the amount of hydrocarbon vaporized at a particular time of elution, based on the corresponding column temperature. Elution time is also known as *retention time* and is calibrated against the boiling point of *n*-paraffin hydrocarbons. Hence, as shown in figure 2–6, SimDist is plotted as a weight percentage of the sample eluted against the corresponding boiling-point equivalent of *n*-paraffins. Heavy oil or bitumen samples contain mostly aromatics and do not elute at the same rate as do the *n*-paraffins because their boiling points do not necessarily fall within the range of the boiling points of the corresponding *n*-paraffins. Hence, determination of the correct boiling-point distribution of the hydrocarbons in bitumen by the SimDist method requires proper calibration and use of a correction factor for highly aromatic heavy oil or bitumen samples.

Once the GC column attains the maximum permissible temperature, the amount of sample eluted through the column is determined. By back-calculation on the basis of the amount of sample injected into the GC column and the amount eluted through the column at a given maximum temperature, the amount retained by the column is theoretically calculated. The amount retained inside the column represents the resid fraction present in the bitumen sample that corresponds to that temperature.

A chief advantage of the SimDist method is that one can determine much higher distillable temperatures than could be achieved using a commercial process. Another advantage is that, because of the availability of highly improved computer software, the SimDist curve can be sliced to any desirable temperature as needed and divided into various hypothetical boiling range fractions, without actually distilling the crude.

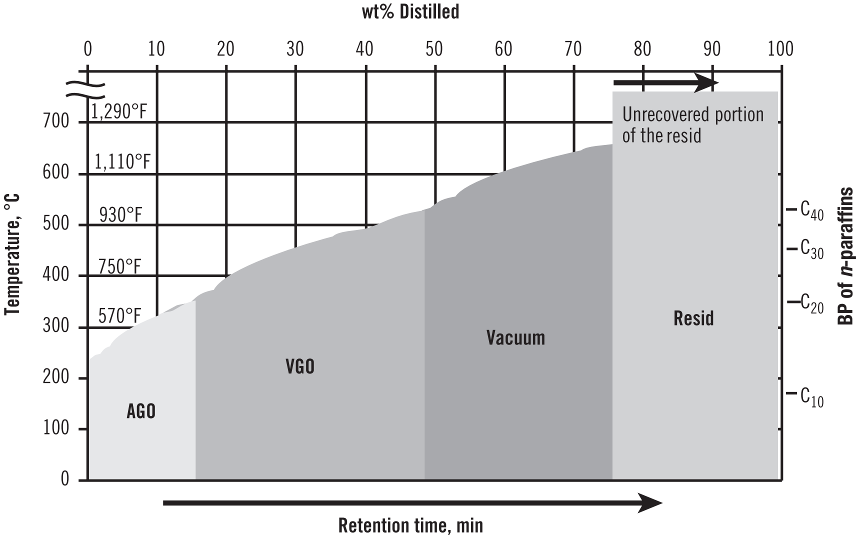

Fig. 2–6. Typical example of HTSD of whole bitumen. BP = boiling point.

An HTSD graph of a typical Alberta bitumen is shown in figure 2–6. The curve shows boiling-point distribution characteristics (e.g., the amount distilled off at a particular temperature). Analysis of the SimDist curve for this particular bitumen feedstock is done as follows, by dividing it into several fractions/groups:

- First, the portion that is distillable below 350°C (i.e., AGO) is considered. The amount of AGO in the bitumen sample is 15 wt%.
- Next to be considered is the portion that can be distilled under vacuum (i.e., VGO), equivalent to atmospheric boiling-point range of 350–535°C. The amount of VGO (350–535°C) yield from the curve is 33 wt%.
- Hence, the total amount of distillable fraction (i.e., AGO + VGO) present in the bitumen is 48 wt%.
- Thus, the resid fraction (535°C+) in the bitumen, which is not distillable below 535°C, is 52 wt%.
- Even though it is not commercially possible to distill any crude up to 660°C (as fig. 2–6 shows), HTSD could recover 75 wt% of the bitumen hydrocarbons at 660°C. In other words, 75 wt% of the bitumen is distillable below 660°C.
- Hence, the 25 wt% of the bitumen that was not recovered by the HTSD at 660°C is defined as the resid, which boils above 660°C.

Hence, two types of resids are reported here from the same SimDist curve—namely:

- Resid of 535°C+ (1,000°F+), which is 52 wt% of the bitumen
- Resid of 660°C+ (1,220°F+), which is 25 wt% of the bitumen

Figure 2–6 also shows that the 535°C+ resid fraction contains carbon structures that are equivalent to more than C_{40} hydrocarbons. The vacuum gas oil (350–535°C) fraction consists of hydrocarbons approximately in the range of C_{20}–C_{40}. The AGO fraction (<350°C) consists of hydrocarbons below C_{20}.

Resid/Residue/Residuum

Resid is a term widely used as a truncated form of residue or residuum. It is the portion of the bitumen that remains after vacuum distillation. It usually refers to the fraction that remains after vacuum distillation by using a cut point at the equivalent temperature at atmospheric pressure around 525–575°C (950–1,300°F), depending on the method of distillation used. In a given barrel of bitumen, about half of it is 535°C+ (1,000°F+) resid (fig. 2–2); this is the most difficult fraction to handle, both for transportation and for processing, because most of the heteroatoms, most of the metals, and all of the asphaltenes are concentrated into the resid fraction.

The term *atmospheric residue* is used for the portion that remains after atmospheric distillation of bitumen. This terminology can lead to confusion, because the atmospheric residue is also equivalent to any blend of vacuum residue and VGO. For example, one can vary the residue content to a low value by blending with VGO and still call it an atmospheric residue, even though during atmospheric distillation one would not find such a blend.

Importantly, multiple terminologies are used for resid. Resid is also referred to as *residuum*, *residue*, *vacuum bottoms*, or *topped bitumen*. Use of so many names interchangeably should be avoided, because it can confuse newcomers to the heavy oil industries. This is currently an issue because of the heavy oil industry's novelty—that is, simultaneous discoveries (sometimes countries apart) and a lack of information sharing have prevented the establishment of a uniform terminology. Either *resid* or *residue* should be strictly used for the unprocessed resid fraction of the crude heavy oil or bitumen. Once processed, the resid is either called *pitch*, when processed thermally, or *asphalt*, when processed by solvent extraction; thus, even though many people wrongly use these terms to refer to resid, pitch and asphalt have discrete meanings.

Comparison of resid versus distillate

The amount of resid content in a sample of bitumen and the detailed characteristics of the resid are of great importance to the heavy oil industry. This is because they serve as a basis for the choice of upgrading process and operating conditions, discussed in detail in chapters 7 and 8.

As shown in figure 2–7, Alberta bitumen contains 45–50 wt% of the amount distillable below 535°C and 50–55 wt% vacuum resid, boiling above 535°C (1,000°F). The distillate portion is further divided into two fractions: the yields of AGO are 10–15 wt% and those of VGO are 30–35 wt% of the whole bitumen.

Comparison of asphalt and de-asphalted oil

The quality of the resid fraction plays an important role in bitumen processing. Thus, a further classification of the resid after distillation is shown in figure 2–7.

The resid is further subjected to de-asphalting by use of *n*-paraffin as a solvent. The purpose is to prepare feedstock for future processing. Yields and properties of the asphalt and the de-asphalted oil (DAO) depend on the solvent and process conditions used. The resid contains about 45–50 wt% of asphalt, and the remaining 50–55 wt% is DAO. These data are valuable for the evaluation of resid upgrading processes.

This asphalt can be used in the road construction industry. Asphalt could be also used as fuel, but it would cause serious emission problems. It could, however, be used as a good source of feedstock for gasification or coking. DAO can be prepared as feedstock either for the catcracking unit or for hydrocracking unit. DAO is also a good blendstock for VGO.

Bitumen, as well as the resid properties, is characterized by the concentrations of S, N, metals, CCR, and asphaltenes. The higher the concentrations are of any of the above materials, the lower will be the quality of the bitumen. Figure 2–8 shows the distribution of the heteroatoms, metals, and CCR in the resid and the distillate as compared to the whole bitumen.

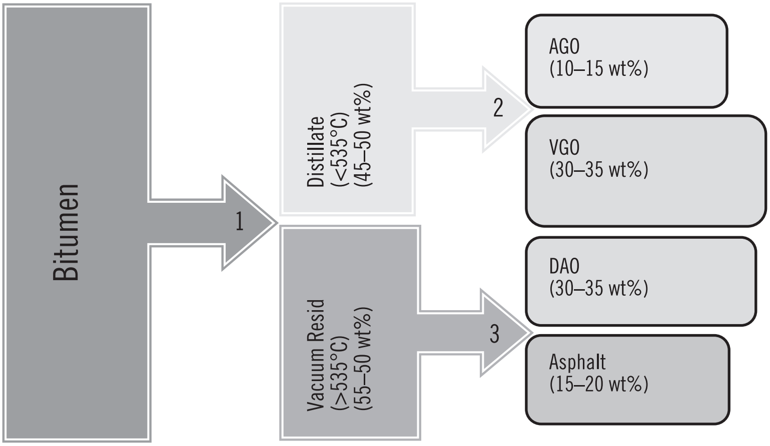

Fig. 2–7. Classification of Alberta bitumen based on distillation and solvent extraction (based on wt% of the bitumen sample)

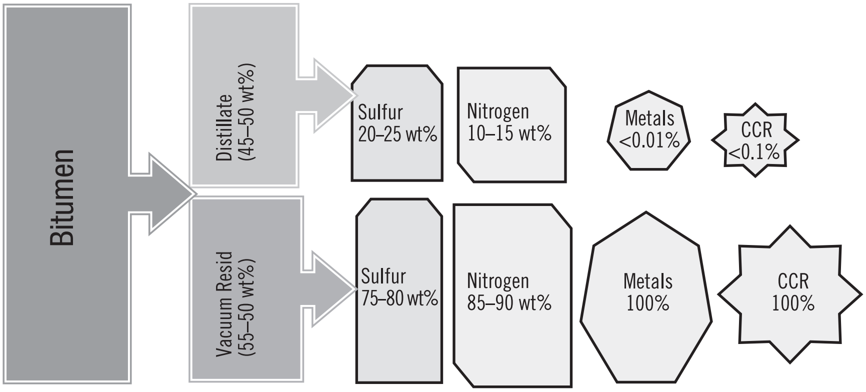

Fig. 2–8. Relative concentrations of S, N, metals, and CCR in resid and distillate (based on wt% of the respective components in bitumen)

Results show that 75–80 wt% of the sulfur and 85–90 wt% of the nitrogen present in the bitumen are actually present in the resid fraction. All 100% of the metals and CCR present in the bitumen come from the resid itself. Hence, if the resid is removed from the bitumen, then more than 75% of the detrimental effects (for details, see the discussion of upgrading, in chap. 7) of the processing of bitumen will be removed. However, if we don’t use the resid at all, then we will lose 50% of the crude, which is still commercially usable.

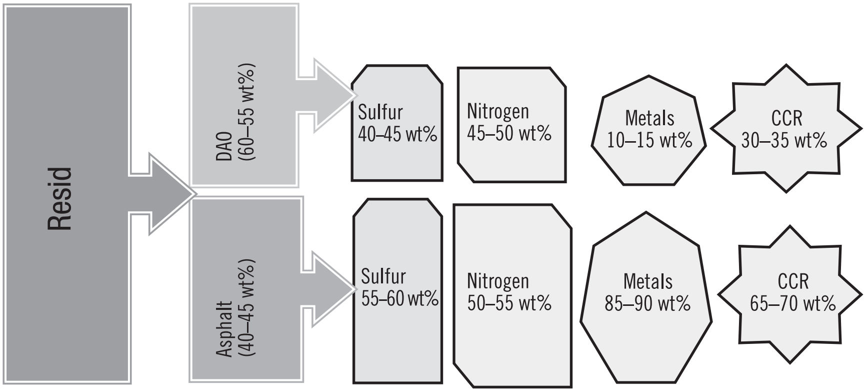

Fig. 2–9. Relative concentrations of S, N, metals, and CCR in asphalt and DAOs of the resid (based on wt% of the respective components in the resid)

Figure 2–9 compares the distribution of heteroatoms, metals, and CCR in the asphalt with that of the DAO. The concentrations of heteroatoms, metals, and CCR are higher in the asphalt fraction as compared to the DAO. Asphalt contains just over 50% of the sulfur and nitrogen of the resid, but it consists of about 90% of the resid metals and about 70% of the resid CCR. Thus, if the asphalt is rejected before processing of the resid in a refinery, especially in a catalytic process, then the cause of the deactivation of the catalyst will be considerably reduced; this is because the CCR and metals are the main cause of the process upset.

Metals

Various types of metals are found in the bitumen, all of which are located in the resid fraction. The concentration of vanadium is always highest of all the metals present in the bitumen and is almost double that of the nickel (tables 2–1 and 2–2). Most of the nickel and vanadium are present in the form of organometallic complexes, with a cyclic aromatic structure attached through nitrogen bonds; these are commonly known as *porphyrins*.[5]

Figure 2–10 represents a typical porphyrin structure where vanadium is bonded with nitrogen, enclosed in a five-member ring (i.e., as a pyrrole). Nonporphyrin metals are mostly present in the asphaltene fraction. The stability of vanadium-porphyrin is greater than that of the nickel-porphyrin.

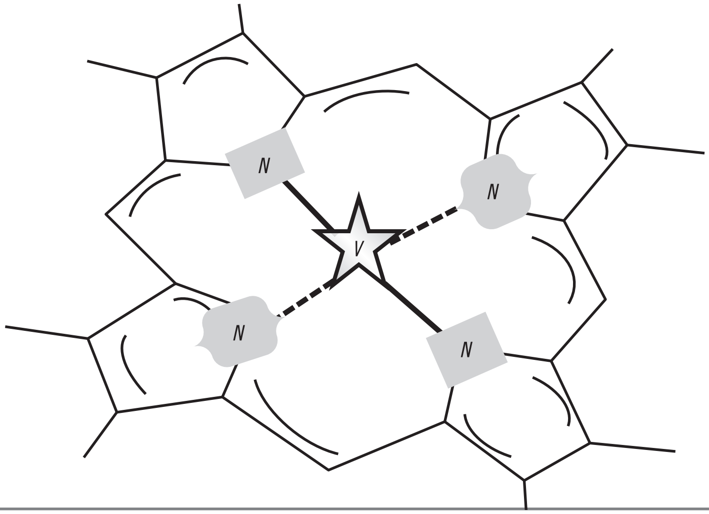

Fig. 2–10. Example of a proposed vanadium-porphyrin ring structure in bitumen

Calcium, potassium, sodium, iron, and silica are also present in the bitumen as water-soluble salts. These are easy to remove compared to the porphyrin groups.

All metals are undesirable components of bitumen. They are detrimental to the catalytic processes and cause catalyst deactivation and corrosion.

Oxygen and TAN

The oxygen content in bitumen is usually less than 1 wt%, but some higher concentration numbers can be seen, usually caused by the atmospheric oxidation of the asphaltenes during handling. Oxygen in the crude is mostly responsible for the acidity of the crude, because most of the oxygen is present as carboxylic group. The acid functional group of crude oil is also known as *naphthenic acid*, although they are mostly present in aromatic (ring) or aliphatic (chain) structures. Acidity of any crude is measured in terms of TAN value (total acid number), also known as the *basicity number*, originating from the type and amount of base used for titration. (TAN is expressed in units of milligrams KOH per gram sample; see also chap. 3.) The higher the TAN value is, the higher will be the sample's acidity. Bitumen falls in the category of high-acid (TAN >1) crude because its TAN value is mostly above 2.0. The market value or demand of a crude oil decreases with the increase in TAN value because of its highly corrosive behavior. Other oxygenated compounds in the bitumen are present as phenolic functional groups. Note that, unlike sulfur and nitrogen, almost all of the oxygen in the bitumen is present in the VGO fraction and not in the heavier resid fraction.

CCR

One of the major properties that is commonly used for thermal or catalytic processing of heavy crude and bitumen is the carbon residue, or CCR value. (The full name *Conradson carbon residue* comes from the designer of the particular laboratory analytical technique used for the measurement of CCR discussed below.) Almost all of the CCR in the bitumen is present in the resid fraction of the heavy crude (figs. 2–8 and 2–9), and the CCR measurement is usually done on either the resid fraction or the whole bitumen but not on the distillate fraction.

The CCR value indicates the propensity of the feedstock to form coke during a thermal process. The CCR number may vary from 15 wt% to 25 wt% depending on the origin of the bitumen. The CCR value can be used to predict the amount of coke formation in a delayed-coker operation. As a rule of thumb, the amount of coke yielded in a delayed-coking process is about 1.5 times that of the CCR number. However, this method should not be used to estimate the actual coke yield in a commercial delayed-coker operation, as several other factors—such as aromaticity, sulfur content, and metal content—also influence coke yield. The CCR value also indicates the tendency of a feedstock to foul on the surface of a furnace.

The value of CCR represents a particular analytical technique (American Standard Test Methods [ASTM] D-189) used for the measurement of the carbon residue. There are two other major analytical techniques used for the measurement of carbon residue, namely *Ramsbottom carbon residue* (ASTM D-524) and *microcarbon residue* (ASTM D-4530). The values of each technique are not interchangeable; thus, before using any data on carbon residue determination, readers should find out which technique was used.

Molecular Weight

The measurement of the true molecular weight of heavy oil or bitumen is difficult. In particular, the nondistillable residues and asphaltene aggregates are the most difficult to measure. Results are strongly dependent on the types of solvent used, their polarity, and their solubility; the presence of contaminants also affects the results. If molecular weight is desired, then it is recommended not to measure the molecular weight of the whole bitumen or heavier fractions together, but rather to measure the distribution of molecular weight over a wide range of fractions, as may be obtained by using gel permeation chromatography (GPC) or size-exclusion chromatography. For more details, readers may consult an excellent review on molecular weight of heavy crudes by Altgelt and Boduszynski.[6]

Challenges Facing Bitumen Characterization

Because bitumen is a semisolid at normal conditions, it is hard to handle—and even more difficult to sample properly for analysis. When steam is used during production, bitumen forms emulsions with the water that are extremely difficult to break. Therefore, sampling of bitumen is a great challenge, and a reservoir core sample or live sample is extremely difficult to obtain. Every step of the handling of a sample changes the composition if proper protocols are not followed; a great deal of experience is required in order to handle the bitumen. Protocols may vary between laboratories; moreover, data interpretation varies depending on the experience of the scientists/engineers.

Some engineers and scientists use computer-modeling techniques widely applicable for lower-molecular-weight conventional oil to predict the properties of the heavy oil or bitumen. However, because of the complexity of the bitumen molecules, often these models fail to make correct predictions. For example, simply molecular weight, viscosity, or density of bitumen (and especially of a blend) cannot be predicted correctly even today with computer models. Hence, there is no guarantee that the predicted values based on those models will be the same as the real values.

Figure 2–11 summarizes the trend in the variation of major properties of crude oil as a function of API gravity. With the increase in the API gravity of a crude oil (decrease in density/specific gravity), the viscosity of the crude decreases exponentially—from a million for a very heavy unconventional crude (API <10°) to below 100 mPa·s for a very light conventional crude (API >40°). The concentrations of heteroatoms and metals increase as the crudes get heavier, and the value of a crude oil decreases at the same rate. Bitumen, which falls in the low-API range (<10°), has high sulfur (>5 wt%), nitrogen (>5,000 ppm), and metal (>1,000 ppm) contents. Similarly, asphaltenes and CCR contents increase (>15 wt%) with the decrease in API gravity (<10°) of the crude, and the values decrease to almost zero with the increase in API gravity above 40°.

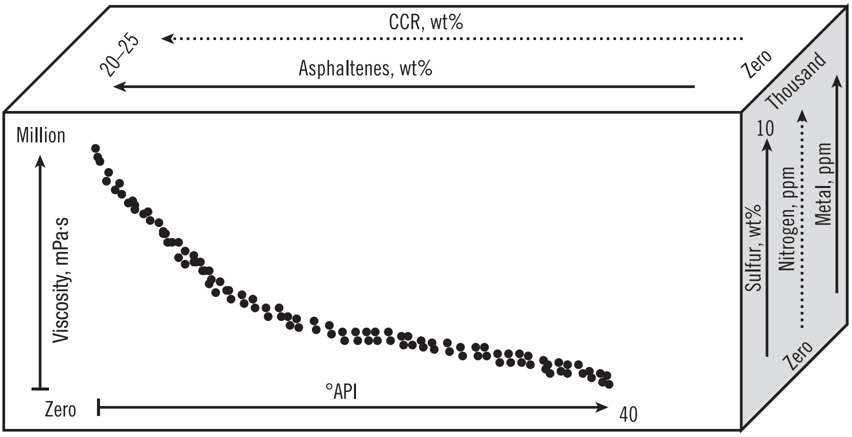

Fig. 2–11. Trend in variation of average values of various properties of crude oil with API gravity

For example, one could predict that light conventional crude of API gravity greater than 40° would contain almost no asphaltene or CCR and almost no metals. The same crude is expected to have a very low amount of sulfur (<1 wt%) and nitrogen (<100 ppm), although the values depend on the origin of the crude. However, the properties of synthetic crude oil will highly depend on the history of the processing conditions.

References

1 Speight, J. G. 2000. *The Desulfurization of Heavy Oils and Residue*. 2nd ed. New York: Marcel Dekker, pp. 98–100.

2 Gray, M. R. 1994. *Upgrading Petroleum Residues and Heavy Oils*. New York: Marcel Dekker, pp. 16–22.

3 Ibid.

4 Mullins, O. C., E. Y. Sheu, A. Hammami, and A. G. Marshall, eds. 2006. *Asphaltenes, Heavy Oils, and Petroleomics*. New York: Springer Verlag; Strausz, O. P., and E. M. Lown. 2003. *The Chemistry of Alberta Oil Sands, Bitumen, and Heavy Oils*. Calgary, AB: Alberta Energy Research Institute publication.

5 Speight, 2000.

6 Altgelt, K. H., and M. M. Boduszynski. 1994. Chap. 4, Properties of heavy petroleum fractions, in *Composition and Analysis of Heavy Petroleum Fractions*. New York: Marcel Dekker.

ANALYTICAL TECHNIQUES

3

Importantly the introduction of heavy oil brings changes to petroleum laboratories. The methods familiar to analytical chemists for conventional oils may not be applicable to unconventional crudes. For example, the most important characteristics—such as very low API gravity (<10°), high viscosity (>10,000 cP) at normal conditions, and much higher sulfur (>5 wt%) concentrations in bitumen—cannot be analyzed using the same protocols as have been used for the conventional crudes or refinery products.

The major problem with heavy oil/bitumen is the handling of the sample, because of its high viscosity and water content. Water makes such a strong emulsion with bitumen that it is hard to break. Complete dehydration of the sample for analytical purposes is a problem, and the composition of the bitumen sample is altered during the process.

Similarly, the possibility of mishandling the sample occurs in the laboratory while subsampling at higher temperatures to make the heavy oil/bitumen mobile. Thus sampling at different temperature conditions at various stages could result in phase separation, resulting in a completely nonrepresentative sample.

Hence, the reliability of the data is dependent on sampling technique, in addition to analytical technique. Analytical work should initially be limited on the basis of the demands of the data, to allow reliable interpretation; ultimately, commercial evaluation may require the use of a much more detailed assay. Thus, it is necessary to develop a simple and accurate method of analysis that enables the user to assess the feedstock or product qualities and to evaluate the process—not only to decrease the analytical cost but also to obtain reliable analytical data.

This chapter discusses most of the important properties and the analytical methods used to create a simple assay database. So that analytical chemists consult the standard test specifications and use the right laboratory equipment for a particular analysis, exact details of the analytical procedures are avoided here; for simplicity, ASTM protocol numbers are cited here (for summary, see table 3–1), and analytical chemists are referred to those protocols for a more detailed discussion.

Nonanalytical chemists or engineers may refer to those ASTM numbers when requesting a sample analysis or when comparing among the assay database from different laboratories.

Especially for researchers, the easiest way to handle and characterize bitumen samples is by carrying out a minimum number of analyses, listed in table 3–1, and comparing the data and properties. In general, these data are sufficient for the initial evaluation of various feedstocks or their derived products. For bitumen-upgraded synthetic crude products, which can be handled the same as any conventional crude, commercially established analytical methods for conventional crude can be used.

Table 3–1. Recommended initial analytical test runs for raw bitumen

Property	Units	ASTM protocol #	Note
Density	kg/m^3	D-5002	
Specific gravity @ 60/60°F		D-1298	
API	Degree API	D-287/D-5002	Calculated from specific gravity
Viscosity/Kinematic viscosity	mPa·s/cSt/cP	D-445	Maximum at three temperatures
Simulated Distillation/HTSD		D-2887/D-7169	Also available high temp SimDist
Resid (1,000°F+)	wt%/vol%		Calculate (recovery temperature may be changed as needed)
Sulfur	wt%	D-129*/D-4294**	*Bomb method (old method); **X-ray technique (new method)
Nitrogen/Basic N	ppm	D-4629/UOP 269	Basic N is usually less than half of total N
Asphaltene	wt%	D-4055/IP-143/D-6560	Report the solvent used
CCR	wt%	D-189/D-4530	Report the technique used
Total acid number (TAN)	mg KOH/g sample	D-664	
Vanadium/Nickel/Iron/ Calcium/Total metal	ppm	D-3605/D-5185	AA/ICAP technique for inorganic ash
Carbon/Hydrogen	wt%	D3178/D-5291	Combustion technique used for coal/coke
Fractional distillation/vacuum distillation for detailed assay	wt%	D-2892/D-1160	
Water % sediment BS&W content	wt%	D-4007	

In addition to collection of the above data, several other analyses need to be performed to evaluate or optimize a process condition. Examples of these other analytical processes are given in table 3–2. Not all properties are mentioned because the purpose here is to note only some of the important analyses regularly done to characterize a feedstock and its derived products.

For detailed assays, fractionation of the feedstock and product need to be done in the laboratory. The distillates are split into categories based on their various boiling-point ranges, such as naphtha, kero, diesel, light gas oil, and heavy gas oil. Not all analyses are done on all fractions; rather, analysis is done selectively on the basis of the relevant need for, importance and reliability of, and ability to interpret the data. The following section describes the significance of certain important properties as they relate to the analytical techniques used to characterize the feed and product samples.

Table 3–2. Suggested properties for the second set of analysis for feed and upgraded products

Property	Comments
Atmospheric distillation	To collect the atmospheric gas oil for further analysis.
Vacuum distillation	To collect the vacuum gas oil and resid for further analysis.
Detailed types of sulfur	To determine S distribution in various fractions by GC.
Basic nitrogen	Types of nitrogen distribution.
Toluene insoluble	Amount of solid in the crude.
PONA	ASTM D-3239/D-2549/D-2786; this is done only on distillate fraction.
SARA	ASTM D-2007; column chromatography done on resid fraction or whole bitumen
Ash content	ASTM D-482.
Watson/UOP factor Kw	This is a calculated value to characterize aromatic/paraffinic crude.
Aniline point	ASTM D-611.
Pour point	ASTM D-6749.
Bromine number	ASTM D-1159; on distillate only.
Viscosity calculation at different temperatures	ASTM D-341; calculation from a viscosity-temperature graph.
Salt content (NaCl)	This is important before processing of heavy crude, expressed as lb NaCl/1,000 bbl; if >10, considered high salt crude.

Density and API Gravity

Density is an important factor for the petroleum industry because the crude oil and its refined products are sold by volume, rather than by weight. The standard method for measuring density in the oil industry is *specific gravity* at 60/60°F (15.6/15.6°C). Because the density or specific gravity scale covers an extremely narrow range for a wide variety of crude oils with various properties, the American Petroleum Institute (API) adopted a wider scale, expressed in *degrees API*, defined as follows:

$$°\text{API} = \frac{141.5}{\text{specific gravity @ 60/60°F}} - 131.5 \qquad \textbf{(3–1)}$$

In this scale, API gravity varies widely—from 50–60° for condensates, 30–50° for lighter crudes, 20–30° for medium crude, 10–20° for conventional heavy crude, below 10° for unconventional (extra-) heavy crude/bitumen, to below 5° for vacuum resid.

API gravity is an inverse scale of specific gravity. The API value of petroleum hydrocarbons decreases with the increase in specific gravity and increase in aromaticity.

In a laboratory, the specific gravity of bitumen is usually measured by a standard method (see table 3–1), using a pycnometer, at a temperature of 60°F. Then, the corresponding API value is calculated using equation 3–1.

The API value of water is 10°, and that of bitumen is below 10°, meaning it is heavier than the water. The API value of extraheavy oil is also below 10°; thus, it is also heavier than the water. That explains why bitumen is situated below the water table inside the reservoir. By contrast, the API value of conventional heavy oil is of above 10° and is lighter than the water.

The API value of bitumen is slightly higher than that of water at a temperature above 130°C (265°F).[1] This is an important property of bitumen that happens because of a swelling effect at higher temperature (i.e., volume increases as temperature increases); hence, bitumen becomes lighter than water at that temperature and floats above the water, facilitating the hot-water extraction process of oil sands (discussed in chap. 5).

Viscosity

After density, viscosity is the next most important characteristic of bitumen, because it plays a major role in the production of bitumen from the subsurface reservoirs and its subsequent transportation through the pipeline to a refinery. Viscosity is the primary fluid property targeted by the heavy oil recovery process. As discussed in chapter 1, alongside our original definition of bitumen, heavy oil and bitumen may be classified more accurately on the basis of viscosity, rather than API gravity.

The most commonly used units for viscosity are *centipoise* (cP) and, for kinematic viscosity, *centistokes* (cSt), which is defined as the viscosity, in cP, divided by the specific gravity. In the metric system, viscosity is represented by the units of millipascal-seconds (mPa·s).

It is much easier to measure the viscosity of conventional crude oil as it flows at normal temperatures. However, because bitumen does not flow at normal conditions, its viscosity measurement is complicated. Because viscosity is highly dependent on temperature, the viscosity of bitumen can be measured at higher temperatures (>40°C), where it flows by itself. The capillary viscometer method (ASTM D-445), used for the measurements of the viscosity of conventional crude at normal conditions, cannot be used for bitumen, especially at normal temperatures.

Because there is a need to measure the viscosity of bitumen at room temperature, special viscosity measurement techniques were developed for highly viscous liquid—for example, using bob-and-cup and cone-and-plate viscometers. Details of these techniques are given in an excellent review article on viscosity by Seyer and Gyte.[2] In these techniques, the viscosity of bitumen at normal temperatures is measured on the basis of *shear* effects, rather than conventional *flow* effects. Because bitumen is almost solid at room temperature, this technique is suitable at lower temperatures. This technique has its own limitations because the temperature of the system rises as a consequence of the frictional effect. Hence, exact experimental temperature for the viscosity measurement cannot be determined accurately. Because the value of the viscosity of bitumen is high, error induced in its measurement is also high; therefore, great care is needed in viscosity measurement.

Figures 3–1 and 3–2 are adapted from the curves presented by Seyer and Gyte.[3] Only some of their data are used, to reduce the level of detail for simplicity's sake.

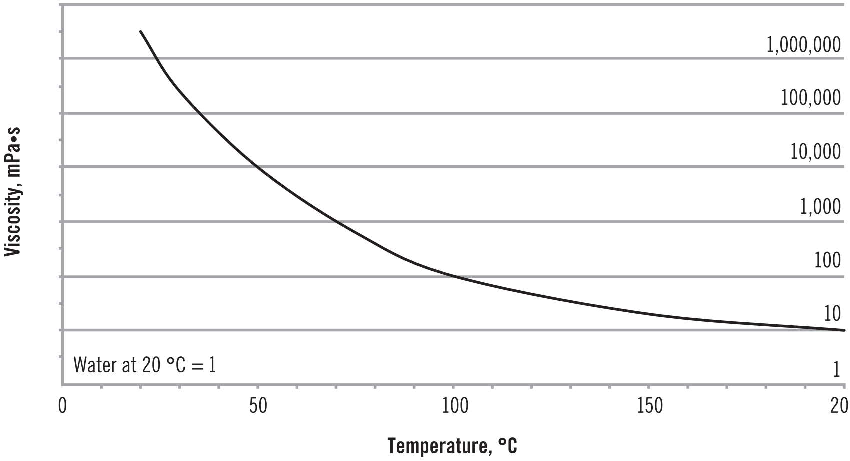

Fig. 3–1. Typical variation of viscosity of bitumen with temperature

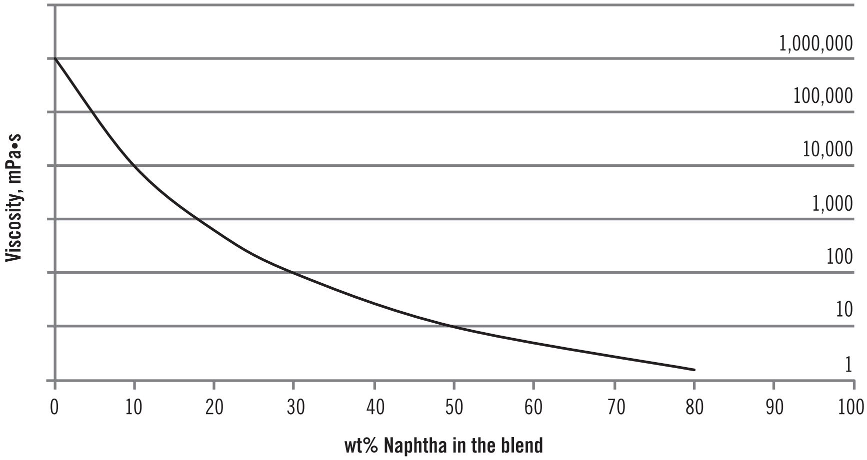

Fig. 3–2. Typical variation of viscosity of bitumen blend with the addition of naphtha diluent at 20°C

Viscosity versus temperature

Figure 3–1 presents a graph of the variation of viscosity with temperature for Athabasca bitumen. Viscosity is exquisitely sensitive to temperature, decreasing exponentially—from a value of 1 million at room temperature to below 100 mPa·s at 100°C.

Over the years, attempts have been made to predict the viscosities of bitumen at different temperatures. The first basic equation to predict the viscosity was developed by Walther and was presented at the 1937 World Petroleum Congress:

$$\ln\ln(\gamma + 0.7) = m\ln T + b \tag{3–2}$$

where γ is the kinematic viscosity (in cSt), T is the absolute temperature (273 + °C), and m and b are constants for a particular oil. Equation 3–2 permits a straight-line plot of kinematic viscosity versus temperature within a certain temperature range. The values of the constants are determined from known viscosities at known temperatures, and then viscosity at an unknown temperature is calculated. However, the values of the constants in equation 3–2 have been modified by different researchers to predict the viscosity more accurately.

If kinematic viscosities of any liquid hydrocarbons at two temperatures are available, then the kinematic viscosity at any other temperature (within a limited range) can be determined from a standard chart (see ASTM D-341).

Viscosity versus diluent

The viscosity of bitumen also varies with its dilution. Figure 3–2 shows that the blending of bitumen with a very light hydrocarbon, such as naphtha, will decrease the viscosity exponentially, similar to the case of decrease in temperature. The addition of only 10 wt% naphtha decreases the viscosity from 1 million to 10,000 millipascal-seconds, and the addition of a further 10 wt% (i.e., total 20 wt%) naphtha causes the viscosity to go down below 1,000 millipascal-seconds, making it mobile. This is one of the reasons why lighter hydrocarbons, such as naphtha or condensates, are used as diluent to transport bitumen through pipelines (discussed in chap. 6).

