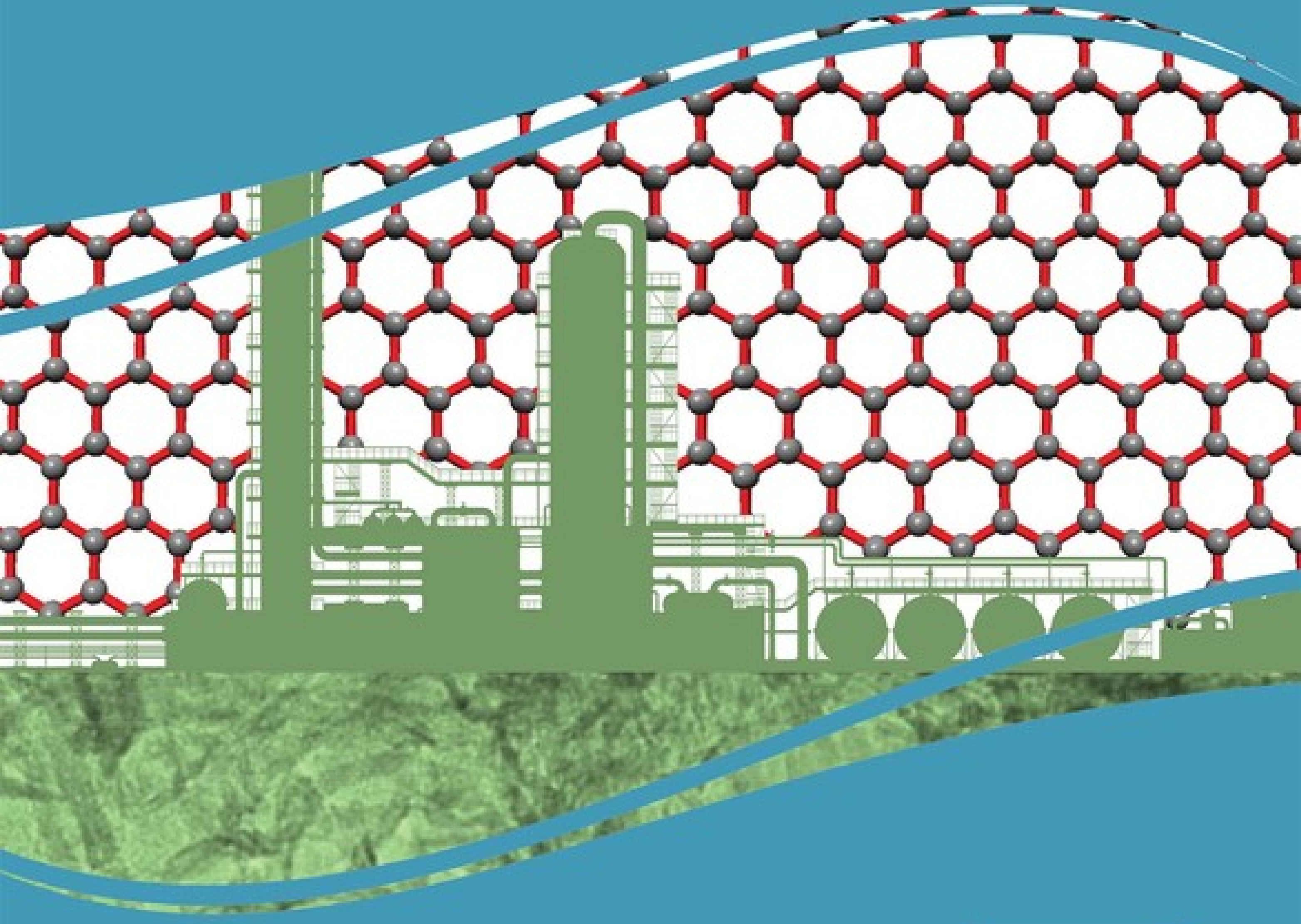
Premier Reference Source

Applying Nanotechnology to the Desulfurization Process in Petroleum Engineering



Tawfik A. Saleh

IGI GLOBAL
DISSEMINATOR of KNOWLEDGE

Applying Nanotechnology to the Desulfurization Process in Petroleum Engineering

Tawfik A. Saleh
Department of Chemistry, King Fahd University of Petroleum and Minerals, Saudi Arabia

A volume in the Advances in Chemical and Materials Engineering (ACME) Book Series

ENGINEERING SCIENCE REFERENCE
An Imprint of IGI Global

Published in the United States of America by
Engineering Science Reference (an imprint of IGI Global)
701 E. Chocolate Avenue
Hershey PA, USA 17033
Tel: 717-533-8845
Fax: 717-533-8661
E-mail: cust@igi-global.com
Web site: http://www.igi-global.com

Library of Congress Cataloging-in-Publication Data

Applying nanotechnology to the desulfurization process in petroleum engineering / Tawfik A. Saleh, editor.
pages cm
Includes bibliographical references and index.
ISBN 978-1-4666-9545-0 (hardcover) -- ISBN 978-1-4666-9546-7 (ebook) 1. Petroleum--Refining--Desulfurization--Materials. 2. Petroleum--Refining--Desulfurization--Technique. 3. Nanostructured materials. I. Saleh, Tawfik A., editor.
TP690.45.A66 2016
665.5'3--dc23
2015033323

This book is published in the IGI Global book series Advances in Chemical and Materials Engineering (ACME) (ISSN: 2327-5448; eISSN: 2327-5456)

British Cataloguing in Publication Data
A Cataloguing in Publication record for this book is available from the British Library.

For electronic access to this publication, please contact: eresources@igi-global.com.

Advances in Chemical and Materials Engineering (ACME) Book Series

J. Paulo Davim
University of Aveiro, Portugal

ISSN: 2327-5448
EISSN: 2327-5456

MISSION

The cross disciplinary approach of chemical and materials engineering is rapidly growing as it applies to the study of educational, scientific and industrial research activities by solving complex chemical problems using computational techniques and statistical methods.

The **Advances in Chemical and Materials Engineering (ACME) Book Series** provides research on the recent advances throughout computational and statistical methods of analysis and modeling. This series brings together collaboration between chemists, engineers, statisticians, and computer scientists and offers a wealth of knowledge and useful tools to academics, practitioners, and professionals through high quality publications.

COVERAGE

- Wear of Materials
- Composites
- Electrochemical and Corrosion
- Heat Treatments
- Fracture Mechanics
- Ductility and Crack-Resistance
- Fatigue and Creep
- Metallic Alloys
- Coatings and surface treatments
- Biomaterials

IGI Global is currently accepting manuscripts for publication within this series. To submit a proposal for a volume in this series, please contact our Acquisition Editors at Acquisitions@igi-global.com or visit: http://www.igi-global.com/publish/.

The Advances in Chemical and Materials Engineering (ACME) Book Series (ISSN 2327-5448) is published by IGI Global, 701 E. Chocolate Avenue, Hershey, PA 17033-1240, USA, www.igi-global.com. This series is composed of titles available for purchase individually; each title is edited to be contextually exclusive from any other title within the series. For pricing and ordering information please visit http://www.igi-global.com/book-series/advances-chemical-materials-engineering/73687. Postmaster: Send all address changes to above address.

Titles in this Series

For a list of additional titles in this series, please visit: www.igi-global.com

Quantitative Structure-Activity Relationships in Drug Design, Predictive Toxicology, and Risk Assessment
Kunal Roy (Jadavpur University, India)
Medical Information Science Reference • copyright 2015 • 727pp • H/C (ISBN: 9781466681361) • US $295.00 (our price)

Handbook of Research on Recent Developments in Materials Science and Corrosion Engineering Education
Hwee Ling Lim (The Petroleum Institute, UAE)
Engineering Science Reference • copyright 2015 • 493pp • H/C (ISBN: 9781466681835) • US $325.00 (our price)

Processing Techniques and Tribological Behavior of Composite Materials
Rajnesh Tyagi (Indian Institute of Technology (BHU), Varanasi, India) and J. Paulo Davim (University of Aveiro, Portugal)
Engineering Science Reference • copyright 2015 • 464pp • H/C (ISBN: 9781466675308) • US $225.00 (our price)

Handbook of Research on Diverse Applications of Nanotechnology in Biomedicine, Chemistry, and Engineering
Shivani Soni (Alabama State University, USA) Amandeep Salhotra (City of Hope National Medical Center, USA) and Mrutyunjay Suar (KIIT University, India)
Engineering Science Reference • copyright 2015 • 820pp • H/C (ISBN: 9781466663633) • US $395.00 (our price)

Innovative Applications and Developments of Micro-Pattern Gaseous Detectors
Tom Francke (Myon, Sweden) and Vladimir Peskov (CERN, Switzerland)
Engineering Science Reference • copyright 2014 • 303pp • H/C (ISBN: 9781466660144) • US $215.00 (our price)

Handbook of Research on Nanoscience, Nanotechnology, and Advanced Materials
Mohamed Bououdina (University of Bahrain, Bahrain) and J. Paulo Davim (University of Aveiro, Portugal)
Engineering Science Reference • copyright 2014 • 617pp • H/C (ISBN: 9781466658240) • US $365.00 (our price)

Quantum and Optical Dynamics of Matter for Nanotechnology
Mihai V. Putz (West University of Timisoara, Romania)
Engineering Science Reference • copyright 2014 • 527pp • H/C (ISBN: 9781466646872) • US $180.00 (our price)

Advanced Solar Cell Materials, Technology, Modeling, and Simulation
Laurentiu Fara (Polytechnic University of Bucharest, Romania) and Masafumi Yamaguchi (Toyota Technological Institute, Japan)
Engineering Science Reference • copyright 2013 • 354pp • H/C (ISBN: 9781466619272) • US $195.00 (our price)

www.igi-global.com

701 E. Chocolate Ave., Hershey, PA 17033
Order online at www.igi-global.com or call 717-533-8845 x100
To place a standing order for titles released in this series, contact: cust@igi-global.com
Mon-Fri 8:00 am - 5:00 pm (est) or fax 24 hours a day 717-533-8661

Table of Contents

Detailed Table of Contents

Chapter 1
Sulfur in Petroleum: Petroleum Desulfurization Techniques.. 1
Waqas Ahmad, University of Peshawar, Pakistan

This chapter describes the occurrence of organosulfur compounds in petroleum, their detrimental effects and various techniques for removal of these compounds. The sole commercial desulfurization process i.e. HDS is broadly discussed in terms of reaction conditions, different types of catalysts used, reactor design and mechanistic pathways in the process. The shortcomings of HDS and needs for developing new desulfurization techniques is also described. Various newly developed research techniques for desulfurization are also discussed with their technical backgrounds, commercial overview, advantages and shortcomings in the light of literature reports. These techniques include, Adsorptive desulfurization, Bio-desulfurization, Precipitative desulfurization, and Oxidative desulfurization with its sub types like ODS using H2O2- Polyoxometalates (POM), ODS with Ionic liquids, Photo-oxidative desulphurization and Ultrasound Assisted ODS.

Chapter 2
Sulfur and Nitrogen Chemical Speciation in Crude Oils and Related Carbonaceous Materials 53
Sudipa Mitra-Kirtley, Rose-Hulman Institute of Technology. USA
Oliver C. Mullins, Schlumberger-Doll Research, USA
Andrew E. Pomerantz, Schlumberger-Doll Research, USA

This chapter gives an overview of sulfur x-ray absorption near edge spectroscopy (XANES) studies performed on some carbonaceous materials, viz. crude oil and related materials (asphaltenes, kerogens, bitumens, and resins), and coals. Thiophene, sulfide, sulfoxide, sulfone, pyrite, and sulfate are found in varying amounts in these materials. In source rock bitumens, sulfoxide is more abundant than in the kerogens, while within the kerogens, the less aromatic Type I samples show a smaller ratio of thiophenic/sulfidic sulfur than in Type II samples. Petroleum asphaltenes have a similar sulfur chemistry, regardless of the source or the burial depth. Resins and oil fractions retain the polar sulfoxide species of the parent oil similar to the more polar asphaltenes fractions. More aromatic sulfur species also dominate in the more matured coals than in the younger coals. Studies of nitrogen XANES also reveal that aromatic forms of nitrogen prevail in samples with increased aromatic carbon.

Chapter 3
Cleaner Energy Fuels: Hydrodesulfurization and Beyond 84
Neha Sareen, Banaras Hindu University, India
Subrato Bhattacharya, Banaras Hindu University, India

Today, SO2 pollution has become a glaring problem especially in India and China. Thus, desulfurization of fossil fuels has become an essential area of research. Advances in experimental sciences to explain the desulfurization mechanism will be beneficial to the rational designing of more effective HDS catalysts. Several reaction pathways involving desulfurization of thiophene have been compiled. Also, a repertoire of the desulfurization pathways encountered in the author's laboratory has been provided. The results will not only throw light on some unusual mechanisms of desulfurization process but also break the popular belief that desulfurization is limited to C-S bond cleavage only. The reactions may also serve as a basis for engineering optimal catalysts for future applications.

Chapter 4
Nanocomposites and Hybrid Materials for Adsorptive Desulfurization 129
Tawfik A. Saleh, King Fahd University of Petroleum and Minerals, Saudi Arabia
Gaddafi I. Danmaliki, King Fahd University of Petroleum and Minerals, Saudi Arabia
Taye Damola Shuaib, King Fahd University of Petroleum and Minerals, Saudi Arabia

Desulfurization (removal of S compounds) of fuels is an important research topic in recent years. Several techniques have been reported to remove the sulfur-containing compounds in fuels. One of these techniques is adsorptive desulfurization (ADS) (removal based on chemisorption and physisorption) which has received much attention because of low energy consumption and facile operation condition. This chapter discusses the methods employed under this technique and the types of nanocomposites and hybrid materials (adsorbents) that have been investigated as potential adsorbents. The strategies to enhance sulfur adsorption capacity and main challenges will be discussed.

Chapter 5
Carbon-Based Nanomaterials for Desulfurization: Classification, Preparation, and Evaluation 154
Tawfik A. Saleh, King Fahd University of Petroleum and Minerals, Saudi Arabia
Taye Damola Shuaib, King Fahd University of Petroleum and Minerals, Saudi Arabia
Gaddafi Ibrahim Danmaliki, King Fahd University of Petroleum and Minerals, Saudi Arabia
Mohammed A. Al-Daous, Saudi Aramco, Saudi Arabia

The special interest in ultra-low sulfur diesel (ULSD) is informed by the need to comply with the strict government policy on low sulfur content of transportation fuels. Better knowledge of different factors that concern deep desulfurization of fuels is important to achieve ultra-low sulfur fuels and cheaper way of producing ULSD. Both the capital and operating cost of the adsorptive desulfurization process is cheaper compare to the conventional hydroprocessing. The need to produce more volume of fuel such as diesel with very low sulfur content from low grade feed stocks like heavy oil and light cycle oil (LCO) in order to meet up with the global demand for sulfur-free fuels is pertinent. Several on-going researches are pointing to the use of adsorbents for removal of sulfur compounds from the hydrocarbon refining stream. In this chapter, varieties of carbon nanomaterials suitable for adsorptive desulfurization are discussed. The approach is feasible for commercial applications with any adsorbent of an adequate lifetime of activity as well as high capacity.

Organosulfur compounds show a negative environmental impact because of SOx emissions by combustion of fuel oils. As a consequence, removal of sulfur is becoming a worldwide challenge. The hydrodesulfurization (HDS) process achieves limited performances in the case of refractory S-containing aromatic compounds, such as thiophene and substituted benzothiophenes (BTs), which require highly energy-demanding conditions (high temperature and pressure conditions). Oxidative desulfurization (ODS) is considered the most promising alternative to HDS. During ODS treatment, the organosulfur compounds are oxidized to corresponding sulfoxides and sulfones, which can be successively removed by extraction with polar solvents. Different stoichiometric oxidants have been used in the ODS processes with a different degree of efficacy and environmental impact. The design and development of catalytic procedures can increase the ODS energy efficiency as well as make it more economical and environmentally acceptable. Here we describe the advances in nanostructured organometallic catalysis and biotechology applied to ODS treatment.