Furthermore, there is a need to predict the viscosity of a blend, and several equations serve that purpose. However, the most commonly used method to predict the viscosity of crude blends is ASTM D-341, along with the Rafutas index method. The blending index is given as follows:

$$I = f(\gamma) = 23.097 + 33.468 \log\log(\gamma + 0.8) \tag{3–3}$$

where I is the Refutas index and γ is the kinematic viscosity. In this method, the viscosity of each hydrocarbon component in the blend is determined first, and then the Refutas index of the blend is calculated as follows:

$$I_\beta = \sum_{i}^{n} I_i W_i \tag{3–4}$$

where I_i is the Refutas index and W_i is the weight fraction of the component i. Kinematic viscosity γ of a blend is calculated from equation 3–3 once the Refutas index value I_β of the blend is known from equation 3–4.

Readers are cautioned to use data derived from these equations carefully, because they are not valid over a wide range of temperatures or diluents. Also note that some researchers in different laboratories modify the values of the constants to meet their expected results. There is almost always a deviation between the predicted value and the real value (because models based on ideal cases will differ from reality).

The viscosity of a blend is strongly dependent on the molecular weight of the diluent used.[4] For example, the higher the molecular weight is of a diluent (e.g., methane [16], ethane [30], or toluene [92]), the higher will be the amount of the diluent required in order to meet the same viscosity at the same conditions.

Viscosity of visbroken liquid

Banerjee et al. have carried out viscosity measurements of a bitumen feedstock and its mildly thermally cracked visbroken product samples by using shear techniques in coaxial cylinders.[5] Bitumen samples were placed between two cylinders, and torque was applied at various shear rates, measuring stress at a constant temperature. Viscosity was calculated as the ratio between stress and shear rate.[6]

In the same study, it was observed that the viscosity of a visbroken product was quite sensitive to air exposure. Viscosity was significantly lowered, by about 50%, when oxygen was excluded from the reaction system. With no particular explanation, visbreaking of Athabasca bitumen was found to be more sensitive to oxygen than that of the Cold Lake bitumen.[7]

Asphaltene Analysis

The asphaltene fraction of bitumen is separated either from the resid or from the whole bitumen by precipitation using a normal paraffin as a solvent. It is purely a physical separation, with no resultant chemical change in the structure of asphaltene. In a laboratory setup, asphaltene is separated by adding almost 40 times its volume of *n*-pentane, *n*-hexane, or *n*-heptane. The mixture is agitated for an hour in an ultrasonic bath at constant temperature; then, after the mixture is filtered, the solid material is dried and collected as asphaltenes.

Commercially, by contrast, lower hydrocarbons—such as propane, butane, or a mixture of both—are used. Yields of asphaltenes are dependent not only on the type of solvent used but also on the length of time the feedstock is kept in contact with the solvent.

Several standard ASTM methods (e.g., D-2006, D-2007, D-4124, or IP -143) are used to determine the quantity of asphaltenes by use of various solvents. Readers should refer to those methods for more details.

SARA Analysis

Classification of bitumen into its four major groups, SARA (saturates, aromatics, resins, and asphaltenes), is done by several methods.[8] With the development of new analytical techniques, now it is done either by high-performance liquid chromatography or on a micro scale more popularly by TLC-FID (thin-layer chromatography with flame ionization detector), using an Iatroscan instrument. By contrast PONA analysis (see chap. 2) is done strictly on distillate fractions by chromatographic and mass-spectroscopic techniques per ASTM D-3239, D-2549, or D-2786.

Figure 3–3 represents the various steps involved in SARA analysis of bitumen on the basis of combined solubility and adsorption characteristics in a chromatography column.[9] The sample is recovered by evaporating the solvent in a rotator evaporator. The amount of solvent required in order to elute any sample is directly related to the amount of sample retained in the column. However, the amount of solvent required can be visually estimated by noticing the change in color of the solvent as soon as all the desired sample is recovered. Note that, in this method, the resin is further separated into two fractions—namely, high-density and low-density resin. It is strongly recommended that this procedure be done only under proper protection in the laboratory, using a fume hood, because the solvents are toxic.

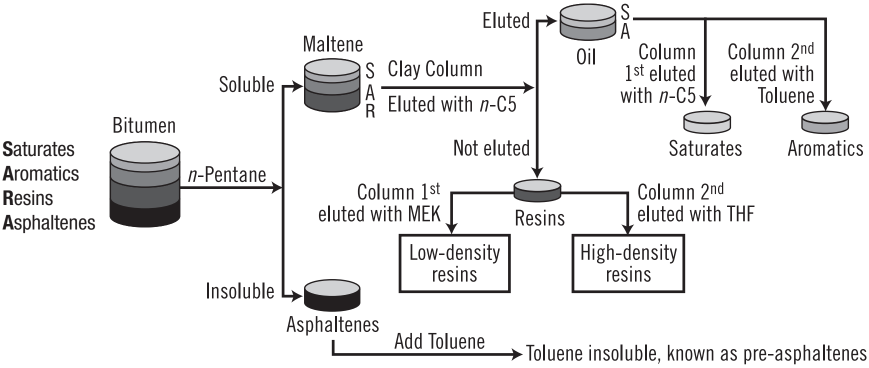

Fig. 3–3. Quantitative and preparative SARA analysis of whole bitumen using column chromatography

Step 1 in figure 3–3 represents solvent extraction of bitumen into asphaltenes and maltenes by using 40 times the bitumen's volume of *n*-pentane as solvent. The mixture is shaken for about 10–12 hours in a normal bath or about an hour in an ultrasonic bath and is then filtered to recover the asphaltene fraction. Maltene is recovered by evaporation of the solvent.

In step 2, the maltene fraction is further separated into resin and oil by column chromatography, using the technique recommended by ASTM D-2007, where the clay column is first eluted by *n*-pentane to recover the oil and the resin fraction is retained in the column.

In step 3 (fig. 3–3), the same clay column is first eluted with methyl ethyl ketone (MEK) to extract a dark-colored oily liquid, which is low-density resin. A further elution with tetrahydrofuran (THF) recovers a dark-colored crystalline semisolid, which is high-density resin.

The pentane-soluble oil fraction obtained in step 2 is further separated in step 4 (fig. 3–3), into saturated and aromatic fractions in an activated silica-alumina column. The saturated fraction is first eluted by *n*-pentane as a colorless liquid. The adsorbed aromatic portion in the column is then eluted by toluene.

Distillation and HTSD

Normal distillation of a heavy crude oil in the laboratory is done in a distillation apparatus per ASTM D-86, for atmospheric distillation, followed by ASTM D-1160, for vacuum distillation under reduced pressure. Another standard test method is ASTM D-2892, for the distillation of crude up to an atmospheric equivalent temperature of 400°C in a fractionating column of 15 theoretical plates. An alternative vacuum distillation method for heavy oil is ASTM D-5236.

Once the normal distillation is complete, then the experimental data are converted to true boiling point (TBP) data at atmospheric pressure or 101 kilopascals (kPa). A distillation curve is then drawn between volume percent (vol%) or wt% distilled versus TBP. This is a time-consuming method; however, the method is indispensable when detailed properties of fractionated products are required.

Capillary-column GC is being used for SimDist, per ASTM D-2887, to determine various boiling fractions of heavy crude oils. The advantage of this chromatographic technique is that the sample that contains a nonvolatile component, such as resid, can be analyzed by injecting simply the diluted original sample (i.e., the way it was when it was received). The unrecovered resid portion of the bitumen could be back-calculated from the amount of sample injected.

Another advantage of the capillary-column GC technique is that the SimDist curve can be sliced at any desired fraction's boiling range, and the yield of the various fractions can then be calculated theoretically. SimDist curves of several samples can be compared directly by overlapping them on the same plot. Recent advancement of this technique can reach more than 700°C (1,300°F), by use of HTSD per ASTM D7169-2005 (based on ASTM D-2887). However, this temperature range is practically impossible to achieve in a commercial vacuum tower in a refinery without cracking the bitumen.

A word of caution

This technique needs careful calibration method in order to identify the components and corresponding equivalent boiling points. For example, SimDist calibration is based on the retention times of normal paraffins and their boiling points; however, aromatic compounds' boiling points do not fall within the same range. Sometimes, researchers refer to average boiling points instead of actual boiling points. Thus, one has to be very careful when using these data, especially when comparing data from different laboratories.

CHNS

In the coal industry, CHNS is determined by ultimate analysis. For bitumen, a similar combustion technique can be used for the analyses of carbon and hydrogen only (e.g., ASTM D-3178). However, sulfur and nitrogen are determined separately by more precise techniques. As the sulfur concentration in the sample changes, the protocol for sulfur determination also changes. For example, in case of bitumen, where the sulfur concentration is higher than 1 wt%, ASTM D-4294 is used. By contrast, for bitumen-derived products, where the sulfur concentration is below 0.5 wt%, ASTM D-1266 may be used; for bitumen-derived hydrotreated products, where the sulfur concentration has been reduced to below 100 ppm, ASTM D-3170 may be used.

The total nitrogen in bitumen can be determined by combustion, using ASTM D-3179. However, for a more precise determination, other methods are preferred, such as oxidation followed by the chemilumenescence (ASTM D-4629); for trace-nitrogen analysis, ASTM D-3431 can be used.

Metals

Metals are usually analyzed in the whole bitumen or in the resid fraction. Metals are first recovered from the sample as ash by combustion. The metals in the ash are then analyzed by inductively coupled argon plasma techniques (ICAP) or by atomic absorption (AA) spectroscopy. Standard methods (e.g., ASTM D-2788 or D-3340) can be used for the determination of metals in heavy oil or its processed products.

TAN

Acidity of a crude oil is measured by a simple potentiometric or pH titration method by neutralizing the acid functional group by using a basic solution, such as sodium or potassium hydroxide (KOH). The TAN value is defined as the milligrams of KOH required to neutralize the acidic group of one gram of the oil sample; thus, the TAN value is expressed in units of mg KOH/g. The TAN value is also known as the *basicity number*.

Water

Accurate analysis of water in a bitumen sample is extremely difficult because of emulsion formation. Usually, the water content is determined by the Karl Fischer titration method in a Mettler-Toledo model DL-32 instrument.

Challenges in Analysis of Heavy Petroleum Fractions

Critical to the characterization of heavy oil or bitumen are the analytical techniques and protocol used by the chemist for the analysis of the feedstock and the product sample obtained from any process or experiments. The characterization of high-molecular-weight species is extremely difficult; nevertheless, there is a definite need to characterize bitumen at the molecular level. Chemists interested in this area must anticipate fractionating the bitumen as much as possible before considering its characterization. Recently there has been great interest in the fractionation and characterization of larger molecules by using high-performance liquid chromatography (HPLC) or, more recently, using supercritical fluid chromatography, in combination with various spectroscopic techniques. Although detailed description of the analysis of heavy oil or bitumen is beyond the scope of this book, analytical chemists interested in the detailed spectroscopic analysis of heavy petroleum fractions may consult the book *Composition and Analysis of Heavy Petroleum Fractions*, by Altegelt and Boduszynski, which describes in detail the combination of a high-performance chromatographic separation followed by various spectroscopic techniques to characterize heavy fractions at the molecular level.[10]

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RECOVERY TO REFINERY

4

The demand for energy is increasing rapidly. The heavy oil and bitumen industry will undoubtedly play a vital role in meeting this challenge. However, tapping into heavy oil reserves is not a short-term solution: it is highly capital intensive, it does not provide an immediate high rate of return or a high profit margin, and the heavy oil business strongly depends on the price differential between heavy crude and light crude. Increasing the profit margin of a company requires the complete integration of upstream and downstream portfolios from recovery to refinery.

Bitumen is exceedingly difficult to handle, recover, transport, and refine. The most difficult challenge is posed by the *bottom-of-the-barrel* portions—namely, the resids and asphaltenes. In the heavy oil/bitumen business, the purpose is not to find more oil deposits, but rather to maximize the project economics through optimization of each and every step involved. The whole purpose of the business is to convert heavy crude into synthetic crude that will substitute for the conventional crude. The industry needs to develop new technologies to meet those challenges. Even today, few refineries in the United States are capable of processing heavy oil.

The development of oil sands is energy intensive, as compared to the development of conventional crudes. Because the quality of the crude becomes poorer with the increase in density, aromaticity, or impurities, the severity of the processing increases, as does the energy consumption in each step.

Chief among the problems with the Alberta oil sand deposits is its location—far up north, in a harsh climate, and away from major infrastructure. Up front, that increases the cost of capital and the operating expenses, starting with the recovery of the bitumen from the subsurface reservoirs, then proceeding through the transportation of the bitumen either to a nearby upgrader or to a refinery in Canada or the United States.

Another problem facing the bitumen industry is the perception around the world that Canadian bitumen is dirty and high in greenhouse-gas (GHG) emissions (see chap. 11). There is a great ongoing debate on this subject inside and outside the industry.

Major Steps from Recovery to Refinery

In the oil sands business, the entire value chain, from recovery to refinery, needs to be considered, rather than only the single step in which each independent company or a particular group within a big company specializes. This is because the value of bitumen depends on the price at which bitumen producers can sell their product to refineries, in spite of competition from light (conventional) crude producers.

Figure 4–1 represents the major steps involved, from the production of bitumen to its transportation to a refinery gate. Each step in the process needs external energy input, and that should be matched relative to the energy available in the bitumen. As the energy input increases, the operating cost of production and transportation increases. At the same time, the environmental impact of each step needs to be mitigated.

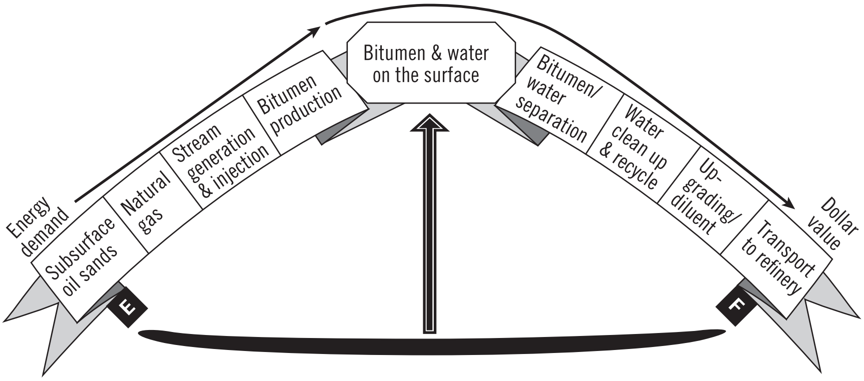

Fig. 4–1. Steps from recovery to refinery in the oil sands

Step 1: Recovery

In the northern-most part of Alberta, the bituminous oil sands are surface mined. The bitumen is then removed from the solid sand and clay particles by a hot-water extraction process (for details, see chap. 5).

In southern Alberta, by contrast, the first step in the recovery of bitumen from the subsurface reservoir involves steam injection. The latest technology for in situ recovery is known by the acronym *SAGD* (pronounced "sag-dee"), which stands for *steam-assisted gravity drainage* (for details, see chap. 5). The steam is produced on the surface by burning off natural gas. As a rule of thumb, about three barrel equivalents of cold water need to be converted into steam to extract one barrel of bitumen.

Next, steam is pumped down the hole, through the injection well. The steam transfers its own heat into the reservoir and raises the temperature enough to decrease the viscosity of the bitumen, making it mobile. Near Fort McMurray, Alberta, the cold reservoir temperature is about 10–12°C. As was shown in figure 3–1, the viscosity of bitumen is more than 1 million mPa·s at those conditions. Steam heats the reservoir to above 200°C to decrease the viscosity, to approach that of water (<10 mPa·s), so that it becomes mobile enough to flow along with the hot condensed water.

The mobilized bitumen, along with the condensed steam (produced water), is then drawn to the surface through the production well. Immersed pumps pull the water/bitumen mixture aboveground.

Surface oil sands are bitumen rich, generally containing more than 10% bitumen, whereas subsurface oil sands usually contain less than 10% bitumen. Surface mining of oil sands followed by hot-water extraction recovers up to 90% of the bitumen. By contrast, the in situ process recovers less than 80% of the bitumen. Thus, mining is more efficient than in situ recovery.

Step 2: Oil/water separation

The first major step after the recovery of bitumen is to separate the components in the water/bitumen mixture. Excess water remains as two distinct phases that can be separated by a simple process (i.e., phase separation). However, part of the water remains as an emulsion, bonded so strongly with the bitumen that it cannot be separated easily. Surfactants are used to break the emulsion, allowing the remaining water to be separated in the dehydration step. Then, the water needs to be cleaned and recycled back into the boiler, to generate more steam. Cleaning of water is difficult and expensive.

Step 3: Transportation

After dehydration of the bitumen, the next major problem is its transportation, because it is not mobile except at high temperatures. This problem is addressed by decreasing the viscosity and increasing the API gravity, so that both meet the pipeline specifications (for details see chap. 6). This is done either by adding naphtha or condensate as diluent or by upgrading the bitumen on site. The upgrading process is briefly explained below (see "Step 4"). One impetus for upgrading the bitumen before transportation is the economic advantage in doing so (explained in the next section).

The most widely used diluent for transportation is condensate, derived from natural gas. Therefore, condensate's availability and price depends on the respective availability and price of natural gas. As the production of bitumen increases, the demand for condensate increases; hence, there will be a shortage of condensate in the near future, and its price is expected to increase. Today, the cost of condensate is already about 25% higher than that of light sweet (conventional) crude. As the price of condensate becomes even higher owing to the increasing demand, upgrading prior to transportation again becomes the better economic option. In addition to upgrading's being independent of condensate availability and cost, the quality of the upgraded product is better than that of the diluted crude. Nevertheless, deciding which route to take is not an easy task for a company.

In further support for upgrading prior to transportation, refineries do not like condensate and usually separate it and return it to the producers at additional cost. Moreover, it is difficult to separate all the condensate at the end of transportation.

Step 4: Upgrading

The goal of the upgrading process is to convert bitumen to a product that producers can sell in the market. Details of the upgrading processes and technologies are discussed in chapters 7 and 8.

As noted above, this can be done before (at the wellhead) or after bitumen's transportation from the recovery point. However, despite the benefits mentioned above, upgrading is still energy intensive and very expensive. The quality of the product is directly related to the degree of upgrading, which in turn is related to the cost of upgrading. Therefore, many factors play a role in determining the decision to build an upgrader and what processes to incorporate.

For example, whether to build an upgrader in Alberta constitutes a difficult strategic decision for the management of any oil company. It represent an extremely slow, multibillion-dollar project that is highly dependent on the price differential between light (conventional) crude and heavy (unconventional) crude. It has been widely observed that the price of crude oil goes through a cycle, making it a challenge to keep the price of crude oil within profitable margins during the whole period of decision making, design consideration, construction, and operation of the upgrader. The effect of the cycle is so strong that as recently as 2008, there was a bust in the heavy oil industry, when Alberta experienced significant disruption, necessitating the postponement or cancellation of most upgrader projects.

Challenges in Establishing the Worth of Bitumen

As previously stated, the bitumen price is heavily dependent on the cost associated with the quality of the crude and the desired quality of the upgraded product. Simply put, as the quality of the crude oil decreases, it takes more energy to upgrade it to the same quality product. The energy requirement is directly related to GHG emissions. There is no clear solution for how to deal with GHG emissions or how to control them economically. Even though the industry generally discusses various steps involved in recovery and upgrading in terms of dollars, a relationship exists between energy consumption and both the energy efficiency of various steps and the economics of the process.

Monetary value

A barrel of bitumen is worth the value of its salable bitumen-derived product, *syncrude*. Hence, the value of bitumen is directly related to the world crude price and competes against the common compatible crudes in North America (e.g., Louisiana Light Sweet, West Texas Intermediate, and Alaskan North Slope) and Europe (e.g., Brent).

Of major concern in the bitumen-upgrading business is the price differential between the heavy crudes and the price of those comparable crudes. As a rule of thumb, the light crude price has to be above $50/barrel (in 2010 dollars, not considering the step of CO_2 capture) to break even with the cost of bitumen production and upgrading. Hence, as the conventional crude price increases, the profit margin in the heavy oil market increases.

For a refiner, the diluted bitumen or the upgraded bitumen is equivalent to the profit they could make on the final refined product. The cost of refining of either bitumen or its product is higher than that of refining conventional crude.

At present, upgraders are immense operations that are capital intensive. To reduce economic risk and the overall cost, future upgraders should be smaller in size and be built at the wellhead. The goal should be to minimize the process of upgrading to pipeline specification, such that the upgraded product can be transported without any diluent through a pipeline either to a nearby refinery or down south, to the United States. The key issues in this scenario are to reduce the overall risk and cost and, even more important, to reduce the environmental impact (for a discussion on clean-bitumen technologies, see chap. 9).

Net energy value

The *net energy value* of the bitumen takes into consideration the total energy required at every step of the process. In mathematical terms, the net energy available from the bitumen is equal to the gross energy in the bitumen minus the total energy required to produce it as a salable product.

In brief, the following are the major energy-intensive steps:

- Generation of steam by burning natural gas and pumping steam downhole
- Pumping bitumen water mixture aboveground
- Water separation, cleaning, and recycling
- Production and handling of diluent to make a bitumen blend
- Derivation of syncrude (in the case of upgrading)
- Control of GHG emissions (in the case of GHG capture)

Hence, energy efficiency of bitumen—in recovery and conversion and in making it into a salable product (i.e., syncrude)—is significantly less than that of conventional crude. However, rather than taking into account the bigger picture including the net energy value and the environmental impact, the oil industry typically takes into account only the dollar values of the salable syncrude. Sure, the dollar values will be ample for companies to make profits; nevertheless, it does not make sense in the long term to have a negative net energy value.

Heating values of common fuels

Table 4–1 provides comparative data on the heating values of some of the most commonly used fuels associated with the oil sands business. On a per-kilogram basis, natural gas has almost 9 megajoules (i.e., 9 MJ/kg) of extra energy as compared to bitumen. Natural gas also burns much cleaner than bitumen because it has no heteroatoms and has a higher H/C ratio. In the SAGD process, natural gas is burned to generate steam (because it is cheaper), and it takes about 1 million standard cubic feet of natural gas to produce 1,000 barrels of bitumen. Hence, there is a great need to reduce the natural gas utilization in bitumen production. A new process concept is proposed in chapter 9 to eliminate the use of natural gas completely.

As shown in table 4–1, asphaltene's heating value (37.5 MJ/kg) is about 15% less than bitumen's (44.5 MJ/kg). In a de-asphalting process, the pitch will have almost the same heating value as the asphaltenes and can be used as a fuel either in a gasifier or blended with coal or petroleum coke (petcoke) for the purpose of burning.

In a coking process (for discussion, see chap. 8), resid is converted into petcoke and synthetic crude oil. Synthetic crude oil has no resid and higher hydrogen content; hence, its heating value of 45.0 MJ/kg is about 14% higher than that of the resid feedstock (39.5 MJ/kg). By contrast, coke is mostly produced from the condensation of the aromatic rings of the asphaltenes with the elimination of hydrogen, thus producing a by-product with a lower energy value (35.0 MJ/kg). Sometimes, petcokes are not suitable for burning because of the resultant atmospheric emissions—namely, oxides of sulfur, nitrogen, and carbon.

Table 4–1. High heating values (HHV) in MJ/kg of certain fuels related to the oil sands business

Fuels	Heating value
Hydrogen	141.8
Methane	55.5
Natural gas	53.0
Condensate	47.5
Synthetic crude oil	45.0
Bitumen	44.5
Resid	39.5
Asphaltene	37.5
Petcoke	35.0

In an ideal case, the petcoke or the pitch, both having heating values of about 65% that of natural gas, may be gasified to generate heat for bitumen production. Thus, a gasifier may be a part of the future upgrader design in Alberta, as discussed in chapter 9. In spite of its high cost of operation, a gasifier has several advantages, including the following:

- Easily capturing CO_2 and compressing it for sequestration
- Producing hydrogen as a by-product for the upgrader
- Replacing natural gas as a heat source
- Safely disposing of heavy metals as slag

This chapter has detailed the steps from the production and recovery of the bitumen from subsurface reservoirs onward. This involves transportation through pipelines and upgrading of bitumen to synthetic crude. Finally, the challenges facing the refinery, to handle the unconventional crude, have been discussed.

BITUMEN PRODUCTION AND RECOVERY

5

Surface Mining

Surface mining was the first technology used for the production of bitumen in Alberta. Even today, about 60% of bitumen production is done through open-pit surface mining, thereby exceeding production by use of in situ technology. However, ERCB has projected that, in the next decade, in situ production will surpass mining production. An excellent review of mining operations in Alberta can be found in the *Oil & Gas Journal*.[1]

Mining is done in the northern part of Alberta, where the overburden depth is less than 75 m (see fig. 1–4). However, about 80% of the known bitumen reserves are at depths greater than 75 m and cannot be recovered by mining operations. There are four major mining operations in Alberta, all in the Athabasca region. The two biggest operators are Suncor Energy and Syncrude Canada, followed by Shell Canada and Canadian Natural Resources.

Before the 1990s, open-pit mining was carried out by using a hydraulic shovel and bucket wheels. Excavated oil sands were then transported in a conveyer belt to the bitumen extraction plant. With the advancement of technologies, the latest mining operations have changed their system to immense shovels and trucking operations.

This is a massive operation. Figure 5–1 shows a simplified diagram of a mining process. Monstrous 400-ton trucks are used for hauling the oil sands to the processing locations. On a typical day, more than a million tons of oil sands are transported, crushed, and then extracted with a quarter-million tons of hot water. It takes four tons of oil sands to get one barrel of bitumen.

The ore materials from oil sands are first crushed in a crusher, to the size of a few inches, and are then transferred to a hot-water rotating slurry tank. Clark and Pasternack pioneered this process when they found that the addition of alkaline material and a surface-active agent is necessary to improve the bitumen extraction process.[2] Later, Bowmen showed that surface-active surfactants are generated as naphthenic acids anyway during the process.[3] In this step of the extraction process, the added alkaline solution (sodium hydroxide) neutralizes the acid functional group of the bitumen to produce surface-active surfactants that break the bitumen/water interfacial tension, to help separate the bitumen from the sand, and to maximize the bitumen extraction process.

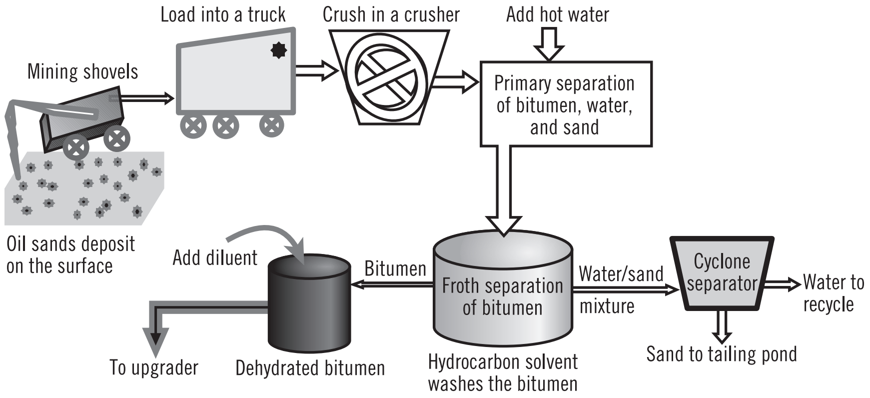

Fig. 5–1. Generalized scheme of a commercial oil sands mining process in northern Alberta

The hot mixture, between 70–80°C, is then transferred to another vessel, usually known as a *primary separation cell*, where bitumen is made into froth by air injection. At that temperature, the froth becomes lighter than water in the presence of air bubbles attached to the bitumen. At this stage, it becomes easier to separate the bitumen from the sand, which drops out by gravity. The separation process is dependent on the solid particle size and the quality of the oil sands.

The bitumen layer is separated, dehydrated, and deaerated, and then hydrocarbon solvent is added before transporting it to an upgrader. Dirty water and sand are directed to a cyclone separator. The water is cleaned and recycled. Wet sand is sent to tailing ponds, where larger particles separate by themselves; however, fine particles remain floating for a longer period of time and create environmental problems.

The mining process is efficient overall, because it is possible to recover more than 90% of the bitumen and recycle more than 90% of the water. The problem with the mining industry, though, is that it leaves a huge environmental footprint by its creation of tailing ponds. By contrast, the in situ processes discussed in the next section leave a much smaller environmental footprint, with no tailing ponds.

In Situ Recovery

By current estimates, the amount of bitumen that is available to be extracted via in situ recovery (steam injection) constitutes approximately 80% of the 1.3 trillion barrels of bitumen in place in the Athabasca oil sands. This covers a wide range in terms of depth, porosity, permeability, and temperature of the reservoirs; in addition, there are variations in the API gravity and the viscosity of the bitumen (fig. 1–4).

Alaska heavy oil is also located at a depth that necessitates use of in situ operations to recover the oil. However, there is no single technology that is optimal for the subsurface production conditions present in Alaska. In contrast, the conditions in Venezuela allow in situ recovery of the extraheavy oil (unconventional heavy crude) in the Orinoco belt by cold production methods. As the name suggests, in this method no heat is added, and it does not require injection of steam. Cold diluent such as nathpha is injected into the reservoirs to decrease the viscosity enough to lift the heavy crude to the surface.[4]

Over the years, various in situ technologies were developed and are still under development that can be used depending on the reservoir conditions. The following sections describe some of the existing technologies, although not all are fully commercial. Details of each and every technology are beyond the scope of this book; however, a relatively in-depth analysis of SAGD is warranted, because it is the fastest growing technology in Alberta. According to ERCB, in situ production will increase to 1.29 million BPD by 2018.[5]

SAGD

SAGD is the most popular steam injection thermal method of recovering viscous hydrocarbons. Although Butler pioneered the development of this technology in the 1970s, it became the focus of more attention only later, in the 1990s.[6]

Figure 5–2 represents a cross-sectional view of the SAGD concept. In the SAGD process, two L-shaped wells—namely, the upper injection well and the lower production well—are placed one above the other. Steam is pumped through the injection well into a viscous hydrocarbon reservoir, while hydrocarbons are produced from the parallel, horizontal production well, which is vertically spaced below the injection well. The injection and production wells are typically located about 5 m apart close to the bottom of the hydrocarbon deposit, about 300–600 m in depth. The horizontal portion of the two wells varies in length from 1,000 to 1,500 m.

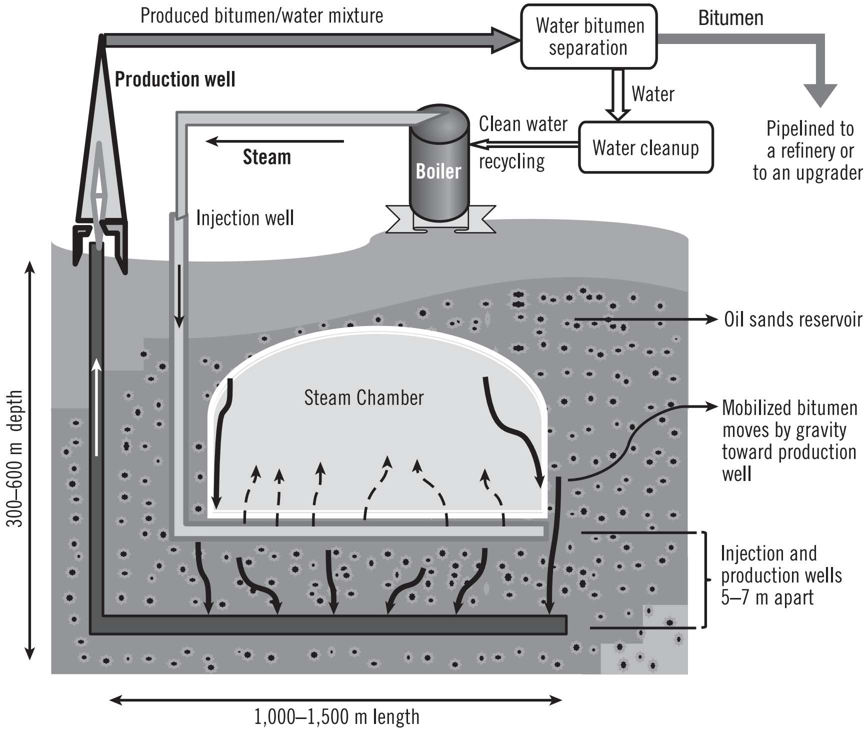

Fig. 5–2. Cross-sectional view of the SAGD concept (not to scale)

SAGD process. In the SAGD process, a steam chamber is created in the reservoir, around and above the horizontal injection well, by injection of steam. As the steam chamber expands upward and laterally from the injection well, viscous hydrocarbons in the reservoir are heated and mobilized, especially at the margins of the steam chamber, where the steam condenses and heats a layer of viscous hydrocarbons by thermal conduction.

The mobilized hydrocarbons (and condensed water) drain under the effects of gravity, moving toward the bottom of the steam chamber, where the production well is located. The mobilized hydrocarbons are collected and produced from the production well. The rate of steam injection and the rate of hydrocarbon production may be controlled with the growth of the steam chamber. It is necessary to ensure that the production well remains located at the bottom of the steam chamber in an appropriate position to collect mobilized hydrocarbons, preferably far from the water in a clean part of the reservoir. Typically, the start-up phase takes three months or more, until communication is established between the two horizontal wells.

Importantly, for efficient production in the SAGD process, conditions in the injection and production wells need to be maintained, so that steam does not simply circulate between the injection and production wells, short-circuiting the intended SAGD process. This may be achieved by controlling steam injection so that the bottom-hole temperature at the production well is below the steam temperature.

A crucial phase of the SAGD process is the initiation of a steam chamber in the reservoir. The typical approach to initiating the SAGD process is to operate the injection and production wells simultaneously with high-pressure steam. However, steam is independently circulated in each of the wells during this start-up phase, heating the hydrocarbon formation around each well by thermal conduction. Independent circulation of the wells is continued until efficient fluid communication between the wells is established. Once the fluid communication is established between the wells, the injection well is dedicated to steam injection while the production well is dedicated to oil production only.

SAGD conditions. Typically, steam is injected through the injection well at a temperature above 200°C and a saturation pressure above 3,000 kPa, to provide high quality steam to mobilize the hydrocarbons. Bitumen has a viscosity close to water's at 200°C, which is enough to pump the bitumen along with the produced water through the production well. A large volume of water is required to be converted into steam, using natural gas as the fuel source. The SAGD heat cycle undergoes several steps that require a lot of energy, accompanied by carbon dioxide (CO_2) emission.

Depending on the characteristics of the reservoir, sufficient pressure must be maintained to lift the produced fluid to the surface. For example, a pressure difference of at least 200 pounds per square inch (psi) is required in order to lift the fluid (bitumen/water mixture) more than 300 m (1,000 ft) to the surface.

Banerjee et al. have patented an improved SAGD process that proposes in situ generation of steam by heating the condensed water with microwaves (MW) or radiofrequency (RF) waves.[7] Frequencies (MW or RF) are directed toward the water molecules; the process is optimized, and the temperature is controlled by adjusting the power level of the MW or RF generators. The intent of this process is to decrease the preheating period, shorten the start-up phase, and improve the steam-to-oil ratio (SOR).