The aim of this chapter is to present the Ni/ZnO nano-sorbent for reactive adsorption desulfurization (RADS) of refinery oil steams. The preparation and modification of nano-sorbent are reviewed. Various characterizations involving in the relation of properties with components, structures and dynamic phase change during RADS, are extensively provided. The mechanisms of desulfurization, sulfur transfer and sulfur adsorption are proposed. The contradictories in literature about active structures and reaction mechanism are discussed and the solutions are suggested. This chapter unfolds the impressive application of RADS of Ni/ZnO nano-sorbent to produce a cleaner gasoline. It also delves into the inadequately engineer areas which require further attention so as to make the RADS process more economic and more efficient. The perspective applications other than gasoline desulfurization are also presented.

Chapter 8

Trimetallic Sulfide Catalysts for Hydrodesulfurization 240

Rafael Huirache-Acuña, Universidad Michoacana de San Nicolás de Hidalgo, Mexico
Gabriel Alonso-Nuñez, National Autonomous University of Mexico, Mexico
Eric M. Rivera-Muñoz, National Autonomous University of Mexico, Mexico
Omar Gutierrez, Instituto Tecnológico Superior de Ciudad Hidalgo, Mexico
Barbara Pawelec, Instituto de Catálisis y Petroleoquímica, C.S.I.C., Spain

The more stringent environmental regulations enacted throughout the world have increased the need of more active hydrotreating (HDT) catalysts, in the petroleum refining industry. Usually, the catalysts used for diesel oil hydrotreatment are γ-Al2O3 supported molybdenum or tungsten sulfides promoted with cobalt or nickel. Current strategies for the design of novel HDS catalysts often include variations in the support formulation, catalyst preparation method and active phase formulation. In this sense, the new generations of catalysts, such as NEBULA®, are based on a totally different concept of bulk-like. In this chapter, we present recent research related to the synthesis, characterization and performance of trimetallic sulfide nanocatalysts for hydrodesulfurization. The present chapter analyses the state of art of the ternary sulfide hydrotreating catalysts.

Chapter 9

Polymolybdate Supported Nano Catalyst for Desulfurization of Diesel 263

Wan Azelee Wan Abu Bakar, Universiti Teknologi Malaysia, Malaysia
Wan Nazwanie Wan Abdullah, Universiti Teknologi Malaysia, Malaysia
Rusmidah Ali, Universiti Teknologi Malaysia, Malaysia
Wan Nur Aini Wan Mokhtar, Universiti Teknologi Malaysia, Malaysia

The Catalytic oxidative desulfurization (Cat-ODS) comprises of molybdenum based catalyst, tert-butyl hydroperoxide (TBHP) as oxidant and dimethylformamide (DMF) as solvent for extraction. A series of polymolybdates supported alumina were prepared using the wet impregnation method. This potential catalyst was characterized by FTIR, FESEM-EDX and XPS for its physical properties. From catalytic testing, Fe/MoO3-Al2O3 calcined at 500°C was revealed as the most potential catalyst which gave the highest sulfur removal under mild condition .The sulfur content in commercial diesel was successfully reduced from 440 ppmw to 88 ppmw under mild condition followed by solvent extraction. Response surface methodology involving Box-Behnken was employed to evaluate and optimize Fe/MoO3/Al2O3 preparation parameters (calcination temperature, catalyst loading, and Fe loading) and their optimum values were found to be 550 ºC, 10 g/L, and 10%. of calcination temperature, catalyst loading, and Fe loading. Based on these results, the reaction mechanisms of peroxy oxygen were proposed.

Chapter 10

Molecularly Imprinted Polymer Nanofibers for Adsorptive Desulfurization 281

Adeniyi S. Ogunlaja, Nelson Mandela Metropolitan University, South Africa
Zenixole R. Tshentu, Nelson Mandela Metropolitan University, South Africa

Desulfurization of fuel oils is an essential process employed in petroleum refineries to reduce the sulfur concentration in fossil fuels in order to meet the mandated environmental protection limit of 10 ppm sulfur. The hydrodesulfurization (HDS) process, which is currently being employed for desulfurization, is limited in treating refractory organosulfur compounds as it only reduces sulfur content in fuels to a range of 200-500 ppm sulfur. Oxidative desulfurization (ODS) is considered a new technology for desulfurization of fuel oils as the process is capable of desulfurizing fuels to reach the ultra-low sulfur levels and can serve as a complementary step to HDS. The chapter discusses, briefly, the oxidation of refractory sulfur compounds found in fuels using vanadium as a catalyst to form organosulfones, a first step in ODS process. The chapter also discusses, in detail, the chemistry involved in molecular imprinting of organosulfones on functional polymers, and the electrospinning of the polymeric matrix to produce molecularly imprinted nanofibers employed for selective adsorption of organosulfones from the oxidized mildly hydrotreated fuels, a second step in the ODS process. Chemical interactions, apart from the imprinting effect, that can be exploited in molecularly imprinted polymers for selective extraction of organosulfones, such as hydrogen bonding, π-π interactions, van der Waals forces and electrostatic interactions, were discussed by employing density functional theory calculations. The possibilities of electrospinning on a large scale as well as prospects for future industrial applications of functional molecularly imprinted nanofibers in desulfurization are also discussed.

Chapter 11

Flue Gas Desulfurization: Processes and Technologies 337

Ricardo del Valle-Zermeño, University of Barcelona, Spain
Josep Maria Chimenos, University of Barcelona, Spain
Joan Formosa, University of Barcelona, Spain

Most of the total quantity of sulfur oxides (SOx) emitted to the atmosphere come from the combustion of fossil fuels, whose preponderance in the energy mix is expected to prevail in the years to come. In order to avoid the damaging consequences that this supposes, the improvement of the removal methods has been the topic of many researches. In this sense, the majority of abatement processes have always been based on wet Flue Gas Desulfurization (wFGD) technologies. In this chapter, the origin, development, deployment and enhancement of the wFGD processes is thoroughly revised. From the early studies on sulfur absorption for commercial purposes to the maturing of the technology fostered by environmental regulations, the chapter covers the aspects that have accompanied FGD research, including the reaction mechanism studies, the main types and configurations, and extending the analysis on the variables, parameters and technical aspects conditioning the process.

The use of nanostructured materials in combination with desulfurizing microorganisms is a promising technique that would improve the desulfurization processes of gaseous fuels, oil, and some wastewater. Nanoparticles are highly versatile and tunable depending on the necessities of each particular contaminated media. The chapter shows the current technological options for the biodesulfurization of natural gas, oil and wastewater produced from the petroleum refining, where the application of nano-sized materials combined with desulfurizing microorganisms would improve the desulfurization capacities. In addition, advantages, disadvantages and opportunities of this hybrid technology are presented.

Biodesulfurization (BDS) process consists on the use of microorganisms for the removal of sulfur from fossil fuels. Through BDS it is possible to treat most of the organosulfur compounds recalcitrant to the conventional hydrodesulfurization (HDS), the petroleum industry's solution, at mild operating conditions, without the need for molecular hydrogen or metal catalysts. This technique results in lower emissions, smaller residue production and less energy consumption, which makes BDS an eco-friendly process that can complement HDS making it more efficient. BDS has been extensively studied and much is already known about the process. Clearly, BDS presents advantages as a complementary technique to HDS; however its commercial use has been delayed by several limitations both upstream and downstream the process. This study will comprehensively review and discuss key issues, like reduction of the BDS costs, advances and/or challenges for a competitive BDS towards its potential industrial application aiming ultra low sulfur fuels.

Preface

Nanotechnology in desulfurization is a fascinating subject of recent origin. The expansion of nanomaterials is the focal point of research and technology that is mostly related to chemistry, physics, applied sciences, petroleum and engineering. Research on nanotechnology has mainly focused on the aspects of synthesis of nanomaterials that have unique chemical, thermal and mechanical properties applicable for a wide range of applications. A variety of properties and phenomena has been investigated, and many of the studies have been directed toward understanding the properties and applications of nanomaterials. Due to their enhanced chemical and mechanical properties, the nanomaterials play promising roles in enhancing the desulfurization. Nanomaterials have properties that are useful for enhancing surface-to-volume ratio, reactivity, strength and durability. In pursuit of the same goal, Applying Nanotechnology to the Desulfurization Process in Petroleum Engineering book offers detailed, up-to-date chapters on the synthesis, properties and technological developments of nanomaterials, and their applications in petroleum.

The first chapter of the book encompasses the occurrence of organosulfur compounds in petroleum, their detrimental effects and various techniques for removal of these compounds. The second chapter covers sulfur x-ray absorption near edge spectroscopy performed on some carbonaceous materials, viz. crude oil and related materials (asphaltenes, kerogens, bitumens, and resins), and coals. The third chapter describes the designing of effective HDS catalysts and desulfurization pathways with some unusual mechanisms of the desulfurization process which break the popular belief that desulfurization is limited to C-S bond cleavage only. The reactions may also serve as a basis for engineering optimal catalysts for applications.

The next two chapters encompass the nanocomposites, hybrid materials and carbon-based nanomaterials for adsorptive desulfurization including preparation and evaluation. The nanostructured transition metal catalysis applied to oxidative desulfurization processes is discussed in the sixth chapter. The aim of the seventh chapter is to present the preparation and modification of Ni/ZnO nano-sorbent for reactive adsorption desulfurization of refinery oil steams. Chapter eight unfolds their various characterizations and the impressive application, including gasoline desulfurization. Trimetallic sulfide catalysts like γ-Al_2O_3 supported molybdenum or tungsten sulfides promoted with cobalt or nickel used for diesel oil hydrotreatment is discussed in chapter eight. Chapter nine presents results of the preparation and structural properties of a series of polymolybdates supported alumina.

Chapter ten, on molecularly imprinted polymer nanofibers for adsorptive desulfurization, covers the processes involved in molecular imprinting of organosulfones on functional polymer networks, and the electrospinning of this polymeric matrix to produce molecularly imprinted nanofibers employed for the selective adsorption of organosulfones from the oxidized mildly hydrotreated fuels, a second step in the oxidative desulfurization process. Moreover, a chapter dedicated to the, “Flue Gas Desulfurization” discusses the origin, development, deployment and enhancement of the wet flue gas desulfurization processes. The chapter covers the aspects, including the reaction mechanism studies, the main types and configurations, and extending the analysis of the variables, parameters and technical aspects conditioning the process.

The last two chapters dedicated to the biodesulfurization and nanotechnology, illustrate the use of nanostructured materials in combination with desulfurizing microorganisms for desulfurization processes of gaseous fuels and oil. In addition, the current technological options for the biodesulfurization, advantages as a complementary technique to hydrodesulfurization, disadvantages and opportunities of this hybrid technology are presented.

In this book, we have tried to cover many aspects of nanomaterials for desulfurization, which is of current interest. This book is written for a large readership, including university students and researchers from diverse backgrounds such as chemistry, petroleum, materials science, physics and engineering. It can be used not only as a textbook for both undergraduate and graduate students, but also as a review and reference book for researchers in these fields. We hope that the chapters of this book will provide the readers with valuable insight into state-of-the-art advanced and functional nanomaterials and technologies. However, it is possible that some topics have been left out owing to constraints on the size of the book and possible errors in judgement. We trust that the preface will be useful to students, teachers and researchers.

The Editor,

Tawfik A. Saleh
Department of Chemistry, King Fahd University of Petroleum and Minerals, Saudi Arabia

Acknowledgment

I would like to acknowledge the support provided by King Fahd University of Petroleum & Minerals. I would like to thank IGI publisher. I would like to express my gratitude to the many people who saw me through this book; to all those who provided support, read, wrote, offered comments, allowed me to quote their remarks and assisted in the editing, proofreading and design. Above all, I want to thank my parents, relatives, wife, children and the rest of my family, who supported and encouraged me in spite of all the time it took me away from them. Last and not least: I beg forgiveness of all those who have been with me over the course of the months and whose names I have failed to mention. Many thanks.

Chapter 1

Sulfur in Petroleum:
Petroleum Desulfurization Techniques

Waqas Ahmad
University of Peshawar, Pakistan

ABSTRACT

This chapter describes the occurrence of organosulfur compounds in petroleum, their detrimental effects and various techniques for removal of these compounds. The sole commercial desulfurization process i.e. HDS is broadly discussed in terms of reaction conditions, different types of catalysts used, reactor design and mechanistic pathways in the process. The shortcomings of HDS and needs for developing new desulfurization techniques is also described. Various newly developed research techniques for desulfurization are also discussed with their technical backgrounds, commercial overview, advantages and shortcomings in the light of literature reports. These techniques include, Adsorptive desulfurization, Bio-desulfurization, Precipitative desulfurization, and Oxidative desulfurization with its sub types like ODS using H2O2- Polyoxometalates (POM), ODS with Ionic liquids, Photo-oxidative desulphurization and Ultrasound Assisted ODS.

INTRODUCTION

Sulfur occurs in crude petroleum in different forms and in varying quantities. But in petroleum the presence of sulfur compounds is undesirable because of several reasons, such as causing corrosion problems, deactivating catalysts in various refining processes and contributing to environmental pollution. The problem of environmental deterioration is increasing steadily as the energy demand increases with growth of the world's population; therefore, worldwide environmental regulation authorities are imposing strict regulations to limit the amount of sulfur in petroleum based liquid fuels.

At present, the commonly used industrial process for removal of sulfur from petroleum is hydrodesulfurization (HDS), which involves treatment of petroleum fractions in a special reactor at high temperature (300-500 ^{o}C) in the presence of a catalyst and hydrogen gas under high partial pressure (30-300 psi). The requirements of HDS process make it a too expensive operation. Furthermore, HDS cannot eliminate certain refractory sulfur compounds from petroleum and therefore cannot attain low level desulfurization

DOI: 10.4018/978-1-4666-9545-0.ch001

under its normal operating conditions. Thus, petroleum desulfurization is a challenging task for the refiners under the current environmental regulations. Keeping in view this scenario, worldwide researchers are striving to develop new desulfurization techniques that are cost effective and more efficient than HDS. In this regard, several new techniques for desulfurization of petroleum have been introduced, including extractive desulfurization, adsorptive desulfurization, desulfurization by polymer membranes, precipitative desulfurization, bio-desulfurization and oxidative desulfurization. All these techniques are still in stages of technological improvements since each one has its own advantages and drawbacks.

This chapter gives detailed account of different types of sulfur compounds occurring in petroleum, their hazardous effects and various processes used for desulfurization of petroleum. The main objectives of this chapter include,

- To identify the nature and types of different sulfur compounds presents in crude petroleum and their distribution in distillate fractions.
- To know various problems associated with sulfur compounds present in petroleum.
- To understand the technological background of different desulfurization techniques and identify the limitations of each.
- To highlight the developments occurred in different desulfurization processes over the past few decades.

1. OCCURANCE OF SULFUR IN PETROLEUM

In crude petroleum, sulphur exists as a non-hydrocarbon constituent in different concentrations. Petroleum crudes obtained from different oilfields contain different quantities and types of sulphur compounds. Generally in heavier crude oil, the proportion and complexity of the sulphur compounds is usually greater than the lighter crudes. The concentration of sulphur in crude petroleum may range from trace amounts to as high as 8 wt%, depending upon its source e.g. the sulphur content in some light Pennsylvanian crude is about 0.05%, in heavy Mexican or Mississippi crude as high as 5% or even more, whereas Middle East crude contain about 2.1% sulfur (Birch et al., 1925).