Steps involved in SAGD operation. As shown in figure 5–2, there are four critical steps involved in the SAGD operation.

Step 1. The volume of water handled in the SAGD operation is represented by the SOR, which is about 3.0; in other words, it takes three barrels of water equivalents of steam to recover one barrel of bitumen. At the start-up phase, the SOR is much higher than 3.0; eventually, it goes down, to about 3.0 at optimum conditions. However, producers are desperately trying to decrease the SOR to decrease their operating costs.

Step 2. The mixture of water and bitumen, after reaching the surface, undergoes several transformations:

- Oil/water separation
- Demulsification
- Water treatment—removing solids, especially silica, from the water comprises the most difficult part
- Recycling of the clean water to the boiler for steam generation

Step 3. Current steam generators are heated with gas-fired boilers, which require millions of British thermal units (BTUs) of energy, equivalent to millions of standard cubic feet (MMSCF) of natural gas, per thousand barrels of bitumen production.

Step 4. The heating period of the SAGD chamber is quite long—about three to four months. The virgin reservoir temperature is 10–12°C, and the average steam saturation temperature and pressure is 235°C at 3,000 kPa (about 430 pounds per square inch). High-quality steam is produced at a high temp and pressure to mobilize the bitumen and lift it aboveground from the reservoir.

Steam generation. As the SAGD process becomes progressively more common in Alberta, technology for high-efficiency steam generation and recycling of produced water (condensed water that comes out through the production well along with bitumen) is increasingly in demand, for both economical and environmental reasons. Steam is generated by separating and treating the produced water and then directing the clean water to a steam generator or boiler. There are various types of steam generators, but the most traditional method uses a *once-through steam generator (OTSG).*

Treating the produced water to make it clean enough to serve as feed water for the steam generator is quite challenging. Several methods, each with its own advantages and disadvantages, are used. Examples include chemical addition, membrane separation, and ion exchange. Details of these processes are beyond the scope of this book.

Hybrid steam/solvent processes

The Alberta Research Council (ARC) in Edmonton is researching a number of hybrid steam/solvent processes that combine SAGD technology with different solvent injection strategies. The new processes are aimed primarily at improving recovery and energy efficiency and reducing water requirements. Examples of enhanced steam processes include the following:

- Expanding-solvent SAGD (ES-SAGD)
- Low-pressure solvent SAGD
- Tapered steam/solvent SAGD
- Steam and vapor extraction process

All the above technologies remain in the investigational stages; therefore, further discussion is not warranted here.

Even though SAGD is effective at producing bitumen from the reservoir to the surface, research has led to continued improvement in the SOR of SAGD through the addition of organic solvents. This improves the thermal efficiency and eventually the cost efficiency of the process. The method is especially suited for reservoir conditions, under which the mobilized heavy oil preferably should have a viscosity of less than 100 mPa·s and should exert enough pressure—usually higher than 2,000 kPa—to lift the mobile bitumen more than 300 m in height.

Hydrocarbon solvents—such as ethane, propane, and butane—are partially miscible in oil. When dissolved in oil, these solvents reduce its viscosity. Two or more solvents are mixed in proportions such that the dew point of the mixture is near the reservoir temperature and pressure. This makes the solvent exist partially in the vapor phase and partially in the liquid phase in the reservoir; the vapor phase helps maintain the pressure, and the partial liquid phase reduces the viscosity of the hydrocarbon in the reservoir, thereby increasing the production of bitumen.

Cyclic steam stimulation

Cyclic steam stimulation (CSS) is a method that was developed in the early 1960s by Imperial Oil as one of the very first steam injection technologies. This is a simplified version of SAGD process, also known as the *huff-and-puff* method. This concept is illustrated in figure 5–3.

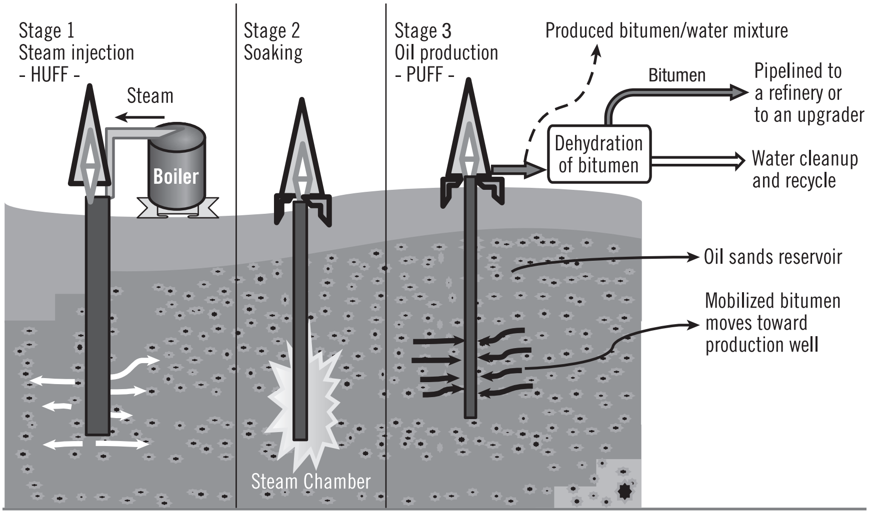

Fig. 5–3. Cross-sectional view of the CSS concept

As shown in figure 5–3, CSS technology uses only one vertical well, for both injection and production. The process involves a three-step cycle:

Step 1: Steam injection (4–6 weeks). In the first step, high-pressure steam is injected into the reservoir until sufficient temperature and pressure is developed. This step, which generally takes about 4–6 weeks, is also known as *huff*.

Step 2: Soaking (2–8 weeks). In the second step, steam injection is stopped and the well is allowed to soak for a few weeks, until the bitumen becomes mobile. During this period, the reservoir is heated to melt the bitumen, and viscosity is reduced enough to make the bitumen flow.

Step 3: Bitumen production (up to a year). In the third step, the mobile bitumen is lifted aboveground through the same well, now acting as a production well. This step, which usually takes several months to a year, is also known as *puff*.

The entire process is repeated until it is no longer economical—which is inevitable, because production decreases with time. The economics of the process depends on the amount of steam required and the cost of steam production. In the CSS process, the maximum recovery obtained is about 20%–25% of original bitumen in place.

Cold heavy oil production with sand

The technology involved in cold heavy oil production with sand (CHOPS) is a cold-production method widely used by small companies for small heavy oil projects. As the name suggests, production occurs by the injection of sand through the well, making the bitumen mobile. The production cost is cheaper than other processes because of the relatively low cost of sand.

CHOPS is used in Canada as a primary recovery process in shallow areas where reservoir temperatures are relatively higher, the viscosity is lower, and there is no mobile water. Venezuela is also a suitable place for this technology, and heavy oil projects in Alaska intend to utilize this technology to avoid the generation of steam.

Vapor-assisted petroleum extraction

Vapor-asssisted petroleum extraction (VAPEX) is a solvent-based process that uses gaseous and liquid hydrocarbon solvents.[8] Vaporized hydrocarbon solvents are injected into the oil sands reservoir. The gas phase of the solvent mixture fills the chamber and increases the reservoir pressure. The liquid phase dissolves into the bitumen at the oil/gas interface, reducing its viscosity and causing it to drain by gravity into a horizontal production well.

Because VAPEX is a nonthermal method, it has the potential to reduce CO_2 and other GHG emissions substantially. It is estimated that, if successful, it may reduce emissions by as much as 85% over thermal processes. Other driving forces for use of VAPEX include the potential to reduce dramatically water consumption, as compared to other extraction technologies, and to lower related water-handling and surface-facility costs. The technology also has significant economic advantages over SAGD, because it can be applied to recover bitumen from zones that are considered too thin for traditional thermal recovery methods. It offers the potential for an upgraded and higher-value product by promoting in situ upgrading. Paraffinic solvents cause asphaltenes to precipitate out and remain behind in the reservoir (i.e., partial upgrading occurs).

Like SAGD, VAPEX uses horizontal well pairs to recover the bitumen. However, the latter process uses a hydrocarbon solvent instead of steam; this eliminates the need to burn fuel (usually natural gas) to create steam, thus resulting in reduced GHG emissions. In addition, the solvent in the VAPEX process can be reused: the vaporized solvents are injected into the reservoir via an upper horizontal well; the bitumen/solvent mixture drains by gravity into the production well, and on the surface, the solvents are separated from the produced bitumen and are recycled.

Research carried out thus far suggests that up to 90% of the solvent used can be recovered and recycled, offering the potential for huge cost savings over other extraction methods. Results have also shown the quality of the produced bitumen to be superior because of partial upgrading, whereby some of the heavier fractions are left in the ground. Although researchers are claiming many advantages, the process is still at an experimental stage.

In situ combustion

During in situ combustion (ISC), heat is generated inside the reservoir chamber by injection of air or oxygen, which causes the heaviest part of the bitumen to burn. The main objective in developing this technology was to eliminate the use of steam—along with those various steps involved in generating steam on the surface, transporting it into the reservoir, and recovering and recycling water. Heat loss during steam injection is a further cause for concern.

In the ISC process, once air or oxygen is injected through an injection well, a combustion front is established by the burning of bitumen. Typically, this generates temperatures over 400°C. As the combustion zone moves horizontally, it thermally cracks the bitumen into lighter fractions that move upward, away from the heated zone. The heavier portion, or coke, formed during the process gets further burned and generates heat. The hot lighter fraction also melts the bitumen in the reservoir and makes it mobile. The mobile oil then moves ahead of the combustion zone, toward the production well.

THAI technology. THAI (Toe-to-Heel Air Injection) is an ISC process developed by Petrobank of Calgary, Alberta.[9] The THAI process combines a horizontal production well with a vertical air injection well. This in situ method is applicable in reservoirs where other steam-based recovery methods cannot be used. According to Petrobank, the THAI process works at lower capital and operating costs than steam injection processes.

An air injection well is drilled vertically at the toe of the horizontal well. Once the bitumen reaches the required temperature and mobility, air is injected into the formation. As the air reaches the heated resource, it starts a combustion reaction. The vertical combustion front moves along the horizontal well (from the toe to the heel of the production well), sweeping the reservoir. As the combustion front develops and temperatures increase, the bitumen is heated to high temperature, at which partial upgrading occurs. The upgraded bitumen is recovered through the production well.

In addition, in a variation of the THAI process called Capri, a catalyst is used in the horizontal well to help precipitate asphaltenes and improve the quality of the upgraded oil. Finally, fire-flooding is an old concept; however, there is still no commercial process available in Alberta.

Challenges Facing In Situ Recovery and Upgrading

Several of the above technologies rely on steam to heat and soften the bitumen underground, allowing it to flow to production wells. Both CSS and SAGD are considered to be economical only in very-high-grade, relatively homogeneous oil sand reservoirs. The Athabasca area, though, mostly consists of heterogeneous reservoirs; only about 10% of the available resources are homogeneous, and only about a maximum of 50% of the bitumen in place can be recovered economically using the currently available technologies.

Selecting a particular in situ technology is very challenging, as it depends on so many factors such as reservoir characteristics, fluid properties, rock properties, ease of drilling, recovery, and production rates. Also needed to be considered are the cost, availability of infrastructure, and the ease of energy utilization. In the case of Alaska, the thick permafrost makes steam injection a challenging task.

The in situ recovery process must take place below the reservoir fracture pressure. Typically, in the Athabasca area, the maximum fracture pressure in the reservoir could be as high as 4,000 kPa. The temperature of the steam injected for the SAGD operation can be a maximum of 250°C, in order not to exceed the reservoir pressure of 4,000 kPa. Thus, there is a limitation to the maximum temperature and pressure that can be attained.

Attempting to upgrade bitumen in situ is an old concept (>30 years old) that has been tried unsuccessfully by many companies and research institutes. However, development of in situ technologies remains an area of interest. For example, the process of *in situ hydro-visbreaking*, with or without catalysts, has been studied extensively in Canada and Venezuela since the early 1980s, and research is still being performed in Alberta.

Many researchers, especially in Canada, are working on developing new technologies to simultaneously upgrade and recover bitumen. One of the most recent interests is in in situ catalytic upgrading, whereby researchers attempt to upgrade heavy oil by cracking heavier molecules into smaller sizes in the presence of an ultradispersed nanocatalyst and hydrogen.[10] This is expected to reduce the density and the viscosity of the bitumen in the subsurface reservoirs before it is recovered aboveground. No public information about this project is yet available; however, if it is successful, this process promises to reduce the cost of production and transportation of heavy oil, as well as to reduce GHG emissions considerably.

It is certain that in situ upgrading will be less efficient than surface upgrading. The following concerns need to be addressed regarding in situ processes:

- There will be uncontrolled mobility of the dispersed catalyst and hydrogen in the reservoir.
- A temperature of at least 350°C is required for hydro-visbreaking, which cannot be reached in a shallow reservoir. In deeper reservoirs, other problems regarding the operating conditions will occur.
- At low pressures (i.e., below fracture pressure [<4,000 kPa]), it would be more beneficial economically and energetically not to attempt to hydrogenate bitumen at all because the reaction will be exceedingly slow. However, residence time is not a limitation in a reservoir.
- Over the years, researchers have tried to generate superheated steam in the reservoir by using a downhole-combustion chamber, where pure hydrogen and oxygen were injected along with water. This involves the extra costs of generating pure hydrogen and oxygen in the field and of recovering, cleaning, and recycling the water. In another attempt, superheated steam was made at the surface and then transported in vacuum-insulated tubing to curtail heat loss.

In summary, to succeed at in situ upgrading, one has to increase recovery, reduce energy demand, lower water consumption, and improve oil properties coming out of the ground to offset the inefficiencies and difficulties associated with the in situ process itself.

Paradigm Shift in Emerging Subsurface Technologies

The majority of the bitumen recovery tests have been done by directly heating the bitumen with steam, to decrease the viscosity and make the bitumen mobile. Several exotic technologies have also been attempted in the industry, and research is still under way on techniques described in this section.

Over the years, attempts have been made to recover oil from shale by using RF or MW dielectric heating. In this process, either the most efficient frequency or a range of frequencies was used to heat the reservoir. The process involves direct dielectric heating of the hydrocarbons; however, it is limited by the penetration depth of the waves through the formation. Frequencies used for RF heating have higher depths of penetration as compared to those for MW heating. Another limitation of MW heating is that MW frequencies are adsorbed only by the polar molecules, thereby transferring the MW energy into heat energy—a process known as *coupling*. Pure hydrocarbons are nonpolar and do not couple in the presence of MW energy.

By contrast, when a molecule with a dipole moment, such as water, is exposed to MW energy, even in the presence of nonpolar hydrocarbon molecules, it gets selectively heated (i.e., without heating the surrounding hydrocarbons). Exploiting this property, Banerjee et al. have proposed a technique to improve the efficiency of the SAGD process by heating the condensed water with MW energy.[11] In the proposed process, a portion of the condensed water is converted back into steam before being transported aboveground, thereby eliminating the cost of recycling the water.

As mentioned above, hydrocarbons in the bitumen are nonpolar and do not couple with the MW energy; thus, MW energy is not capable of either heating or breaking pure hydrocarbon molecules. Banerjee et al. have further proposed to partially upgrade the bitumen at the wellhead using a MW coupling agent.[12] In this method, MW-absorbing coupling agents are mixed with the produced hydrocarbons at the wellhead and are exposed to MW energy. The added materials absorb MW energy and thus produce heat. The heat is transferred by conduction to the hydrocarbons to a desired temperature at which the visbreaking of the bitumen is complete.

Resistive heating—the simplest and most direct heating method—is where electrical insulated heating elements are inserted inside the reservoir. Heat is dissipated through the formation by conduction and radiation. The heat cracks the hydrocarbons adjacent to the heaters and produces volatile liquid. The lighter liquid product is recovered through the production wells; the heavier materials remain inside the reservoir. This process, however, is highly energy intensive; furthermore, because it is expected that the coking around the heating rods will disrupt the conductivity, this process may not be commercially suitable for continuous operation over a long period of time.

For further information on the topics discussed in this chapter, readers may consult the Web sites of the Canadian Association of Petroleum Producers (http://www.capp.ca/canadaindustry/oilsands/) and Suncor (http://www.suncor.com/oilsands/). In addition to the issues of *Oil & Gas Journal* that have been cited in this chapter, PennWell's *International Petroleum Encyclopedia* has been used as a source for general information and will serve as a useful reference for interested readers.[13]

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TRANSPORTATION OF HEAVY OIL/BITUMEN

6

One of the biggest problems in the oil sands industry is the remoteness of the location of the bitumen deposits, in far northern Alberta. The hauling of any material in Alberta is relatively expensive, the infrastructure is limited, and the weather is severe. Transportation of bitumen has become a major issue as the demand for Alberta bitumen increases all over the world.

The majority of the bitumen in Alberta is transported to the United States. The controversial Keystone XL pipeline project by TransCanada, planned to extend from Alberta to the Gulf of Mexico, is under highly publicized debate in the United States (see chap. 11). Moreover, because of the high demand for oil sands energy in Asia, the world market is opening up across the Pacific. China is increasingly interested in participating in the construction of the Northern Gateway, a multibillion-dollar pipeline project by Enbridge, to transport Canadian crude across the ocean via the western coast of Vancouver.

The Canadian oil industry has other concerns, such as whether to upgrade the bitumen in Alberta before transportation. This is not only an economic but also a political decision.

Pipeline Specification

As discussed in previous chapters, bitumen itself is not mobile and is not pipeline transportable. The most common method of transportation of bitumen is to add diluents to reduce the viscosity and make it mobile. A pipeline specification has to be met before the industry will accept the bitumen and its blend. In Canada, this specification is established by the Canadian Association of Petroleum Producers (CAPP) in consultation with Enbridge, a major carrier of crude oil from Canada to the U.S. market.

Key factors for pipeline specifications include the following (for details, see the CAPP and Enbridge Web sites)[1]:

- Density—minimum API gravity of 19° or maximum density of 940 kg/m^3
- Viscosity—maximum value of 350 cSt at pipeline temperature
- Sediment and water content (i.e., BS&W)—maximum limit of 0.5 wt%
- Reid vapor pressure—maximum value of 14.5 psi
- Olefin content less than 1 wt% by PONA analysis (recently introduced) although originally done by bromine number test (where the maximum limit is 10)
- No chlorine in the blend—less than 1 ppm

When a pipeline stream is analyzed and evaluated, the test method should be available, and an ASTM method should be specified for comparison.

Condensate

It is absolutely necessary to alter the bitumen into a material of higher API gravity and lower viscosity to meet the pipeline specification. The most widely used method is to add *condensate* derived from natural gas. Condensates are made of lighter hydrocarbons, in the range of C_5–C_{12}, and above 55°API. A significant amount of condensate is required in order to meet the pipeline specification. Because of the increasing production of bitumen in Canada, the demand for condensate is increasing rapidly, and the industry is facing many serious challenges:

- The cost of condensate depends on the volatile market price of natural gas.
- Usually, the cost of condensate is more than 25% higher than the cost of light (conventional) crude.
- With the increase in demand for condensate will come a shortage of availability of the diluent, and that drives the cost high, too.
- Condensates are not acceptable by the refineries.
- A return pipeline is needed to recycle the condensate.

Synthetic Crude Oil

To address the future shortage of condensate and to meet the above challenges, producers started looking for an alternate option of upgrading the bitumen at the field. In this case, the bitumen is either partially or fully upgraded to synthetic crude oil, or syncrude, as it is generally known. To what extent the bitumen should be upgraded is purely an economical decision. Various upgrader options are discussed later (see chap. 7).

The decision to upgrade the bitumen at the field resolves some of the above problems associated with the condensate, as follows:

- Cost of the syncrude is independent of the price and availability of the natural gas.
- Syncrude is not worth more than the light conventional crude.
- Syncrude is acceptable to the refineries.
- There is no need for a return pipeline.

Transportation Options

Figure 6–1 shows various types of blends available for pipeline transportation of bitumen to the refineries.

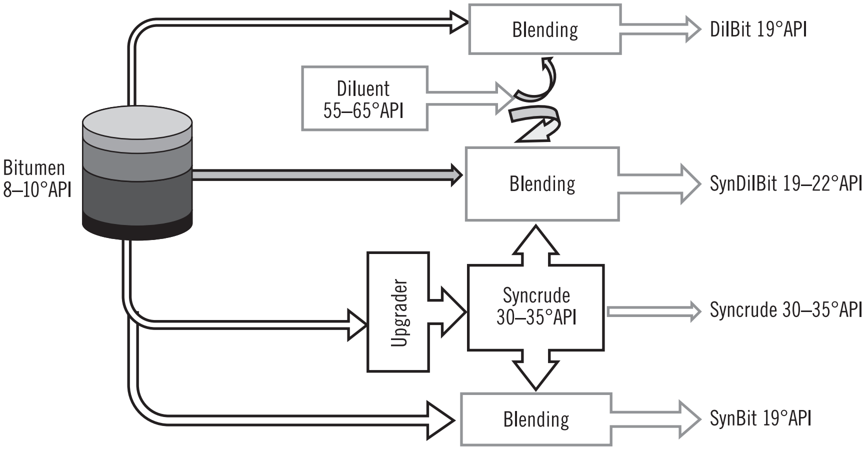

Fig. 6–1. Types of pipeline blends

DilBit

When refinery naphtha or upgrader naphtha is available at the wellhead, the bitumen may be diluted with naphtha or condensate, to meet the pipeline specifications. This diluted bitumen is sold in the market as *DilBit*. The volume of diluent required is about 25%–30%, depending on the API gravity of the diluent. The higher the API gravity is, the lower will be the volume of diluent needed for blending to meet the targeted API value.

The diluent consists of hydrocarbons in the range of C_5–C_{12} and is blended with bitumen that has hydrocarbons greater than C_{30}. Therefore, there are no hydrocarbons between C_{12} and C_{30} in DilBit. This blend is also known as *dumbbell crude*, based on the distribution of the hydrocarbon moieties (i.e., the molecular structure). That distribution makes it difficult for the refiners to handle the blend; moreover, the missing range of hydrocarbons is more valuable for the refiners, because it falls in the range of middle distillate. Examples of DilBit blends include Cold Lake Blend and various Lloyd blends.

Syncrude/SynBit

Another option for the producers is to field upgrade the bitumen into synthetic crude oil that meets pipeline specifications. Even though this is a costly option, it eliminates the need to purchase diluent, and it is independent of the cost of natural gas. As discussed earlier, the resultant increase in production may lead to a shortage of diluent in the near future.

The API gravity of syncrude could vary depending on the upgrading technology used (discussed in chap. 7). For example, if a coker is used, then the API gravity may be around 25–30°, and if hydrogenation is used, then the API gravity could be 35–40°.

As was demonstrated in figure 6–1, operators have two choices when bitumen is upgraded at the field: either sell the syncrude directly to the refiners or to blend the syncrude with bitumen to achieve an API gravity of 19° (i.e., crude suitable for pipelining). Direct synthetic crude is acceptable to the refiners, and usually they prefer syncrude over DilBit owing to three major advantages:

- Unlike dumbbell-shaped DilBit, the syncrude has continuous boiling-point range hydrocarbons.
- Syncrude is a good-quality crude, similar to light conventional crude.
- Refiners do not have to deal with the condensate.

Because syncrude has a much higher API gravity (>19°) than the pipelines require, there is room to blend bitumen with the syncrude. When a synthetic crude is blended with the bitumen, the blend is called *SynBit*. The volume of syncrude needed in the blend is directly related to the API of the syncrude. In Alberta, the most common synthetic crude used for blending is known as OSA (Suncor Oil Sands Blend A) and has an API gravity of 33.0°; it requires 50 vol% of OSA to meet the target API value of 19° when blended with Athabasca bitumen with an API gravity of 7.7°. Suncor also markets a Sour Synthetic Blend, similarly known by the acronym *OSE*, that is a mixture of hydrotreated naphtha, coker gas oil, straight-run gas oil, and Athabasca bitumen.

Syncrude Canada markets a different SynBit known as *SSB* (Syncrude Sweet Blend), which is a mixture of hydrotreated fluid coker product and bitumen. Husky Oil markets a fully upgraded premium-quality synthetic crude known as *HSB* (Husky Sweet Blend).

SynDilBit

It is challenging for the refiners to accept various grades of pipeline blends such as DilBit, SynBit, or syncrudes (discussed in detail in chap. 10). Not all the products are the same; thus, refiners have to know the detailed assays of each and every crude blend before processing them through their refinery or even before purchasing the crude. Not all crudes can be handled by all refiners.

To eliminate the large numbers of synthetic blends in the market and to achieve consistency for the refiners, EnCana (Canadian Oil company) in consultation with other companies decided to market a special blend that meets a consistent assay so that the refiners will not worry about the variation of crude blend quality every time. This blend consists of 65 vol% bitumen where the other 35 vol% is a mixture of condensate, synthetic crude, and some conventional crude. This blend is known as SynDilBit because it close resembles a mixture of SynBit and DilBit.

The targeted assay of SynDilBit is as follows:

- API gravity, 19–22°
- Sulfur content, 2.8–3.2 wt%
- TAN value, 0.7–1.0 mg KOH/g sample
- CCR, 7.0–9.0 wt%

The most widely used SynDilBit in the market is WCS (Western Canadian Select). Another blend is WH (Wabasca Heavy).

Composition of Pipeline Blends

Figures 6–2 and 6–3 show the composition of various types of blends available in the market. Synthetic crude has no bitumen in it; hence, there is no resid in the crude.

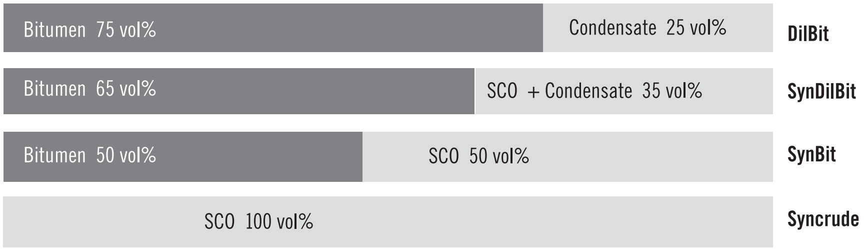

Fig. 6–2. Variation in effective pipeline capacity with type of blend

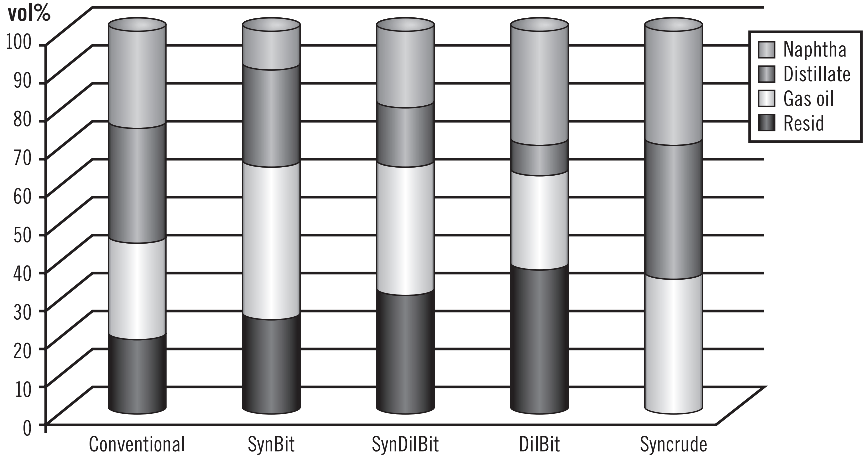

Fig. 6–3. Composition of various types of blends

As shown in figure 6–2, the bitumen concentration in the blend increases from SynBit (50 vol%) to SynDilBit (65 vol%) to DilBit (75 vol%). Hence, for a fixed capacity of pipeline of 100,000 BPD, SynBit would transport 50,000 BPD, SynDilBit would transport 65,000 BPD, and DilBit would transport 75,000 BPD of bitumen. From an economic point of view, although the cost of transportation through the pipeline of a particular volume of blend is the same, on a simple bitumen-volume basis, the amount of bitumen transported per unit volume will be different for the production companies and consequently will affect their economics. Hence, there is a penalty for transporting the diluent.

Figure 6–3 illustrates the detailed composition of various synthetic blends as compared to typical conventional crude. Increase in the bitumen concentration in the blend increases the resid concentration in the same ratio. Conventional crude has the minimum amount of resid (15 vol%) as compared to the other synthetic blends (20–30 vol%). DilBit has the highest concentrations of naphtha (35 vol%) because it is added as a diluent, while syncrude has almost the same amount of naphtha because it is produced from the cracking of the bitumen. Conventional crude has natural straight-run naphtha (30 vol%).

DilBit has very small amount of distillate (5 vol%) because it is not present in either the bitumen or the condensate. It has some gas oil (20 vol%), which comes directly from the bitumen. Syncrude has a large volume of distillate (35 vol%) and gas oil (30 vol%) as cracked product from the bitumen; subsequently, they are proportionately distributed in the synthetic blends. Typical conventional crude consists of about 30 vol% distillate and about 25 vol% gas oil.

Because of the large scale of mining operations as compared to in situ operations, almost all mining development projects are associated with upgraders in the field. This eliminates the diluent demand for the mining projects. By contrast, in situ projects are too small and an upgrader is too expensive to be integrated in the projects. Hence, in the future, because bitumen production is expected to increase through in situ projects, the demand for diluent will therefore increase. For this demand to be met, in situ projects must either include a small-scale field upgrader or partially upgrade the bitumen.

Blend composition and API gravity

The amount of diluent required in order to meet the targeted pipeline specification is directly related to the API gravities and viscosities of the diluent and the bitumen. The higher the molecular weight is of the diluent, the higher will be the amount of diluent required in order to achieve the same API value of the blend.

Figure 6–4 illustrates the amount of diluent required in order to meet pipeline specifications if it were blended with bitumen that has an API gravity of 10° or a density of 1,000 kg/m^3 to make the blend have an API gravity of 19° or a density of 940 kg/m^3. According to the author's experience (not a published work) it has been observed that, for a blend, if the density specification is met, then the viscosity specification of 350 cSt is always met, but not vice versa.

The lower the diluent's API gravity is, the higher will be the volume of diluent required in order for the blend to meet the pipeline specification of 19°API. For example, to make 100 bbl of a blend (bitumen + diluent), it will take 60 bbl of diluent of 25°API, or 50 bbl of diluent of 30°API to meet the pipeline specification. If very light naphtha or condensate of 65°API is used as diluent, then only 20 bbl of diluent will be enough to transport 80 bbl of bitumen of 10°API through the pipeline.

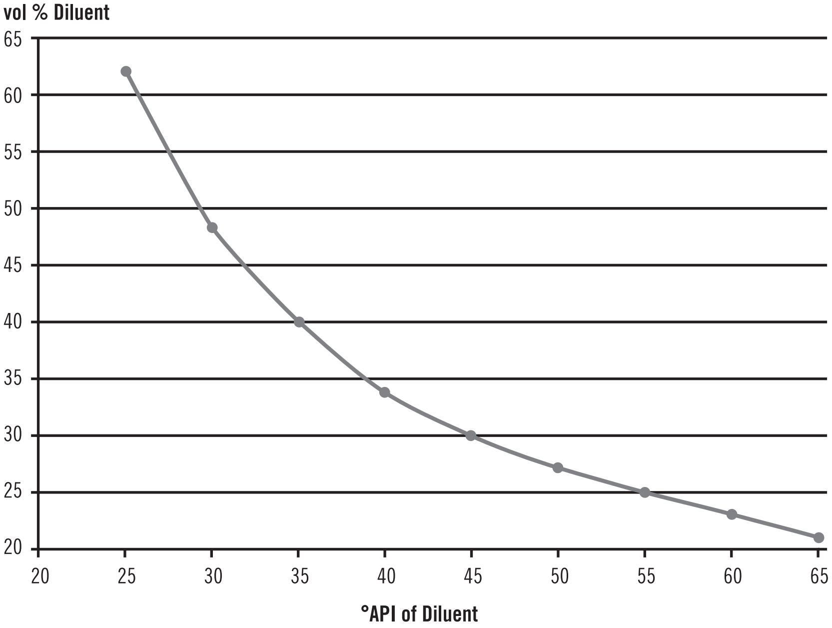

Fig. 6–4. Diluent API gravity and corresponding vol% to meet target of 19°API (given raw bitumen API gravity of 10°)

Care should be taken, however, when blending raw bitumen with a large excess of paraffinic diluent, because of the risk of precipitating the asphaltenes, leading to an increase in fouling. Moreover, if the bitumen has already gone through any partial or full upgrading process(es), the chance of fouling increases much more as compared to when raw bitumen is used.

Orimulsion

Orimulsion is a proprietary technology developed by the Petroleum Research Organization (Pdvsa) of Venezuela, where heavy oil is transported and sold as fuel in the form of an emulsion: a mixture of 70% heavy oil and 30% water with added phenolic or alcohol-based surfactant. Use of this mixture also reduces the viscosity of the heavy oil, thus facilitating transportation of the heavy crude. Initially, Orimulsion was a huge success as a fuel competing with coal in electricity-generation plants because there was no upgrading cost. However, in light of the present disruption in the Venezuelan oil industries (due to internal problems), the present status of Orimulsion is unknown.

Challenges Facing the Pipeline Industries

Stability issues

A milestone for the pipeline industry will be to accept various categories of blends. Every blend behaves differently because the fouling tendency strongly depends on the quality and composition. The fouling tendency of a blend is defined in terms of *stability*. A crude blend is defined as *unstable* when fouling takes place as a result of solid settlement, precipitation of asphaltenes, and sediment or gum formation during transportation. There are economic penalties for transporting such crude blends.

Major stability problems are due to blending incompatibilities. It is common to blend conventional crudes with standard compatible crudes, such as West Texas Intermediate (WTI) or Alaskan North Slope (ANS). Because processed heavy oil and bitumen have different compositions, they may be incompatible with WTI or ANS. It is well known that there are incompatibilities between the high-asphaltene and high-paraffinic crudes. Precipitation of asphaltenes when blending crudes can lead to catastrophic fouling in the pipeline or coking in the preheat train, resulting in net economic loss. The blending of crudes known to be incompatible should always be avoided.

In addition, severely thermally cracked bitumen products, such as coker liquid, contain olefins and diolefins, which cause fouling as a result of polymerization or gum formation. Also, mildly thermally cracked visbroken products are notorious for their instability. A visbreaking study determined that the instability due to sediment formation increases by about 100 times in a mildly visbroken product as compared to raw Athabasca bitumen.[2]

The reason for the increase in instability of the thermally cracked product is that once the asphaltene structure is disturbed as a result of thermal cracking, it starts agglomerating. Consequently, the tendency to precipitate out increases such that it precipitates out into its own liquid. This enhances the rate of fouling.

Stability measurement

Every pipeline blend has to meet stability criteria before transportation. Therefore, it is important for the pipeline industry and for refiners to measure stability before purchasing a blend. Several compatibility models and laboratory tests measure stability and thus can be employed to prevent fouling. Unfortunately, most of these methods are proprietary and not available publicly, for the purpose of standardization; even large oil companies are using different proprietary methods of their own. The following sections describe available, standard laboratory methods to measure the stability of a blend.

Bromine number test. Olefin concentration is measured by titration using a bromine solution per method ASTM D-1159. It is cautioned here that the bromine number should be measured only in distilled product and not on whole crude containing resid, because the latter will give erroneous results. The higher the bromine number is, the higher will be the unsaturated components in the blend and the greater the tendency to foul. The bromine number is expressed as the number of grams of bromine required in order to saturate 100 grams of the test sample (i.e., in units of g Br_2/100 g sample). A bromine number above 10 in a naphtha fraction is considered an unstable product.

Recently, PONA analysis has been introduced as the standard analytical technique for the olefin determination. The maximum limit is set to 1 wt% in a light distillate.

Centrifuge method. Stable emulsion and fine solid particles also cause fouling. It is determined by BS&W measurement by the standard ASTM D-4007 method, and a value of above 0.5 wt% is considered unstable.

Shell Hot Filtration Test. Sediment formation is measured by a standard method known as the Shell Hot Filtration Test. The standard method for the measurement of sediment is ASTM D-4870. In this method, the sample in question is diverted into a hot, sintered filter at 100°C and passes through a Whatman GF/A glass-fiber filter medium. Hot filtration is performed under vacuum by using a steam-jacketed metallic funnel. After filtration, the solid sediment is washed with hot *n*-heptane. The amount of dry sediment retained is weighed. If the amount of sediment collected is greater than 0.1 wt% in the blend, then it is considered unstable (i.e., unsuitable for transportation).

***P*-value test.** This method was developed by Shell (method 1600-80) as a stability test for asphaltenes. In this method, the oil sample is titrated with a known volume of *n*-paraffin, such as *n*-cetane, as solvent. Precipitation is observed under a microscope. This is measured by the maximum amount of *n*-cetane (in ml) added to a gram of oil sample to keep the asphaltenes in solution—that is, when the first indication of the precipitation starts.

The *P* value is calculated as follows:

$$P = 1 + \frac{\text{ml of } n\text{-cetane}}{1 \text{ gram of sample}} \tag{6–1}$$

If the *P* value calculated using equation 6–1 is greater than 1.1, then the solution is considered stable. In other words, if it takes more solvent to precipitate the asphaltenes, then it is more stable.

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2 Banerjee, D. K., W. C. McCaffrey, and M. R. Gray. 1998. *Enhanced Stability of Products from Low Severity Upgrading of Residue*. Internal report, Department of Chemical and Materials Engineering, University of Alberta, Edmonton.

UPGRADING OF HEAVY OIL/BITUMEN

7

Why Upgrade Bitumen?

As discussed in earlier chapters, the virgin (unprocessed) bitumen is not mobile at normal conditions; it has poor cold-flow properties. Hence, raw bitumen and heavy oil are never sold as recovered, because it is not suitable for transportation. It is either transported to the market and sold as diluted bitumen or upgraded in the field and sold as synthetic crude oil.

For the value of the bitumen to be increased so that it may compete with the conventional crude, it is absolutely necessary to increase the quality of the bitumen by upgrading. With the increase in production of bitumen, the market for syncrude will have to be increased, which requires investment by the producer in a heavy oil upgrader. Whether it is attractive to invest in an upgrader will be determined by the price differential between light and heavy crude. A steady price differential market will be required over the planning, design, and construction period, which typically takes several years. Current environmental demand for emission control in heavy oil requires such considerable investment that the profit margins are greatly curtailed. Hence, for an increase in the synthetic crude market to be realized, upstream and downstream interests must be merged.

As shown in figure 7–1, the upgrading of bitumen comprises two stages: primary and secondary upgrading. Primary upgrading is usually carried out either thermally, by the coking process, or catalytically, by the resid-hydrocracking process. In the primary upgrading step the bigger molecules are cracked into lower-molecular-weight molecules to make a desirable distillable product. In both cases, the processed oil's composition is fundamentally different from the virgin oil's composition in terms of sulfur, nitrogen, oxygen, and hydrogen. The gaseous components consist of lighter hydrocarbons, or liquefied petroleum gas (LPG), that are separated and used as fuel. Primary upgrading processes are discussed in detail later in this chapter.

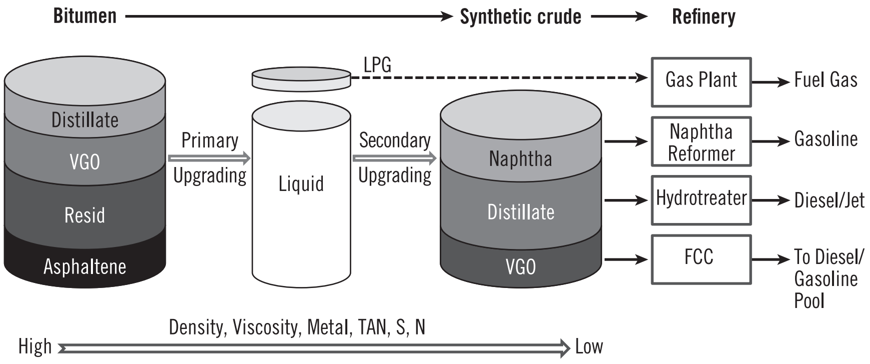

Fig. 7–1. Typical route of bitumen to refinery

In the secondary-upgrading stage, the resulting liquid oil from the primary step is further processed to produce a syncrude that meets the refinery feedstock specifications. The most common process to remove heteroatoms and metals, as well as to saturate the aromatics, is hydroprocessing. This resembles a conventional refining hydrotreating process and is therefore not discussed here in detail.

Thus, syncrude quality depends not only on the properties of the bitumen as feedstock but also on the history of the thermal and catalytic processes that took place. Hence, the syncrude is drastically different from the conventional oil with the same boiling-point distribution. Conventional refineries cannot always handle syncrude owing to its limited catalyst performance.

Syncrude at the refinery gate mainly consists of naphtha, distillate, and heavy gas oil. The naphtha fraction goes to a reformer to be converted into high-octane gasoline. The distillate fraction is treated in a hydrotreater to meet the specifications of diesel, kerosene, and jet fuel. The gas oil fraction is directed to a fluidized catalytic cracking (FCC) unit or to a hydrocracker, to convert the heavier feedstock into diesel and gasoline range products. To find out more about the refining processes, readers may consult additional sources.[1]

Synthetic Crude versus Conventional Crude

Synthetic crude is one of many misnomers in the oil industry. It is neither a synthetic material nor a crude; rather, it is a thermally processed liquid derived from bitumen.

The formation of the synthetic crude oil from the bitumen is dominated by a thermal cracking reaction in an upgrading process. The long-chain paraffinic groups in the residue are likely to cleave β or γ bonds on an aromatic or naphthenic ring, to form lower molecular-weight products with alkyl-aromatics and naphthenic rings in the distillate. When hydrocracking is used instead of coking in the primary upgrading, there will be lower amounts of sulfur and nitrogen in the distillate. Still, secondary hydrotreating is required in order to meet the refinery specifications. Heteroatoms that migrate to the syncrude are resistant to further hydrotreating.

Hydroprocessing of syncrude is a major process in a refinery. It is also difficult, because several reactions occur simultaneously (e.g., the removal of S, N, O, and metals, along with the saturation of aromatics and olefins). Above 400°C, the coking reaction competes with the hydrogenation reaction, and the availability of hydrogen and the reaction pressure dictate which reaction dominates.

The cetane number of the diesel fraction of a synthetic crude is less than that of a conventional crude, and the diesel fraction requires further treatment before use. Paraffin in the bitumen usually moves into the naphtha range after cracking instead of into the diesel range, where it is needed to be for cetane improvement. Aromatic hydrogenation is another way to improve diesel quality; however, it reaches thermodynamic equilibrium and limits the process of naphthenic compound formation.

Fractions of synthetic crude are more aromatic than conventional crude. This property is desirable in the gasoline fraction because it acts as an octane improver; however, it is undesirable in diesel and jet fractions because it gives poor cetane and smoke numbers.

Similarly, the VGO fraction in syncrude is rich in aromatics and heteroatoms, making it difficult to crack in an FCC unit. VGO in syncrude poisons the catalyst faster than VGO in conventional crude. Because of the heavy demand for gasoline in the United States, the cracking of gas oil in an FCC unit is an important process.

Most syncrude is produced by a delayed-coking process. The product is more aromatic and olefinic as compared to conventional crude. This requires sufficient hydrotreating, which a conventional refinery may not be able to handle without major capital investment.

Syncrude is better than conventional crude in certain respects, because it does not contain any resid, asphaltenes, metals, or salt. However, most of these advantages are negated when syncrude is blended with bitumen to produce SynBit.

If a grassroots refinery is built, then the most probable choice would be to design it to handle boutique syncrude refinery feedstock only. The most important advantage will be that no vacuum tower or desalter is required. Syncrude's acidity is lower than that of the conventional crude; hence, metallurgy of the crude tower will be simpler, with the choice being between an FCC unit and a gas oil hydrocracker unit. On the one hand, the FCC product would be more hydrogen deficient and thus would require severe hydrotreating to produce a marketable product. On the other hand, a hydrocracker product would be more hydrogenated than the FCC product and would have the added benefit of controlling the gasoline-to-diesel yield ratio according to market demand. However, the choice of catalyst in a hydrocracker is difficult, because syncrude contains a higher concentration of refractory nitrogen as compared to conventional crude.

Carbon deposits on the catalyst surface are also prevalent in syncrude feedstock owing to higher concentrations of oxygen, nitrogen, and aromatics. The shift in refinery feedstocks from conventional to synthetic crude necessitates the improvement of catalyst quality, toward the selectivity of the desired products.

The overall hydrogen demand is higher in a syncrude refinery than in a conventional crude refinery, even though it does not have to deal with resid or asphaltenes. In general, a conventional refinery cannot handle the unpredictable variation of syncrude properties that would cause an increase in corrosion, fouling, and process upsets.

On the other hand, in the case of hydrogen-addition technologies, a major part of the emission of CO_2 is associated with the production of hydrogen from natural gas and other utilities.

Severity of Upgrading

The following are the biggest problems in processing heavy crudes:

- Low API gravity (<10°) or high density (> 1,000 kg/m^3)
- High asphaltenes (>10 wt%)
- Low H/C ratio (<1.5)
- High metals content (>100 ppm)
- High heteroatom contents (S > 3 wt%; N > 1,000 ppm)
- High acidity (TAN > 2 mg KOH/g sample)
- High carbon residue (CCR > 10 wt%)
- Unknown chemistry of big resid molecules

Because of the aforementioned poor properties of bitumen, severe processing conditions are needed to upgrade it. Severity of the process depends on several factors:

- Temperature
- Total pressure
- Residence time
- Hydrogen-to-feed ratio
- Partial pressure of hydrogen

Severity is usually an indication of resid conversion. The higher the severity is, the higher will be the resid conversion.

Resid conversion is defined as follows:

$$\text{wt\% resid conversion} = \frac{\begin{array}{c}\text{wt of resid in feed} - \\ \text{wt of resid in product}\end{array}}{\text{wt of resid in feed}} \times 100 \qquad \textbf{(7–1)}$$

Similarly, the degree of removal of sulfur, nitrogen, or metals in a secondary hydrotreating process is defined as follows:

$$\text{wt\% S/N conversion} = \frac{\text{wt of S,N in feed} - \text{wt of S,N in product}}{\text{wt of S,N in feed}} \times 100 \qquad \textbf{(7–2)}$$

Of course, in a catalytic process, conversion is highly dependent on the catalyst activity.

Major Upgrading Processes

The first step in upgrading is to separate the lighter, distillable fraction (<535°C [<1,000°F]) from the resid (>535°C [>1,000°F]) by using a vacuum distillation unit. The lighter fraction behaves similarly to the medium-sour conventional crude familiar to refiners. However, handling of the heavier, nondistillable resid poses a challenge. Half of a barrel of bitumen consists of this resid. A key criterion in choosing an upgrading process is the ability to optimize the cracking process for the breaking of the most difficult bigger molecules, to maximize the distillable liquid yield.

Bitumen is deficient in hydrogen, having an H/C ratio of less than 1.5. This calls for the upgrading of bitumen to increase the H/C ratio to above 1.5 in the final product. There are two major ways to increase the H/C ratio—either by rejecting the carbon or by adding hydrogen.

As shown in figure 7–2, there are two major upgrading processes: carbon rejection and hydrogen addition. There are several carbon-rejection options available in the market, and they are all commercially proven and economically attractive residue upgrading options as compared to hydrogen addition. However, carbon-rejection processes typically have a substantial reduction in liquid volume yield, since part of the crude is converted into solid coke or pitch. Details of the individual upgrading technologies are discussed in chapter 8; however, the general processes are described below.

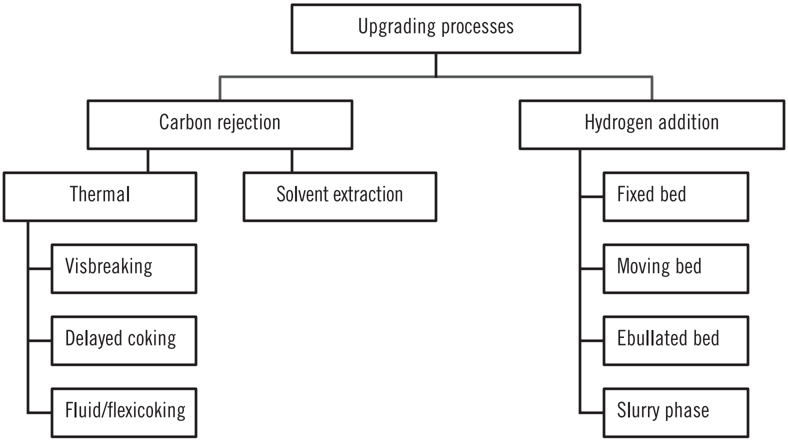

Fig. 7–2. Heavy oil–upgrading options

Carbon-rejection processes

Carbon rejection can be done by a thermal process in which chemical changes take place in the molecular structure of the feedstock, or it can be done by a simple physical process in which highly concentrated bigger carbon structures, such as asphaltenes, are physically separated by solvent extraction. The most fundamental reaction for the upgrading of bitumen is the thermal cracking of the bigger molecules into smaller ones. Cracking of the molecules is dependent on the bond energies. Because there are various types of bonds involved with different bond energies, the thermal reactions are not simple. The following sections describe the various types of carbon-rejection processes.

Visbreaking. The most economical and easiest thermal process is visbreaking. (The terminology comes from viscosity breaking.) It is the oldest technology, in which the heavy feedstock is subjected to mild thermal cracking at a lower severity to reduce the viscosity and to produce fuel oil.

In the visbreaking process, bigger molecules are partially broken, so that the viscosity of the crude is decreased to such an extent that the liquid becomes mobile. This process has its limitations, and the most common problem is the relative instability of the visbroken product. This process is not of much use in the United States and Canada and has only limited use in Europe because there is no market for the residual fuel oil produced in visbreaking. Hence, detailed discussion of the process is avoided.

The thermal cracking takes place in the furnace coil, while the feedstock is travelling through the furnace. The visbreaker temperature is usually 450–500°C in the furnace, and the feed rate is maintained between 1 and 5 minutes. In another type of visbreaker, called a *soaker drum*, the temperature is lowered to 430–450°C, and residence time is increased to 5–8 minutes. The disadvantage of the soaker-drum process is that it forms more coke than the coil-type visbreaking process and requires frequent decoking—at additional cost and handling but yielding the same product qualities.

Most commercial units operate at between 20% and 30% of the resid-conversion range. This is because, as the conversion increases, the product becomes more unstable, owing to asphaltenes precipitation. After visbreaking, the lighter fraction is used as blendstock in the refinery, and the heavier fraction is used as a source of fuel oil.

Coking. The most widely used thermal commercial process is coking. In particular, it is the most dominant process in U.S. refineries, and there is increasing use of coking as an upgrader technology in Canada and Venezuela. In the coking process, the feedstock is subjected to severe thermal conditions (i.e., very high temperature and longer residence times). Under these conditions, the resid conversion is almost 100% complete.

Figure 7–3 represents a proposed reaction mechanism of the formation of coke from a hypothetical resid structure. Through severe cracking, side chains of the aromatic structure are randomly broken to produce aromatic and paraffinic liquids. The big aromatic molecules, with the elimination of hydrogen and polycondensation, ultimately turn into coke (labeled as *coke-1* in fig. 7–3). The liquid product is further cracked and dehydrogenated to produce a highly olefinic liquid product known as *coker oil*, as well as gaseous products. Certain of the olefinic hydrocarbons also undergo polycondensation reactions and produce coke (labeled as *coke-2* in fig. 7–3). Because the coke is derived from a petroleum-based feedstock, it is widely known as *petcoke* in the world market.

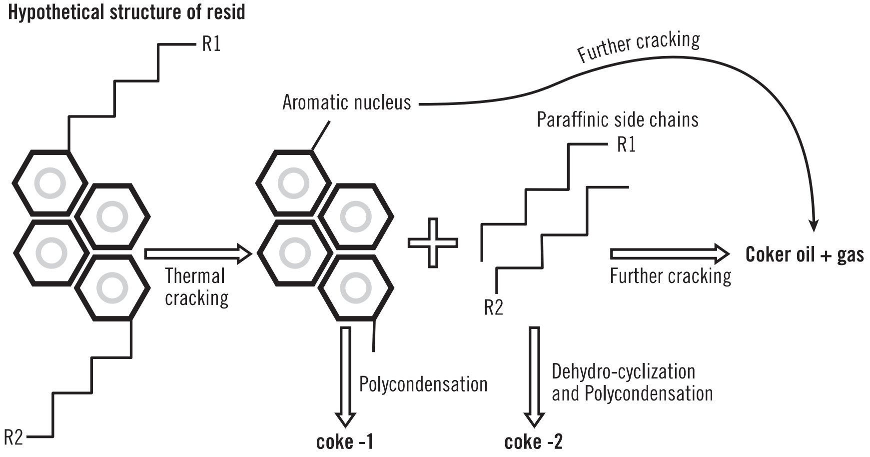

Fig. 7–3. Proposed coking reaction mechanism

In figure 7–3, coke-1 is derived from the aromatic nucleus containing heteroatoms and metals; thus, coke-1 consists of large amounts of sulfur, nitrogen, and metals. Although coker oil has higher market value, the economics of the process is driven by the value of the coke. Coke-2, produced from the paraffinic and aromatic liquid hydrocarbons, contains a much lower amount of heteroatoms and almost no metals. The H/C ratio of coke-2 is expected to be higher than that of coke-1. Coke-2 is more crystalline in structure as compared to coke-1, which is amorphous. Hence, coke-2 has higher market value than coke-1 does.

The yields and properties of coke, coker oil, and gaseous products are highly dependent on the feedstock quality. This is because the severity is maintained at maximum to run the process essentially at 100% resid conversion.

There are two major commercial coking processes:

- Delayed coking
- Fluidized-bed coking (also called fluid or flexicoking)

With the ever increasing bitumen production in Canada, the coking capacity is also increasing rapidly in the United States and Canada. The majority of the commercial coking processes are controlled by the delayed-coking technology. By contrast, in fluidized-bed coking, the net coke yield is less, because part of the coke is burned during the process to generate heat.

Delayed coking. The delayed coker acts as the garbage can of the refinery, into which any unwanted material in the refinery stream is thrown. In delayed coking, the heaviest part—the material that is most difficult to convert—is converted into coke, part of which is then converted into liquid product. The coke yield and its properties are influenced by the feedstock characteristics. The most common feedstock is vacuum residue, containing high sulfur and metals. Coke yield is directly related to the concentrations of asphaltenes and CCR in the resid.

The coking reaction takes place in a drum. The drum outlet temperature is maintained in the range of about 430–450°C (800–850°F) at a pressure of 30–60 psig (pounds per square inch, gauge). The feed is charged at the bottom of the coker drum after being heated in a furnace at a higher temperature (490–500°C [910–930°F]). The material at the bottom of the drum sits for several hours, during which it turns into coke. This coke is porous, allowing the passage of liquid and gaseous products. The coke accumulates from the bottom to the top of the drum; the vaporized product comes out the top of the drum.

Delayed coking is a semibatch process that works in a 24-hour cycle. A typical coking plant consists of two drums. In the first 12 hours, the first drum is filled with coke; then, the feedstock is switched to the second drum. For the next 12 hours, decoking takes place in the first drum while the second drum is filled with coke. The coke is removed from the drum by cutting with high-pressure (~3,000 psig) steam. The coke drops from the bottom of the drum directly onto a conveyer belt or transportation cars (e.g., truck or rail).

Although coking is generally thought of as a good way for refiners to get rid of the low-value dirty material in the feedstock, delayed coking can also be used to produce a high-quality coke that is more valuable and in greater demand than that produced by fluid-coking technology. Commercially, the coke produced from a coker is known as *green coke*. The green coke is *calcined* at very high temperature (1,200–1,350°C) in a rotator kiln before being marketed to carbon and graphite industries. The calcined coke loses its volatile matter and attains a crystalline structure.

Three major types of cokes are produced commercially: *sponge coke*, *shot coke*, and *needle coke*. They differ significantly in properties and end use.

Sponge coke is produced in a delayed coker when resid is rapidly heated and fed into a coker drum. The coke formed is spongy in character and hence gets its name. This coke from Alberta bitumen usually contains most of the sulfur and metals and sometimes is not even suitable for burning, depending on the level of impurities. However, calcined sponge coke with low impurities is used for making anodes in the aluminum industry.

When the coker is operated in such a way that the operator wants to maximize the liquid product yield instead of the coke yield, *shot coke* is formed. As the name suggests, shot coke is usually spherical in shape, and it ranges in sizes. This is the least valuable coke.

The production of *needle coke* involves a special application of delayed-coking technology. This is the most valuable coke. Unlike the other delayed-coking processes, in which the feedstock is resid, in this case, the feedstock is a lower-molecular-weight, highly aromatic resid-free liquid, with very low levels of asphaltenes and of impurities (e.g., metals). The coking reaction is represented by the reaction path to coke-2 shown in figure 7–3, and there is no metal or sulfur in the resultant coke. Because the coke is formed through polycondensation of low-molecular-weight molecules, the coke forms a layered or crystalline structure with no cross-linking; the appearance of these needlelike structures gives this type of coke its name.

Needle coke is processed under extremely strict operating conditions, and most of the information on it is kept proprietary and confidential. The pretreated feedstocks are free of impurities. Examples of such feedstock include slurry oil, decant oil, and thermal tar. Needle coke yield and quality depend on coker operating conditions—such as coker temperature, drum pressure, feed recycle ratio, and steam addition—in addition to the feedstock properties.

Needle coke has a very particular market for the production of graphite electrodes. Needle coke specifications are very strict, with very low sulfur (<0.5 wt%) and less than 100 ppm of metals. Because of its use in the electrode industry, one major property of needle coke that is valued in the market is popularly known as the *CTE value* (coefficient of thermal expansion). The CTE value represents the rate of expansion of the electrode at furnace temperature. Thus, the lower the rate of expansion or the lower the CTE value is, the better will be the quality of the needle coke and the higher will be its market value.

Fluid coking/flexicoking. Compared to delayed coking, which is a semibatched process, fluid coking is a continuous process. As the name suggests, it is carried out in a fluidized-bed riser reactor—that is, coke particles are fluidized by injecting steam at the bottom of the reactor. Resid feedstock is sprayed on the fluid coke particles, which crack into lighter products and coke. The coke is formed as spherical materials on the surface of the original coke. The coke is continuously withdrawn from the bottom of the riser reactor before it becomes too big and is transferred to the adjacent burner, where it is burned.

The lighter, vaporized product leaves the reactor from the top and passes through a cyclone, where entrained coke particles are separated from the hydrocarbons. Hot coke particles from the burner are recycled back into the reactor. Fluid coke is not suitable for further use, because of higher concentrations of impurities as compared to delayed coke.

The fluid coker is run at a higher temperature than the delayed coker, at a range of 520–540°C (950–1,000°F) but at a low residence time, of only a few minutes. Thus, the yield of coke decreases, and the liquid product increases, compared to the delayed-coking operation. The feed cracks more at higher temperature, thereby producing more liquid. The lower residence time is insufficient to polymerize the unsaturated hydrocarbons, thus decreasing the coke yield and increasing the liquid yield.

Hydrogen-addition processes

The processing of heavy crude in the presence of hydrogen is a major step in the upgrading of heavy oil or bitumen. Because bitumen is highly deficient in hydrogen and contains high concentrations of heteroatoms and metals, it is imperative to improve the quality of the upgraded product by removing the impurities; this is done by means of adding hydrogen. The hydroprocessing of heavy oils has been described in detail elsewhere.[2] With the increasing global market demand for clean transportation fuel, the role of hydroprocessing technology is expected to increase.

Hydroprocessing of residue undergoes a series of reactions:

- Hydrocracking. In this first reaction, bigger molecules are cracked, and then the free radicals thus formed are capped by hydrogen, to prevent polymerization reaction toward coke formation.
- Hydrotreating. In this reaction, heteroatoms and metals are removed.
- Hydrogenation. This is the simultaneous saturation of aromatics (i.e., done in concert with hydrotreating).

Hydrotreating is a complicated combination of the following simultaneous reactions:

- Hydrodesulfurization (HDS)
- Hydrodenitrogenation (HDN)
- Hydrodemetallization (HDM)
- Aromatic/olefin saturation

Further, already complex mixtures of reactions become more complicated, because the types of molecules present in the feed are so different that they get removed at different rates. For example, the following are the relative rates of HDS reactions:

thiols or thioethers > thiophenes > benzothiophenes > dibenzothiophenes

As the boiling point of the heavier fractions increases, the removal of sulfur becomes progressively more difficult. In all cases, sulfur is removed as hydrogen sulfide (H_2S), and as the concentration of H_2S increases in the reactor system, the rate of the HDS reaction decreases. Hence, it may be necessary to remove the H_2S online to increase the removal of sulfur. The HDS reaction is also affected by the presence of nitrogen in the system.

The removal of sulfur in a ring structure (e.g., benzothiophene) occurs either with hydrogenation of the ring first or without hydrogenation of the ring. However, in the case of nitrogen in the ring structure, HDN always follows hydrogenation of the ring, subsequently breaking the ring and removing the nitrogen.

Note that the initial step of hydrocracking resid is not a catalytic process, even though there is catalyst present. The first cracking of the aliphatic side chain of the bigger molecules takes place at a temperature above 350°C (>660°F) and is a thermal process. Hydrogenation of the cracked product is a catalytic process.

By contrast, polynuclear aromatic hydrocarbons undergo hydrocracking in the presence of catalyst only. Aromatic rings in the outer layer first get hydrogenated to a naphthenic ring, which subsequently cracks. Hydrogenation of an aromatic ring requires higher pressures (>2,000 psi); hence, the hydrocracking of resid requires a combination of high temperature and high pressure in order to complete the reactions without forming coke. It is easier to hydrocrack polynuclear aromatic hydrocarbons than simple aromatic ring hydrocarbons.

All hydrogenation reactions are highly exothermic. The heat released per mole of hydrogen consumed varies in the range of 60–70 kilojoules per mole (kJ/mol).

In the hydrocracking process, the presence of asphaltenes is a major issue.[3] The most undesirable consequences of their presence are the formation of coke and the precipitation of asphaltenes on the catalyst surface. The actual chemistry behind asphaltene hydrocracking is still unknown.

The severity of the hydrocracking process increases as the feedstock gets progressively heavier and as the desired quality of product increases. The configuration of the reactor and the severity of the hydroprocessing operation for bitumen are different than for lighter (conventional) crude oil.

Catalyst. A number of metal catalysts are available for hydrogenation reactions. Among the most commonly used metals are nickel, chromium, tungsten, molybdenum, palladium, cobalt, iron, and copper. Metal catalysts get poisoned easily in the presence of sulfur and nitrogen. Therefore, oxides or sulfides of the metals are usually used, to avoid poisoning.

Nickel and vanadium porphyrin structures are about four to five nanometers in diameter.[4] During high-temperature operations, the organometallic structure decomposes, and the metals are deposited on the surface of the catalyst. Nickel and vanadium irreversibly cover the catalyst pore and deactivate the catalyst. Thus, the process of deactivation is a metal adsorption process, not a catalyst deactivation process as commonly considered. The thermal deposition of the metals is a very rapid process and usually takes place in the initial stage at the front end of the catalyst bed of fixed-bed hydroprocessing reactors. Hence, the demetallization of heavy oil is carried out in a guard reactor with a proper catalyst pore-size design to capture the metals.

Hydrocracking of heavy crude comprises a combination of reactions—namely, cracking the bigger molecules, followed by their hydrogenation. Usually, bifunctional catalysts are used for this purpose, and these are made of both acid functional groups, for cracking, and active metals, for hydrogenation.

Commercial catalysts are made of a support containing acidic crystalline zeolites and amorphous silica-alumina compounds that provide acid groups. That support is impregnated with active metals—such as palladium, molybdenum, nickel, or tungsten—that provide the hydrogenation activities. Basic nitrogen in the feed, such as pyridine or ammonia, as a product, destroys the acidity of the catalyst and deactivates it.

Researchers are now actively involved in the development of the latest generation of *ultradispersed* (UD) homogeneous catalysts for the hydroprocessing of heavy oil and bitumen.[5] All slurry-phase hydrocracking technologies under development are switching to UD catalysts (discussed in chap. 8). UD catalysts are made of nanoparticles of active metals (e.g., Ni, Mo, Co, and W). They are injected as liquid phase into the reaction zone, either in solution or as an oil-water emulsion. The active nanocatalyst is formed inside the reactor and is dispersed throughout the oil phase.

There are two main advantages of using a UD catalyst over a solid support–based catalyst:

- Because of its nano size, it has high surface-area-to-volume ratio and is much more active than the solid support–based catalyst.

- Because there is no solid support, metals from the bitumen feedstock cannot be deposited into and plug the pore volumes; thus, the catalyst remains active for a longer period of time.

The concentration and the partial pressure of hydrogen in the hydroprocessing of heavy oil are very important. Increasing the hydrogen increases the quality of the final product, decreases the reactor temperature needed for the same reaction, and decreases the rate of deactivation of the catalyst. Thus, for economic reasons, it is essential that the hydrogen be recycled as much as possible and that a higher partial pressure of hydrogen be maintained. Inside the reactor, the recycled hydrogen should be kept as pure as possible.

Hydroprocessing reactors. The main purpose of the hydroprocessing of bitumen during the upgrading process is to prepare the upgraded product as quality feedstock for the refiners. Most of the metals need to be removed so as not to plug the pore volume of the FCC or hydrotreating catalysts, and the basic (alkaline) nitrogen compounds need to be removed so as not to destroy the acid sites of the FCC catalyst. Basically, the lower the impurities content is in the feedstock, the better it is for the refiners.

Over the years, generations of heavy oil hydroprocessing—and especially hydrocracking—technologies have been developed. Improvements in the reactor design from one generation to the next have contributed most to the improvement of catalyst activity by controlling metal deposit and coking. The following sections describe examples of several generations of hydroprocessing reactor designs, developed over a quarter of a century.

Fixed-bed hydrocracker. This is the first generation of hydroprocessing reactor and was designed to treat lighter crude with low sulfur, nitrogen, and metals. With the increasing impurities in the heavier feedstocks, the deactivation rate of the catalyst increased. As a consequence of plugging the catalyst pore size with the metals in the crude, catalyst life was reduced drastically and process shutdowns were frequent. With conventional heavy oil around a 15–20°API range and a metal content below 100 ppm, refiners were able to handle the fixed-bed process for some time, using swing beds and guard reactors.

Moving-bed hydrocracker. The fixed-bed reactor system was improved in the next generation, by the development of moving-bed catalyst systems. The catalyst bed was moved by gravity from top to the bottom, and by doing so, the deactivated catalyst was replaced periodically.

Ebullated-bed hydrocracker. As unconventional heavy oil/bitumen (<10°API) with a much higher metal content (>100 ppm) started coming onto the market, the fixed-bed and moving-bed processes became prohibitively expensive to maintain. In the next generation of hydroprocessing technology, the catalyst bed was expanded upward by fluidizing the bed with liquid flow, with continuous addition and replacement of the catalyst. This technology is also called an *expanded-bed* process.

Ebullated-bed reactors were successful in handling heavier feedstock, such as atmospheric or vacuum resid, having not only high metal concentrations but also high asphaltenes and CCR contents. The main purpose of this development was to make the catalyst life no longer be an issue. The two most commercialized technologies in the market today are LC-Fining, by Chevron Lummus Global, and H-Oil, by Axens/IFP.

The problem with this design is that it requires a relatively high hydrogen partial pressure and a very high catalyst replacement rate. Hence, the process becomes expensive. Another set of problems are scale-up issues, because the reactor is complicated with the combination of liquid and solid flow and expansion of the bed at severe conditions. Because of the fluidization of the catalyst, the attrition rate is high and requires a high-mechanical-strength catalyst.

The ebullated-bed process is limited to high conversion rates (<80 wt%) in a single reactor system with no resid recycling. The problem that arises is the formation of insoluble sediments. This gummy substance, if not controlled properly, causes operational problems or fouling. The tendency to form sediments depends on the quality of the feedstock and on the operating conditions. The higher the conversion is, the greater will be the amount of sediment formation. Because of sediment formation, a fixed-bed process is limited to even lower conversion (<50 wt%) levels.

Slurry-phase hydrocracker. Coke formation, metal deposition, and sediment formation all cause rapid catalyst deactivation. Big molecules, such as asphaltenes, are believed to be mostly responsible for these problems. The problems encountered in the ebullated-bed process were partially resolved by developing the slurry-phase reactor, in which solid additives and a microsize catalyst were added along with the resid feedstock. Because the catalyst enters and leaves the reactor at the same rate along with the feed, catalyst life and deactivation of catalyst are not issues in this case.

The slurry-phase reactor is designed for very high conversion (>90 wt%) of residue without recycling in a single-pass system. The emphasis is on hydrocracking, rather than hydrotreating. For the cracking process to be increased, the reactor temperature must be maintained at a higher temperature, thereby leading to coke formation. However, coke formation is suppressed by adding finely powdered inert carbon-based additives and catalyst. The coke is deposited on the additive surface and carries over with the flow of the liquid, which allows the system to run without fouling.

Challenges in Upgrading of Bitumen

The upgrading industry today faces a highly competitive global market. To meet this challenge, upgraders are seeking cost-effective and energy-efficient ways of converting heavy crude into a lighter product. However, the complexity of a big molecular structure makes it more difficult and expensive to develop innovative technologies in this area.

Heavy crude or bitumen typically requires intensive processing to yield quality products. With increasingly stringent environmental regulations being placed on transportation fuel, the complexity of processing heavy crude is increasing. New upgrading process concepts for converting bitumen or resid are at various stages in development—from laboratory scale to commercial application. Every process condition and severity is different. The degree of severity of upgrading bitumen is measured by the degree of conversion of the resid fraction into synthetic crude. Most bitumen-upgrading processes can be made up of combinations of separations (distillation or de-asphalting), followed by thermal processing (coking or visbreaking) or catalytic hydroprocessing of the resid.

Another main challenge in upgrading bitumen is to control the atmospheric emission of the oxides of carbon, sulfur, and nitrogen. Controlling emissions is also a big part of the oil sands recovery operation because CO_2 is produced during the generation of steam by burning natural gas. However, in the case of upgrading, not all carbon is emitted as CO_2; it depends on the types of process used. In the case of the carbon-rejection process, a part of the carbon is converted into a solid, such as coke or asphalt, and therefore considerably reduces the emission of CO_2. However, the handling and accumulation of coke/pitch is an environmental concern, as this by-product usually contains high concentrations of sulfur and metals from the bitumen feedstock.