Based on their nature, sulfur compounds in petroleum, may be divided in two categories i.e. sulfur in organic form and in inorganic form. In inorganic form sulfur is present as H_2S, elemental sulphur, and pyrites which are dissolved or suspended in crude petroleum. In organic form the sulphur is bounded to a hydrocarbon molecule as a heteroatom, these compounds may be classified as thiols, sulfides, thiolanes, thiophenes, benzothiophenes, benzonapthothiophenes and their alkylated derivatives (Agarwal et al., 2009).

On the basis of their reactivity, sulphur compounds occurring in crude petroleum may be classified in two classes, namely active sulfur and inactive sulfur compounds. Active sulfur compounds are those which directly react with metals and causes corrosion, including H_2S, mercaptans, elemental sulphur and lower sulphides. The active sulfur compounds impart corrosive action to the sour crudes, but due to their high reactivity these compounds can be easily removed from petroleum. The second class, inactive sulfur compounds cannot react readily with metals and it includes aromatic sulphur compounds i.e. thiophene, benzothiophene, dibenzothiophenes, benzonapthothiophenes and their alkyl substituted derivatives, etc.

Due to their limited reactivity, these compounds particularly the alkyl dibenzothiophenes, are difficult to eliminate through normal operating conditions of hydrodesulfurization (Gray et al., 1995), and hence these are referred as refractory sulphur compounds (see Figure 1).

2. DISTRIBUTION OF SULFUR COMPOUNDS IN DISTILLATE FRACTIONS

Among the distillate fractions obtained from crude oil, the distribution of the sulphur compounds is not uniform, rather it vary from fraction to fraction depending upon their boiling points. The concentration as well as the complexity in the structure of the sulphur compounds increases in various distillate fractions with the increase in boiling points (Heinrich G et al., 2001). In light distillate fractions sulphur is generally present in a very simple identifiable form, mostly as reactive forms of sulfur compounds such thiols and sulfides that can be removed easily by extraction or sweetening processes. On the contrary, in case of heavy distillate fractions or residual portions of crude oil having a high boiling point, organic sulfur occurs in more complicated form i.e. as a heteroatom in polyaromatic compounds bearing limited reactivity and therefore difficult to remove (Ahmad, 2013). The distribution of different classes of organosulphur compounds among various distillate fractions is presented in the Table 1.

Crude oil contains different classes of organic sulphur compounds including thiol, sulfides and thiophenes. H_2S and sometimes elemental sulphur are mostly found in dissolved form. The elemental

Figure 1. Representative sulphur compounds present in petroleum

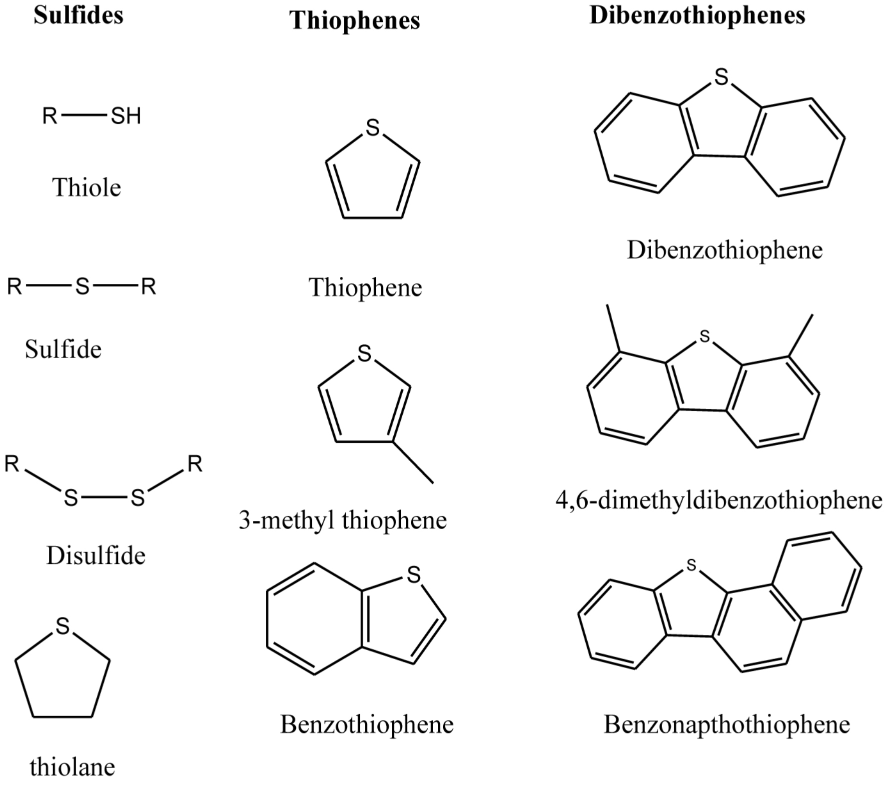


Table 1. % Distribution of various classes of sulphur compounds among different distillates (wt %)

Distillate Fractions	B. P range (^{o}C)	Thiols	Sulfides	Thiophenes	Higher Thiophenes
Naphtha	70–180	50	50	Rare	–
Kerosene	160–240	25	25	35	15
Diesel	230–350	15	15	35	35
Vacuum gas oil	350–550	5	5	30	60
Vacuum residue	>550	Rare	Rare	10	90

(Javadli et al., 2012).

sulphur reacts with thiols in low boiling fractions and produce H_2S, which causes the corrosion problems (Ahmad, 2013). Most of H_2S is flushed off along with gaseous hydrocarbons e.g. methane, ethane, propane, butane etc. which are removed from crude on oil field. Due to the high boiling point of elemental sulphur, it shifts to higher boiling point fractions during the distillation process. The oxidation of H_2S present in petroleum gases and gasoline may also lead to production of elemental sulfur.

In light distillate fractions the commonly present sulfur compounds include thiol, aliphatic sulfides, and simple thiophenes. The main sulfur compounds in gasoline include thiols, aliphatic sulfides and disulfides as well as cyclic sulphides. Thiophenes usually do not occur in straight run gasoline but are present in FCC gasoline that is obtained from cracking of the heavier fractions. As shown in Table 1, in light distillate fractions with boiling point ranging from 70 to 180 ^{o}C i.e. naphtha, about 50% of the sulphur compounds occur as thiol and the same proportion as sulfide, whereas thiophenes are present only in trace amounts. Ronald, *et al.* (Martin et al., 1965) showed that in a gasoline sample, about 61% of total sulfur was present as thiophene and 25% as dibenzothiophenes whereas 11% as sulfides, 2% as disulfides and only 1% was in the form of thiols. Similarly, various classes of sulfur compounds in FCC and RFCC gasoline in China were thiols, sulphides, disulphides and thiophenes with relative distribution of 10, 20, 3 and 68%, respectively (Yin et al., 2002). Furthermore, in catalytically cracked naphtha, the sulfides are mostly aliphatic and cyclic, whereas the thiophenes are mostly mono-, di- or tri-alkyl thiophenes (Yin et al., 2004). Various types of common sulfides and thiophenes identified in catalytically cracked naphtha are presented in Table 2.

Kerosene oil also contains types of sulphur compounds similar to those found in gasoline, however the proportion of thiophenes and dibenzothiophenes is higher than thiol and disulfides. A kerosene oil sample obtained from Midle East crude with 0.05% wt sulphur, was shown to contain about 6% of thiols, 45% of various aliphatic sulfides, 2% of thiophenes and 47% of multi ring thiophenes, mostly consisting of 2 and 3 rings (Martin & Grant, 1965).

In diesel oil, sulfur compounds are mostly as sulfides and disulfides, various types of thiophenic compounds such as beonzothiophene, dibenzothiophenes, benzonapthothiophene, and a number of other

Table 2. Common sulfides and thiophenes present in FCC naphtha

Sulfides	Butyl-methyl sulfide, Butyl-ethyl sulfide, Tert-pentyl methylsulfide, Tert-butyl isopropyl sulfide, Tert-pentyl ethylsulfide, Tert-pentyl iso-propyl sulfide, Iso-propyl butylsulfide.
Thiophenes	Thiophene, 2-Methyl thiophene, 3-Methyl thiophene, Tetrahydro thiophene, Iso-propyl thiophene, Methylethyl thiophene, Dimethyl thiophene, Trimethyl thiophene.

alkylated thiophenes. As shown in Table 1, the proportion of thiophenic sulfur compounds in diesel is about 70%. In variously treated diesel oil, such as RFCC, FCC, visbreaker, delayed coker and hydrofined diesel oil, the sulfur compounds identified by using two dimensional gas chromatography were similar to that of straight run diesel oil i.e. aliphatic sulfides and alkyl derivatives of benzothiophenes and dibenzothiophenes. Furthermore, in the case of cracked diesel, the proportion of DBTs is higher than in straight run diesel (Hua et al., 2003). The light cycle oil LCO with boiling range 220-337 ^{o}C mostly contains alkyl substituted benzothiophenes (BT) and dibenzothiophenes (DBT). Quantitative distribution of various thiophenes in LCO, was found to be as: thiophenes (1.9%), C_1-BT (9.5%), C_2-BT (15.1%), C_3-BT (22.1%), DBT (2.2%), C_1-DBT (11.8%), C_2-DBT (15.9%) and C_3-DBT (20.9%) (Nylén et al., 2004).

In case of heavier distillates i.e. asphalts, shale oil, atmospheric residue, bitumen, etc. sulfur occurs in even more complex forms; mostly as condensed heteroaromatics, thiols and traces of sulfides, whereas no H_2S or elemental sulphur is present. According to Borns, *et al.,* in oil sands derived bitumen, only 38% sulfur is aliphatic and the rest are aromatics with a high molecular weight in the 200 to 700 m/z range (Shi et al., 2010). Furthermore, heteroaromatic sulphur compounds containing multiple S atoms like one, two and three sulphur atoms (S_1, S_2 and S_3) may also be found, with S_1 being present in high proportion (71%), and S_2 and S_3 in smaller proportions (11 and 1%, respectively). Variety of hetero-atomic aromatic compounds also occurs in bitumen which contains S, N and O in a same molecule or ring.

Like bitumen, shale oil contain sulphur compounds of great complexity. The majority (up to 90%) occurs as thiophenes and benzothiophenes and only traces of alkyl sulfides and disulfides may be found. Table 3 exhibits some typical heterocyclic sulphur compounds identified in Paraho shale oil (Willey et al., 1981). Sulphur compounds in petroleum residues are similar to those occurring in oil sand bitumen, VGO and shale oil, which could not be eliminated through HDS process. The refractory sulfur compounds in residue portion, are often associated with asphaltenes, which contain high amounts of nitrogen, sulfur and various metals and resembles to polymeric material (Ahmad, 2013).

3. DETRIMENTAL EFFECTS OF SULPHUR COMPOUNDS IN PETROLEUM

Sulfur compounds are associated with a variety of problems, and are therefore removed from petroleum products. Below is an overview of the major problems caused by sulfur compounds in petroleum.

Table 3. Some organosulphur compounds present in oil sahle (Paraho Shale)

Benzothiophenes	• Benzothiophene, • 5-ethylbenzothiophenes, • 3-methylbenzothiophene, • Dibenzothiophene
High Mol. Wt. Benzothiophenes	• phenanthro[4,3-b]benzothiophene, • naptho[2,1-b]benzothiophene, • triphenyleno[4,5-b,c,d]thiophenes, • anthra[1,2-b]benzo[d]thipophene, • dinaptho[1,2-b:2-1,d]thiophene, • benzo[b]naptho[2,3-d]thiophenes, • phenanthro[2-1,b]thiophene chrysene, • phenanthro[9,10-b]thiophenes

3.1 Malodorous

The irritating pungent smell of sour petroleum crudes is due to the presence of sulfur compounds, particularly H_2S and mercaptans (McKetta, 1992.). These compounds are not only malodorous but also toxic, therefore handling and processing of the petroleum products with objectionable odor creates health hazards and nuisance to the workers. Besides, most of these compounds often bear corrosive character, influencing the fuel quality. The bad odor is removed from the crude petroleum through sweetening processes or by various refining processes in the refining industry (Hobson et al., 1984).

3.2 Corrosion Problems

The corrosive nature of sour crude petroleum and light distillate fractions is due to some of the sulfur compounds like H_2S, elemental sulphur, lower aliphatic sulfides and mercaptans, which are highly reactive towards metals and thereby causes the corrosion in the distribution systems and equipment in the petroleum refineries (McKetta, 1992.; Wood et al., 1925). When these compounds are present abundantly in crude oil or light distillate fractions, they cause corrosion by reacting directly on the metals surfaces. Corrosion damages storage tanks, pipes and equipments, reducing not only their durability but also leading to high repair and maintenance costs (Ahmad, 2013). Such type of corrosion in petroleum products is assessed by means of the relative degree of corrosivity using the copper strip corrosion test (ASTM D 130).

Apart from direct corrosion, sulfur compounds also cause indirect corrosion by producing SO_x which damage the internal linings of pipes, boilers and parts of the engine, boilers or piping (Ma et al., 2007). During combustion of fuel containing sulfur in the boilers or internal combustion engines, organic sulfur is oxidized and set free as SO_x, which leads to formation of H_2SO_4 by combining with water vapors present in the flue gases. As the temperature decreases, the acid condenses on various metal surfaces like linings of tubes, cylinder, internal parts of the engine, etc. and causes the corrosion of these parts, thereby decreasing their durability (Ahmad, 2013). Various techniques are used to combat such corrosion; these include application of metal plating as protective coatings, increasing the metals temperature to avoid the condensation of acid, using different additives in the combustion chamber. Similarly addition of additives to the flue gas stream or increasing the temperature of incoming gases by auxiliary heating systems is also carried out to avoid the acid precipitation on the metal surfaces (Hobson & Petroleum, 1984).

3.3 Deactivation or Poisoning of Catalyst

The major disadvantage of the sulfur compounds in petroleum is that they deactivate the base metals and precious metal catalysts used in a number of refining processes for downstream processing of petroleum and other catalytic environmental operations (B.C. Gates et al., 1979; Kent, 2010; Ma et al., 1994). During these processes, sulphur species are selectively adsorbed over the surface or active sites of metals present in the catalysts, thereby causing inactivation or reducing of their activity. This loss of activity occurs after the formation of metal sulfides when sulfur compounds contact the surface of Cu, Ni, Co etc. For instance, sulphur impurity on ppm level in the feed is sufficient to reduce the activity of nickel catalyst many folds in just a few days. Generally, sulfur species are irreversible poisons for most catalysts e.g. heavy metals like Hg, Pb, As. Hence, regeneration of the catalyst by air, O_2, or steam treatment becomes a difficult task (Froment et al., 1987; Kent, 2010). However, in some cases where precious metals are reversibly poisoned, these can be regenerated by removing sulfur compounds from the gas stream (Kent, 2010). Other examples of reversible poisons are nitrogen compounds like cyanide and ammonia, whereas vanadium is an irreversible poison.

In various processes e.g. catalytic hydrogenation, reforming, isomerization and alkylation, sulphur is selectively adsorbed on the catalyst surface as H_2S or organic sulfides, and blocks the adsorption of any other species, hence leading to partial or complete loss in the activity of the catalyst. The degree of deactivation of the catalyst depends on the extent of the surface coverage, which may be mechanistically categorized as geometric blocking or by long range electronic effects. In case of a partially covered surface, deactivation results from the combined geometric blocking and long range electronic effects. On the other under high surface coverage, loss in activity is resulted only by geometric blocking (Ahmad, 2013). In combustion operations, SO_2 and SO_3 from sulfur compounds may form active metal sulfates after being adsorbed over the metal surface (Kent, 2010). Pt supported on Al_2O_3 used for reduction of the combustion emissions is also deactivated in the similar manner; the SO_2 produced during combustion is oxidized to SO_3 by Pt which subsequently is adsorbed on the carrier surface (Al_2O_3) to form the corresponding sulfate. The sulfate slowly covers the surface of the carrier, causing Pt occlusion and leading to loss in the activity of the catalyst.