Challenges in Catalyst Development

The hydrogenation reaction strongly depends on catalyst activity. Thus, researchers are continuously trying to improve the qualities of the catalysts for hydroprocessing of this bitumen. The unknown complex chemistry of bitumen—especially asphaltenes with polycondensed aromatic structure (size > 30 angstrom) and very high molecular weight (>1,000)—is mostly responsible for creating difficulties in the catalytic conversion of bitumen. For treatment of these bigger molecules, the pore size of the catalyst should be bigger. Because these molecules diffuse slowly, they end up blocking the pore mouth, either by coking or by metal deposition. Once the pore is blocked, the active surface area within the pore is not effectively available for hydrogenation, thus deactivating the catalyst.

One of the most remarkable improvements over the years has been the dramatic decrease in catalyst particle size. With the development of technologies from one generation to the next—from fixed-bed to ebullated-bed to slurry-phase—the catalyst particle size has decreased from over 10,000 microns to below 100 microns.

In the latest catalyst development, researchers are moving away from the high-surface-area support and are developing supportless UD nanoparticle catalysts.[5] Several of the newest generations of slurry-phase processes inject catalyst precursors in liquid phase inside the reactor along with the feedstock, and then the active nanoparticle catalyst is generated in-situ at the reaction conditions.[6] Liquid catalysts are usually made of oil-soluble organometallic compounds or water-soluble salts that break down at reactor temperatures to form active metal sulfides.

Because there is no support—and, therefore, no pore—in the nanocatalyst, there is no issue of blocking the pore volume. Hence, catalyst activity remains for a longer period of time. Because of a very high surface-area-to-volume ratio, these nanocatalysts are highly active and could be even reused by recycling the unconverted pitch—that is, where all the catalyst particles remain after distillation of the liquid product.

The biggest challenge still remains the recovery and regeneration of the catalyst from the liquid phase. The costs of these catalysts are extremely high. Disposal of the spent catalyst also represents a daunting environmental concern. Details of the nanocatalysts are still proprietary information; they are still under development.

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POTENTIAL HEAVY OIL—UPGRADING TECHNOLOGIES

8

This chapter outlines commercial, as well as several semicommercial, or *emerging*, upgrading technologies that will have applications mostly at the wellhead, for upgrading. Although many of the emerging technologies discussed here may not be of academic interest, the concepts have been tested, in either a pilot-scale or a demonstration-scale unit, and have the potential for future commercial or semicommercial applications.

The discussion of results or the comparison of particular emerging technologies is intentionally avoided. Hence, the processes are discussed in general terms throughout. Interested readers may, however, contact the original source of any particular technology.

Technology and Feedstock Properties

The choice of a technology strongly depends on the characteristics of the feedstock and the quality of the product. Figure 8–1 illustrates various preferred feedstock qualities for which a given technology will be most suitable. For example, if the feedstock consists of very-poor-quality vacuum resid or pitch of API gravity close to zero (i.e., very high CCR/asphaltenes [>25 %], sulfur [>5%], and metals [>500 ppm]), then the preferred choice would be a carbon-rejection process; this is because hydrogen-addition technology would be prohibitively expensive and difficult to operate.

However, resid fluidized catalytic cracking (RFCC), though a carbon-rejection process, cannot be used for a feedstock with high impurities, because the catalyst replacement rate would be extremely high and the operation would be difficult. Only a low-resid feedstock with very low CCR, asphaltenes, and metal content could be used for an RFCC plant.

By contrast, when the quality of the feedstock is relatively good, various resid hydrocracking processes are available, depending on the degree of impurities. Key targets of the hydrocracking process are the cost and ease of operation. The main cost is catalyst utilization and hydrogen consumption. The deactivation rate of a catalyst is directly related to the metal and coke deposition on the catalyst surface.

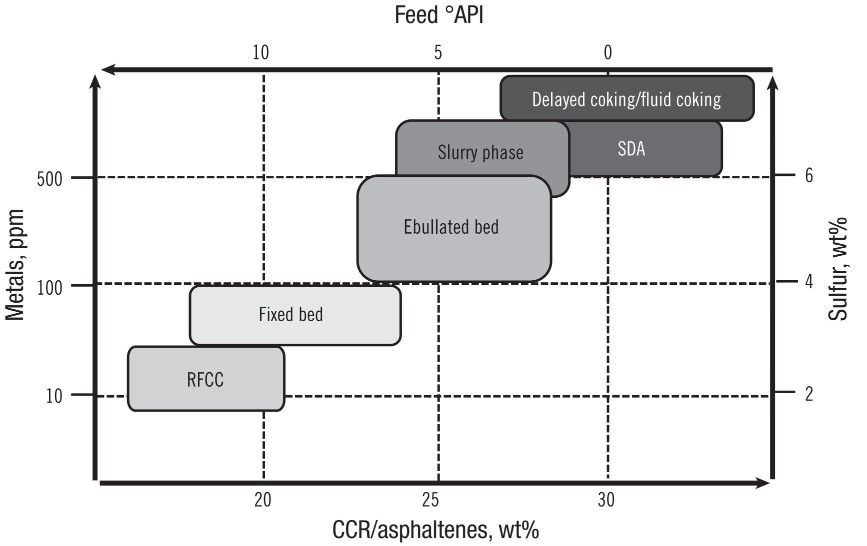

Fig. 8–1. Potential choice of upgrading technology based on feedstock properties

A fixed-bed reactor can tolerate a minimum catalyst deactivation rate at low metal (<100 ppm) and CCR/asphaltenes (< 20 wt%) concentrations in the feed. At higher metal concentrations, the ebullated-bed technology, where online catalyst replacement is done, is more suitable, to avoid frequent shutdown of the fixed-bed operation. Ebullated-bed technology can treat vacuum resid feed of lower API gravity (<5°) and can tolerate higher impurities (>100 ppm). However, with the increase in impurities, the ebullated-bed catalyst replacement rate increases, and the cost of operation is even higher. For treatment of even poorer-quality vacuum resid of much higher metals content (>500 ppm), the slurry-phase technology is more suitable, because catalyst deactivation rate is not an issue. Thus, slurry-phase technology could handle a feedstock similar to that of a delayed coker.

In the first step of the crude distillation process, a typical barrel of Alberta bitumen will yield 15 vol% AGO and another 43 vol% VGO. These two straight-run fractions combined (58 vol%) could be treated in a conventional refinery through the existing plants. However, the remaining 42 vol% vacuum resid requires special processing to make it suitable for further refining into cleaner fuel.

All technologies discussed below are based on Alberta resid, fractionated from Alberta bitumen as feedstock. The typical properties of this resid are shown in table 8–1. Note that the bitumen characteristics resemble those shown previously, in figure 2–2 and table 2–1.

Table 8–1. Typical properties of 525°C+ resid fraction from Alberta bitumen

Properties, units	Average value
API, degrees	2.5
n-C_5–asphaltenes, wt%	19.0
CCR, wt%	24.5
Sulfur, wt%	5.5
Nitrogen, wt%	0.6
Metals V/Ni, ppm	800/200
Kinematic viscosity @100˚C, cSt	100,000

Carbon-Rejection Technologies

Commercial technologies

Delayed coking and fluid coking are the oldest commercial technologies for carbon rejection. Consequently, most of the commercial data are openly available in the literature.

Delayed coking. The most widely used bitumen-upgrading technology is delayed coking because the process is simple and economical. The process was developed more than 50 years ago; however, basically there has been no major improvement in the process since then. The overall process is not efficient; the vacuum resid is heated to above 500°C (> 930°F) in a furnace and is then fed into a coker drum, where the temperature drops 430–450°C and coke accumulates for over 10–12 hours. Coking produces less than 80 vol% or 70 wt% poor-quality liquid, and about one-third of the feed carbon is converted into low-value coke.

As shown in figure 8–2, a typical commercial delayed-coking plant consists of two drums. While the first drum is charged with hot feedstock at the bottom and is being filled with coke, the second drum is decoked. Usually, it runs on a 24-hour cycle.

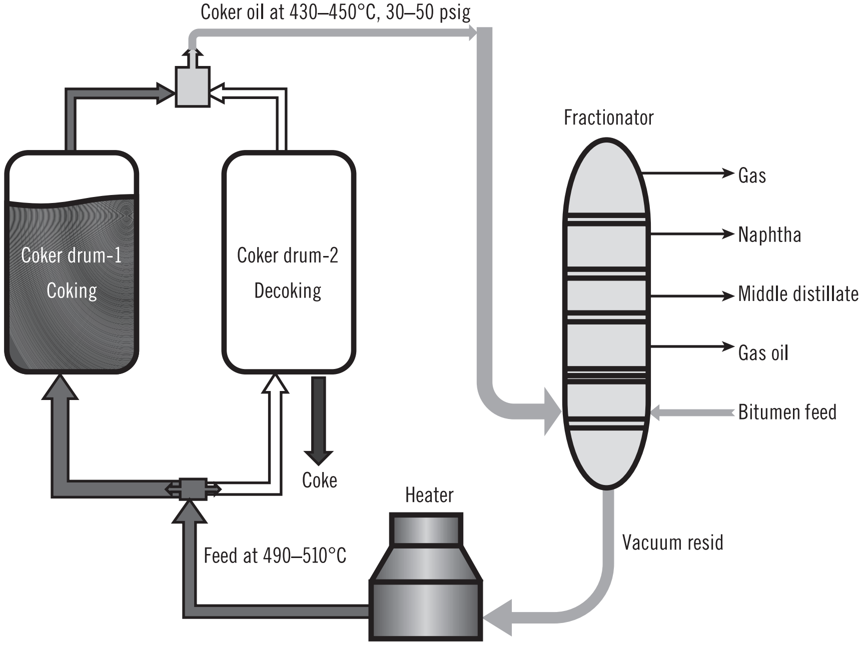

Fig. 8–2. Schematic of delayed-coking technology

The liquid vapor exits from the top of the drum and is directed to a fractionator. The product is highly unsaturated and requires hydrotreating even for short-term storage or for pipeline transportation. The top portion of the drum usually develops a foaming problem; subsequently, carryover of the foam causes operation problems. Operators use silicon-based antifoaming agents to avoid the foaming problem. However, those antifoaming agents deteriorate catalysts in the downstream hydroprocessing of coker oil.

Some delayed-coker operators recycle distillate or gas oil to improve the liquid yield and decrease the coke yield. The advantage of recycling in terms of yield is about 1–5 wt%, and the economical justification of recycling depends on the product quality and yield.

Delayed coking has limited flexibility in terms of operating conditions as compared to the hydrogen-addition processes. The liquid phase has a residence time of hours, but the vapor phase has a residence time of only a few minutes.

There is a narrow window of temperature available for the operation of the commercial delayed coker because the coker-drum temperature is controlled by the furnace temperature, which is limited by the rate of fouling on the furnace wall. However, not much economic benefit results from running a coker at very high temperatures, as the results in figure 8–3 show; liquid yield increases and coke yield decreases by less than 5 wt% with the increase of 25°C in coker-drum exit temperature. The results shown in figure 8–3 are for 5°API resid feedstock.

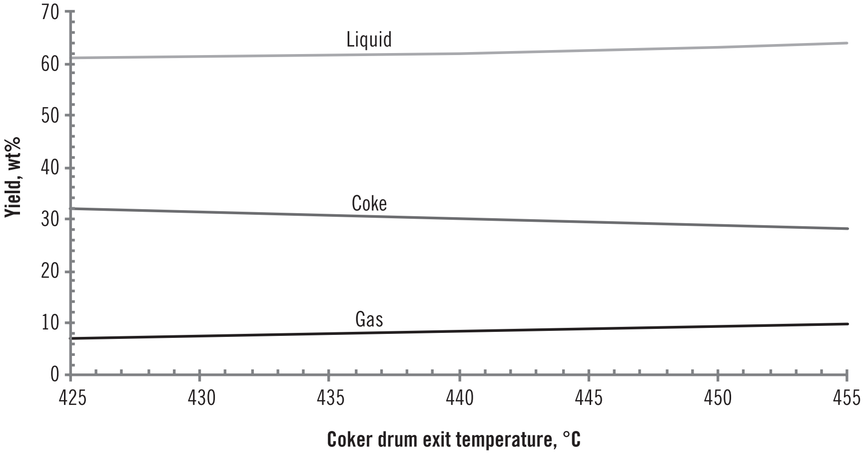

Fig. 8–3. Influence of coker-drum exit temperature on product yields

Commercial delayed cokers are run at a nominal pressure of 20–50 psig. If the operator wants to increase the coke yield and decrease the coker oil yield, then there is an advantage to running it at a higher pressure; otherwise, if the purpose of the coking operation is to increase the oil yield, then a lower pressure is preferred. However, the maximum yield advantage is less than 5 wt% when pressure is increased from 20 to 50 psig.

Figure 8–4 illustrates a typical range of expected product yields as a function of the API gravity (or CCR value) of the feedstock. When vacuum resid of 2.0°API is used as feedstock for the delayed coker, only a little over 50 wt% liquid and about 40 wt% coke is produced, with the remaining 10 wt% being C_1–C_4 hydrocarbons, H_2S, and some hydrogen. As the feedstock API gravity increases or the CCR value decreases, the liquid yield increases and the coke yield decreases; however, the total gas yield remains almost constant, within a single percentage point. When whole bitumen of 10°API is used instead of the vacuum resid as feedstock, the liquid yield increases, approaching 70 wt%, and the coke yield decreases, to just below 30 wt% of the feed.

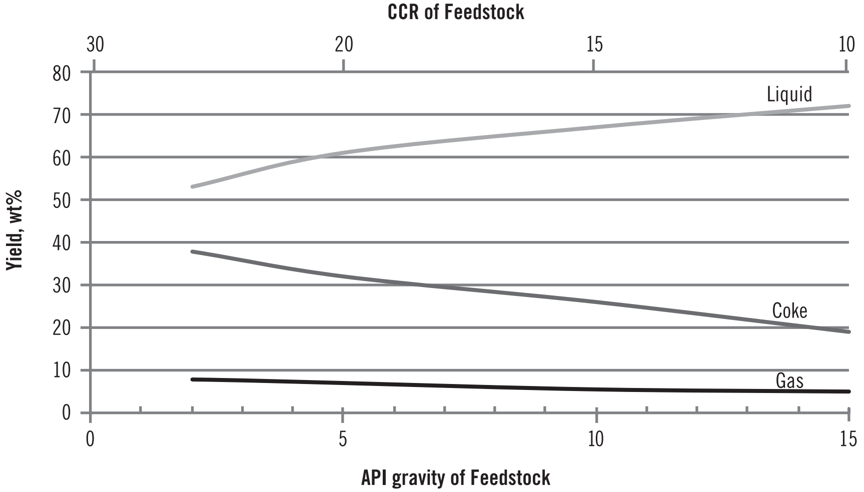

Fig. 8–4. Variation of product yields with API/CCR of feedstock. API gravity is given in °API and CCR in terms of wt%.

The increase in liquid yield and decrease in coke yield with the increase in API gravity (or decrease in CCR value) of the feedstock are not necessarily because of the efficiency of the coking process. Rather, these improvements are due to the cracking of the additional heavier distillable liquid already present in the feed as well, as due to the relatively lower resid content in higher-API-gravity feedstocks.

A typical coker liquid consists of about 50 vol% gas oil, 20 vol% middle distillate, and 30 vol% naphtha. Thus, most of the liquid product in the coker is in the heavier and lighter ranges, rather than in the middle range.

A typical gaseous product stream from a delayed coker consists of about 30 wt% C_1, 25 wt% C_2, 20 wt% C_3, and 15 wt% C_4 hydrocarbons; that is, the concentration of hydrocarbons decreases with the increase in carbon number. The remaining 10 wt% in the gaseous stream consists of H_2S, although the yield of H_2S depends on the concentration of sulfur in the feed. Most of the higher gaseous hydrocarbons are olefinic in nature.

Because delayed coking is a carbon-rejection process, it rejects feed carbon as coke and releases feed hydrogen. However, most of the hydrogen is consumed in producing less-useful, gaseous hydrocarbons instead of liquid; for example, methane consumes the maximum amount of hydrogen. Another major cause of consumption of the hydrogen is that it reacts with the feed sulfur in the vapor phase to produce H_2S. A small amount (<0.05 wt%) of pure hydrogen is always yielded by a coking process.

There are various types of sulfur and nitrogen species in the feedstock, and most of those species are strongly bonded with the asphaltenes and resid fractions in a ring structure (see discussion in figs. 2–8 and 2–9). Most of those sulfur and nitrogen species remain in the coke after the coking process. The benefit of coking is that more than 50% of the feed sulfur and more than 60% of the feed nitrogen remains in the coke and is rejected as a solid—without reacting with hydrogen and not producing H_2S or NH_3. This reduces the costs of the hydrogen consumption, of the cleaning of the off-gas stream, and of the handling of sulfur or nitrogen. Another advantage of delayed coking over hydrogen addition is that more than 90% of the metals in the feed are transferred to the coke, instead of into the liquid phase.

Fluid coking/flexicoking. Whereas delayed coking is a batch process, designed to yield higher coke, fluid coking, developed by Exxon, is a continuous process, to maximize liquid yield and minimize coke yield. Flexicoking is an extension of fluid coking in which a part of the coke is gasified; hence, the coking process is the same, and the coker-oil yield has no net effect in flexicoking compared to fluid coking. Figure 8–5 illustrates the fluid-coking technology with the extension to a flexicoker via an integrated gasifier.

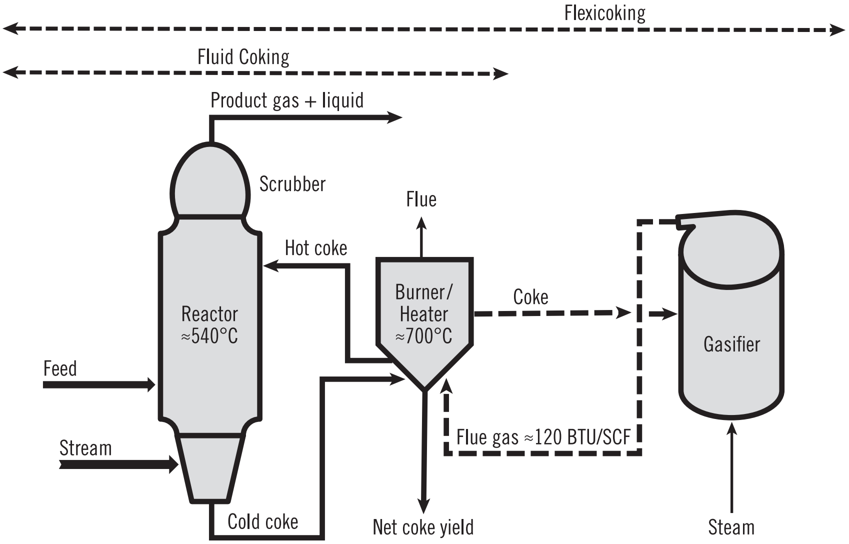

Fig. 8–5. Schematic of fluid/flexicoking technologies

A a result of the fluidization of the bed, the coker is able to run at a higher temperature and a shorter residence time as compared to a delayed coker. This allows higher cracking of the bigger molecules and less time for polycondensation toward coke formation. Thus, the liquid yield increases by about 2–3 vol%, and the net coke yield (part of the coke is burned or gasified) decreases by more than 20–25 wt% in fluid coking as compared to delayed coking

In fluid coking, a burner is used to burn a part of the coke. The disadvantage is that sulfur and nitrogen in the coke are burned to produce oxides of nitrogen and sulfur (NO_x and SO_x, respectively). In flexicoking, the burner is replaced by a heater and part of the coke is directed to a gasifier, where coke is converted into low-heating-value (~120 BTU/SCF) flue gas in the presence of steam. Flexicoking's chief advantages are that, under the gasification condition, almost no emission of toxic gases occurs and low-BTU gas is used as fuel to heat the coke.

In the fluidized-bed coking process, the biggest problem is controlling the size of the fluidized coke particles after fresh coke starts depositing on the surface of the original coke. When not controlled properly, the coke starts to agglomerate and settle inside the reactor, ultimately forcing a shutdown of the operation.

Emerging technologies

Heavy-to-Light (HTL) upgrading process.[1] This technology was originally developed as the Rapid Thermal Process by Ensyn Group of Canada, which was acquired by Ivanhoe Energy of the United States. This is an emerging technology, and process data are not available publicly.

The HTL upgrading process is intended to be a small-scale field-based upgrader whose liquid product meets pipeline specifications, such that it will not require any diluent for transportation. According to Ivanhoe, at standard operating conditions and in once-through mode, the HTL process yields 90 vol% liquid that meets the pipeline specification for viscosity of <350 cSt at normal temperature but that does not meet the target API gravity of 19°. Nevertheless, Ivanhoe has claimed that the HTL process can be run in a different mode that uses recycling and, although yielding only 80 vol% liquid, meets both viscosity and API specifications.

As shown in figure 8–6, HTL upgrading is based on the principle of fluid coking; however, it is essentially a visbreaking technology. In this process, sand is used as a heat-transfer source (i.e., instead of coke in a fluid coker), and hot bitumen is sprayed on the circulating hot sand at a very high temperature (i.e., higher than in a fluid coker) and over a very short residence time (i.e., shorter than in a fluid coker). These operating conditions allow the heavy molecules to crack into lower molecules—hence producing a lower-viscosity liquid product and some coke. All the coke formed on the sand surface is burned in a reheater, to heat the sand. Hot sand is then recycled back into the reactor.

The basic concept of the HTL process is not new, except in that the process reduces the residence time to the extent that severe cracking does not take place. Two previous technologies of the early 1980s—namely, the LR process, developed by Lurgi, and the ART process, developed by Englehart—were based on fluidized-bed technology, and both used inert solid as heat-transfer medium.

The HTL process was tested in a 200 BPD demonstration plant in California. Ivanhoe is now attempting to build a commercial plant in Canada.

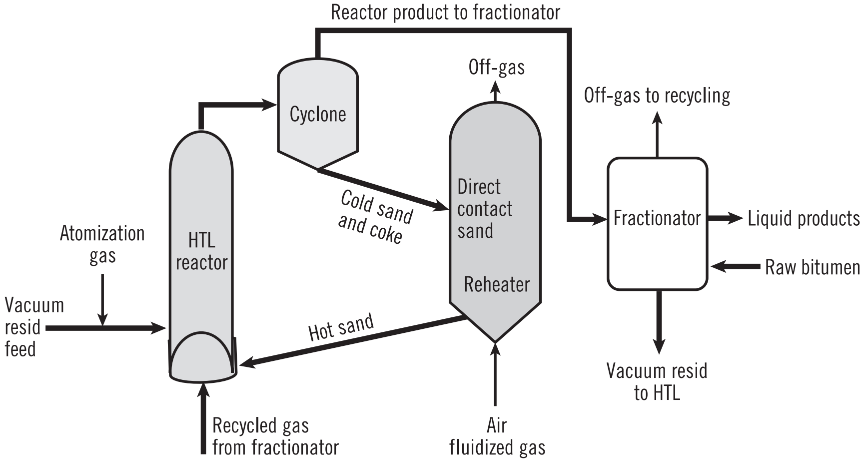

Fig. 8–6. Schematic of HTL process

I^{y}Q upgrading.[2] The I^{y}Q technology was developed by ETX of Calgary, Alberta. The process is based on fluidized-bed coking. However, as shown in figure 8–7, the main difference between I^{y}Q and any other fluidized-bed process is that the hot solid bed is added to one end of a horizontal reactor; the bed is fluidized perpendicularly, but the bed moves horizontally along the length of the reactor and exits from the other end of the reactor. In contrast to other well-mixed fluidized-bed processes, the I^{y}Q bed moves as a plug flow from one end to the exit end. ETX claims that this reactor design provides about 9% by volume higher yield of bottomless synthetic crude than a delayed coker, with less coke formation and lower gas yields.

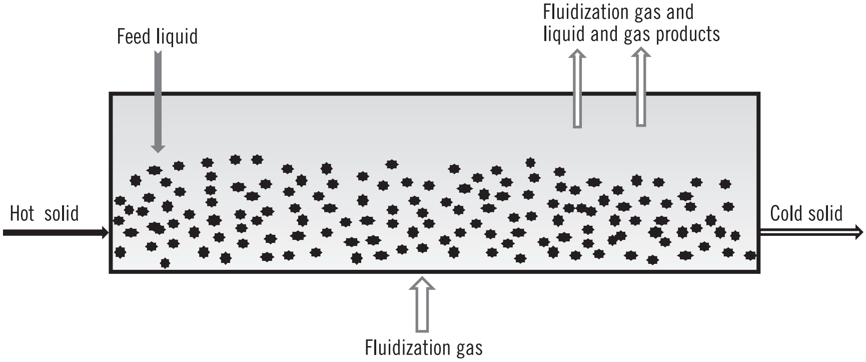

Fig. 8–7. Schematic of I^{y}Q process

This is an emerging technology, and the process information is not publicly available.

Solvent De-asphalting

Solvent de-asphalting (SDA) is a process wherein relatively lighter and more-paraffinic molecular hydrocarbons are physically separated from the heavier polycondensed aromatic molecules by solvent extraction, using hydrocarbon solvents in the range of C_3–C_6. Usually the solvent-to-feed ratio varies between 3 and 10. Because SDA is a physical separation process, there is no chemical change between the feed and the product. However, unlike distillation, the process does not separate on the basis of molecular weight.

SDA is a simple economical process to remove the dirtiest part of the bitumen. The depth of separation is based on solvent type, temperature, and pressure of extraction. The economics of the process is highly dependent on the recovery and recycling of the solvent. The purpose of applying SDA to bitumen processing is first to remove the most difficult-to-upgrade portion of the bitumen and then to send the relatively cleaned up de-asphalted oil (DAO) to an upgrader.

Figure 8–8 represents a typical example of the variation of DAO yield with the types of solvent used. The higher the molecular weight of the solvent is, the higher will be the amount of DAO yield or less the amount of asphaltenes/pitch yields. As the DAO yield increases, the quality of the DAO becomes poorer. Thus, the lower the molecular weight of the solvent is, the less will be the amount of DAO yielded but the better will be the quality of the product. In addition to the increase in impurities (S, N, or metals), API gravity decreases and CCR increase, along with the increase in DAO yield.

De-asphalting is not an attractive process if the de-asphalted pitch has no market. DAO is also not a good-quality product when compared against the products of other upgrading processes. DAO is a poor-quality feedstock, especially for hydroprocessing; moreover, as the quality of the DAO decreases, the rate of poisoning of the catalyst increases.

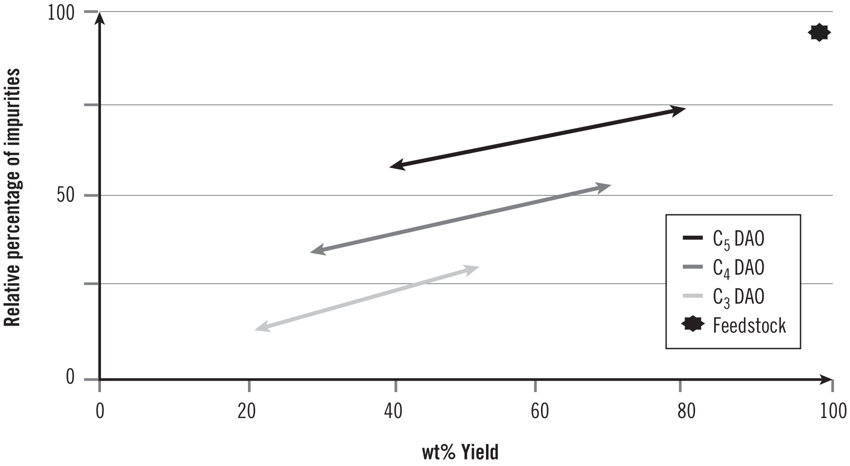

Fig. 8–8. Variation of DAO qualities and yields by solvent type

The following sections give examples of SDA processes. One commercial process and one emerging process are described.

Commercial SDA process—Residual Oil Supercritical Extraction[3]

There are two major commercial SDA processes: Residual Oil Supercritical Extraction (ROSE), which process is currently licensed by KBR; and Demex, a process developed by UOP. Because ROSE is the most widely used commercial SDA process in the world, a brief description is warranted.

Figure 8–9 shows a simplified diagram of the ROSE process. The feed is mixed with the solvent in the first separator, where asphaltene is precipitated out as solid; the DAO with solvent is directed to a second separator, where the solvent is recovered and the DAO is separated. The first separator works at a subcritical condition, and the second separator (the solvent recovery section) works in the supercritical condition. A maximum amount of solvent is recovered and recycled.

The depth of separation is controlled by the temperature, pressure, and solvent type. For discussion of detailed results of the ROSE process, readers may visit KBR's Web site.

In chapter 4 (see table 4–1), heating values of various fuels were given. Asphaltene, which is similar to SDA pitch, has a heating value of 37.5 MJ/kg, almost 20% more than that of petcoke. Thus, the pitch can be burned as fuel, either alone or as a blend with petcoke or coal. KBR has developed a process to convert pitch into pellets, to be sold as fuel.

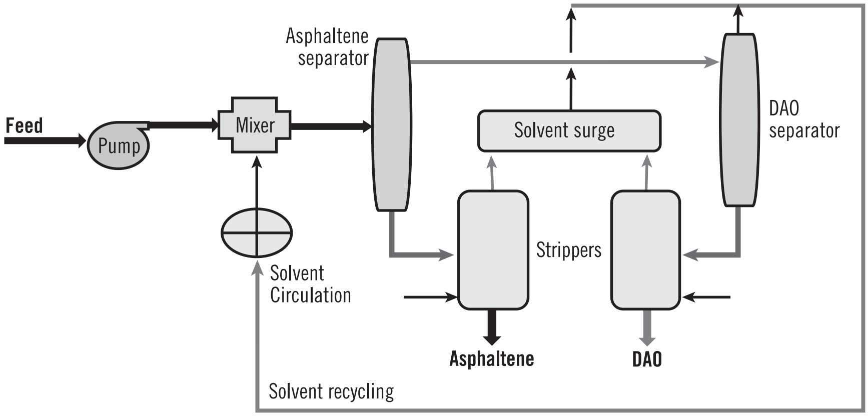

Fig. 8–9. Schematic of ROSE process

Emerging SDA process—Selective Separation Recovery Process[4]

The Selective Separation Recovery Process (SSRP) is an emerging technology developed by the University of Beijing, China, for the upgrading of Alberta bitumen. As shown in figure 8–10, SSRP uses three or more separating columns and extracts bitumen into more fractions (e.g., DAO, resins, and asphaltenes) than the ROSE process does. However, separation into several fractions does not necessarily translate into a better process, because the impurities are distributed proportionally in the fractions.

The SSRP process claims that it operates at 20% less solvent as compared to ROSE; hence, the operating cost would be lower. However, SSRP operates the extraction section at supercritical conditions—thus, at much higher pressure than in the ROSE process—which might ultimately increase the operating cost.

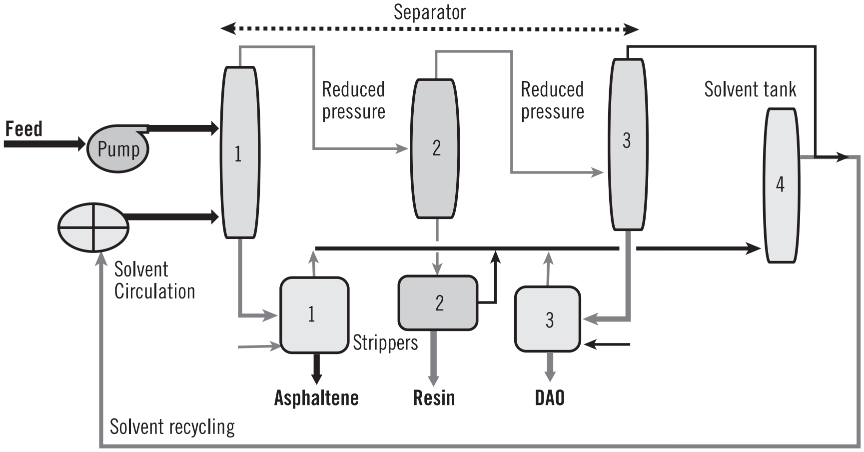

Fig. 8–10. Schematic of SSRP process

For typical Alberta bitumen extracted by this method, the approximate process yields are as follows:

- DAO, 70%
- Resin, 8%
- Asphalt, 22%

However, the separation into additional fractions is directly related to the distribution of poor-quality materials. For example, the resin fraction contains more than twice the CCR and metals as compared to the DAO fraction.

Hence, comparison of the two different SDA processes is difficult; one is not necessarily better than the other. The economics of each process depends on the ultimate use of the end products.

Hydrogen-Addition Technologies

Unlike carbon-rejection processes, hydrogen-addition processes have more flexibility in process conditions and product slates. Depending on the nature of the feed, types of contaminants, and the process conditions, hydroprocessing can produce boutique synthetic crude in accordance with market demand.

The biggest advantage of the hydrocracking process is that, at a high conversion level (i.e., >90%), it can yield more than 100 vol% light sweet synthetic crude. This crude has a broader market, appeals more to refiners, and can demand higher price. Thus, there is a much lower financial risk for the owners of hydroprocessing upgraders than for the owner of coking-based upgraders. The economics of upgrading processes is highly dependent on the resid conversion level.

In response to recent worldwide interest in and development of slurry-phase hydrocracking technology, this chapter includes descriptions of several emerging slurry-phase technologies. However, results and operating conditions of individual technologies are not discussed, in favor of a general overview of the hydroprocessing of Alberta resid. Most of the results discussed in the following sections are valid within a small margin of error for any emerging slurry-phase technology; the final result, though, may vary depending on the types of catalyst and feedstock. Readers interested in obtaining detailed information on any particular technology may contact the respective process developers.

Note that in a commercial hydrocracking process, resid hydrocrackers should be followed by a hydrotreater to improve the quality of the product. Data below are from pilot plant studies that were not accompanied by secondary hydrotreating. Although most of the results reported here are based on personal experience, further information may be found in various books and reports.[5]

Process parameters

Resid conversion is the metric for all hydrocracking processes, and it is directly related to the severity of the operation. The exact severity of the conditions is usually proprietary information of the companies. The catalyst plays an important role in the hydrogenation of the cracked product. New slurry-phase technologies under development are switching to the use of a homogeneous UD nanocatalyst.

Severity is a combination of the following conditions (usual ranges are specified):

- Reactor temperature, 440–460°C
- Space velocity, 0.5–1.5 h^{-1}
- Hydrogen pressure, 10–20 MPa

The key factors involved in evaluation of the resid hydrocracking process are discussed in the next sections. These results are averages and are intended to provide readers with a guideline for technical evaluation; however, for the economic evaluation of a particular technology one should obtain the project-specific results.

Product yields

The success of any process is measured in terms of the various product yields, the most important of which is the yield of the most valuable product—in this case, the yield of the syncrude (C_5–525°C) fraction. As shown in figure 8–11, yields of syncrude and gaseous products increase with the increase in resid conversion. Syncrude yield increases from 50 wt% to 80 wt%, and C_1–C_4 hydrocarbons yield almost double, from 3.5 wt% to 7.0 wt% with the increase in conversion from 55 wt% to 92 wt%. The higher the sulfur content in the feed and the higher the severity is, the more sulfur will be converted into H_2S.

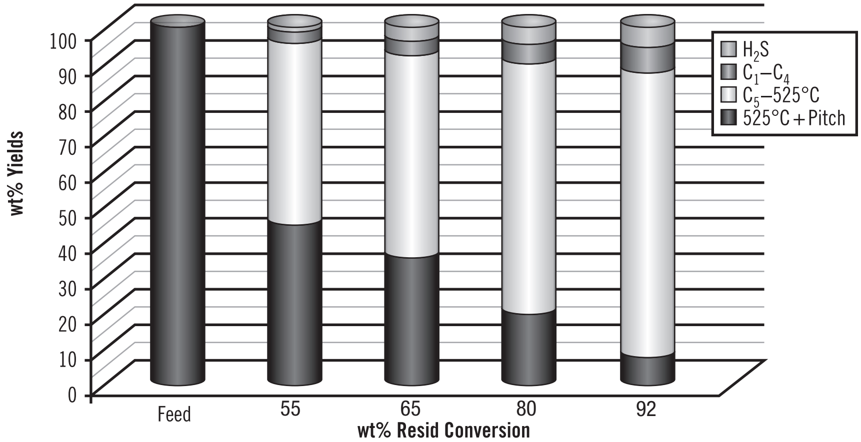

Fig. 8–11. Variation of product yields with resid conversion

Liquid API

The goal of the hydro-conversion processes is to produce a high-quality syncrude for the refiners. API gravity is a base-case measurement for the quality of crude. Refiners pay a premium price for higher-API crude.

Figure 8–12 shows the variation of API gravity of the liquid product as a function of resid conversion for two cases:

- C_5+ total liquid (including pitch)
- Syncrude (i.e., C_5–525°C)

At the 55 wt% conversion level, the total C_5+ liquid product has an API gravity of 15°. At the 65 wt% conversion level, the API gravity increases to 19.5°. Thus, at 55 wt% conversion, a low-API and poor-quality liquid is produced that does not even meet the pipeline specification of 19°API. If the producers intend to sell the whole liquid product, then it is recommended that, for a liquid product that at least meets the pipeline target, the hydrocracker should run at a minimum 65 wt% conversion level. However, it is above the 90 wt% conversion level that the total C_5+ liquid API gravity exceeds 30°, which is a good-quality refinery feedstock.

If the producers intended to sell the syncrude only, then the API of the liquid is always of good quality and always exceeds the pipeline target. The API gravity of synthetic crude oil increases from 25° to 32° with the increase in conversion from 55 wt% to 92 wt%. At higher conversions, not only does the API gravity increase but, at the same time, the volume yield of syncrude increases, from about 75 vol% to 100 vol% (fig. 8–13). Liquids are sold in volumes in the petroleum industry; hence, maximizing volume and API gravity of the syncrude increases the profit margin of the producers at high conversion levels.

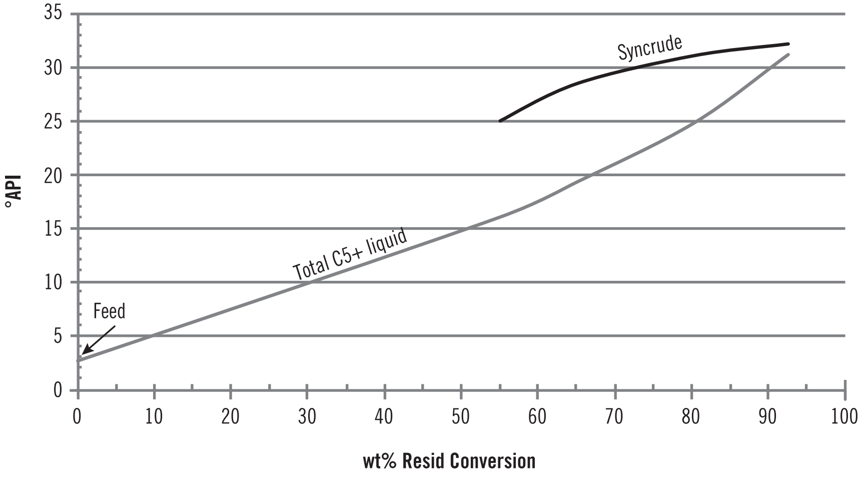

Fig. 8–12. Variation of liquid product API gravity with resid conversion. C_5+ includes pitch.

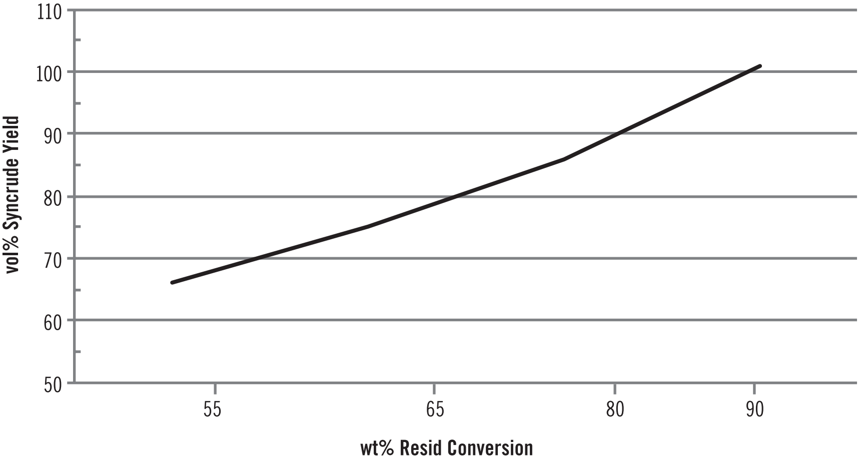

Fig. 8–13. Variation of percent by volume syncrude yield with resid conversion

Above 90% by weight resid conversions, volume yields of both C_5+ liquid and syncrude exceed 100%. Readers should note that in a commercial operation, secondary hydroprocessing of syncrude is done using a fixed-bed hydrocracker and hydrotreater. Above 90 wt% resid conversion, the total liquid volume yield (combining two steps) is expected to exceed 105 vol% with respect to the feed volume.

Liquid composition

The quality of a crude oil is measured by its composition. For a refiner, crude oil's worth depends on the refining capabilities and capacities. For example, a refiner with coking capability would prefer to buy a crude oil with resid and not a syncrude without resid; a refiner would prefer to receive a low-sulfur crude if they do not have a sufficient hydrotreater capacity to hydrotreat the feedstock.

Figure 8–14 shows a typical composition of C_5+ liquid yield at various resid conversion levels. Usually, the distillate fraction is the most valuable fraction for the refiners to produce diesel and jet fuel, and the volume of distillate almost doubles, from 25 vol% to 50 vol%, with the increase in conversion from 55 wt% to 92 wt%.

The next most important fraction for refiners is naphtha to produce gasoline, and the average naphtha content varies in the range of 15–20 vol%. Another valuable fraction for the refiners is the gas oil as FCC feedstock, the volume of which varies in the range of 20–30 vol% in the syncrude with the increase in resid conversion.

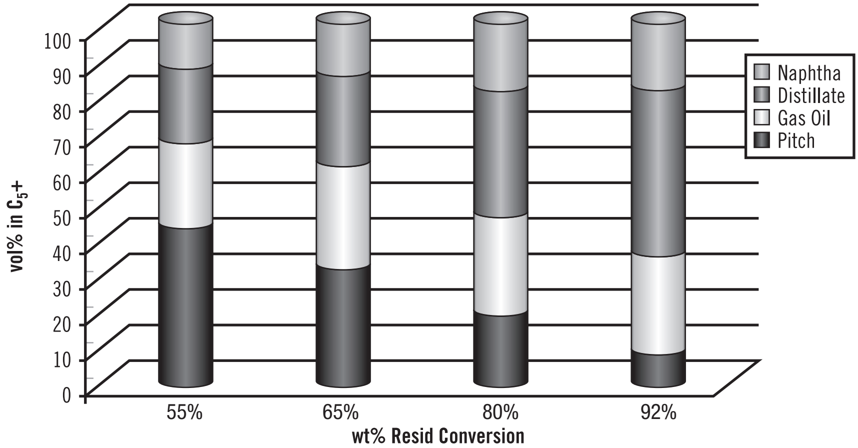

Fig. 8–14. Variation of C_5+ liquid composition with resid conversion

In a commercial slurry-phase hydrocracking process, the unconverted pitch fraction (especially at higher conversion) must be removed before transportation or sale to the refiners. This fraction would be highly detrimental to the refining process, because it may contain asphaltenes, sediments, metals from the catalyst, and metals from the feedstock. Asphaltenes must be removed to avoid instability of the liquid stream, which could cause fouling in the pipelines or in the heaters, and metals would deactivate the downstream hydroprocessing catalysts.

Gaseous hydrocarbons

The total yield of gaseous hydrocarbons (i.e., C_1–C_4) in a gaseous stream increases almost linearly, from 4 wt% to 7 wt% of the feed with the increase in resid conversion from 55 wt% to greater than 90 wt%. As illustrated in figure 8–15, the concentrations of hydrocarbon decrease with the increase in carbon number from C_1 to C_4. This is a clear indication of increase in cracking of bigger molecules at higher severities.

Higher concentrations of methane in the gaseous stream have two main disadvantages:

- Methane consumes more hydrogen—that is, four per carbon atom, during the formation of methane.
- Methane is more difficult to remove from hydrogen—thus, loss of hydrogen occurs during the purification of a recycled hydrogen stream.

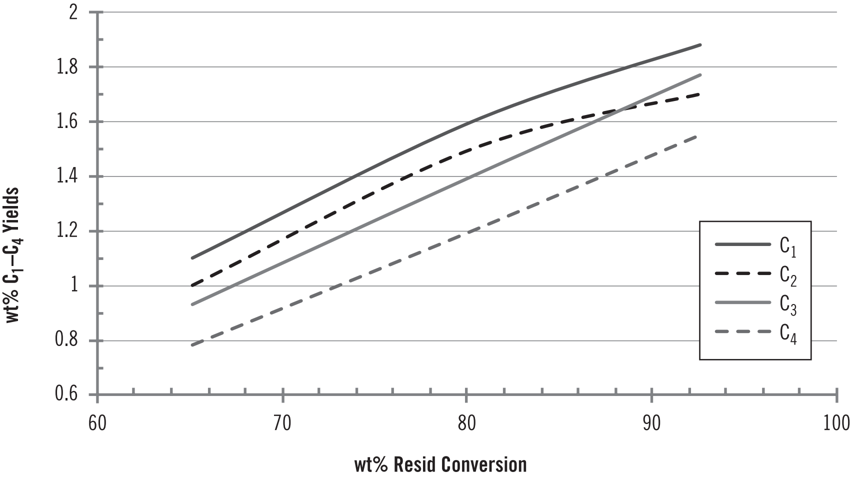

Fig. 8–15. Trend in variation of C_1–C_4 yields with resid conversion

Hydrogenation Efficiency

There is no direct measurement of catalyst activity, or *hydrogenation efficiency*. However, it is an important factor, because hydrogen improves the quality of the syncrude and is an important operating cost. If hydrogenation is not effective, then severe fouling in the reactor may result. Important factors that affect hydrogenation efficiency are discussed in the following sections.

Desulfurization

One of the goals of syncrude production is to meet the sulfur and nitrogen specifications for the refiners. As the demand for clean fuel increases, it is necessary to clean up as much sulfur as possible from the high-sulfur bitumen feedstock before delivery of the syncrude to the refiners. In the hydrocracking process, bigger molecules containing sulfur and nitrogen are cracked, and part of the heteroatoms then reacts with hydrogen to produce hydrogen sulfide and ammonia. Figure 8–16 shows the trend in percentage of sulfur removal with resid conversion.

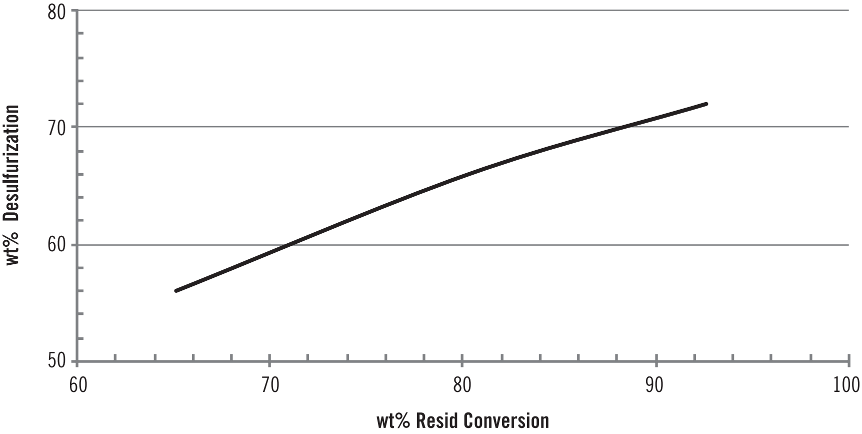

Fig. 8–16. Trend in variation of sulfur removal with resid conversion

More than 50 wt% of the sulfur in the feed is removed at the 65 wt% conversion level, and desulfurization increases to more than 70 wt% when the cracking process exceeds the 90 wt% conversion level. However, desulfurization activity is strongly dependent on the properties of the feed and the stability of the catalyst.

Desulfurization is an example of HDS activity. Similarly, HDN (nitrogen removal) and HDM (metal removal) activities also depend on the process scheme and the hydrogenation efficiency. The total hydrogenation efficiency is measured by the rate of HDS, HDN, and HDM.

Asphaltenes and CCR conversion

Other major criteria for hydrogen efficiency measurement are the conversions of asphaltenes and CCR. Figure 8–17 illustrates the trend in variation of conversion of both asphaltenes and CCR with resid conversion. In an ideal case of 100% hydrogenation efficiency, the asphaltenes and CCR conversions should lie on the same $Y = X$ curve, along with the resid conversion. However, as shown in figure 8–17, the asphaltenes-conversion curve is a straight line, increases with resid conversion, and has the tendency to move toward the $Y = X$ curve (although it always remains slightly below the $Y = X$ curve). Above the 90 wt% resid conversion level, the asphaltenes-conversion curve is close to (within 5% of) the $Y = X$ curve.

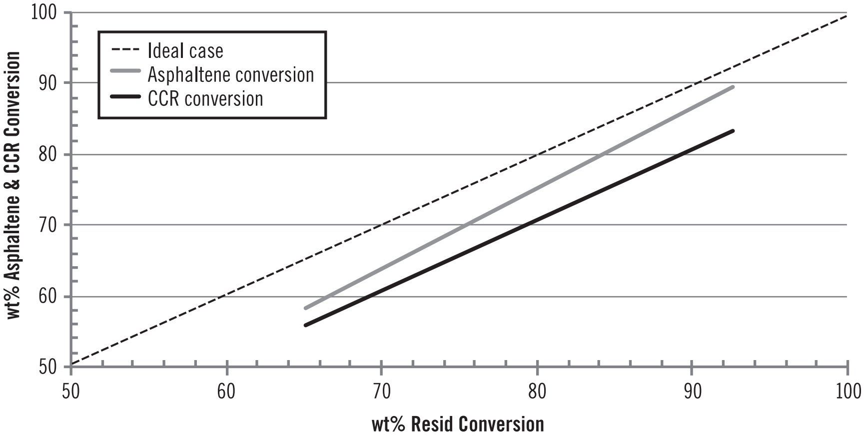

Fig. 8–17. Trend in variation of asphaltenes and CCR conversion with resid conversion

Further, as shown in figure 8–17, the CCR conversion curve is also a straight line. However, it always remains below the asphaltenes-conversion curve and almost parallel to the $Y = X$ curve (just within a 10% difference).

The preceding results clearly indicate that the rates of asphaltenes and CCR conversions are directly dependent on the resid conversion. Further, the efficiency of asphaltenes conversion is always higher than that of the CCR conversion (throughout the process conditions).

Hydrogen consumption

The actual hydrogen consumption is based on the chemistry of the process, which includes not only removal of heteroatoms and metals but also hydrogenation of aromatics and hydroconversion of bigger molecules, such as asphaltenes. Hydrogen consumption is directly related to the catalyst activity and feedstock properties. Figure 8–18 shows the trend in hydrogen consumption with conversion, and hydrogen consumption increases almost linearly, from 850 to 1,250 SCF/bbl with the increase in conversion level from 65 wt% to above 90 wt%.

Note that the amount of chemical hydrogen consumption does not necessarily directly reflect the efficiency of a process. A process may report lower hydrogen consumption because of any of the following reasons: the catalyst activity is poor, the degree of conversion is lower, the quality of the liquid product is poor, or the type of feedstock was of better quality.

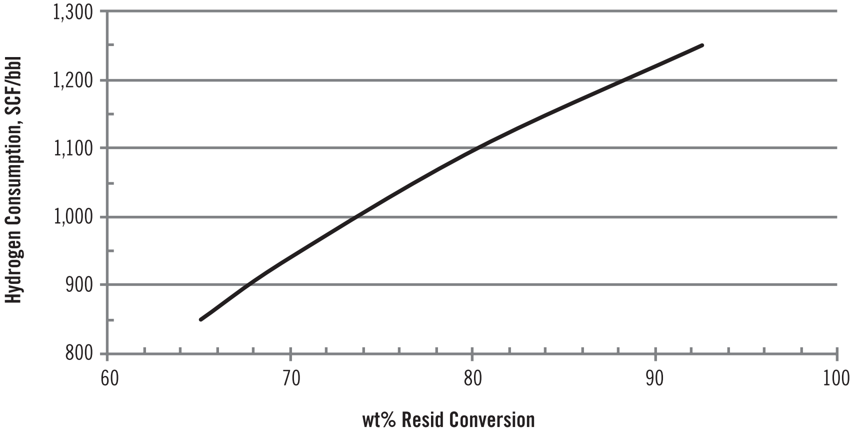

Fig. 8–18. Trend in variation of chemical hydrogen consumption with resid conversion

Chemical hydrogen consumption values should not be used as a metric for the evaluation of hydroprocessing technology. Nevertheless, the main cost of hydrogen is based on volume of hydrogen added, which is the hydrogen-to-oil ratio in the reactor; the partial pressure of hydrogen; and the percentage of hydrogen recycled. The degree of purification of the recycled hydrogen—and, hence, the cost of purification—is an important factor, because the partial pressure of hydrogen in the reactor inlet is dependent on the hydrogen purity, which in turn affects the hydroprocessing reaction.

Resid Hydrocracking Technologies

Ebullated-bed technology

Ebullated-bed technology is the only currently running commercial resid hydrocracking process that can treat vacuum resid from heavy oil. There are two commercial ebullated-bed processes in wide use: LC-Fining (Chevron Lummus Global) and H-Oil (Axens/IFP). (Although another ebullated-bed process, called T-Star, exists, it was designed to treat heavy gas oil; originally developed by Texaco but now licensed by Axens/IFP, T-Star is fundamentally similar to H-Oil.)

Chevron has developed and commercialized several hydroprocessing concepts for various types of feedstocks over the years. The commercial LC-Fining is specifically designed for resid feedstock. H-Oil was originally developed and licensed by the Hydrocarbon Research Institute of Princeton, New Jersey (HRI) and was then acquired by the French Petroleum Institute, IFP, which has since become part of Axens. Because of the similarities between LC-Fining and H-Oil, separate detailed discussions of those two technologies are not warranted here; however, a large body of literature information is available about both.

A general overview of an ebullated-bed process is given in figure 8–19. The system is so called because the fine catalyst particles, added from the top of the reactor, are suspended in the liquid feedstock, which is added from the bottom of the reactor, along with hydrogen. The upward expansion of the catalyst bed is controlled by the upward flow of the oil. There is a radioactivity detector to control the liquid level of the expanding bed. The expanding bed allows the catalyst to be recovered online, without disturbing the process conditions, while the catalyst is regenerated and recycled back; the catalyst is collected from the bottom of the reactor.

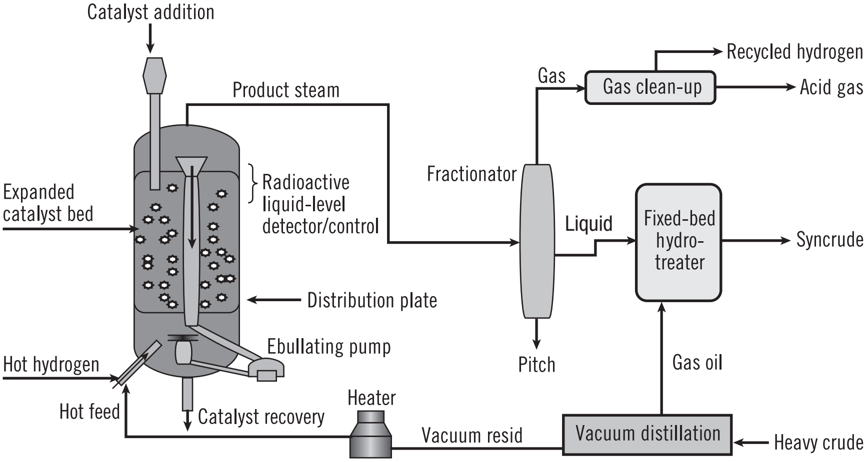

Fig. 8–19. Schematic of ebullated-bed reactor design and process

Vacuum resid is the feedstock of the process. A single-reactor train usually runs at 60–65 wt% conversion levels without recycling. To increase the conversion, the system runs multiple trains in series. Even so, the maximum conversion is limited to the 80–85 wt% conversion level.

The product stream exits the reactor from the top and is fractionated into three major fractions:

- Gaseous stream. The product stream is cleaned, and hydrogen is recovered and recycled. The hydrocarbon is used as a fuel source.

- Syncrude. The liquid stream from the reactor is usually sent to a hydrotreater, because additional hydrotreating is required before blending in order to stabilize the product and meet the refinery specification.
- Pitch. In some commercial processes, the unreacted pitch is sent to another plant, such as a delayed coker or an SDA unit.

Moving-bed technology

Moving-bed technology was developed to overcome the difficulties in operation of fixed-bed technology when relatively higher concentrations (>100 ppm) of metals are present in a conventional feed. In a moving-bed process, the fresh catalyst is added at the top, and the spent catalyst is withdrawn at the bottom of the reactor. The system requires special equipment to operate at high pressure. However, as the feed becomes heavier and the metal concentration increases beyond 100–200 ppm, it becomes more difficult to operate the process at higher conversion levels.

There are three main moving-bed processes:

- OCR (online catalyst replacement), developed by Chevron
- Hycon process, developed by Shell
- Hyvahl process, developed by IFP

Because of the limited applications of these processes, especially in North America, detailed discussion is beyond the scope of the present text.

Slurry-phase technology

Emerging slurry-phase hydrocracking technologies are being developed by various groups all over the world. Over the past quarter century, there has been a great deal of interest in the development of slurry-phase hydrocracking technology. Despite a surplus of experience in running commercial and semicommercial plants (combining experience in VCC, CANMET, HDH, and EST proprietary technologies), there is no commercial unit running today anywhere in the world; however, as of mid-2011, Eni announced that they are constructing a commercial 23,000 BPD plant in Italy based on the EST technology they developed (see the section “Stages of Development,” below, for further discussion).

The main objective of a slurry-phase process is to achieve greater than 90% resid conversion in a single-train system, without recycling. A general overview of a proposed slurry-phase process is shown in figure 8–20. The reactor is simple—made of a high-pressure empty cylinder (with no internal components)—and looks much less complicated than the ebullated-bed reactor. Nevertheless, it is a three-phase process, using an *up-flow bubble-column reactor*, and the "*hydrodynamics*" of the reactor is complicated enough to make the operation much more difficult than it looks. Engineers apply results of *cold-model* hydrodynamic studies to the actual reaction conditions; however, this usually does not work. Thus, *hot-model* studies, despite being expensive and more difficult to do, are needed, to build confidence in a commercial-scale design.

The biggest problem during operation of the slurry-phase reactor is the need to maintain optimum conditions of three phases—namely gas holdup, liquid holdup, and solid holdup. All three are interrelated—that is, once one goes up, another goes down. High gas holdup will create more foaming and will decrease liquid holdup. However, the process requires higher liquid holdup in order to achieve high conversion. An increase in pressure increases gas holdup, and the process requires a high pressure of hydrogen. If the solid holdup increases, then it would affect both liquid and gas holdups. Solid settlement is also a significant problem. Therefore, running a commercial plant at optimum condition is absolutely necessary, and a very small window of operating conditions exists in which a greater than 90 wt% conversion level can be achieved.

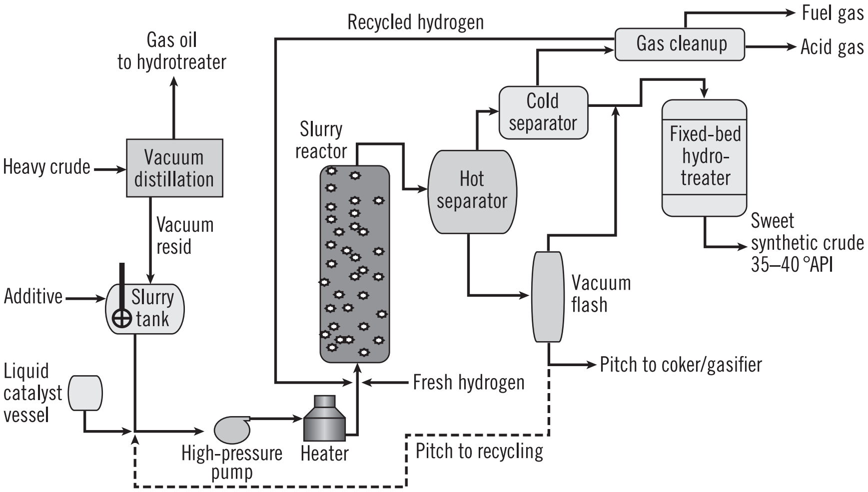

Fig. 8–20. Schematic of proposed slurry-phase upgrading process

Four major concerns need to be addressed in the design of a slurry-phase reactor:

- Solid settlement
- Foaming
- Hydrogen starvation (i.e., coking/fouling)
- Catalyst activity

In the end, the success of an operation of a slurry-phase bubble-column reactor is solely dependent on the experience of the operators.

In the early days of their development, slurry-phase reactors used finely ground fresh solid catalyst or additives. The concentration of the additives ranged from 2 wt% to 5 wt% of the feed, and the particle size ranged from 50 to 500 microns. Additive was slurried with the heavy oil feedstock and fed into the reactor. The main purpose of the solid additive was to maintain the solid holdup of the reactor and to suppress coke deposition.

More recently, however, with the development of a homogeneous catalyst system, liquid-phase catalyst precursor is injected into the system. The type of catalyst and point of injection depends on the developer and is mostly confidential. Homogeneous catalyst is made of either oil-soluble or water-soluble complex organometallic compounds, and the metal concentration varies from 500 to 1,000 ppm. Also, in certain cases, an inert solid is added (1–2 wt%) to the feedstock in a slurry tank and is then slurried with the resid feedstock before entering the reactor. The slurry, along with the catalyst, is heated close to the reaction temperature in a heater before being fed to the bottom of the reactor. Hot hydrogen is also fed to the bottom of the reactor. Hydrogen passes through a distributor at the inlet. Everything fed at the bottom flows upward, cocurrent, along the whole length of the reactor. This is a well-mixed reactor, and the temperature throughout the reactor is controlled within 1°C. This is a highly exothermic reaction, and runaway temperature is exceedingly common, eventually coking up the reactor. Fine control of the temperature is essential, which is usually done by injecting quench hydrogen.

All products, including catalyst, exit from the top of the reactor and first go through a high-pressure hot separator, where the heavier portion is separated from the lighter one. The bottom of the hot separator is vacuum-flashed to recover the maximum amount of carryover lighter liquid. In a future commercial plant, the bottom pitch either will be sent to another unit, such as a coker, an SDA, or a gasifier, or will be partially recycled back to the reactor.

The top stream from the hot separator then goes through a cold separator, where the gaseous stream is separated from the lighter liquid product. The gaseous stream is cleaned, and hydrogen is separated and purified before being recycled back to the reactor.

In a future commercial plant, syncrude (without pitch) will be directed to a hydrotreater. The end product would be a stable higher-quality sweet synthetic crude.

The biggest disadvantage of the homogeneous catalyst system in particular is that all the metals from the feed and the catalyst remain in the liquid phase, and after fractionation they are mostly concentrated in the pitch. So, it is essential to separate the pitch before selling the liquid product. Because of the very high concentrations of the metals in the pitch, it is not environmentally friendly, and it can be neither disposed of nor burned off. Another disadvantage is that the homogeneous catalyst is made of traditional expensive metals, such as cobalt, nickel, molybdenum, and tungsten, and it is particularly difficult to recover them; as yet, there is no cost-effective method to recover the catalyst.

Stages of Development

Figure 8–21 lists various slurry-phase technologies developed over the past quarter century. These are further classified among several stages of development.

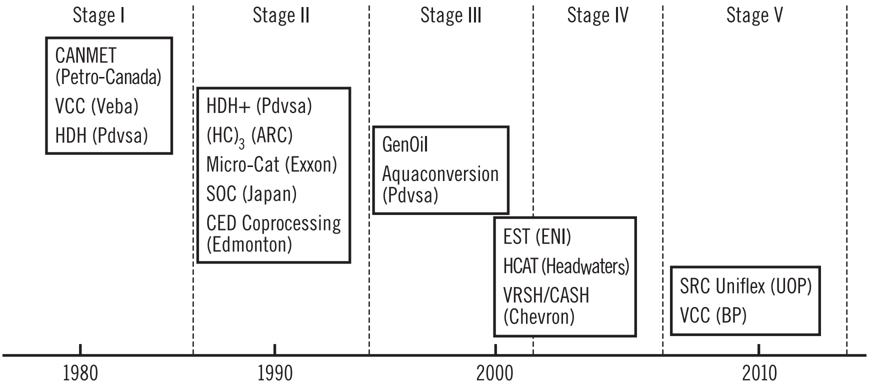

Fig. 8–21. Various slurry-phase hydrocracking technologies over time

First stage

This phase describes the pioneering work done simultaneously by three groups:

- CANMET process, by CANMET Energy Research Laboratory, in Canada
- VCC process, by Veba Oel, in Germany (although this technology was originally developed much earlier for coal liquefaction)
- HDH process, by Pdvsa's Intevep laboratory, in Venezuela

In all cases, solid iron-based catalyst and carbon-based additives were used to control the coke formation. All three processes were tested at very high (>90 wt%) conversion levels in commercial and semicommercial-size reactors. The CANMET process was run in a 5,000 BPD commercial plant in the Petro-Canada refinery in Montreal, and the plant stopped operation in the late 1990s. The VCC commercial plant of 3,500 BPD in Bottrop, Germany, was initially run with heavy oil and, in the mid-1990s, was run with plastic wastes for economic reasons; in the late 1990s, the whole plant was dismantled. The HDH process was tested in a 150 BPD semicommercial plant in the late 1980s in Bottrop, Germany.

Second stage

This stage of development started with the utilization of a liquid-phase homogeneous catalyst:

HDH PLUS. The HDH process using heterogeneous catalyst was originally developed by Pdvsa in Venezuela in the early 1980s.[6] Later in the program, in the mid-1990s, when the HDH process switched to use of a dispersed homogeneous catalyst, the name was changed to *HDH+*. The HDH+ process was successfully tested at close to 95 wt% resid conversion levels in Pdvsa's demonstration plant at the Intevep laboratory, near Caracas, Venezuela. Using vacuum resid feedstock from Venezuelan heavy crude and traditional nickel-moly–based homogeneous catalyst, the syncrude yield was more than 100% by volume. In the early 2000s, while Pdvsa was trying to commercialize this technology in one of its refineries, the political situation in Venezuela disrupted the process, leaving the fate of this technology to be determined; however, in 2010, IFP announced that they will be joining with Pdvsa to commercialize the process.

$(HC)_3$. The Alberta Research Council (ARC), in Edmonton, has been active in developing the $(HC)_3$ process, which uses a special formation of a micron-size colloidal hydrocracking moly-based homogeneous catalyst.[7] They claimed that the special catalyst was designed to convert asphaltene molecules and have achieved greater than 95 wt% resid and asphaltenes conversions, producing a syncrude of greater than 35°API. While the process was tested in a small-scale pilot plant, for a while ARC attempted to scale it up directly to a much bigger size semicommercial plant. Eventually, the process was sold to Headwaters in the United States (see also "HCAT," below).

Micro-Cat and Aurabon. Early on, Exxon developed the Micro-Cat process, which used a well-dispersed micron-size moly-based homogeneous catalyst. Very little information is now available on either the success or the failure of development of the process, and no activities have been reported for a long period of time.

During the same period, UOP developed the Aurabon process using a moly-based homogeneous catalyst. After unsuccessful attempts to commercialize the process, they abandoned it too.

It seems both the technologies are withdrawn. Therefore, further discussion of both processes is unnecessary.

Super Oil Cracking (SOC). The SOC process was developed by Japan Energy to convert heavy crude into light naphtha at a very high temperature and pressure, using a moly-based liquid catalyst and a carbon-based solid support. After it was tested in a pilot-scale unit, the process was directly demonstrated for a while at a commercial scale in a refinery in Japan.

CED coprocessing. Canadian Energy Development (CED), in Edmonton, Alberta, developed two coprocessing technologies, for the simultaneous upgrading of Alberta bitumen and coal, based on slurry-phase technology.[8] Unlike other slurry-phase processes, finely divided coal, instead of inert carbon-based additives, was mixed with the oil. Results clearly showed that the combination of coal and oil had a synergistic effect and that the total syncrude yield was higher than in the only-oil case. In 1992, after detailed technical and economical feasibility studies, CED submitted a project report to the Alberta Government proposing to build a commercial plant, the "Canadian Energy Upgrader" in Alberta; however, because of the poor economic situation of the energy sector at that time, the project was never started.

Third stage

Two technologies are described here, even though they do not resemble a slurry-phase process. Their inclusion is, however, warranted because both are based on hydroprocessing technology and use water as a source of hydrogen.

GenOil Upgrader. This hydroprocessing technology was developed by GenOil of Edmonton, Alberta.[9] The purpose of this technology was to develop a field-based unit to upgrade bitumen at the wellhead. The pilot plant reported to have used pure hydrogen produced from water by electrolysis, and hydroprocessing was done in a fixed-bed reactor. For the future commercial scale upgrader, GenOil plans to introduce a combination of moving-bed and fixed-bed reactors and also plans to convert the pitch into hydrogen.

Aquaconversion. This process was developed based on the same concept as that of HDH+ technology at Intevap, in Venezuela.[10] The process is based on steam cracking in the presence of homogeneous catalyst. They claimed to have generated hydrogen radicals from water using alkaline catalyst and consequently added the hydrogen catalytically (nickel-based) to upgrade the heavy oil. The purpose of developing this process was to use it as a field upgrader at the wellhead and to upgrade the heavy oil to produce pipeline-quality product. They claim to have tested the process in a commercial scale plant in Venezuela. Lately, UOP was involved in licensing the process, but there is no news of any activities now.

Fourth stage

Slurry-phase technologies reported here are the latest most active processes, where the process developers are close to commercialization.