Generally, during catalytic hydrotreatment processes, the sulfur compounds present in the feed form H_2S under a high partial pressure of H_2, increasing its concentration in the recycle gas stream, and leading to deactivation of the catalyst unless it is removed. The H_2S is known for being a reversible poison for Pt and it deactivates the catalyst used in recyclization and hydrogenation reactions. In the earlier designs of catalytic reforming reactors, the removal of H_2S gas from the recycle stream was effectuated by absorption with steam and di-ethanolamine. In modern units, the sulfur from the feed is removed through catalytic HDS, and then the feed is subjected to reforming. In most practices, sulfur in the feed is reduced to about 0.5 ppm or less, in case of using high sulfur feed, problems of low catalysts activity and poor products yield are encountered. Similarly, during the pretreatment of the feed, it is necessary to reduce sulfur contents to a few ppm before subjecting to catalytic reforming in case of using naphtha as feed and also for catalytic isomerization of C_4 to C_6 paraffins.

Pre-sulfidation of the catalyst may be used to overcome the deactivation problem up to some extent in certain processes. The catalyst is pre-sulfided with various sulfur precursors before the reaction, the so called sulfided catalyst can efficiently catalyze hydrogenation reactions even if strong inhibitors like H_2S and NH_3 are present. In addition, the sulfided catalysts also resists early deactivation through coke deposition (Absi Halabi et al., 1996).

3.4 Influence of Octane Number in Gasoline

It has been shown that in gasoline, the presence of sulfur compounds tend to resist the susceptibility of octane boosting with the addition of the octane improvers like tetra-methyl-lead (TML) and tetra-ethyl-lead (TEL) (Magyar et al., 2005). Studies have shown that different classes of sulfur compounds decrease the octane number of gasoline and its response to tetraethyl lead. The thermal decomposition products of different sulfur compounds show susceptibility to TEL, and hence reduce its response to raise the anti-knocking.(Ryan, 1942)

Similarly, the gasoline obtained through fluid catalytic cracking (FCC gasoline) contains high concentration of aromatics and olefins as well as sulfur compounds. Generally sulfur compounds are eliminated through hydrodesulphurization, however the during this process olefins and aromatic saturation occurs due to which the octane number of the gasoline decreases (Babich et al., 2003), and in order to meet the octane rating according to standard fuel specifications additional processing is required, which leads to increased operating cost of the gasoline.

3.5 Health Effects

Sulphur compounds, particularly some condensed thiophenes, are known to cause adverse effects on human health i.e. carcinogenic or mutagenic, on exposure to a certain level (Braid et al., 2005; Willey et al., 1981). H_2S is a malodorous compound that produces strong irritating odors and causes headaches on short time exposure and on long duration exposure might lead to unconsciousness (Gruse et al., 1960). Some thiols (-C-SH) have also a stinging repulsive odor and are strong irritants that can be very toxic at high concentrations. For instance methylmercaptan can be smelled at level below 0.002 ppm, and at above this concentration its harmful affects starts. Thiols may cause nausea, vomiting, headache, coughing, lung irritation and inflammation of eyes, throat and nose on exposure to high concentrations. Under severe conditions of high concentrations, long term exposure to high concentrations of thiols may also leads to uncomfortable breathing, muscular spasms or unconsciousness, however effects of irritation disappears soon as the affected individual is brought to breath in fresh air. Furthermore, as thiols are highly soluble in fats, soon after contact they are readily absorbed in the skin.

Like other sulfur compounds, low molecular weight sulfides are also malodorous. The dimethyl- and diethyl-disulphides are relatively less toxic and have less repulsive odor than thiols, but still their smell can be observed at very low concentrations, up to a range of 0.0001 to 0.002 ppm. Under high concentrations, sulfides can cause irritation of eyes, throat, nose and muscular paralysis.

3.6 Contribution to Atmospheric Pollution

Sulfur present in petroleum products is converted to SO_2 during combustion, which is liberated in to the atmosphere where it causes serious environmental pollution problems such as acid rain while contributing to photochemical smog. Also, SO_2 is directly harmful to animals and vegetation.

3.6.1 Direct Effects of SO_2 in Atmosphere

SO_2 is a colorless gas having piercing pungent odor and is very harmful to man, animals and vegetation; its main source is the conventional fuels containing sulfur compounds, which are utilized for transportation and in the industry [34]. The effect of SO_2 on humans primarily appears on the respiratory tract causing its irritation and constriction, which leads to increased resistance in air passage. These effects are more pronounced in persons suffering from respiratory weakness and sensitized asthma. The irritation effects are experienced when the individuals are exposed to SO_2 level of 1-2 ppm in air, SO_2 level of 5-10 ppm causes severe bronchial spasm, whereas the level of 500 ppm may lead to death (Manahan, 2010).

A combination of SO_2 and smoke in air, which usually occurs when smog is formed by temperature inversion layer, leads to a widespread disaster that affects not only humans but also animals. Several incidents happened across the world in the past when high SO_2 level was trapped in smog. In Meuse River Valley, Belgium such incident occurred in December 1930, when the SO_2 level in the atmosphere raised to 38 ppm, leading to the death of approximately 60 people and many cattle. Similarly, in October

1948 in Pennsylvania, United States of America, the SO_2 level reached 2 ppm, and caused the death of about 20 people and the illness of more than 40% of the population (Sharma, 2007). In December 1952 in London, heavy smog with 1.3 ppm SO_2 and 4 mg/m^3 of smoke, lasted for five days, during which approximately 12000 deaths occurred (Davis, 2002). These deaths were mainly caused due to pneumonia, bronchitis and related respiratory problems. A similar accident occurred in London in December 1962, but this time the number of the deaths was small i.e. about 700, which was due to the implementation of the Clean Air Act, in 1962 (Manahan, 2010; Sharma).

High levels of SO_2 are also injurious to plants, causing a condition called leaf necrosis in which the edge of the leaf and its petiole is damaged. The chronic effect of $SO_{2,}$ chlorosis, appears as yellowing of the leaf. It has been found that low level chronic effects of exposure to SO_2 are more damaging than exposure to high dose for short durations (Varshney et al., 1979). Furthermore, the SO_2 also damages the plants and aquatic flora in rivers and lakes indirectly by causing acid rain.

3.6.2 Acid Rain

The SO_2 released during combustion of fossil fuels containing sulfur compounds is photo-catalytically oxidized to SO_3 in the atmosphere [37]. In atmosphere, under humid conditions SO_3 reacts with water and form H_2SO_4.

$$2SO_2 + 2O_2 \rightarrow 2SO_3 \tag{1}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{2}$$

In a similar way, the oxides of nitrogen forms HNO3 in atmosphere, and when these acids combine to cause acidic precipitation, this is termed as acid rain. Today, acid rain is a major environmental problem; it is not only hazardous to living beings but it also damages the non-living objects. The acid rain adversely affects the biota and its surroundings.

Acid rain primarily affects soil by leaching action. Acid rain dissolves and washes away the nutrients that are needed for plants development and growth, thereby rendering soil less fertile. Furthermore, the acidic washing also dissolves the harmful substances present in certain soils i.e. Hg, Al, Pb, As etc., further polluting the fresh water bodies, vegetation and finally reaching human food chain. Certain beneficial microbial cultures in soil that cannot survive under low pH conditions are also destroyed by acid rain (Harrison et al., 2007). The acid rain has damaging effects on forests as well (Manahan, 2010), due to decreasing the soil fertility by washing away the important nutrients, the growth and development of forest vegetation, particularly large trees is retarded. Furthermore the acid rain damage the waxy coating on the leaves and needles of the large coniferous trees, causing dead brown spots on it, due to which they lose their photosynthetic activity. The infected trees weaken and become vulnerable to diseases, insect manifestations, cold weather and draught. The trees at peaks or high altitude remains in direct contact with the acidic clouds, hence these are at more risk of adverse effects.

The acid rain runoff drains into fresh water bodies like lakes, streams and marshes, where it disturbs the aquatic life. The fresh water is commonly neutral, with pH in the range of 6- 8, and is suitable for supporting the aquatic life. The aquatic flora and fauna is very sensitive to high or low pH, therefore the acid rain which lowers the pH of fresh water bodies greatly threaten their survival. Acidic water mainly affects the reproduction and growth of the organism living in water (Morris, 1989; Singh et al., 2007).

Another main deleterious effect of the acid rain is the damage of structures made of metal or stone like statues, buildings, automobiles etc. when exposed for long durations (Singh & Agrawal, 2007). The famous historic buildings and statues across the world like the Taj Mahal in Agra (India), the Parthenon in Athens (Greece), the stonework of Lincoln Castle in Lincolnshire, England etc. have been damaged by acid pollution.

The human health is not harmed directly by acid rain but indirectly through intoxication of the food chain. The acidic water leaches the toxic substances from soil and leads them to the fresh water bodies, from where they find their way to the food chain by directly consuming the contaminated water or utilize the animals or plant grown therein (Singh & Agrawal, 2007). For example in Sweden, several lakes have been found contaminated with Hg, which is leached by acid rain from the surrounding soils, and the residents are abandoned to use fishes as food from these lakes.

4. DESULPHURIZATION OF PETROLEUM PRODUCTS

Concerning the nuisance due to sulfur compounds in the form of environmental pollutant, health effect and hurdling in the refining processes, it is important to remove sulfur from petroleum derived fuels prior to their usage for energy. In order to stop the serious environmental deterioration, the worldwide environmental regulatory authorities have implemented serious rules and regulations to limit the concentration of sulphur in transportation and industrial fuels. The environmental protection agencies in developed countries like US, Japan and in Europe, the level of total sulfur contents has been set to 10 ppm for gasoline, whereas 15 ppm for diesel oil (Largeteau et al., 2012; Stanislaus et al., 2010).

Sulfur compounds are removed from petroleum and petroleum derived products through the process referred as desulphurization process. Today hydrodesulphurization (HDS) is the only process used by refineries worldwide for desulfurization of petroleum, but researchers are struggling to introduce new desulfurization processes that should be more efficient and cost effective than HDS. The preceding sections include discussion on the HDS as well as new desulfurization techniques brought to scene by researchers.

4.1 Hydrodesulphurization (HDS)

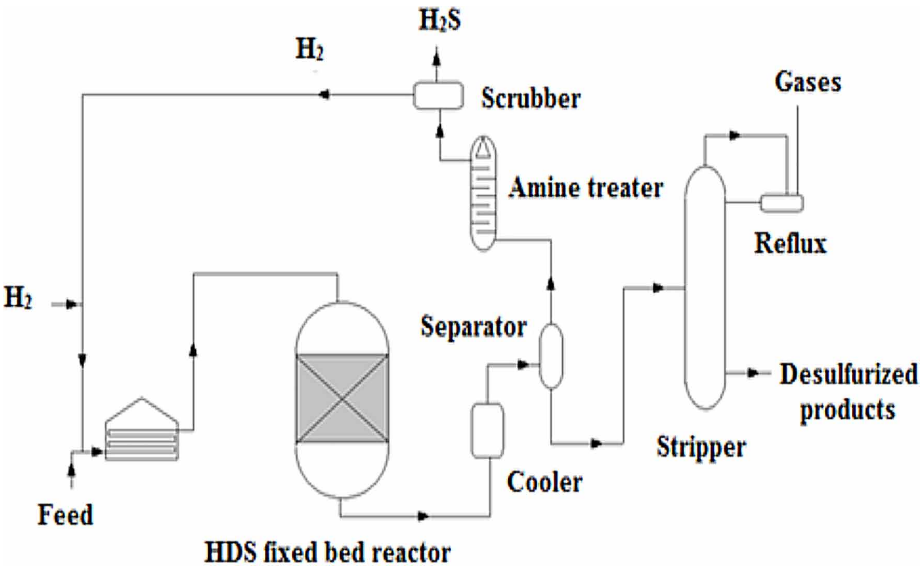
Hydrodesulphurization (HDS) process was discovered in 1930 and is used since then as a most common industrial process for desulfurization of petroleum. In HDS process, feed is treated with hydrogen gas in a specially designed reactor under high partial pressure and elevated temperature in the presence of a catalyst. The organically bonded sulphur is converted into H_2S during the reaction, which is separated from the feed in the stream of flue gases. The conventional HDS process commonly operates at temperature ranging from 300 to 450 ^oC and pressure of 30 to 300 psi, however the process conditions may vary depending on the nature of feed and its sulfur contents as well as the degree of desulphurization required (Javadli & Klerk, 2012). In conventional HDS, the catalysts mostly used are sulfided CoMo type or NiMo and CoMo supported on Al_2O_3 (Furimsky, 1996; Knudsen et al., 1999; Ma et al., 1994;

Shafi et al., 2000; Vasudevan et al., 1996). The advanced HDS operation is used for deep desulfurization of high sulfur feed, and carried out under severe conditions of temperature and pressure, i.e. at elevated temperature and high pressure, over the catalysts using advanced supports.

In HDS unit, the feed which may be naphtha, kerosene or gas oil is mixed with hydrogen gas and heated in a fire heated tubular furnace to up to 315 and 425 °C temperature. The vaporized feed is then pumped into a fixed bed reactor packed with catalyst under pressure up to 70 bars. During the process, the compounds of sulfur and nitrogen present in the feed react with H_2 to form H_2S and NH_3. The products from the reactor are passed to a cooler, and then to a separator. In the separator, the gases consisting of H_2S and H_2 are separated from the liquid product, high-pressure gas rich in H_2 is recycled to the HDS reactor and the low-pressure gas rich in H_2S is passed to amine contactor for removal of H_2S gas. The flue gases can be used for heating the furnaces. Liquid products are pumped to the stripping column, where remaining H_2S, gases and other impurities are then removed as desulfurized product (see Figure 2).

In the HDS process, the reactions of sulphur compounds involve the removal of sulfur atom as H_2S. In case of thiols or sulfides, the reaction proceeds through S-C bond breakage, and subsequently by S-H and C-H bonds formation. The reactions of thiophenic compounds are somewhat complex for which two pathways are proposed, hydrogenolysis and hydrogenation (Babich & Moulijn, 2003). The hydrogenolysis pathway proceeds via direct removal of S atom from the molecule by simultaneous cleavage of C-S bond and formation of S-H bond. The hydrogenation pathway involves successive addition of hydrogen to the carbon atoms and subsequently leads to the removal of S from the aromatic ring. In case of aromatic sulfur compounds, generally both reaction pathways proceed in parallel, however the nature of the catalysts can steer the preference of either pathway. It is commonly known that the NiMo catalyst favors the hydrogenolysis pathway, and CoMo catalyst enhances the hydrogenation. In case of DBT, only hydrogenolysis reaction occurs, whereas in case of alkyl-DBT both hydrogenolysis and hydrogenation reactions proceed (Knudsen et al., 1999; Ma et al., 1994; Vasudevan & Fierro, 1996).

Figure 2. Typical HDS unit



During the HDS process, the order of reactivity of various oragnosulphur compounds is as:(B. C. Gates et al., 1997; Shafi & Hutchings, 2000).

Th > R-Th > BT > R-BT > DBT > R-DBT > 4-R-DBT > 4, 6-R_2-DBT

where, Th = Thiophene, R = Alkyl group

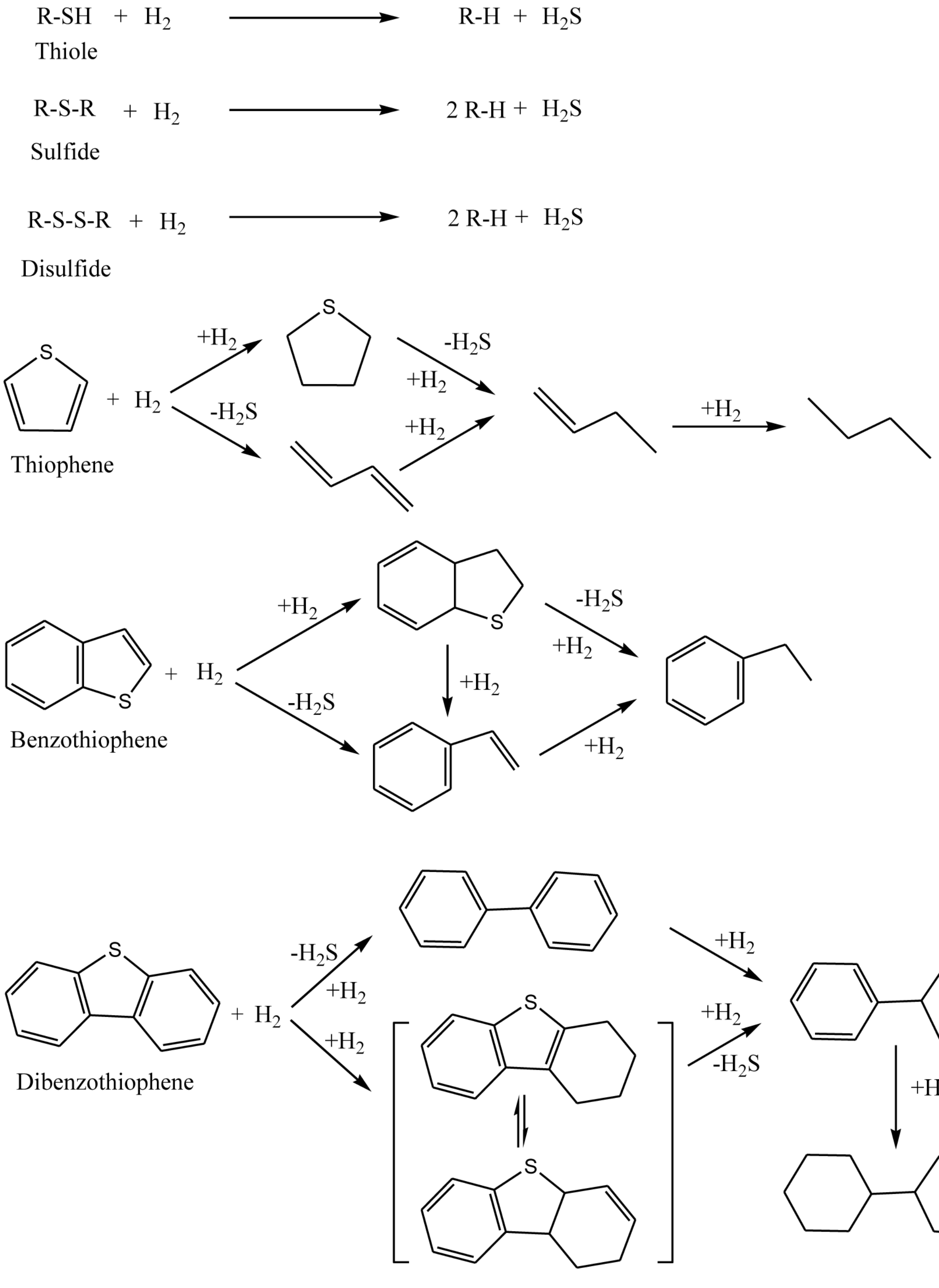
Due to resonance stabilized structure and the alkyl side chains which encounters stearic hindrance, the alkyl-BT and alkyl-DBT, particularly 4,6-dialkyl-DBT are highly resistant to HDS under normal operating conditions (Campos-Martin et al., 2010; Javadli & Klerk, 2012). In order to treat these refractory sulfur compounds in distillate fractions, HDS operation requires severe conditions, i.e. high hydrogen partial pressure, low space velocity and elevated temperature. On the other hand, many side reactions occur under these conditions, which include the olefin and aromatics saturation and coke formation. In light distillates fractions i.e. FCC naphtha, the saturation of olefins and aromatics leads to substantial decrease in the octane number, whereas the enhanced coke formation under high temperature, causes catalyst deactivation. Also the application of severe operating conditions is limited by the design of HDS reactor (Babich & Moulijn, 2003).

Several efforts have been made on development of active catalyst systems and reactor design to enhance the efficiency of the HDS and eliminate the refractory sulfur compounds as well as to avoid the problems outlined above. Various new catalysts were developed by considering the choice of active species, proper support and exploring best synthetic routes for the catalyst.

Recent research has introduced some new support materials with improved efficiency, including MCM-41, Titania (TiO_2) and Alumina (Al_2O_3), HY zeolites, Carbon, etc. (Olguin et al., 1997; Segawa et al., 2000; Song et al., 2003). With the interest of finding the active catalysts, Akzo Nobel catalyst preparation technology designed a highly active catalyst which is thermally and mechanically stable and with a good product quality. This catalyst consists of CoMo & NiMo and was named Super Type II Reactive Sites (STARS) catalyst. The catalysts worked well in case of high sulfur containing feeds, allowing to reduce the sulfur contents from 1000 ppm to up to 1-2 ppm (Brevoord E et al., 2000; EOR, 2000; Song & Ma, 2003). Akzo Nobel also developed another catalyst which is referred as NEBULA (New bulk activity) with a bear high hydrotreatment activity in the sulfide form (Mayo S et al., 2001). The catalyst is very suitable for hydrotreatment process under harsh condition and high hydrogen pressure. Criterion catalyst and technologies, also introduced some new catalysts named Criterion NiMo and CoMo CENTINAL catalysts, which are designed for treatment of different feeds under different condition (W., 2001). NiMo CENTINAL is the favorite catalyst for HDS of low sulphur content feeds under high H_2 pressure, whereas CoMo CENTINAL is preferred for high sulphur feeds and under low H_2 pressure. The addition of various noble metals such as Pd, Ru and Pt has also been reported to enhance the activity of active catalytic species. On the other hand, the addition of noble metals increases the susceptibility to sulfur poisoning (Song & Ma, 2003) (see Figure 3).

Apart from improving the catalyst activity, developments in the reactor design also boosted the HDS efficiency. Generally the conventional HDS processes use fixed bed reactors, where the feed and hydrogen are supplied concurrently. In this setup the complete sulfur removal at the outlet is limited due to high concentration of H_2S and hydrogen. To overcome this problem, ABB Lummus Technology designed a new two stage reactor with counter current supply of feed and hydrogen. In this reactor design the H_2 and the feed are supplied from the bottom and top respectively while both stages are packed with catalyst beds. In the first reactor stage, the feed and hydrogen current are put into contacted concurrently and

Figure 3. HDS reaction of different sulphur compounds
(Babich & Moulijn, 2003).



the sulphur resistant catalyst is used. In the second stage, the feed is counter currently contacted with hydrogen, allowing to obtain efficient removal of H_2S while favoring the mixing of olefins and H_2S (Song & Ma, 2003).

The Institute of Petroleum France (IPF) developed new HDS processes named T-Star process, which was designed for treating heavy feed stocks, which are commonly associated with high production of coke. In this process, the ebullated bed type reactor was used by fluidizing the catalyst bed by means of a fast stream of feed and hydrogen. Because of the intimate contact of the catalyst and the reactants, the process efficiency is very high and less coke is produced whereas no overheating of the catalyst or bed plugging or channeling is encountered. Furthermore, the activity of the catalyst can be controlled by adding or drawing the catalysts particles into or from the reactor (Krishna et al., 2000).

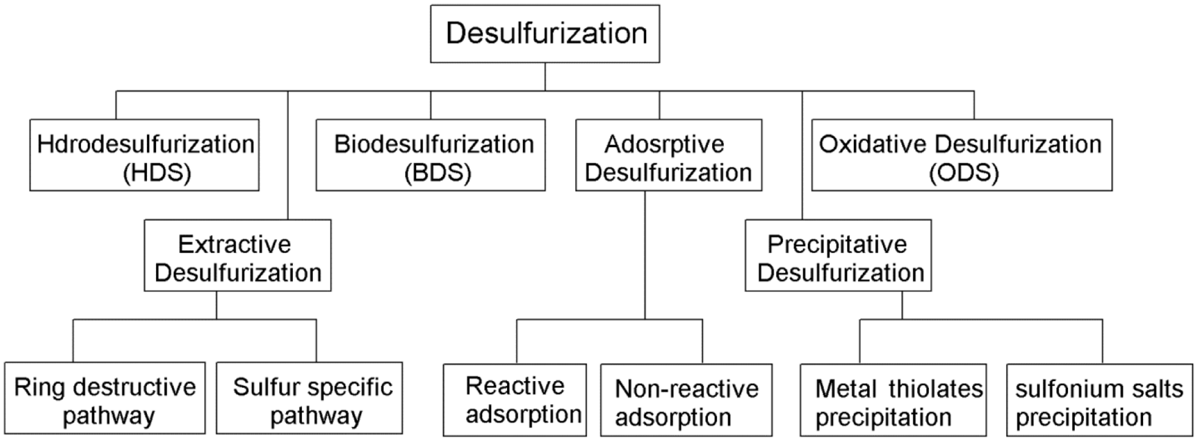
5. ALTERNATIVE DESULFURIZATION METHODS

Although many advancement are brought in the HDS process, the technology is still considered very expensive because of using costly hydrogen, specialized reactors and severe conditions of temperature and pressure, especially when dealing with a high sulfur feed (Ron et al., 2004). Besides, the process efficiency is limited by reduced reactivity of alkylated benzothiophenes as well as by the deactivation of catalyst by coke formation and H_2S (Babich & Moulijn, 2003). Therefore less expensive and more efficient desulphurization techniques must be sought as alternatives to conventional HDS. As a result of extensive research in this field, some new desulfurization techniques have been suggested, as detailed in the preceding sections (Babich & Moulijn, 2003; Campos-Martin et al., 2010; Javadli & Klerk, 2012) (see Figure 4).

5.1 Extractive Desulphurization (EDS)

As a rule like dissolves like or simply polar substance dissolve in polar solvents and vice a versa, hence sulfur can be removed from petroleum by extraction using an appropriate solvent. Extractive desul-

Figure 4. Various techniques for desulphurization of petroleum



phurization (EDS) involves removing sulphur compounds from the petroleum by transferring it into a solvent in which their solubility is higher than the petroleum hydrocarbons. Apart from bearing a high solubility for sulphur compounds, the solvent should be less expensive, immiscible to petroleum and with a different boiling point to that of sulphur compounds. Thus, the removal could be accomplished easily.

The EDS process operates at ambient conditions and is applicable in industry. The solvent and feedstock are allowed to mix in the mixing tank, by virtue of their solubility in the solvents, and the sulfur compounds are transferred to the solvent. The solvent is then removed from the feedstock in the separator section before being recycled after removal of the extracted sulfur compounds through distillation.

A number of patents are available on the EDS of petroleum. The commonly used solvents for EDS include ethanol, acetone (Izumi Funakoshi et al., 1998), polyethylene glycols (Forte, 1996), various amines (Yuji Horii et al., 1996), dimethyl formamide (DMF), misetyl oxide, furfural, dimethyl sulfoxide (DMSO) and N-methylpyrolidone (NMP) (H. Rang et al., 2006). Commonly two or more solvents are blended together and used for EDS i.e. acetone: ethanol mixture or tetraethyleneglycol: methoxytriglycol mixture, in order to enhance the extraction of organosulphur compounds. Early studies showed that the EDS of various distillate fractions using polyethylene methylether achieved approximately 30% of sulfur removal (Pfüller et al., 2003). However, later researchers reported that using a blend of- 30 wt% aqueous acetone, methanol, misetyl oxide and formic acid, up to 86 -96% desulfurization range is attained in different distillates fractions (Funakashi et al., 2002).

EDS cannot remove all types of sulfur compounds and therefore in different distillates fractions the overall desulfurization efficiency is very low. However, it has been reported that when EDS is employed in combination with other processes like hydrotreatment and oxidation, the efficiency of the process can be markedly enhanced (H. Rang et al., 2006). For gas oil, the sulphur content can be reduced to up to 71% by extraction with polyethylene glycol and dimethylether while deep desulfurization of gas oil was attained by successive hydrotreatment and extraction (Pfüller & Walstra, 2003). Similarly, in the case of kerosene, extraction followed by hydrotreatment achieved 94% of sulfur removal (Forte, 1996). The efficiency of the EDS can be further enhanced when the sulfur compounds are previously oxidized and extracted with polar solvents. However this process will be discussed in detail in later sections.

The immiscibility of the solvent and the hydrocarbons in the feed is necessary in order to separate the sulfur compounds. On the other hand, it reduces the solubility of the sulfur compounds and hence the extraction capacity, leading to low desulfurization yields. Furthermore, other compounds apart from sulphur species can be extracted during the process and reduce the feed oil recovery. In case of heavy oils, when increasing the temperature for reducing the viscosity and easing the mixing, the solvent may suffer loss due to evaporation (Javadli & Klerk, 2012).

In the last decade, a new class of liquids termed as ionic liquid (IL) were introduced as potential alternatives to organic solvents. IL are thermally and chemically stable and have low vapour pressure, which makes them very suitable for extractive desulfurization. Several types of IL based on alkylimidazolium cations and $CuCl^-$, $Cu_2Cl_3^-$, $Cu_3Cl_4^-$ anions have been investigated for EDS of model and commercial oil. These IL were aimed to remove thiophene by π-complexation, although the complexing agents dissolved in gasoline. The IL, $[BMIM]Cu_2Cl_3$ is able to extract close to 23% of sulfur from gasoline (Campos-Martin et al., 2010). Some other IL containing alkylimidazolium cation and various other anions like hexa-flourophosphate $[BMIM]PF_6$, tetra-flouroborate $[BMIM]BF_4$ (S. Zhang et al., 2002), ethylsulfate $[EMIM]EtSO_4$, octylsulfate $[BMIM]OcSO_4$ (Wasserscheid et al., 2004), dibutylphosphate [BMIM][DBP], bistrifluoro methylsulfonylimide [HMIM[Tf_2N] (Planeta et al., 2006), diethylphosphate [EMIM][DEP] etc. (Nie et al., 2007) were used for extractive desulfurization of model and commercial oil. The high efficiency IL could lower the sulfur in diesel to as low as 10 ppm.

Similarly various pyridinium based ionic liquids containing tetrafluoroborate anion and various alkylpyridinum cations like *N*-hexylpyridinium, *N*-butylpyridinium, and *N*-octylpyridinium tetrafluoroborate, have also been used for EDS of liquid fuels (H. Gao et al., 2008). Moreover, some of the IL can be regenerated and reused. However, their overall desulphurization efficiency is very small, also resulting in the extraction of aromatic compounds.

5.2 Adsorptive Desulphurization

Adsorptive desulphurization involves the selective adsorption of the organosulphur compounds in the light distillates on a suitable adsorbent. The process may be operated in column mode or batch mode. During the process, as the feed contacts the solid adsorbent, the sulphur compounds are adsorbed on its surface .The process can be operated in cycles until the sulphur breakthrough is attained. Different characteristics of the adsorbent material influence the efficiency of the adsorptive desulfurization; these include the capacity of adsorption, stability, selectivity, regeneration ability and durability etc.

Based upon the interaction of the organosulphur compounds with the adsorbent, adsorptive desulphurization may follow two different approaches including physical adsorption and reactive or chemical adsorption. In physical adsorption, Van der Wall forces are responsible for binding the sulphur compounds onto the sorbent surface. During this process, the sulfur compounds are adsorbed on the adsorbent without changing their structure. Since the sulfur compounds are held to adsorbent by physical forces, less energy is required for regenerating the adsorbent.