EST. EST technology was developed by Eni in Italy.[11] Within the last decade, they have successfully developed the technology from 0.3 BPD pilot plant test run to 1,200 BPD demonstration plant test run. Eni announced that they have already started construction of a 23,000 BPD commercial plant and expected to complete the construction at the Sannazzaro refinery before the end of 2012.[12]

Because of the EST process's unique feature set and its being close to commercial status, a more-detailed description of the process is provided here. Figure 8–22 shows a block diagram of EST process. Unlike other slurry-phase processes, EST is designed to run at almost 100% resid conversion through process integration of a slurry-phase hydrocracker with

SDA unit. The hydrocracker product is de-asphalted in an SDA unit. The asphaltene is recycled back to the hydrocracker to extinction. The DAO is further hydrotreated to directly produce light transportation fuel, without producing any heavy fuel or pitch. In the process traditional moly-based homogeneous catalyst is used, and the catalyst is recycled along with asphaltenes after de-asphalting of the liquid product stream. There is almost no waste stream left in the process.

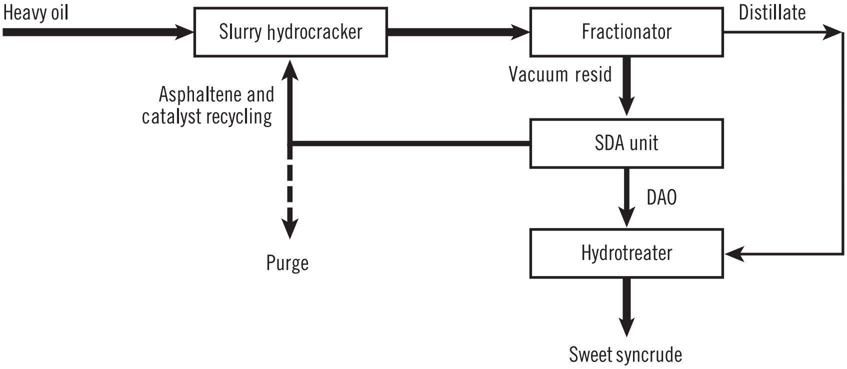

Fig. 8–22. Block diagram of EST process developed by Eni

HCAT. The parent version of HCAT is the $(HC)_3$ process discussed above. Headwaters acquired $(HC)_3$ and changed the name to HCAT after basically improving the catalyst system to achieve better mixing and higher conversion. Like EST, this process also intends to recycle the resid fraction, along with the catalyst, to achieve greater than 95 wt% conversion and to produce high-quality light syncrude. In a recent news release, Headwaters Heavy Oil reported that Neste Oil's Porvoo refinery, in Finland, is the first commercial implementation of the HCAT upgrading technology.[13] Headwaters is licensing and working on commercializing the process.

Chevron Activated Slurry Hydroprocessing (CASH)/Vacuum Resid Slurry Hydrocracking (VRSH). Based on the principle of slurry-phase technology, Chevron initially developed the CASH process using a moly-based highly dispersed homogeneous catalyst. In the mid-2000s, they further developed the proprietary process to convert heavy resid into light transportation fuel, called the *VRSH process*. All the activities are confidential; however, Chevron's Web site reports that they have tested the process in several pilot-scale plants and are ready for a semicommercial test run; Chevron claims to have achieved 100% resid conversion using slurry hydrocracking technology.[14] The principal goal of this technology development is to further expand their hydroprocessing portfolio and to be able to convert heavy crude directly into clean transportation fuel.

Fifth stage

This stage of development consists of two projects, whose original developers are listed in the first stage (see also fig. 8–21).

SRC Uniflex. This process is the latest version under investigation by UOP. After analyzing the potential of CANMET process, UOP acquired the technology licensing rights from Natural Resources Canada.[15] To convert heavy oil directly into high-quality fuels, UOP intended to improve the CANMET process by process integration through use of their own hydrotreating processes. The product from the high-conversion CANMET process was fractionated and individually hydrotreated in Unionfining and Unioncracking reactors. UOP's eventual goal is to produce ultralow-sulfur gasoline and diesel as finished products.

VCC. In 2002, Bristish Petroleum (BP) acquired Veba Oel and consequently now also owns the Veba Combi Cracking (VCC) slurry-phase hydrocracking process (discussed earlier). To the author's knowledge, this is the first time BP has had access to the latest generation of hydroprocessing technology. BP is planning to improve the process to handle the bottom of the heavy crude and convert it into clean transportation fuel as required by law in Europe. BP recognizes that it is in their interest to improve the technology portfolio.

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UPGRADER PROJECT SCENARIOS AND THE FUTURE OF CLEAN-BITUMEN TECHNOLOGY

9

The main purpose of the operation of any commercial upgrader is to meet reasonable project goals for cost, schedule, and operability—and, ultimately, to keep the profit margin high. It is essential for energy companies to consider environmental effects and incorporate highly innovative technologies at a certain cost. Even though new technologies entail considerably more risk to implement than do commercial ones, the responsibility to mitigate this risk belongs to the developers of these emerging technologies. Certain technologies failed to get off the ground, because early on, developers focused on completion, skipping pilot plant work or scale-up steps and substituting models and engineering for reliable basic experimental data. Furthermore, some leading energy companies have demonstrated that they have no courage to take the risks even to investigate, much less implement, new technologies.

This chapter highlights various scenarios for the potential design of *clean-bitumen* upgraders that deploy commercial resid conversion technologies. This discussion is especially pertinent to the situation in Alberta, where the processes of in situ recovery and surface upgrading have been integrated. Another topic of discussion in this chapter is the application of residue gasification for the production of hydrogen, heat, and power for these integrated plants. Integration and cogeneration allow the process to generate power and heat from its own feed, reducing overall energy demand as compared to the case where power and steam were generated separately from external sources.

In brief, this proposed project is a stand-alone upgrader, independent of external sources. It is done in an environmentally sensitive way—hence, the name clean-bitumen technology. Critics may say that the proposal does not make economic sense; nevertheless, it definitely makes environmental sense. This project does not burn a cleaner fuel to get a dirtier one. In fact, this project becomes more feasible with the implication of strict environmental regulations and with improvements in the efficiencies of the technologies, such as gasification, carbon capture, and bitumen upgrading. Moreover, although this may not make economic sense today, it definitely will if the oil price jumps back to the 2008 level, of above $130/bbl; in that year alone, the industry spent more than $20 billion in Alberta.

Natural gas, with the highest H/C atomic ratio, is a much cleaner energy source compared to not only bitumen but any other fossil fuel. It is strongly recommended not to burn the cleanest hydrocarbons to generate steam for the recovery of the dirtiest hydrocarbons. Natural gas is used as a feedstock in the steam methane reformer (SMR) unit, to produce hydrogen for the upgraders. Natural gas is also a main source for condensate production for pipeline transportation of bitumen. The cost of upgrading and transportation is highly dependent on natural gas availability and price, and natural gas prices are notoriously volatile. If the utilization of natural gas is avoided for the production, upgrading, and transportation of the bitumen—and if one replaces the bitumen-derived fuel with the same natural gas for vehicles (although this concept is not popular in North America)—then the overall environmental effect will be much better than the current methods (see chap. 11).

The factors that influence the utilization of more-expensive gasifiers instead of burners include the reduction in GHG emissions, the easy capture of CO_2, the use of enhanced oil recovery (EOR), the production of hydrogen, and the safe disposal of the solid-waste stream. The ultimate aim of this proposal is to use the least valuable part of the bitumen itself as a source of fuel for the production of syngas. For example, asphalt or vacuum resids are the most difficult portion of the bitumen to handle, as well as the most expensive to upgrade. So why upgrade them? Indeed, removing the resid portion instead facilitates subsequent upgrading of the resid-free bitumen (see arguments in chap. 2). Another advantage of using the gasifier is that the metals in the resid will exit as vitrified slag and can be disposed of safely, whereas the metals in any other form cannot be disposed of in an environmentally safe manner.

Before further discussion of the future options, it will be worthwhile to review some of the current upgraders in Alberta. They are extremely large in size and capital intensive. They represent high-risk investments, are not efficient for environmental control, and come with issues about the disposal of by-products.

Present Commercial Upgraders[1]

There are currently four major upgraders in Northern Alberta, all associated with the integration of mining projects. None of the major upgraders includes a gasifier, although the proposal has been on the table to expand it in the near future. However, the fifth and latest upgrader, located in Long Lake, Alberta, is the only project integrated with the SAGD operation that includes a gasifier.

The five upgraders in northern Alberta as of this writing are listed in table 9–1. The combined capacity of all five upgraders is about 1.3 million BPD.

All the upgraders listed in table 9–1 consist of atmospheric and vacuum towers, and vacuum resid is fed to the main upgrading reactor. As shown above, the main upgrading process is coking, hydrocracking, or a combination of both. The liquid product from the upgrader is further hydrotreated to produce the final product.

The only upgrader in southern Alberta is along the border with Saskatchewan. This is the Lloydminster (Husky/Biprovincial) upgrader, of capacity 72,000 BPD and consisting of two technologies: an ebullated-bed H-Oil process and a delayed coker. The pitch from the H-Oil hydrocracker is fed into the coker. Liquid products from the hydrocracker and hydrotreated coker are blended together to produce high-quality syncrude.

Table 9–1. Upgraders in northern Alberta

Upgrader name	Capacity, BPD	Upgrader type
1. Alberta Oil Sands Project (AOSP)	255,000	LC-Fining (hydrocracking)
2. Canadian Natural Resource, Horizon	135,000	Delayed coking
3. Suncor's Voyageur/Millennium	440,000	Delayed coking
4. Syncrude's Oil Sands[a]	407,000	LC-Fining and fluid coking
5. Long Lake	72,000	Proprietary OrCrude process, hydrocracking, and gasifier

[a] A part of the vacuum resid is fed to the LC-Fining, and the LC-Fining pitch, along with the rest of the vacuum resid, is fed to the coker.

Long Lake upgrader[1]

The Long Lake upgrader is unique in being integrated with SAGD and a gasifier. This 72,000 BPD upgrader has a capacity of expected syncrude production of 58,000 BPD. Its goal is to produce low-sulfur (<10 ppm) premium sweet synthetic crude of 39°API. The upgrader is owned by OPTI Canada, a joint venture with Nexen; both are Canadian companies based in Calgary.

As shown in figure 9–1 the upgrader consists of a proprietary, OrCrude process combined with a commercial Shell gasifier and a Chevron Lummus Global fixed-bed hydrocracker. The OrCrude process consists of a distillation unit, an SDA unit, and a thermal cracking unit. All information on this process is confidential.

The partially upgraded liquid product from the OrCrude process is directed to the hydrocracker. The gasification unit converts asphaltenes from the SDA plant into syngas. The syngas is used partly to produce hydrogen for the hydrocracker and partly to heat the water to generate steam for the SAGD process. This process partially reduces the natural gas demand. Recently (in July 2011), the Chinese national oil company, CNOOC, had proposed to acquire part of OPTI Canada.

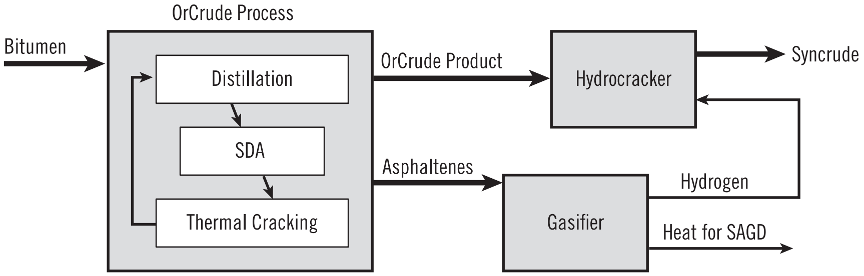

Fig. 9–1. Schematic of Long Lake upgrader by OPTI/Nexen

Clean-Bitumen Upgraders

The future approaches proposed here concentrate on smaller-scale field-based upgraders, operating at milder conditions to minimize upgrading, to yield a pipeline-transportable product of at least 19°API and maximum viscosity of 350 cSt at pipeline temperature. The economic impact of such future clean-bitumen options will be highly dependent on the price of the final blend product that a producer can get. It is a challenge to implement the options discussed below; however, they will completely eliminate dependence on the following:

- Natural gas utilization for steam generation for in situ production
- Natural gas utilization for hydrogen production (by SMR)
- Purchase of diluent for transportation of bitumen

Further, clean-bitumen options will eliminate GHG emissions through CO_2 capture and will reduce emissions of toxic gases (NO_x/SO_x emissions).

Calculations for these upgrader scenarios are based on the following assumptions:

- Production yields 100,000 BPD (given as an example and for easy calculation; actual upgrader size may be much smaller depending on the site specific project) of raw bitumen of 8°API and sulfur content of 5.0 wt% (average API gravity and S content of Alberta bitumen).
- Heating value of natural gas is 950 BTU/SCF.
- Natural gas consumption is 900 SCF/bbl of bitumen production at SOR of 3.0.
- Efficiencies are 95% for a burner and 90% for a gasifier.
- Heating value of vacuum resid is 17,000 BTU/pound.
- Heating value of coke is 14,500 BTU/pound.
- Heating value of SDA pitch is 16,000 BTU/pound. This is an estimated value. It depends on the quality of the pitch. In a real commercial study, the actual heating value of the pitch used must be experimentally determined.
- Heating value of fuel gas. Although the fuel gas's heating value will depend on the gas composition, for simplicity (considering that the main component in natural gas and fuel gas is methane), it is assumed here that the heating values are close. In an actual feasibility study, the fuel gas's composition would need to be determined from experimental data by GC analysis to calculate the exact heating value.
- Energy required to capture CO_2 is not considered in this study, because the value will depend on the site-specific project.
- Coking data of SDA asphalt are not available, because they will depend on the quality of the asphalt. However, for simplicity, it is here considered that the coking of asphalt will behave the same as vacuum resid. Again, for a real feasibility study, actual experimental data would be required.
- Hydrogen is produced by the gasification of the bitumen or its by-products. Syngas (a mixture of $CO + H_2$) thus produced is converted into hydrogen by a water gas shift (WGS) reaction

(for details, see the "Hydrogen Production and Gasification" section, below).

A majority of the results discussed below have been mathematically determined using the data that were commercially available as of the date of this publication. For simplicity's sake, approximate (i.e., rounded) figures are used. (For a more rigorous financial analysis, one should use project-specific experimental data with proper feedstocks.)

Base case

In the base case, no bitumen upgrading is done, natural gas is used as fuel for steam in SAGD, and a purchased diluent is used for DilBit transportation. Figure 9–2 shows the base-case scenario of bitumen production that has been widely used in Alberta since the beginning of in situ recovery by use of the SAGD process. For bitumen production of 100,000 BPD, three times that volume (300,000 BPD) of water equivalence must be converted into steam to be injected into the reservoir. Production of the steam requires that 92 million standard cubic feet per day (MMSCFD) of natural gas be burned. The CO_2 generated by the burning of natural gas is not easy to capture, because it is done in a low-pressure burner. The bitumen is dehydrated, after which the water is cleaned and recycled back into the boiler.

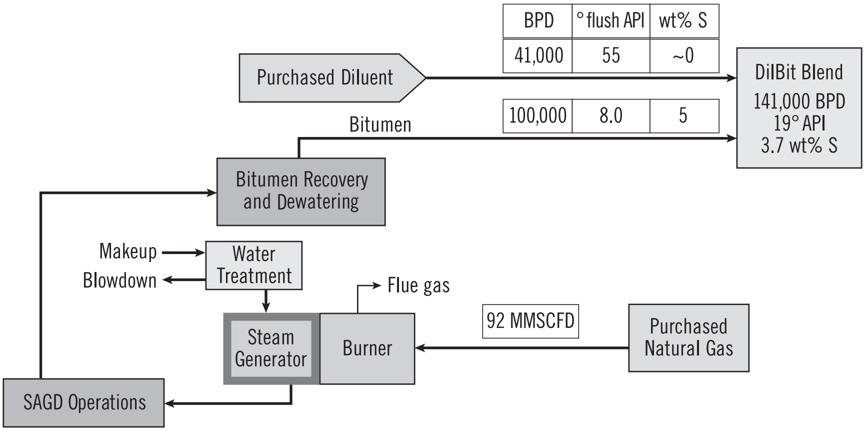

Fig. 9–2. Block diagram for base case

The bitumen is then blended with the diluent of 55°API to meet the pipeline specification of 19°API and maximum viscosity of 350 cSt at pipeline temperature. For typical Alberta bitumen of average API of 8.0°, producers need to purchase an additional 41,000 BPD of diluent to meet the specification. The DilBit blend of volume 141,000 BPD (S content 3.7 wt%) is then transported and sold to a refinery. Some refiners dislike the condensate, so they return it to the producers, requiring additional costs of transportation through a return pipeline.

Option 1: Vacuum flash unit

In this scenario, a vacuum flash unit is used for partial upgrading, along with vacuum resid for the gasifier and purchased diluent for DilBit. The burning of natural gas for SAGD is totally eliminated by replacing it with vacuum resid. Because there is no real upgrading of the bitumen, purchased diluent is still needed for transportation. Because almost half of a barrel of bitumen consists of a better-quality VGO, it is recovered through vacuum flash (a less expensive crude vacuum distillation unit), and the lower-quality vacuum resid is then used as fuel for the gasifier.

Figure 9–3 shows that the energy required to generate enough steam for 100,000 BPD of bitumen production comes from the gasification of 14,500 BPD of vacuum resid. The resid is produced by processing 28,000 BPD of bitumen in a vacuum flash unit. The remaining 72,000 bbl of the bitumen is bypassed and blended with the VGO produced, resulting in a blend of 85,500 BPD of 8.8°API that contains 4.7 wt% sulfur. Thus the blend needs diluent to meet the pipeline specification. Hence, the operator is still dependent on the availability and cost of an additional 32,000 BPD of diluent from another supplier in order to transport and sell the blend to a refiner.

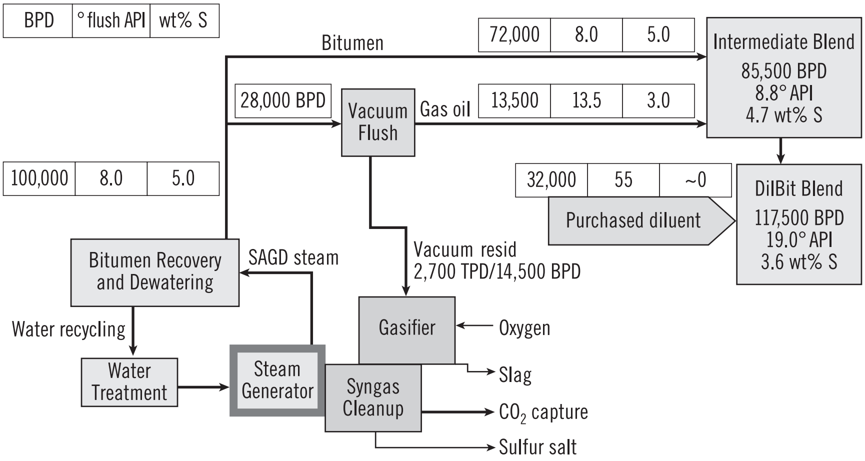

Fig. 9–3. Block diagram for option 1

Because of the gasification of vacuum resid, there is no emission of toxic gas, and the CO_2 is captured and either stored underground or used for EOR. The solid-waste stream exits as a clean slag from the gasifier that is disposed of easily.

Option 2: Delayed-coker unit

Eliminating the diluent demand in option 1, option 2 proposes fully upgrading part of the bitumen to produce the required amount of syncrude for transportation. In this scenario, a delayed-coker unit is used as the main upgrader, along with coke for the gasifier, syngas for the hydrogen, and coker oil as diluent (fig. 9–4). Enough coke is produced from the delayed coker to meet the feedstock demand for the gasifier. Also, enough hydrotreated coker oil is produced as syncrude to eliminate the need to purchase any diluent for the transportation of bitumen.

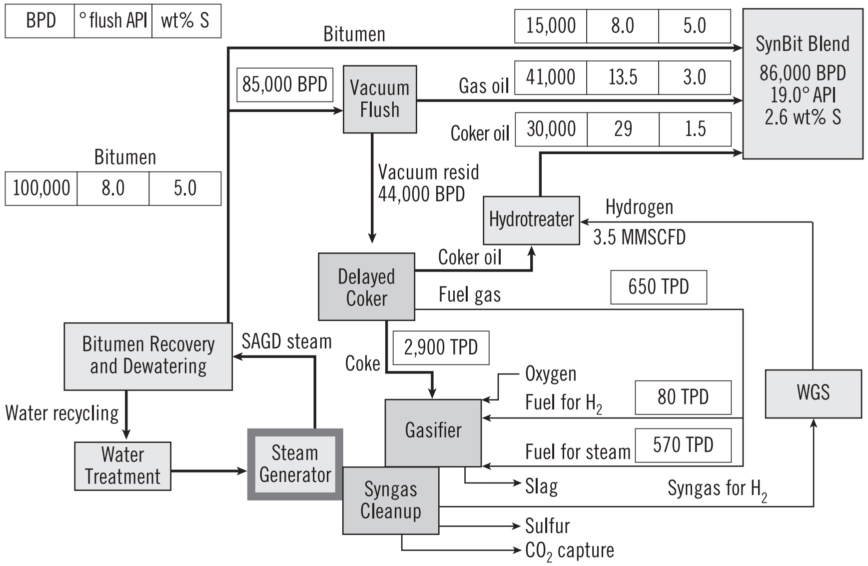

Fig. 9–4. Block diagram for option 2

For the natural gas to be replaced by coke, 3,400 metric tons per day (TPD) of coke is needed to meet the fuel requirement. However, in this option, the delayed coker produces additional C_1–C_4 hydrocarbons that could be used as fuel for the gasifier. The coker oil is hydrotreated before blending, to stabilize the product. The hydrogen for the hydrotreater is produced from the syngas generated in the gasifier, replacing natural gas and the SMR unit. A part of the syngas is directed through a WGS reactor to produce hydrogen. Another part of the syngas is burned in a burner to produce steam.

For the generation of 44,000 BPD of vacuum resid as feedstock for the coker, 85,000 BPD of bitumen is processed through a vacuum flash unit. This also generates 41,000 BPD of VGO of 13.5°API for the blend.

The delayed coker produces 30,000 BPD of coker oil of 29°API with a sulfur content of 1.5 wt%. The stream is hydrotreated to stabilize the product, consuming 3.5 MMSCFD of hydrogen. The coker oil is blended with the VGO, and 15,000 BPD of bypassed raw bitumen, producing 86,000 BPD of SynBit of 19°API with a sulfur content of 2.6 wt%, is sold directly to a refiner.

The delayed coker also produces 2,900 TPD of coke and 650 TPD of fuel gas; both were used as feedstocks for the gasifier. For the generation of enough syngas to produce enough hydrogen for the hydrotreater, 80 TPD of fuel gas was fed to the gasifier, and an additional 570 TPD of fuel gas is needed to produce enough steam for the production of bitumen by SAGD. In this option, no coke is left as a waste stream. As was the case with burning the coke, gasification of coke produces no emission of toxic gas, and the CO_2 is again captured and either stored or used for EOR. The solid-waste stream exits as a clean slag from the gasifier that is disposed of easily.

Because coker oil is used as diluent, this option is not dependent on the purchase of diluent. This is a stand-alone process, independent of external cost or availability of natural gas, hydrogen, or diluent.

Option 3: SDA unit

In this option, the main upgrader is the SDA unit, replacing the vacuum flash unit; the SDA unit is used for partial upgrading, along with asphalt for gasifier and purchased diluent for DilBit. As in option 1, there is no significant upgrading in this process to produce a pipeline-transportable product; the process is dependent on the purchase of diluent for transportation. The asphalt produced after de-asphalting is used as fuel for the gasifier.

Some companies use a vacuum distillation unit before the SDA unit. However, an atmospheric distillation unit may be used instead of a vacuum unit, to justify the use of SDA and to minimize the cost.

Figure 9–5 shows a typical case, where it is assumed that atmospheric resid is used as feedstock in a typical commercial SDA unit with C_4 as solvent. The atmospheric distillation unit processes 44,000 BPD of bitumen, producing 37,500 BPD of atmospheric resid and 6,500 BPD of AGO of

25°API (S content 2.3 wt%). The remaining 56,000 BPD of bitumen is bypassed for blending.

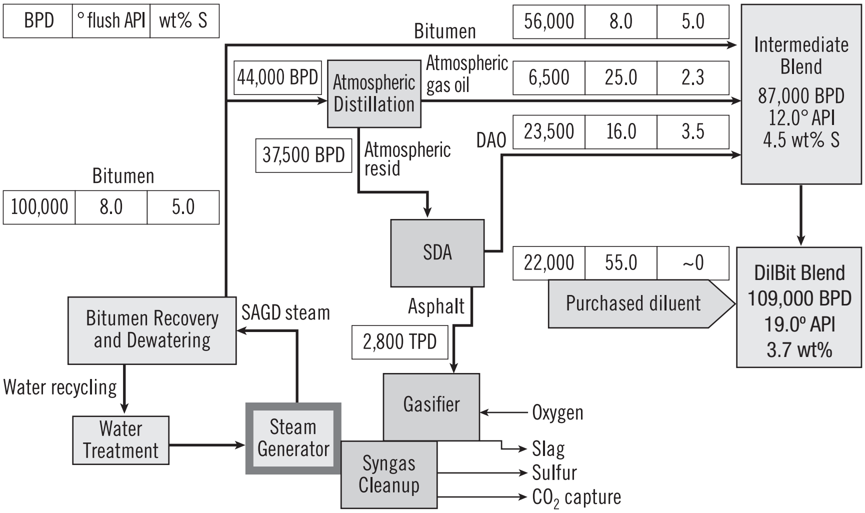

Fig. 9–5. Block diagram for option 3

The SDA unit yields 2,800 TPD of asphalt and 23,500 BPD of DAO of 16.0°API and sulfur content of 3.5 wt%. All the asphalt is gasified to generate syngas for the steam boiler.

A final intermediate blend of 87,000 BPD is made from bypass bitumen, AGO, and DAO. This blend has an API gravity of 12.0° and a sulfur content of 4.5 wt%. Thus, the producer needs to purchase an additional 22,000 BPD of diluent to meet the pipeline specification to transport it and sell it to the refiner. The DilBit blend production is 109,000 BPD of 19°API with a sulfur content of 3.7 wt%.

Option 4: SDA and delayed-coker units

Eliminating the need of a diluent in an SDA upgrader, option 4 adds a delayed coker to the upgrading process scheme in the previous scenario, along with coke for the gasifier, fuel gas for the SMR, and syncrude as the final product. Asphalt from the SDA unit is directed to a coker to produce coke and coker oil. The coke, along with the fuel gas from the coker, is gasified to generate heat for SAGD. Hydrotreated coker oil is used as diluent. Part of the fuel gas is converted into hydrogen through an SMR reactor for the hydrotreater. As an alternative, the fuel gas could be gasified into syngas and then converted into hydrogen in a WGS reactor, as in option 2. The final decision depends on the project-specific economics.

As shown in figure 9–6, all 100,000 BPD of the bitumen is processed through the atmospheric distillation unit, to generate 14,500 BPD of AGO and 85,500 BPD of atmospheric resid. Of this, 83,500 BPD of the resid is processed through an SDA unit, and the remaining 2,000 BPD is diverted to the gasifier to meet the heat balance for steam generation.

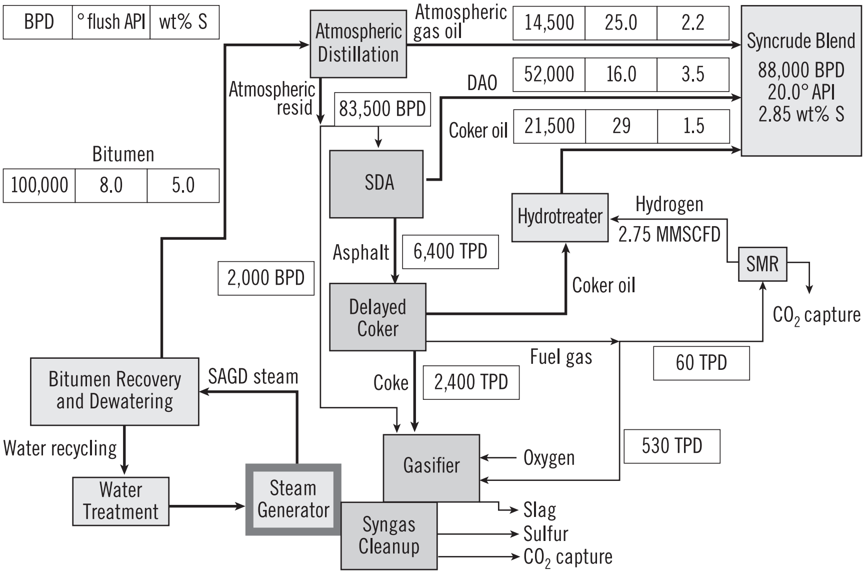

Fig. 9–6. Block diagram for option 4

An SDA plant yields 52,000 BPD of DAO and 6,400 TPD of asphalt. The asphalt in then subjected to coking in a delayed-coker plant. Asphalt is converted into 2,400 TPD of coke and 21,500 BPD of hydrotreated coker oil of 29°API with a sulfur content of 1.5 wt%. Because there are no experimental data available for coking of this particular asphalt, for simplicity's sake, it may be assumed that the coking reaction proceeds similarly to that of vacuum resid. However, readers are cautioned that, for real economic analyses, experimental data on that particular asphalt coking are needed.

In addition, the coker also produces 590 TPD of C_1–C_4 fuel gas. Instead of natural gas, a part of the clean fuel gas is used in an SMR unit to produce hydrogen. Meeting the hydrotreater's demand for the stabilization of coker oil before blending requires 60 TPD of fuel gas to produce 2.75 MMSCFD of hydrogen. Generating enough steam for the bitumen production necessitates the gasification of all 2,400 TPD of coke along with 2,000 BPD of bypassed atmospheric resid and the remaining 530 TPD of fuel gas. Of the coker oil thus produced, 21,500 BPD is blended with the 52,000 BPD of DAO and 14,500 BPD of AGO, yielding 88,000 BPD of syncrude blend of 20.0°API with a sulfur content of 2.85 wt%. This syncrude is sold in the market and, because there is no raw bitumen or resid in the blend, does not contain any resid.

Option 5: Hydrocracker unit

In the final option, a hydrocracker unit is used for upgrading, along with pitch and resid as fuel for the gasifier, syngas for the hydrogen, and SynBit as the final product. Option 5 illustrates an example of a slurry-phase reactor used for the hydroprocessing of heavy oil at a 93 wt% resid conversion level in a single-reactor system. The proposed design is independent of natural gas utilization or diluent. Hydrogen for the hydrocracker is produced from its own products: C_1–C_4 hydrocarbon gases and hydrocracked pitch.

Figure 9–7 shows the option 5 scenario. Of 100,000 BPD of bitumen, 95,000 BPD is processed through the vacuum flash unit, to meet the demand for pitch as fuel for the generation of steam for SAGD, as well as for the production of hydrogen. A part of the resid, 37,500 BPD, is diverted to the hydrocracker as feedstock, and the remaining 11,500 BPD goes to the gasifier.

The syncrude yield from the hydrocracker is 39,000 BPD of 32°API with a sulfur content of 1.2 wt%. The syncrude is further hydrotreated to stabilize the products and the total hydrogen consumption for the process is about 43 MMSCFD, with anticipated catalyst consumption of 2–3 TPD. The hydrocracker produces an additional 750 TPD of pitch, along with 590 TPD of fuel gas. Meeting the daily hydrogen demand of the hydrocracker necessitates that a part of the pitch, 340 TPD, and all of fuel gas be gasified, and the equivalent syngas is routed through a WGS reactor.

Bypassed resid (11,500 BPD) and the rest of the pitch (410 TPD) are also fed to the gasifier, to meet the heat balance for steam production. The major advantage of selecting a combination of slurry reactor and gasifier is that all the metals in the feed and the catalyst remain in the pitch. This leads to the formation of a vitrified slag that can be disposed of under environmental regulations.

Hydrocracker syncrude is blended with 46,000 BPD of vacuum gas oil and 5,000 BPD of bypassed raw bitumen to produce a final product of 90,000 BPD of SynBit of 21°API and sulfur content of 2.4 wt% that is sold to refiners. Final SynBit API gravity is higher than the required pipeline specification of 19°API; thus, the producers may claim a premium price for the SynBit or may blend some more purchased bitumen if available.

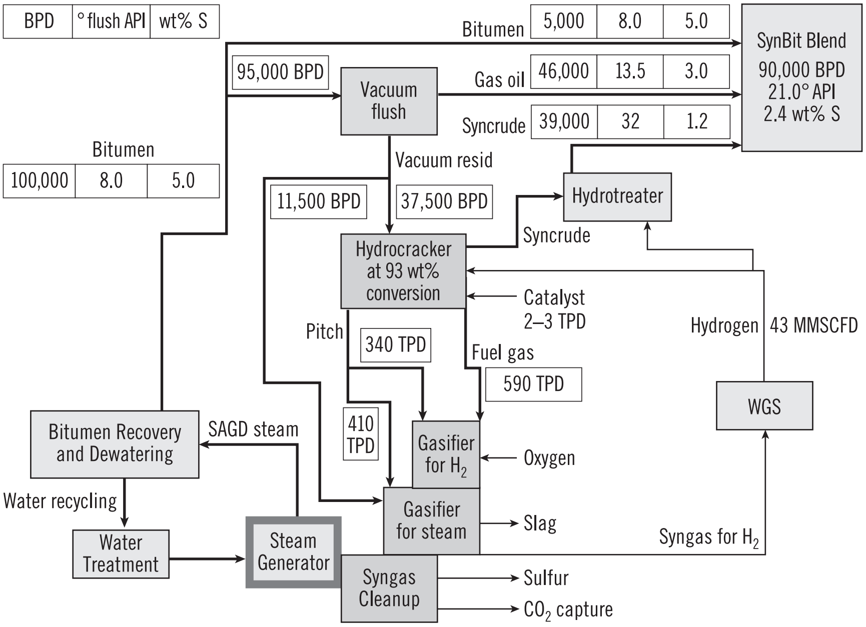

Fig. 9–7. Block diagram for option 5

The Black Diamond Process

The Black Diamond process is a new upgrader design concept consisting of an integrated two-stage process. The concept is based on modified versions of two U.S. patents awarded to the author.[2]

As shown in figure 9–8, the top portion of the upgrader consists of a hydrocracker that is directly integrated at the bottom with a POx (partial oxidation) unit. The top one-third of the hydrocracker is in the vapor phase, and the bottom two-thirds is in the liquid phase controlled by a liquid-level detector. The bitumen feedstock is added at the top of the liquid phase. Unlike in other upgrader designs, bitumen is fed directly into the hydrocracker without fractionation in the present upgrader. Thus the process design does not require any external vacuum flash or distillation unit, thereby eliminating the equipment and capital cost. Catalyst and fresh hydrogen are added at the bottom of the hydrocracker. As the feed flows downward by gravity, the remaining feed gets progressively heavier and is hydrocracked. As they form, the cracked lighter hydrocarbons flash out and exit from the top. The catalyst circulation and flashing of the vapor phase is enhanced with the help of hot hydrogen addition at the bottom and upward flow.