In case of reactive adsorption, the sulfur compounds are fixed to the adsorbent via chemical bonding and therefore the nature of the sulfur compounds may be altered. The sulphur compounds are commonly attached to the adsorbent mostly as sulphides, and thereby removed from the feed stock. In some cases the chemosorbed sulfur compounds are further altered by treatments like hydrogenation etc. to set free the sulfur atom from the parent hydrocarbon molecule.

The regeneration of the adsorbent may be performed by strong heating in air or solvent washing, and the sulfur removal as hydrogen sulfide or sulfur oxides, depends on the nature of the adsorbent and the sulphur compounds as well as on the and regeneration process employed (Babich & Moulijn, 2003). It has been found that the regeneration is easy but selectivity is limited in case of physisorption based adsorptive desulphurization, whereas reactive adsorption is highly selective however regeneration is quite difficult and complex (Hernández-Maldonado et al., 2004a, 2004b).

In the literature, several different types of materials have been used as adsorbents for adsorptive desulfurization of various distillate fractions like model oil and gasoline, naphtha, diesel and jet fuel oil. The most common are activated carbon, zeolites 5A and 13X (Mikhail et al., 2002; Salem, 1994; Salem et al., 1997), Si_2O_3 & Al_2O_3, MOF (metal organic framework) (Brieva GB et al., 2010; Irvine R L et al., 1999), modified composite oxides (Zhou et al., 2006), SBA-15 (McKinley et al., 2003), ZSM-5, MCM-41, Faujasite (Hernández-Maldonado et al., 2002; Velu et al., 2003), etc. Activated carbon is a very efficient adsorbent for high sulphur feed but generally attains low level of total desulfurization; in contrast, zeolite 13X is efficient in attaining deep desulphurization of low sulphur feeds. The application of these two adsorbents in a two stage reactor constitutes an industrially viable process, where the first stage consists of a bed of activated carbon which merely lowers the sulfur contents of the feed and the second stage comprises of a bed of 13 X zeolite which further attain deep desulfurization. Activated carbon, silica and zeolites are very efficient in removal of alkylated DBTs from the high sulfur feed i.e. containing around 1200 ppm total sulphur.

Another approach exploited by reactive adsorptive desulphurization involves the π-complexation between a metal on the adsorbent surface and organosulphur compounds. As the π bond is relatively stronger than Van der Wall's attractions of physical adsorption, the sulphur compounds are more efficiently removed from the feed. Various transition metals like Ag, Cu, Co, Zn, Ni, Ce, etc. over various supports e.g. zeolite Y, MCM-41 and silica gel, are being used for this purpose (Hernández-Maldonado et al., 2005; Hernández-Maldonado & Yang, 2002; Ma et al., 2005; McKinley & Angelici, 2003; Tian et al., 2005; Velu et al., 2003). Clay adsorbents like bentonite clay loaded with π-complex forming species such as Fe^{+3}, Cu^{+1},Cu^{+2} or modified with $KMnO_4$ etc. have also being applied for model gasoline (Tang et al., 2011).

The IRVAD process is a commercial adsorptive desulphurization process for gasoline that was developed by Black and Veatch Pritchard engineering company, employing selective adsorbents containing alumina (Babich & Moulijn, 2003; Song & Ma, 2003; R. T. Yang et al., 2003). The process involves the counter current contact of feed and adsorbent in a multistage reactor with a feed to adsorbent ratio of 4:1 under atmospheric pressure and temperature of 240 ^{o}C. The process showed 90% of desulfurization efficiency in pilot plant experiments for coker naphtha and FCC gasoline (Babich & Moulijn, 2003).

Another commercial desulfurization process called S-Zorb process was introduced by Phillips Petroleum Co. (USA), based on simultaneous hydrotreatment and adsorption (Song & Ma, 2003). In this process the feed, usually gasoline or diesel is combined along the adsorbent and gaseous hydrogen in a fluidized bed hydrotreatment reactor under 2 to 20 bars pressure, at a temperature between 340 to 410 ^{o}C. During the process, sulphur is bounded to the adsorbent material, consisting of a metal oxide like Zn and Ni supported on alumina and silica (Gyanesh P. Khare et al., 2000). The efficiency of the process is close to 98%, using a 1100 ppm sulfur gasoline and allowing to reduce the sulfur content to up to 25 ppm while slightly reducing olefins content to about 3%. This process commercially started for operation in 2001, in Phillips Petroleum Co. refinery, at Texas Philips.

5.3 Precipitative Desulphurization

The conversion of organosulphur compounds into insoluble precipitates by means of different precipitating agents constitutes the basis of precipitative desulphurization. The sulfur compounds precipitate into a insoluble form that can be easily removed from the feed stock through filtration or gravity settling. Different precipitating agents follow different reaction chemistry to accomplish the conversion of soluble sulfur compounds into insoluble precipitates in the liquid hydrocarbon fuels e.g. formation of metal thiolates, S-alkyl sulfonium salts and charge transfer complex.

Thiols (mercaptans) in light distillate fractions or crude petroleum can be converted into metal thiolates by reacting with metal oxides or hydroxides, the metal thiolates formed are solid that can be easily recovered from the feed (Reid, 1966; Tiers et al., 2000). In this process, the hydrocarbon feed is contacted with various active metal oxide or hydroxide; thiols are changed into metals thiolates through a hetrogeneous phase reaction and can be separated from the feed through a filtration process. The metals thiolates can be treated with dilute acid to recover the original thiole and the respective metal salts; the choice of acid depends upon the metal salt desired. The process occurs under ambient condition and therefore no specialized reactor is required.

$$MO + 2R\text{-}SH \rightarrow M(SR)_2 + H_2O \tag{3}$$

$$M(SR)_2 + 2HNO_3 \rightarrow M(NO_3)_2 + 2R\text{-}SH \tag{4}$$

Precipitative desulfurization has been investigated with a number of metal oxides and hydroxides using model or real oils as feed. PbO and $Hg(OH)_2$ has shown to be highly active in precipitating various types of thiols under ambient conditions at 1 h reaction time. (Nehlsen et al., 2003, 2004). In addition, MnO_2 is also found to be efficient in removing thiols from crude oil as well as distillate fraction, however its reaction is completed after almost 3 h (M. Shakirullah et al., 2009).

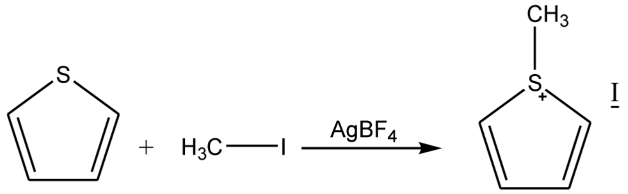
Other approach of precipitative desulphurization is based on conversion of heterocyclic sulfur compounds i.e. thiophenes into solid precipitates of S-alkylsulfonium salts using suitable alkylating agents. Shirashi, *et al.,*(Shiraishi, Tachibana, et al., 2001; Shiraishi, Taki, et al., 2001) showed that thiophenes in the model and real oil react with alkyl halides such as CH_3I in the presence of $AgBF_4$ as a catalyst, forming solid participates of S-alkylsulfonium salts, which can be separated from the hydrocarbon feed. The process was investigated for desulfurization in catalytically cracked gasoline containing 100 ppm sulfur, which showed that the sulphur content of the feed was decreased to up to 30 ppm. In this process the only problem encountered was the competitive alkylation of the aromatics and the olefins along with the alkylation of sulfur compounds, limiting its efficiency. On the other hand, during this process the olefinic content is decreased significantly, still the octane number of the treated CCG was higher than the CCG (See Figure 5).

Another technique of precipitative desulfurization utilizes the idea of precipitating the aromatic sulphur compounds in the hydrocarbon stream as a charge transfer complex (Meille et al., 1998; Milenkovic et al., 1999). In this process the thiophenic compounds are converted into a charge transfer complex by π complexation with an efficient π–acceptor compound. Model experiments on 4,6-DMDBT dissolved in a solvent was carried out with a π –acceptor (tetranitro-9-fluorene), in which the suspended precipitate was formed, the precipitated complex could be removed by filtration. However, like in alkylation based process, the competitive reactions of the non sulphur aromatics limits the efficiency of this process as well.

5.4 Biodesulphurization (BDS)

The biodesulphurization process relies on the chemosynthetic bacterial strains for reducing the sulfur content of petroleum, by metabolizing sulphur compounds in the hydrocarbon stream. In comparison to HDS, biodesulphurization is an economic process since it operates under mild conditions of temperature and pressures i.e. below 50 °C and atmospheric pressure (Kaufman et al., 1998; Linguist LK et al., 1999;

Figure 5. Formation of S-alkyl sulfonium salts

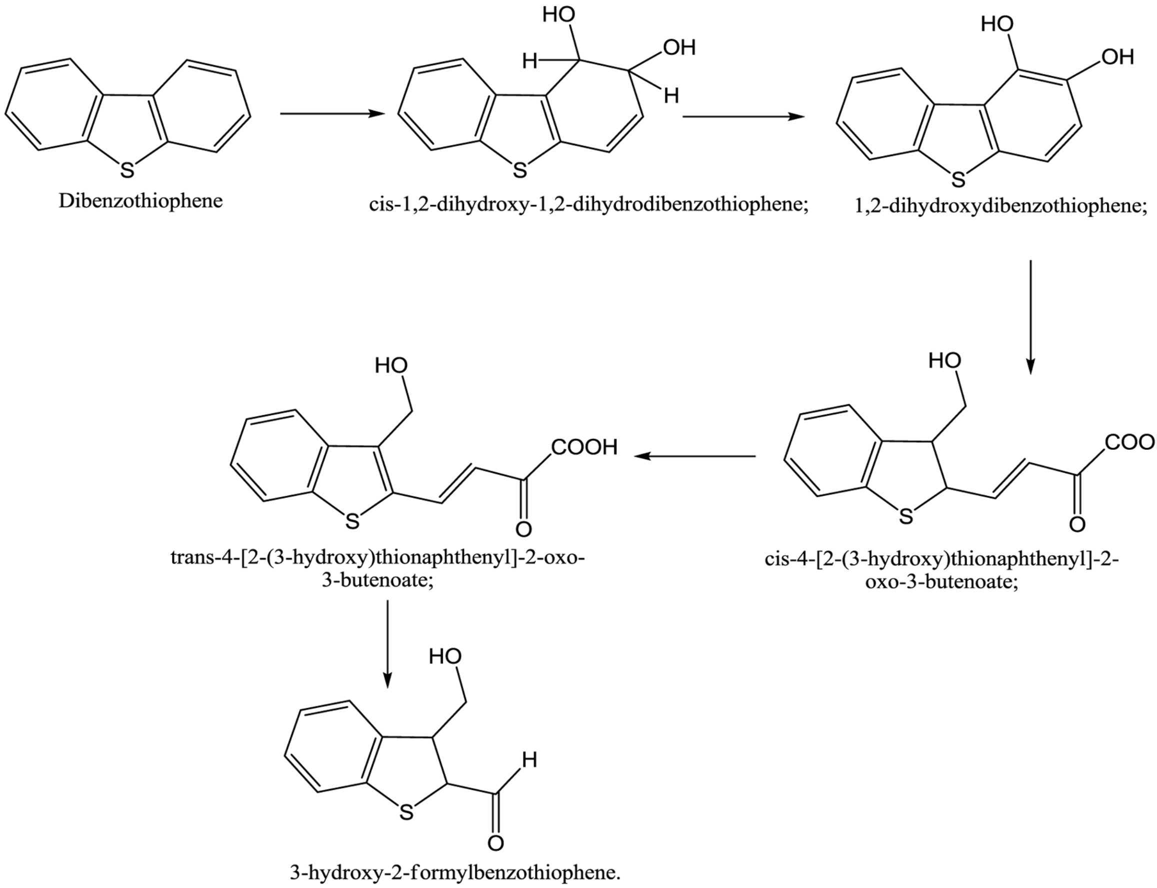


Pacheco MA et al., 1999). Depending on the type of the bacterial strains used, BDS involve different mechanistic approaches in which sulfur is eliminated from the feedstock, however two major pathways namely ring destructive and sulphur specific oxidation pathway are worth mention (Campos-Martin et al., 2010).

In case of ring destructive pathway, the cleavage of thiophenic ring results from the oxidation of sulfur or carbon atoms of the ring, termed as Kodama pathway. The oxidation products are immiscible to the hydrocarbon phase because of their polar nature and therefore they can be separated from the feed through extraction with polar solvents. The Kodama pathway was investigated by Denome et al. (1993), who showed that enzymes produced by *Pseudomonas* strain 18, carry out the di-oxygenation of the peripheral aromatic ring of the DBT that results in the ring cleavage. The final oxidation product formed is 3-hydroxy-2-formylbenzothiophene, which is water soluble and transfers to aqueous phase.

Another approach for ring destructive pathway was proposed by Afferden (M. v. Afferden et al., 1993), in which *Brevibacterium sp*. triggers the oxidation of sulphur atom in the DBT ring, ultimately resulting in the release of a sulphur atom in the form of sulfites or sulfates. As the ring destructive pathway involves the loss of carbon atoms from the aromatic skeleton, the calorific value of fuel is decreased and hence the process is considered to be not favorable for the Industry hence (Campos-Martin et al., 2010) (see Figure 6).

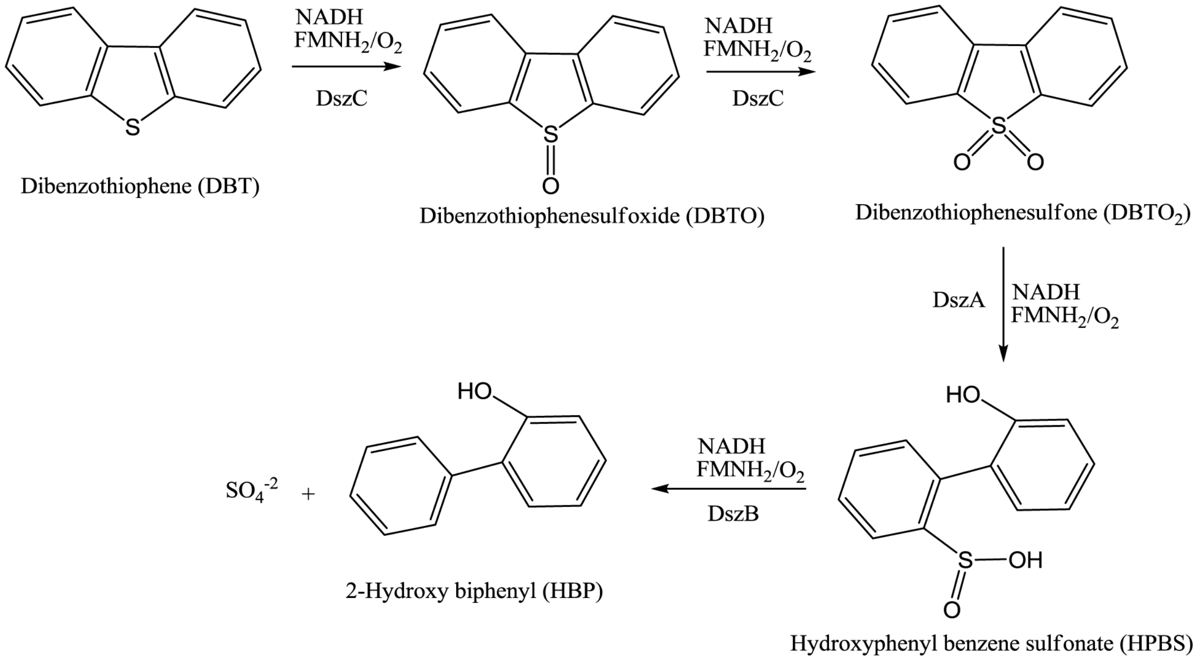
Figure 6. DBT metabolism via Kodama pathway



Sulphur specific oxidation pathway, also termed as 4-S pathway, was proposed by Kilbane (Kilbane, 1989) and it involves the successive and selective oxidation of sulfur atoms in the thiophenes ring (Figure 7). In the case of DBT, this leads to the formation of DBT sulfoxides, followed by DBT sulfone, hydroxybiphenylsulfinate (HBPS) and hydroxybiphenyl (HBP), whereas sulfur is ultimately eliminated as SO_3^{-2} or SO_4^{-2}. Van Afferden et al. investigated the 4-S pathway with a specie termed as *Brevibacterium Sp for* oxidizingd DBT to DBTO and further to $DBTO_2$, releasing free sulfur as SO_3^{-2} or SO_4^{-2} from $DBTO_2$ (M. Afferden et al., 1990) (see Figure 7).

Various aerobic strains such as *Rhodococcus erythropolis* can selectively remove the sulphur atom from the thiophenic ring without losing the total carbon atoms of the molecule (Kirimura et al., 2002). Other species include the *Gordona*, *Nocardia*, *Mycobacterium*, *Agrobacterium*, *Klebsiella*, *Xanthomonas*, thermophile *Paenibacillus* species etc. (Javadli & Klerk, 2012). *Rhodococcus* species encode a set of of genes, named as Dsz. These genes produce four types of enzymes, DszA, DszB DszC and dszD. These enzymes consecutively oxidize DBT to DBTO, $DBTO_2$, 2-(2-hydroxybiphenyl)-benzenesulfinate (HPBS), and 2-hydroxybiphenyl, respectively and finally inorganic sulphur is released. The DszC and DszA are monoxygenase enzymes. The DszC enzymes oxidizes DBT to DBTO and $DBTO_2$, and it require oxygen and $FMNH_2$. The DszA also require oxygen and NADH, and it convert sulfones into sulfinate i.e. HBPS. The DszB is a sulfinse enzyme, which catalyze the conversion of HBPS to HBP. Similarly the DszD is an oxidoreductase enzyme which oxidizes NADH and reduces $FMNH_2$. The oxidation pathway involves these enzymes to remove the sulfur compounds(Denome et al., 1994; M. Z. Li et al., 1996; Mohebali et al., 2008; Oldfield C Fau - Pogrebinsky et al., 1997; Piddington et al., 1995). The overall oxidation process is given as following.

Figure 7. Sulphur specific oxidation or 4S pathway for DBT degradation



$$DBT + 3O_2 + 4\ NADH + 2\ H^+ \rightarrow\ 2HBP + SO_3^{-2} + 3H_2O + 4NAD^+ \qquad (6)$$

As HBP is left behind in the hydrocarbon stream i.e. feed hence no loss to the fuel value of the feed occurs in the selective oxidation pathway. BDS of light crude and heavy crude oil (with S content 0.4 and 1.9%) was investigated using *Pantoea agglomerans* D23W3, the sulfur removal efficiency in both fractions was found to be 61% and 63%, respectively (Javadli & Klerk, 2012).

Aerobic BDS is associated with risks of explosions or fire hazards and the production of byproducts. These reasons led to consider the cloning of desulphurization genes into anaerobic hosts. The anaerobic BDS offers the advantage over aerobic BDS, since it does not involve the formation of undesired oxidation byproducts such as coloring and gummy products which is common in aerobic BDS (McFarland, 1999).

The use of a sulfate-reducing bacterium, *Desulfovibrio desulphuricans* M6, allows extending desulfurization of heavier crudes (Kim et al., 1990; B. H. Kim et al., 1995; Lizama et al., 1995). Further investigations indicated that, aromatic sulphur compounds are more susceptible to the reductive degradation of the bacteria than the aliphatic sulphur compounds. BDS of different thiophenic sulphur compounds was also examined using *Desulfovibrio desulphuricans* M6, which shown that the conversion of benzothiophenes was 96% and that of DBT was 42% (Kim et al., 1990).

To improve the efficiency of the BDS process, several critical aspects such as reactor design, oil-water separation and recovery of the products or by-products are required to be developed. Recent research on the reactor design suggests that the use of multistage air lift reactors offers low costs for mixing the feed, enhanced reaction kinetics during the process and a continuous growth or regeneration of the microbes within the reactor. The breaking of the stable emulsions formed by the mixture of feed oil, water and microbes could be circumvented with the application of hydrocyclones for attaining an efficient separation of clean oil and water. Instead of using single phase aqueous system for removal of sulphur in BDS, application of two phase system comprising of aqueous and alkane solvents give a high efficiency. Using refined products, such as diesel or gasoline instead of viscous crude petroleum as a feed in the BDS process can solve the problems of creating two phase oil-water systems with retarded efficiency (Ahmad, 2013).

In the last few decades, researches brought tremendous advancements to BDS, however there are still several shortcomings in the process, including the storage, shipment and use of microbes within the industrial environment and logistics of sanitary handling, which makes the BDS a commercially unviable process (Javadli & Klerk, 2012).

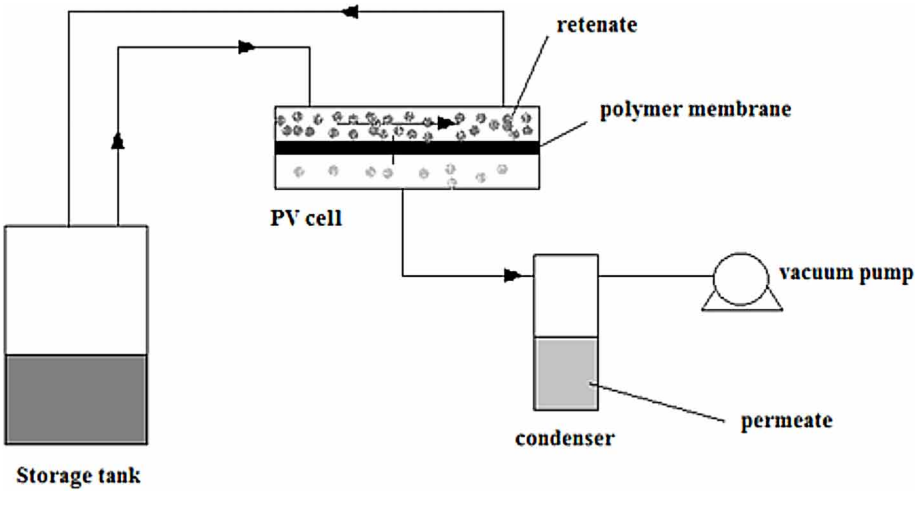
5.5 Desulfurization by Polymer Membranes (PV Process)

Polymer membranes are used to remove sulfur compounds from light distillate fractions by the pervaporation (PV) technique, in which the sulfur compounds are selectively permeated from the feed through reduced pressure across the membrane (Lin et al., 2009). The polymer membrane is fixed in a cell, and preheated feed is introduced and pumped downstream of the membrane by a vacuum pump. A condenser or cold trap is also provided between the cell and the vacuum pump. Under reduced pressure the sulfur compounds from the feed diffuses into the polymer membrane along with some hydrocarbons, permeating through the membrane as vapor and collected in the condenser as liquid permeate. The sulfur free feed is removed and sent to storage and sulfur rich permeate can be hydrotreated to remove sulfur. For a continuous operation the feed is allowed to contact the membrane on its one side, and the vacuum is applied on the other side to build a continuous pressure gradient. The semipermeable membrane works as a separation media in the process, the sulfur compounds are removed from the feed on the basis of their affinity or relative diffusivity to the polymer membrane. The amount of feed components permeating through the unit area of the membrane in unit time is referred as flux, whereas the ratio of the amount of sulfur in feed to that in permeate is characterized as sulfur enrichment factor. These two parameters are of main concern in the operation of pervaporation process. A general sketch of the process is shown in Figure 8.

A variety of polymer membranes has been used for desulfurization of light distillates, such as polethyeneglycol (PEG) (Lin et al., 2006), polydimethylsiloxane (PDMS), polyimide (PI) (Qi, Wang, et al., 2006; Qi, Zhao, et al., 2006; L. Wang et al., 2006), Nafion (Saxton et al., 2002), polysulfone (PS) (Plummer M A et al., 2002) etc. Grace Davison Company patented a number of polymer membranes for desulfurization of gasoline, including PUU, PERVAP 1060 and PI (White LS et al., 2004), they reported that PUU exhibit high sulfur enrichment however the flux for PUU was very small i.e. 0.1 kg/m^{2}h. ExxonMobil Research and Engineering Company invented a process based on non-ionic and ionic membranes, the non-ionic membranes used included PVP and CTA whereas the ionic membrane included Nafion RTM (Minhas et al., 2004; Minhas et al., 2002; Saxton & Minhas, 2002). In the case of catalytically cracked naphtha containing 1990 ppm sulfur, the PVP membrane was found to produce retenate with 120 ppm sulfur, whereas the CTA membrane gave the permeate containing 5000 ppm sulfur from catalytically cracked naphtha having 1880 ppm sulfur. Marathon Oil Company also investigated a process for removal of sulfur from naphtha by using a number of membranes including Nanofiltration SR-90, Ultrafiltration G-10 and polysulfone SEP-0013, out of which polysulfone gave the maximum sulfur enrichment.

In order to enhance the desulfurization efficiency, the performance of the polymer membrane can be improved by various modifications like crosslinking, grafting, filling, blending and copolymerization etc. For example the crosslinking of PEG, not only make it insoluble in gasoline but also decrease its swelling due to which it retains good selectivity (Lin et al., 2006). Besides the crosslinking of PEG, the sulfur enrichment factor for model gasoline increased from 3.31 to 7.31and for FCC gasoline increased from 1 to 3.05. However it was found that with increasing crosslinking in PEG, total permeation flux was reduced. Qi et al. investigated desulfurization of model gasoline by using polymer composite of

Figure 8. Scheme of the polymer membrane based desulfurization process



PDMS and AgY zeolite, with which increase in total flux was attained (Qi et al., 2007b). these authors also studied the separation of model sulfur compounds by mixed matrix membrane of PDMS and AgO_2 as filler, and found that selectivity and permeability was an issue for the modified and unmodified membranes (Qi et al., 2007a). Lin et al. reported that in desulfurization of gasoline with PEG and PU blended membranes, high permeation flux and sulfur enrichment factor was achieved (Lin et al., 2008). Li et al. studied the desulfurization of model gasoline with hybrid membranes of PDMS and $Ni^{+2}Y$ zeolite, results shown that with increasing amount of $Ni^{+2}Y$ in the membrane, the permeation flux increased however the sulfur enrichment factor first increased and then decreased which was attributed to the presence of defective voids in the membrane (B. Li et al., 2008). Similarly Kong et al. synthesized PEG and PES composite membranes which exhibited high flux and sulfur enrichment factor (3.37 kg/m^2h and 3.63, respectively) in case of FCC gasoline. The key operating parameters which influence the efficiency of the desulfurization by polymer membrane include the feed temperature, permeate pressure and sulfur contents of the feed and the feed flow rate.

The Grace Daviso Company was the first to introduce a high efficiency commercial membrane desulfurization process for gasoline in the name of S-Brane technology. The pilot plant was operated in October 2001 and it can reduce the sulfur content in gasoline to up to 30 ppm with the capacity of one barrel per day (Lin et al., 2009). A demonstration plant of S-Brane technology for desulfurization of naphtha with capacity of 300 bpd was installed in Conco Philips, Bayway Refinery in 2003. The plant operated continuously for 6 months, indicating the industrial viability of the process (Zhao X et al., 2004). Trans Ionic Corporation has also developed a commercial process for desulfurization gasoline range products, which is called TranSep process. The unique feature of the process is the use of venture nozzle and a fluid for recovery of permeate under atmospheric pressure, hence eliminating the expensive refrigeration process for condensation of the permeate (Robert C S). In spite of extensive technological advancement, there are several problems in the membrane based desulfurization process which needs attention of the researchers such as high energy requirements, loss in octane number, economic assessments and coupling optimizations.

5.6 Oxidative Desulphurization (ODS)

Oxidative desulphurization (ODS) was early introduced in 1970s, but recently the process has gained popularity as HDS alternative techniques for achieving deep desulfurization in petroleum. The ODS is based on selective oxidation of sulfur compounds in hydrocarbon fuel, followed by removal of the oxidized compounds from the feed through extraction or adsorption (Campos-Martin et al., 2010; Javadli & Klerk, 2012). In this process the nature of the organosulphur compounds is altered by oxidation with a suitable oxidizing agent, followed by separation. Hence the overall ODS process basically consists of two processes, namely the oxidation and extraction or adsorption. An appropriate oxidant is used to selectively oxidize the sulfur compounds in hydrocarbon stream into respective sulfoxides and then to sulfones, which possess relatively higher polarity than the parent sulfur compound. Because of their high polarity the oxidized sulfur compounds can be removed from feed through liquid-liquid extraction or adsorption process. The attraction of the ODS process is that it operates under mild conditions, mostly atmospheric pressure, mild temperature (below 100 ^{o}C) and reaction time ranging between 30 to 100 min. The sulfur compounds in the feed are oxidized by reacting with an oxidant in a vessel under normal conditions. The oxidants include organic peracids, molecular oxygen, ozone and hydroperoxides, etc. and a suitable oxidation catalyst is also added to enhance the oxidation efficiency. After the oxidation is completed, the treated feed is transferred to a extraction vessel where the oxidized sulphur compounds are removed by extraction with a polar solvent system. In the case that the oxidized sulfur compounds are removed by adsorption on a solid adsorbent, column adsorption or batch adsorption may be used (see Figure 9).

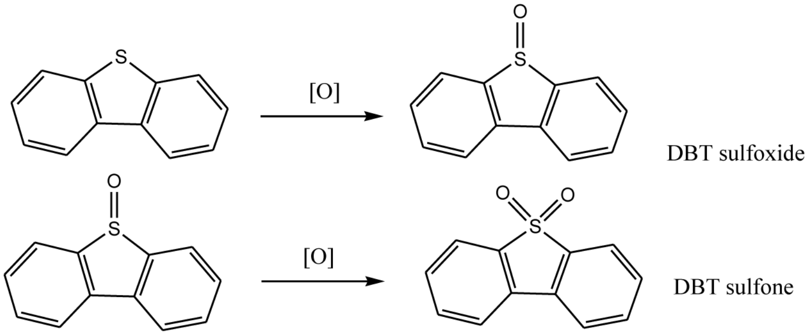
The order of reactivity of different sulfur compounds in the ODS has been found to be as (Otsuki et al., 2000);

4,6-DMDBT > 4-MDBT >DBT > BT > Th

The reactivity of the sulfur compounds increases due to the electron donating effects of alkyl side chains as the electron density on the sulfur atom increases for the electrophilic attack on the oxygen. This reactivity order is the opposite for the HDS reactivities, since the most resistant compounds to be treated by HDS are the most reactive in ODS.