Bitumen-derived pitch from the hydrocracker exits from the bottom and directly enters the POx unit through a pressure-controlled letdown-valve system. The purpose is to utilize the heat from the hydrocracker into the POx unit to minimize energy demand. The hot pitch is directly gasified by catalytic steam gasification instead of by adding pure oxygen to generate syngas. The syngas from the POx unit is cleaned and further divided into two streams:

- The first portion, integrated with the WGS reactor system, enables the facility to generate sufficient hydrogen for the hydrocracker.
- The second portion is diverted to a syngas burner to generate high-pressure, high-quality steam to drive the SAGD process for the production of bitumen.

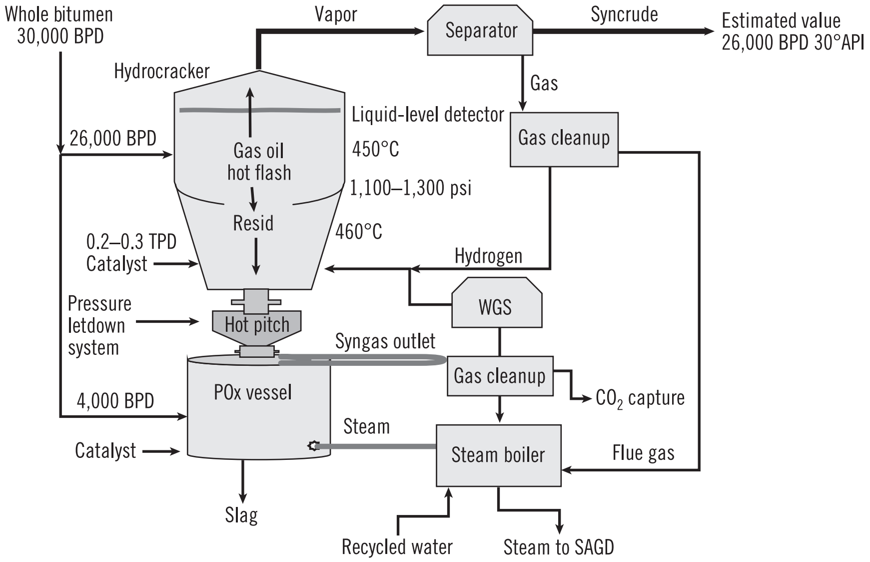

Fig. 9–8. Diagram of the proposed Black Diamond process

There is much less waste product stream because the feed metals, catalysts, and other solids are solidified inside the gasifier to produce a solid waste that is suitable for disposal in a landfill.

Avoiding high solid and catalyst concentrations inside the reactor—as well as operational problems usually associated with that solid (e.g., pressure-controlled letdown-valve operation, slurry-pump operation)—is accomplished by use of a liquid catalyst, instead of a solid catalyst. However, some inert solid will be required in order to provide surface area for adsorbing coke and metals.

The space-velocity calculation of this reactor design is more complex than for a regular tubular slurry-phase technology, because the volumetric flow of liquid varies significantly as feed flows from the top to the bottom of the reactor. Because the feed is bitumen, instead of vacuum resid, the volumetric feed rate at the top of the reactor is about 2.5 times higher than the vacuum resid in the middle portion of the reactor. Because the AGO, the VGO, and the hydrocracked product flash in the upper part of the reactor and exit overhead, the downward liquid volumetric flow declines at a rate proportional to the decline experienced by the fraction remaining in the liquid phase. When the resid conversion is 80 wt%, the flow rate exiting the bottom of the reactor and entering the POx unit is only 10 wt% of the total bitumen fed at the top. As shown in figure 9–8, the hydrocracker is bigger in size at the top as compared to the bottom, where it is connected to the POx unit. This slightly larger reactor is thought to justify eliminating the pretreating vacuum tower.

The top hydrocracker portion operates at variable temperatures, which are higher toward the bottom of the reactor (around 460°C) and gradually decrease toward the top to 440°C. The hydrogen partial pressure is higher at the bottom and decreases at the top. The total pressure in the system is around 1,100–1,300 psi, which is much lower than in corresponding commercial hydrocracker plants.

Unlike LC-Fining or other tubular slurry-phase reactors, in which all liquid and vapor fluids flow out the top of the reactor, in the present design, only the vapor can exit from the top of the reactor, because there is a liquid-level controller at the top. This means that the entire *hydrocrackate* product must flash before it can exit the reactor. The resid flows downward by gravity and comes in contact with higher temperatures, where fresher catalyst and a higher partial pressure of hydrogen accelerate the conversion of resid into lighter product. At the bottom of the hydrocracker, the unreacted resid or pitch is transferred periodically into the POx unit through a pressure-controlled letdown-valve system.

As shown in figure 9–8, the commercial plant is designed for 30,000 BPD of bitumen production at the wellhead. A part of the bitumen stream (~4,000

BPD) is diverted to the POx unit to match the heat balance, so that enough syngas can be generated for both steam generation, for the production of bitumen, and hydrogen production, for the hydrocracker to produce syncrude. The steam generator also includes flue gas from the hydrocracker. The whole design maximizes energy efficiency through process integration: steam gasification of pitch; production of hydrogen from pitch and water; and recycling of hydrogen.

The hydrocracker unit processes 26,000 BPD of bitumen and converts a minimum of 80 wt% resid into synthetic crude. The overhead vapor stream, containing reactor product and hydrogen-rich gas, is routed to a separator. Hydrogen-rich gas is separated and recycled back. Separated liquid product is cooled and depressurized, and it produces a good-quality syncrude.

The syncrude product yield is estimated to be about 26,000 BPD of about 30°API. The syncrude mostly consists of middle distillate and gas oil with less naphtha, because most of the resid would crack into distillate and some naphtha before exiting the reactor. One has the flexibility either to blend more purchased bitumen, to make it pipeline-transportable (i.e., 19°API) SynBit, or to sell the 30°API syncrude product at a premium price to the refiners.

The pitch stream from the hydrocracker bottoms is gasified in the POx unit in the presence of steam, instead of oxygen, to minimize the cost. This is similar to a steam reformer, in the presence of a suitable catalyst. The syngas balance for the production of hydrogen and heat for SAGD steam is achieved by gasification of an additional raw-bitumen stream (4,000 BPD) as needed. The gaseous streams containing CO_2 and other acid gases are scrubbed, removed, and captured in an absorber and are then routed to underground partially depleted reservoirs.

The Clean-Coal-Bitumen Process

The purpose of this section is to inform readers about the concept and availability of the clean-coal-bitumen process—that is, the simultaneous upgrading of coal and heavy oil. This process is a combination of clean-coal and clean-bitumen technologies integrated with a gasifier to reduce emissions and capture CO_2 and is especially valuable for countries rich in coal resources but highly dependent on imported oil. The economics of the process is benefitted by the conversion of two low-value feedstocks (i.e., coal and heavy oil) into transportation fuel. Moreover, at a very high crude oil price (>$100/bbl), the economics of this process would be even better, because of the advantage in terms of cost of feedstock; in some countries, the worth of the coal used is a fraction of that of imported crude.

The concept of coprocessing is not new. HRI in New Jersey (an H-Coal process) (now owned by Axens/IFP) and CANMET in Ottawa, Ontario, developed this process in the late 1980s. This process provides important improvements in both coal liquefaction and heavy oil upgrading, as follows:

- In coal liquefaction, the coal-derived recycled oil is replaced with heavy oil.
- In heavy oil upgrading, additional synthetic crude through synergistic effect from relatively low-value coal feedstock (i.e., worth less than bitumen).

Figure 9–9 shows a block diagram of a proposed commercial clean-coal–bitumen plant, based on a study done by the author and coworkers.[3] In this case, 30,000 BPD of raw Alberta bitumen is first vacuum distilled to recover 14,000 BPD of VGO and 16,000 BPD of resid. In the coal-preparation area, 2,200 TPD of run-of-mine subbituminous coal is crushed and dried. Alberta subbituminous coal contains about 20%–23% moisture and 10%–15% ash; this provides equivalent dry-ash–free coal of about 1,500 TPD of organic material that could be converted into liquid. Crushed coal is then mixed with vacuum resid in a slurry tank, and the slurry is then pumped to a high-pressure tubular slurry-phase reactor. A coprocessing reactor runs between 450–470°C and 15–20 MPa hydrogen pressure.

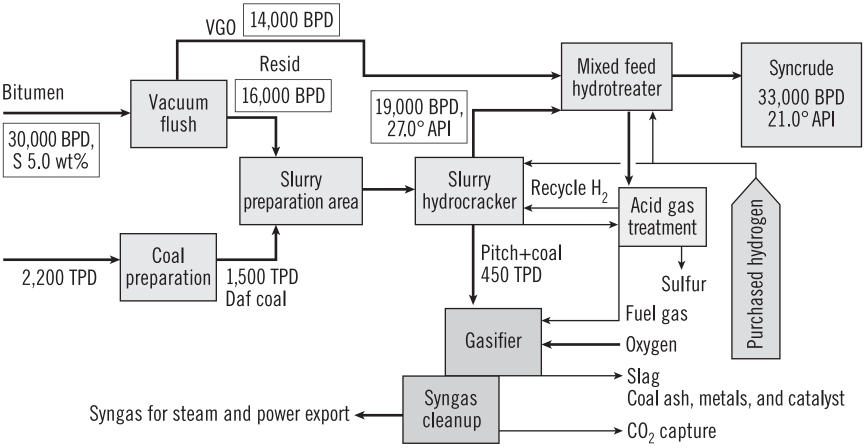

Fig. 9–9. Block diagram of clean-coal-bitumen process

Based on the resid content plus coal in the feedstock, the total conversion of organic coal plus resid exceeds 85–90 wt% under the operating conditions. The total hydrogen consumption is about 2.5–2.8 wt% of the organic feed.

The reactor product stream is separated into a gaseous stream, pitch plus unreacted coal, and synthetic crude. Coprocessing yields 19,000 BPD of resid-free synthetic crude of 27°API that is diverted to a mixed-feed hydrotreater to further remove sulfur and nitrogen. Usually, coal consists of a higher percentage of nitrogen than the heavy oil; thus, synthetic crude needs severe hydrotreating to remove the nitrogen. Coprocessed liquid usually contains a higher percentage (35–40 vol%) of naphtha and less distillate (30–35 vol%) and gas oil (25–30 vol%).

Straight-run VGO from the vacuum flash unit is also directed to the hydrotreater. Here, it is blended with the syncrude to produce a final blend of 33,000 BPD of 21°API that is sold to the refineries.

The recovered hydrocracker bottoms (450 TPD) consist of unreacted resid, unconverted coal, and ash. The bottom stream is gasified to generate heat for steam in SAGD and power for the upgrader plant. All CO_2 emissions from this gasifier could be easily captured and buried underground. The original calculation did not include hydrogen production and total heat balance; hence additional fuel and hydrogen need to be purchased.

All the metals—consisting of ash from the coal, metals from the heavy oil, and added catalysts—form a vitrified slag. This comes out of the gasifier as a nontoxic solid that can be disposed of or buried in an environmentally acceptable way.

Hydrogen Production and Gasification

As discussed in earlier chapters, bitumen is a highly hydrogen-deficient material, and upgrading thus requires considerable quantities of hydrogen. Several hydrogen plants are under construction in Canada to meet such demands for hydrogen. The most common method of commercial hydrogen production is SMR, wherein natural gas (mostly methane) is the most common feedstock.

The SMR reaction takes place in the presence of high-pressure steam and catalyst, as follows:

$$CH_4 + H_2O \quad \leftrightarrow \quad CO + 3\,H_2 \quad \Delta H\ 206\ \text{kJ/mol} \tag{9–1}$$

This is a strong endothermic reaction; hence, it requires a lot of energy to produce hydrogen. The syngas thus produced consists of three times the volume of hydrogen as compared to that of carbon monoxide. However, the H_2 to CO ratio changes depending on the molecular structure of the hydrocarbon feedstock.

The CO thus produced is further converted into hydrogen in a CO shift reactor (WGS) as shown below in equation 9–3.

Today, because of the high demand for hydrogen, refiners and upgraders are looking for alternate technologies. Gasification of low-value by-products—such as coke, pitch, vacuum resid, and gaseous hydrocarbons—gives the most suitable feedstocks for the upgrader scenarios discussed earlier in this chapter. The gasification technology is still not widely used for hydrogen production, but only because of its high capital and operating costs. However, it is still advantageous to use gasification, considering environmental issues and the flexibility of the wide ranges of low-value feedstocks.

Unlike SMR, gasification is based on partial oxidation of carbon or hydrocarbons; thus it is an exothermic reaction, as follows:

$$CH_4 + ½\,O_2 \quad \leftrightarrow \quad CO + 2\,H_2 \quad \Delta H\ {-520}\ \text{kJ/mol} \tag{9–2}$$

The heat produced in reaction 9–2 is used for the second step, a moderately exothermic reaction (WGS reaction), where in the presence of steam CO is converted into additional hydrogen and CO_2, as follows:

$$CO + H_2O \quad \leftrightarrow \quad CO_2 + H_2 \quad \Delta H\ {-41}\ \text{kJ/mol} \tag{9–3}$$

In theory, the two steps combined (reactions 9–2 and 9–3) yield three volume units of hydrogen per volume unit of methane; in practice, though, the actual yield depends on the efficiency of the two steps and the type of feedstocks.

The two most commonly used commercial gasifiers are the Texaco process (now owned by GE) and the Shell process. Both are mostly used for the conversion of low-value carbonaceous feed, such as coal and petcoke, by partial oxidation into syngas. Gasifiers operate at very high temperatures of 1,100–1,500°C and high pressures in the range of 500–1,200 psig. Higher pressure has advantages in recovering hydrogen and capturing CO_2. Hot syngas from the gasifier is cooled, cleaned (i.e., sulfur recovery), and converted into petrochemicals and hydrogen. Hot syngas is cooled with water, and the waste heat is used for steam production. The slag from a gasifier is an inert material and can be disposed of easily, with no environmental problem.

There is a worldwide interest in carbon capturing and storage (CCS). There are technologies available for CCS; however, political and environmental pressure will be needed to implement them. As discussed earlier, in new upgrader projects, CSS could be applied as part of the upgrading facilities along with gasification technology. Concentrated CO_2 under pressure could be separated from the synthesis gas either by chemical process or by physical methods. Captured CO_2 could be compressed further and pumped down underground for enhanced oil recovery (EOR) and sequestration. This could provide producers with additional economic advantages through increased production and tax incentives.

The most expensive operating costs for the gasification technology result from the cryogenic air-separation unit and acid gas removal from the syngas prior to further processing. For the production of high-purity hydrogen, the pressure swing adsorption (PSA) unit is preferred, although other technologies (e.g., membrane separation or the cryogenic process) could be used, depending on the purity and recovery of hydrogen required.

Importantly, gasification is advantageous not only for hydrogen production but also for its ability to convert heavy carbonaceous feeds, such as coal, resid, or bitumen, into clean liquid hydrocarbons via syngas. Conversion of syngas to liquid hydrocarbons is achieved using a very old process (developed in early 1920s) known as the *Fisher-Tropsch synthesis* (FT synthesis), named for its famous developers. The major products of these conversions are a series of straight-chain alkanes, alkenes, and oxygenated hydrocarbons. In particular, the diesel product from FT synthesis is of higher value, with a much higher cetane number (>50) and no sulfur and nitrogen, than the corresponding bitumen/oil-derived diesel.

The only commercial operation based on FT synthesis, using coal as feedstock in CTL (coal-to-liquid) process and gas as feedstock in GTL (gas-to-liquid) process, is conducted by the South African state-owned oil company SASOL.

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CHALLENGES FACING CONVENTIONAL REFINERIES WITH UNCONVENTIONAL OIL

10

A conventional refinery may process one type of crude or several types, depending on the pipeline supply logistics. If a refinery handles several crudes being processed in sequence over a length of time, then refiners need to adjust the refinery process conditions on the basis of the quality of the crude. If all crudes are conventional crude and compatible to each other, then refiners may blend the crudes to reduce the changes they have to make in the refinery process conditions in order to increase the production and economics of operation.

When oil sands–derived raw bitumen, or the upgraded bitumen product, is diluted with condensate or synthetic crude and pipelined to a refinery, such a change in the type of blend creates a big challenge for the refiners, requiring them to make several adjustments. (For a detailed description of the differences between conventional crude and synthetic crude, see chap. 7.)

Figure 10–1 depicts a conventional refinery, illustrating the types of different synthetic blends that could arrive at the gate of a refinery. Four blends are shown in figure 10–1: syncrude, SynBit, SynDilBit, and DilBit (for details, see chap. 6). For simplicity, approximate rounded figures are used for the composition of the blends almost at the same ratio as that of the real blends. There are atmospheric and vacuum towers in a refinery, but they are not shown in figure 10–1, for simplicity's sake. The center of figure 10–1 shows capacities of various plants in a 100,000 BPD conventional crude refinery (e.g., the refinery has a naphtha reformer of 25,000 BPD capacity, a distillate hydrotreater of 30,000 BPD capacity, an FCC plant of 25,000 BPD capacity to treat VGO, and a delayed coker of 20,000 BPD capacity to handle the resid). The four boxes around the refinery show four different synthetic pipeline blends and their compositions in thousands of barrels per day (KBPD), the total volume of each blend being 100,000 BPD.

The following sections review the difficulties facing a conventional refinery on the arrival of a synthetic blend. Figure 10–1 is used as a reference example for comparing capacities when using each of these blends of unconventional oil.

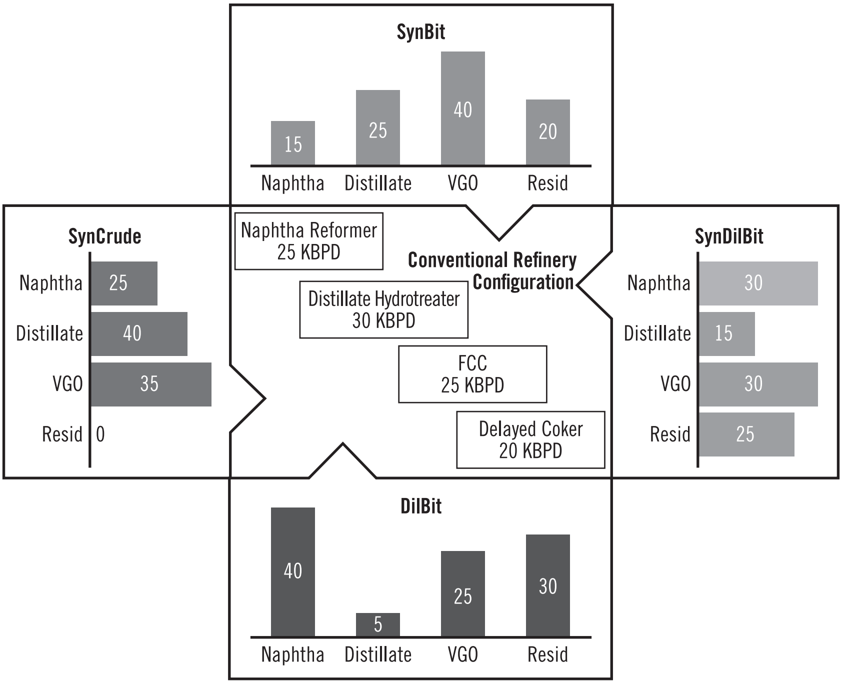

Fig. 10–1. Composition of blend types at the gate of a conventional refinery

Difficulties in Refining Syncrude

When conventional crude is replaced by synthetic crude, the biggest challenge for the refiners is that synthetic crudes are not compatible with conventional crude. The molecular level properties of each synthetic crude vary considerably, based on its history (i.e., processing and origin). First, refiners have to change the catalysts and the process conditions (severity) of each and every plant. Second, because the syncrude has no resid, a refinery with a delayed-coker unit will not be able to process anything through the coker. However, the naphtha reformer will run at its full capacity of 25,000 BPD, while the distillate hydrotreater and the FCC units will have to deal with excess volumes (by 10,000 BPD each) of feedstocks. These all have economic impacts on the refineries.

Difficulties in Refining SynBit

When the syncrude is replaced by the SynBit at the refinery gate, it leaves the refiner with an excess volume (40 KBPD) of VGO; consequently, the refinery will need to build another FCC unit to handle it. The refiner has to decide what to do with the VGO before receiving the SynBit. By contrast, the because there is not enough of naphtha and distillate in the blend, the naphtha reformer and distillate hydrotreater will receive less feedstock and thus will both run at lower capacities. If a refinery were to run its two plants at 20%–40% lower capacity, it would have a negative impact on the profit margin. However, in this case, the only advantage to the refiner is that the coker will run at full capacity, because SynBit has 20 KBPD of resid.

Difficulties in Refining SynDilBit

The SynBit may be replaced by SynDilBit, a mixture of synthetic crude, condensate, and bitumen. This blend contains high concentrations of naphtha (30 KBPD) coming from the condensate and syncrude, 30 KBPD of VGO coming from the syncrude and from the raw bitumen, and 25 KBPD of resid coming from the bitumen.

The refiners will face problems with the distillate hydrotreater, which will run at half capacity because the amount of distillate is only 15 KBPD, while the other three plants (i.e., the naphtha reformer, the FCC unit, and the coker) will have to handle an excess 5,000 BPD of each feedstock. If a refinery were to decide to process SynDilBit for a longer period of time, then they might increase the capacities of all the three plants and decrease the capacity of the distillate hydrotreater. However, this represents a major investment for the refiners.

Difficulties in Refining DilBit

When the SynDilBit is replaced by the DilBit, or dumbbell crude, at the refinery gate, the refiners will suddenly receive a very large volume (40 KBPD) of naphtha, because it is added as a diluent. In most cases, the DilBit contains very light condensate (not naphtha). Because refiners usually do not prefer those lighter hydrocarbons, they may return it to the producers despite the additional cost of shipping it back. In addition, there is a very low distillate fraction (5%) in the blend because the fraction is not present either in the condensate or in the bitumen. Thus, the distillate hydrotreater will have a supply of feedstock of only about 15% of its capacity. Consequently, production of diesel/jet fuel will be very low and may not meet the market demand. This will also have a considerable negative impact on the refinery's profit margin.

In DilBit, there are gas oils and resid from the bitumen itself. The FCC will run at its full capacity of 25 KBPD; however, the quality of the gas oil is poorer than that of the gas oil from the conventional crude, even though they share the same boiling range. The life of the FCC catalyst will decrease if the refiners use the same catalyst for bitumen-derived gas oil. Hence, the operating cost of the FCC unit will increase.

The resid concentration is about 50% more in DilBit as compared to the coker capacity. Consequently, refiners must either deal with the excess resid or increase the coker capacity.

Besides the simple problems discussed above, when switching to nonconventional feedstocks, refiners may face more difficult challenges, such as corrosion and fouling. Bitumen is a high-acid, high-asphaltene, and high-sulfur crude that accelerates corrosion and fouling in the refinery. High-acid crude could be handled only by changing the metallurgy of the wall of the reactors, which is impractical for an existing plant. Thus, if a grassroots refinery is built, then it should be designed on the basis of a boutique feedstock that will be processed through the refinery for a long period of time.

FINAL THOUGHT—GOING GREEN

11

Finally, on September 2, 2011, just as I thought I had finished writing this book, the idea for this chapter came to me at 30,000 ft, flying from the United States to Canada, as I was reading that day's issue of the *Globe and Mail*. The business section drew my attention because several pages were devoted to Alberta oil sands, discussing in particular the issues related to two proposed pipelines from Alberta: the Gateway pipeline, going west toward Vancouver; and the Keystone XL pipeline, going south toward the Gulf of Mexico. Pictures showed the demonstrations on the previous day that took place in the United States against the Keystone XL pipeline project, with one noticeable poster reading, "No more dirty oil sands."[1]

What the demonstrators believe in depends on who they listen to, among so many pundits. Especially in the media and political lobbying, scientific facts are ignored.

Today's biggest challenge is to handle the recent rapid rise in the energy demand all over the world. Therefore, the question becomes, Can we manage without the Alberta oil sands? The answer, at least for today, is no.

It is true that the oil sands and bitumen are dirty; nevertheless, there is an environmentally responsible way to handle these resources. Further, although the oil industries depend on high profit margins, it is their responsibility to handle the matter in an environmentally responsible way—at any cost. Most important, the industry needs to improve its image by communicating with the public and using solid scientific data to back up practices. Finally, the people in the United States need to understand that they will be much better off dependent on the dirty oil from Canada than on oil from the rest of the world, unless they choose to stop driving.

In the preface, I mentioned that it is not desirable to burn cleaner natural gas to recover dirty bitumen. Instead, it makes better sense to use part of the bitumen for its own production. The options discussed in chapter 9 represent an integrated approach to reducing GHG emissions for bitumen production and upgrading by using the bitumen-derived fuel in a gasifier.

Let us see what we can do with the natural gas instead of burning it for the production of SAGD steam. For example, presently, bitumen producers are burning 92 MMSCFD of natural gas to generate steam for the production of 100,000 BPD of bitumen (see fig. 9–2). If we do not burn the natural gas for the bitumen production (as discussed in chap. 9) and instead run vehicles with the same amount of natural gas, which burns much cleaner than the bitumen-derived gasoline, the results would be as follows:

- Gasoline has a heating value of 115,400 BTU/gallon.
- Assume that a gasoline car drives at a rate of 25 miles per gallon.
- Strictly on the basis of heating value (950 BTU/SCF) and not efficiency, a gallon of gasoline is equivalent to about 125 SCF of natural gas, or one can drive 25 miles using 125 SCF of natural gas or LNG.
- Hence, with 92 MMSCFD of natural gas, it will be possible to drive 735,000 vehicles within 25 miles per day.
- Or, one can imagine that in Alberta's capital city of Edmonton, with a population of 800,000, everyone could drive their cars 25 miles per day using the same amount of natural gas, as long as it is not used for any bitumen production.

So, the conclusion is that, if we do well-to-wheel CO_2 emissions calculations from bitumen production to exhaust emission from transportation fuel, there will be an significant overall reduction in environmental emissions, especially achieving more than 99% lower SO_x and 90% lower NO_x emissions from LNG vehicles—a huge change compared to cars propelled by bitumen-derived gasoline.

As far as CO_2 emission is concerned,

- One car driving 25 miles per day with one gallon of gasoline emits about 20 pounds of CO_2.
- One car driving 25 miles per day replacing one gallon of gasoline with 125 SCF of natural gas emits about 12 pounds of CO_2.
- Thus, replacing gasoline with natural gas for vehicles will decrease 8 pounds of CO_2 emissions per car per day.
- Hence, 735,000 vehicles will decrease CO_2 emissions by 5.88 million pounds or 2,670 TPD. According to *National Geographic*, conventional crude production emits 128 pounds/bbl of CO_2, as compared to 364 pounds for mining operations and 388 pounds for in situ operations per barrel of production and upgrading.[2]

Thus, the bitumen-derived gasoline emits three times more CO_2 (in production and upgrading) than does the conventional, crude-derived gasoline; hence, it emits even higher levels of CO_2 than natural gas production.

- It is true that gasoline, being liquid, has higher energy density and is easier to handle and transport as compared to LNG; however, the overall carbon emission is much higher from the bitumen-derived gasoline.

Thus, not only does natural gas cost less than the bitumen-derived fuel, but it also emits much less GHG as compared to gasoline (in emissions from both production and exhaust). Although it is true that the natural gas emits more methane (a GHG) as compared to the gasoline, the nonmethane GHG emissions offset the total emissions.

Note that the carbon emissions from coal-fired power plants are much higher than for the oil sands in Alberta. There is no nuclear reactor in Alberta.

Is Nuclear Energy a Viable Solution?

Environmentalists do not like nuclear energy either, even though it is the cleanest energy available. Again, which pundits are they listening to?

Not long ago, serious thought was given to using nuclear reactors as a source of clean energy for the production of Alberta bitumen. This really is an interesting concept: through the integration of two energy industries (i.e., petroleum with nuclear), the oil industry would be dedicating itself to reducing emissions and going relatively green.

The case was so serious that, at the 2008 Oil Sands and Heavy Oil Technologies Conference, Atomic Energy of Canada showed the benefit of using a nuclear reactor to reduce CO_2 emissions for bitumen production. According to them, it will take a nuclear reactor of capacity 1,000 megawatts electrical (MWe) to produce enough steam for a SAGD operation at SOR of 2.5 for 300,000 BPD of bitumen production.[3] There are zero emissions from nuclear energy, and this may be the only way to meet the CO_2 emissions target.

Is nuclear really a solution of the future? Especially after what happened in Japan in March 2011, the question must be weighed carefully.

Currently, in-situ bitumen production in Alberta exceeds 1 million barrels per day. So it will take four nuclear reactors of 1,000 MWe capacity each to meet the energy demand just for the bitumen production.

Then, what about the additional energy required for further upgrading and refining of the bitumen to transportation fuel? And what about the emissions from vehicle tailpipes?

Does this mean we could have nuclear-powered vehicles? No, not yet! What about electric vehicles? We already have started down that path, and that would definitely make for a greener, carbonless solution. However, that's assuming that the power comes from nuclear energy, not coal. Who will pay for it? Will environmentalists allow it? Ultimately, economics drives the decision, not the environment. What about alternative clean energy? We have a long way to go, but we have enough time. Let us discuss that in the next book.

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APPENDIX A: GLOSSARY

API gravity: Used in the petroleum industry as a density scale, defined mathematically by equation (3–1). Named after the American Petroleum Institute (API).

Asphalt: A product from deep distillation or extraction by paraffinic solvent, similar to asphaltenes.

Asphaltenes: The heaviest and most concentrated aromatic fractions of bitumen that precipitate out in the presence of normal paraffin and are soluble in benzene or toluene. (See also *pre-asphaltenes*.)

Atmospheric gas oil (AGO): The liquid portion recovered under atmospheric distillation below 350°C.

Atmospheric resid: The undistillable fraction that remains after atmospheric distillation of a crude oil. Usual temperature of distillation is 350°C (660°F); therefore, the atmospheric resid is that found at 350°C+ (660°F+) and is often referred to in those terms.

Barrels of oil equivalent (BOE): Units used for the comparison of various energy sources with an energy equivalent to that of a barrel of oil. Specifically, 1 BOE = 5.8 million BTU.

Biodegradation: Degradation of hydrocarbons by natural environment or bacteria or other biological means.

Bitumen: Naturally occurring highly viscous hydrocarbons of viscosity greater than 10,000 cSt at reservoir conditions and API gravity less than 10°, recovered only by thermal process or mining and usually used in reference to the crude obtained from the oil sands in Alberta.

Carbon residue: What remains when a sample is pyrolyzed in an inert atmosphere. This indicates the tendency of a crude to form coke. Various methods are used, and usually the names indicate special equipment used for the analysis of the residue (e.g., Conradson residue [CCR], micro residue, or Ramsbottom residue).

Coke, calcined coke, and green coke: In a commercial operation, the raw coke formed during delayed coking is green coke. Before being sold to carbon and graphite industries, green coke is calcined (or heated to a very high temperature) to reduce the volatile matter and increase the crystalline structure, the product of which is calcined coke.

Coking: A thermal cracking process wherein there is no hydrogen and catalyst. The bigger molecules crack into lower-molecular-weight hydrocarbons and solid coke.

Condensate: A mixture of very light hydrocarbons recovered from a gas reservoir or natural gas and used as diluent for bitumen transportation.

Conventional crude oil: The type of crude that can be recovered from the reservoir by conventional means (e.g., by pumping).

Conventional heavy oil: Hydrocarbons in the range of 10–21°API that can be recovered along with the conventional oil.

Coprocessing: Simultaneous upgrading of coal and heavy oil.

Cracking: A series of reactions that takes place by breaking bonds (e.g., C–C, C–S, C–N, or C–H) of heavier molecules into smaller molecules.

Crude oil: A naturally occurring liquid hydrocarbon mixture generally defined by its physical properties.

Dead oil: Gas-free heavy oil used as a sample for analysis in the laboratory.

De-asphalted oil (DAO): The portion of bitumen recovered by *n*-paraffin solvent extraction.

Extraheavy oil (unconventional heavy oil): Heavy oil that cannot move by itself and cannot be recovered by conventional means. Extraheavy oil falls below 10°API, with viscosity less than 10,000 cSt.

Gasification: Conversion of carbonaceous materials into syngas at high temperature and pressure.

Heavy oil: In general, heavy oil refers to a crude petroleum hydrocarbon of below 21°API.

Hydrocracking: The process of cracking the C–C bond accompanied by the addition of hydrogen, where bigger molecules in the heavy oil are transferred to the lower-molecular-weight liquid oil.

Hydrogenation: The process of adding hydrogen to remove contaminants (e.g., S, N, and metals) and to saturate the unsaturated olefins or aromatics.

Live oil: Actual core sample from the reservoir with gas.

Maltene: Portion of the whole bitumen soluble in n-paraffins.

Oil sands: Bitumen-soaked sand, located mostly in Alberta.

Pitch: A semisolid product, equivalent to a resid, that is obtained through the processing of heavy oil or bitumen.

PONA: Paraffins, olefins, naphthenes, and aromatics.

Porphyrin: Metals in heavy oil that are chelated with nitrogen bonds in a ring structure.

Pre-asphaltenes: The portion of asphaltene that is insoluble in benzene or toluene.

Produced water: Water that comes out through the production well along with the heavy oil (in the case of offshore drilling) or bitumen (in the case of SAGD).

Residue/residuum/resid: Nondistillable portion remaining after atmospheric or vacuum distillation of heavy oil, usually referred to by the equivalent atmospheric temperature at which it was distilled (e.g., 535°C+ [1,000°F+]).

Resin: Portion of the maltenes adsorbed by silica gel or clay column and not eluted by *n*-pentane.

SARA: Saturates, aromatics, resins, and asphaltenes.

Simulated distillation (SimDist): Method of quickly determining the boiling-point distribution of a crude oil sample by GC.

Steam methane reforming (SMR): Method of production of hydrogen from natural gas by using steam.

Syngas: Mixture of carbon monoxide and hydrogen as product from a gasifier.

Synthetic crude oil (SCO; also called *syncrude*): A product resulting from the upgrading of heavy oil or bitumen that does not contain residue.

Tar: Highly viscous material resulting from destructive distillation of bitumen or coal.

Tar sands: Term incorrectly used to refer to oil sands, which, by definition, are not a tar. (See also *tar*.)

Upgrading: Conversion of heavy oil into lighter oil.

Vacuum gas oil (VGO): The portion distilled under vacuum as volatile material after atmospheric distillation. Usually, this is the fraction at 350–535°C (660–1,000°F).

Vacuum resid: Material remaining undistilled at maximum temperature achievable under vacuum without thermal decomposition of the crude oil. The equivalent atmospheric temperature of distillation depends on the vacuum applied; in this book, for simplicity, 535°C+ (1,000°F+) is used.

Water gas shift (WGS) reaction: Method of production of hydrogen from syngas by using steam.

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APPENDIX C: COLLABORATORS

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Prof. S. L. Chawla	IIT, Delhi	
Dr. K. L. Mallik	Indian Institute of Petroleum, Dehradun	Later became General Manager, Lubrizol India Ltd, Bombay
Prof. Dr. Docent V. Vantu	Institute of Petroleum and Gas (IPG) , Ploiesti, Romania	Fellow of the Romanian Academy of Sciences
Dr. V. Matei	IPG Ploiesti, Romania	
Prof. K. J. Laidler	University of Ottawa, Ontario	Recipient of numerous international honors and awards in chemical kinetics
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[a] Listed in chronological order of collaboration, from 1970 to the present.

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