During the extraction process, when the oil treated by selective oxidation is mixed with an immiscible polar solvent, phase separation occurs and the oxidized products migrate to the polar solvent phase. The aqueous or polar solvent phase rich in oxidized sulfur compounds is then conveniently separated from the feed oil by decantation or gravity separation. The extraction solvents should be polar in nature and should have a boiling point higher or lower than the oxidized sulphur compounds so the sulfur compounds could be removed from the solvent by distillation. For the selection of the extraction solvent other properties of the solvent may also be taken into account such as freezing point, surface tension, viscosity, and density, etc. Several type of solvents have been used for extraction purpose in the ODS process, which includes dimethyl sulfoxide, N-methylpyrollidone, acetonitrile, furfural, methanol, and dimethylformamide, etc. (Sobati et al., 2010; Zannikos et al., 1995). According to different researchers the sulfur extractability of all the solvents is not same, some solvents are highly efficient in extracting oxidized sulfur compounds although may also lead to extraction of the aromatic components of the feed (Campos-Martin et al., 2010). In order to enhance the sulfur extraction efficiency and to avoid the extraction of non-sulfur aromatics, usually azeotropic mixture of various solvents with water is employed for extraction (Ali et al., 2006). After oxidation, the oxidized sulphur compounds may also be removed from the feed through adsorption process using adsorbents such as silica, alumina and activated carbon etc. (Javadli & Klerk, 2012; Ma et al., 2007).

Figure 9. Oxidation of sulfur compounds



Among all the non HDS techniques, only the ODS process seems to be the promising alternative to HDS, because it offers several advantages over the rest of desulfurization methods.

1. The ODS process do not require costly hydrogen and a specialized high temperature and high pressure reactor.
2. The process operates under mild conditions of pressure and temperature, which makes it an economic process.
3. The solvent and the extracted oxidized sulfur compounds can be recycled.
4. The refractory sulfur compounds (alkyl-substituted dibenzothiophenes) can be efficiently removed by ODS, which are difficult to be treated by HDS under its normal operating conditions, hence the ODS can attain deep desulfurization.

Maintaining selectivity and efficiency in oxidation of sulphur compounds among the olefins, aromatics and cycloalkanes in non-polar medium and selection of the most appropriate oxidant is a challenging task in the ODS process. Extensive research in this field suggests the application of some novel oxidants, catalysts and use of different techniques in oxidation process.

Many types of oxidation systems are utilized for efficient conversion of sulfur compounds. Some reported the use of several of inorganic oxidants in the ODS process, which included nitric acid (Tam et al., 1990a), nitric oxide (Tam et al., 1990b), $KMnO_4$, sodium perchlorate (Shakirullah et al., 2010) and ozone etc. (Paybarah et al., 1982). However in most cases the inorganic oxidants requires a polar solvent or aqueous medium for enhanced efficiency, on the other limits the interaction of the oxidant and the sulphur compounds in the petroleum due to immiscibility. Many other oxidation systems used in the ODS process are mentioned below.

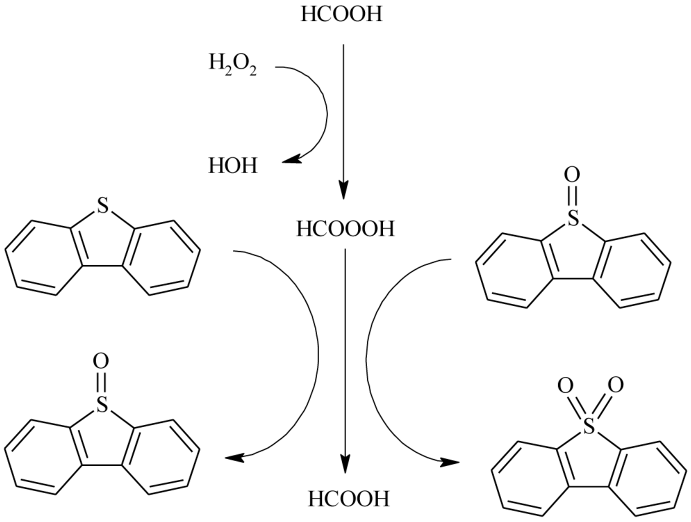
5.6.1 ODS with Organic Peracids

Organic peracids are extensively used as selective oxidants for oxidation of aliphatic and aromatics sulphur compounds. However because of the explosive nature of organic peracids and due to their storage and handling problems, they are produced in-situ during the ODS processes by reacting organic acids and H_2O_2 (Campos-Martin et al., 2010). For this purpose, formic acid and acetic acid are the best choices among various organic acids, and are most widely used in the presence of H_2O_2 as efficient oxidants for ODS processes (Gaofei Zhang et al., 2009). The oxidation of sulfur compounds with organic acids in combination with H_2O_2 involves the generation of peroxy radical from the resultant peracid, which selectively oxidizes the sulphur compounds (see Figure 10).

Desulfurization of gas oil was investigated with H_2O_2 and CH_3COOH oxidation system followed by solvent extraction and close to 90% of the sulfur content was decreased at 90 °C and after 30 min reaction time (Zannikos et al., 1995). Using the same oxidants and a mixture of acetonitrile and water for extraction, Shirashi, *et al.* carried out ODS of light oil, which resulted in depletion of the sulphur level to less than 50 ppm (Shiraishi et al., 2002). Formic acid in combination with H_2O_2 also constitutes an efficient oxidation system for selective oxidation of aromatic sulphur compounds, which has been extensively utilized for ODS model oil and real oil samples (De Filippis et al., 2010; Dehkordi et al., 2009; Otsuki et al., 2000).

Although the use of organic peracids produced in-situ provides a highly efficient route for the selective oxidation of organosulphur compounds in petroleum, large amounts of H_2O_2 and other organic acid are

Figure 10. Oxidation of dibenzothiophene by peracids



consumed, leading to increased operating costs. The efficiency of ODS could be enhanced with a lower consumption of H_2O_2 and organic acid using a heterogeneous catalyst. In peracids oxidation system, the catalyst enhances the production of peroxy species, which are responsible for oxidizing of the organo-sulphur compounds during the ODS process. Desulfurization of fuel oil by H_2O_2/HCOOH oxidation system showed a 60% sulfur removal, however using activated carbon as catalyst in the system yielded a maximum 95% desulfurization (Yu et al., 2005). Several types of catalysts are being used to enhance the efficiency of ODS with peracids, these includes EDTA, activated carbon, Na and Mg-silicates (Hao et al., 2005), silica gel (CHEN et al., 2006), molecular sieves loaded with various metal oxides(CHEN Lanju, 2007), transition metal salts (de Souza et al., 2009), and sodium bicarbonate (Deshpande et al., 2004). These heterogeneous catalysts promote the generation of peracid radicals, which further accelerate the oxidation of sulphur compounds, and in turn leads to enhanced desulphurization yields. However, the maximum efficiency of the oxidant cannot be utilized because of the phase transfer limitations between polar oxidants and non-polar oil phases. The immiscibility of the phases delays the interaction between oxidant and sulfur compounds and hinders the activity of the oxidants and hence the desulfurization efficiency. But if a surface active agent is introduced, the phase transfer limitations could be minimized. The application of various surfactants as phase transferring agents has been practiced in advanced ODS processes as discussed in detail in the later sections.

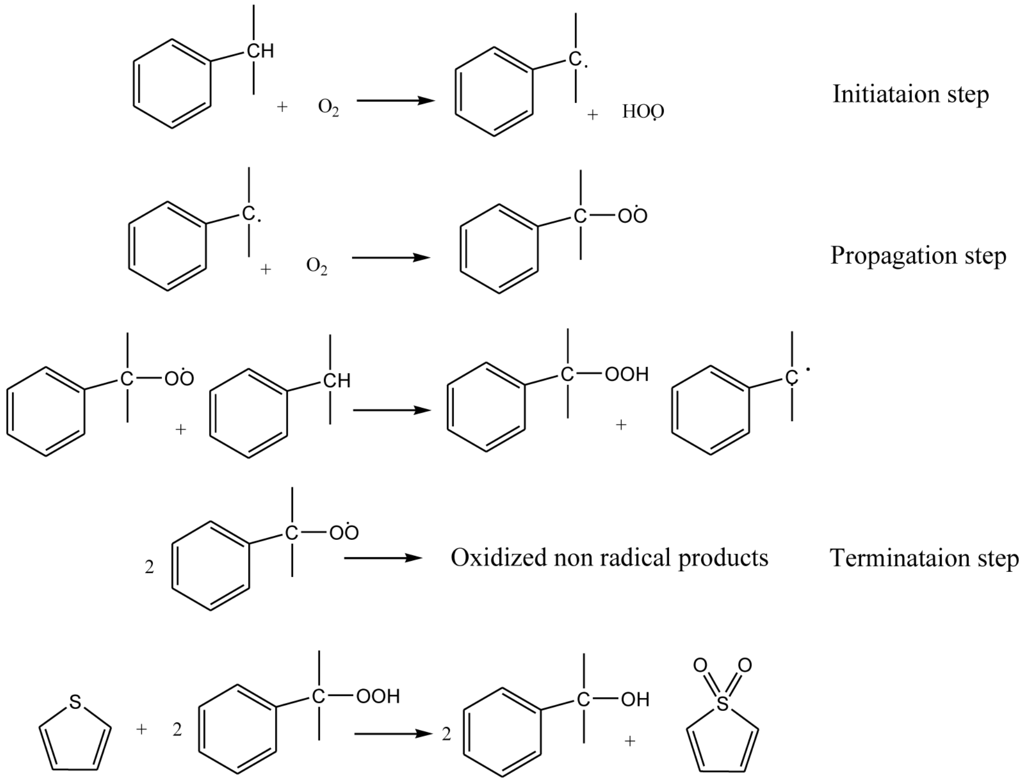
5.6.2 ODS with Air or Molecular Oxygen

Air or molecular oxygen cannot directly oxidize the sulfur compounds but only in the presence of a hydro peroxide source generally alkyl aromatics, at elevated temperature i.e. 100 to 200 °C and near atmospheric pressure. The application of auto-oxidation for the ODS of the heavy oil and distillates fraction has been studied extensively (Javadli & Klerk, 2012). Air or molecular oxygen can also oxidize sulfur compounds at lower temperature, but the reaction requires an initiator (oxygen carrier) or a catalyst.

Generally the high temperature auto-oxidation process involves the formation of a hydroperoxide intermediate by the attack of molecular oxygen on alkyl aromatics, which selectively oxidizes the organosulphur compounds. The production of hydroperoxide follows a free radical mechanism. The alkyl aromatics present in the heavy distillates fraction serves to form hydroperoxide during oxidation with air or molecular oxygen. In heavy oil, the oxidation by molecular oxygen leads to the removal of sulphur in the form of SO_2, whereas in light distillates fractions sulfur is separated as sulfoxide and sulfone, mostly by extraction or adsorption process. Such type ODS has been widely studied in case of various oil fractions, where the hydroperoxide is produced in situ by molecular oxygen using different types of catalysts. The organosulphur compounds that are present in jet and diesel oil have shown to be efficiently oxidized at 120 °C by O_2 and using CuO as catalyst, due to the in-situ generation of hydroperoxides (Sundararaman et al., 2010). The production of hydroperoxide is found to be dependent on the amount of the alkyl aromatics available. Under a high concentration of alkyl aromatics in the feed, the production of hydroperoxides is higher, leading to an increase in the rate of sulfur oxidation. As the alkyl aromatics are more abundant in diesel oil than jet oil, the desulphurization attained in diesel oil was higher. The desulphurization yield in the absence of the catalyst has shown to be very low, which reveals that the catalyst promotes the formation of hydroperoxides (see Figure 11).

With the use of different types of catalysts the efficiency of ODS by air or molecular oxygen is markedly enhanced. Sampanther, *et al.,* (Sampanthar et al., 2006) employed MnO_2 & Co_2O_3 supported on Al_2O_3 as catalyst for the ODS of diesel oil by air oxidation (under pressure of 0.1 MPa and temperature

Figure 11. Oxidation of thiophene by my molecular oxygen



range of 230 to 300 °C), and using NMP as extractant, the sulfur concentration of the feed was reduced to 60 ppm from the initial of 400 ppm. This study also revealed that the ODS process was associated with decrease in the aromatic contents of the feed (from 46.4 to 12.5%), and an increase in the olefin contents (from 2.4 to 3.6%), which was resulted by the free radical mechanism involved. The study also indicated that the sulphur atom from the organosulfur compounds was removed in the form of SO_2. Similarly the ODS of different model sulfur compounds by air (0.1 MPa and 400 °C) in the presence of various catalysts including CuO and ZnO supported on Al_2O_3, and Cu & Pt supported on CeO_2 also indicated that during the process sulfur is removed as SO_2 (Y. Lu et al., 2008). Song, *et al.* studied the ODS of Jet oil by air oxidation (0.1 MPa) at lower temperature (50 °C) using nitrates and bromides of Fe(III) loaded on activated carbon (Ma et al., 2007), and reported that the efficiency of the catalyst increases as the Fe loading increases.

Oxidation of sulfur compounds by molecular oxygen under mild conditions i.e. low temperature and atmospheric pressure occur only in the presence of an initiator usually an aldehyde, such process is of great importance for ODS application. Several types of aldehydes have been used with molecular oxygen for ODS of various distillate fractions (Venkateshwar Rao et al., 2007). The notable aldehydes used include isobutyraldehyde, benzaldehyde, n-octanal and hexanal etc. It has been shown that during this process, the interaction of molecular oxygen and aldehydes first leads to the formation of acyl radical, then to peroxy-acyl radical and ultimately to a per-acid. It is actually the per-acid produced that oxidizes the sulphur compound through transfer of oxygen.

The ODS of diesel oil containing 447 ppm sulfur was studied using O_2 and iso-butyraldehyde oxidation system, when the oil was extracted with acetonitrile the sulphur contents were reduced to about 77 ppm and when further subjected to column adsorption on silica gel the sulfur level was decreased to 31ppm (Venkateshwar Rao et al., 2007). In similar type low temperature ODS based on O_2/aldehyde oxidation system, catalyst like cobalt salts and iron pthalocyanin complexes have also been used to enhance the desulfurization efficiency (Murata et al., 2003; Zhou, Li, et al., 2009). Application of tert-butyl hydroperoxide as initiator was shown to readily increase the conversion of DBT from 85 to 96% conversion in ODS using air and isobutyl aldehyde (Guo et al., 2011).

Studies indicated that ODS based of molecular oxygen not only suffers from oxidation of non-sulfur moieties, but also involve the formation of undesirable oxidation products like sediments and gums mostly in case of heavy oils (Javadli & Klerk, 2012).

5.5.3 ODS with Organic Hydroperoxides

The selective oxidation of sulfur compounds can also be effectuated with organic hydroperoxides, which are extensively used for ODS applications. Various hydroperoxides employed in the ODS processes include tertiary-butylhydroperoxide (TBPH) (Chica, Gatti, et al., 2006), cumenehydroperoxide (Chang et al., 2010), cyclohexanoneperoxide (X. Zhou et al., 2006) and tert-amylhydroperoxide (Zhou, Gai, et al., 2009) etc. Among these, TBHP is highly efficient, and hence is widely used in ODS studies. EniChem/UOP and Lyondell Chemicals have patented several ODS processes which involve TBHP as oxidant (Karas LJ et al., 2004; G. R. a. L. M. Karas LJ, 2008; Kocal JA, 2001; Kocal JA and Branvold TA, 2002; Z et al., 2005). The Lyondell chemical process involves the separation of oxidized sulfur compounds by extraction, whereas the ODS processes by EniChem/UOP employs adsorption for removal of oxidized products. However, TBPH is very costly and as it contains very low free available oxygen(17-10%) therefore its consumption during oxidation process is very high, which limits the efficiency of these processes.

Generally, a catalyst is required for the efficient oxidation of sulphur compounds by hydroperoxides. Several types of heterogeneous catalysts have given promising results, mostly containing transition metals like Ti, W, V and Mo, loaded on different supports such as alumina, silica, titania, mesoporous MCM-41 etc., (Campos-Martin et al., 2010).

A number of researchers have investigated that Mo supported on different supports, when used with hydroperoxides for ODS, show high desulfurization activity (Chica, Gatti, et al., 2006; Ishihara et al., 2005; Venkateshwar Rao et al., 2007; D. Wang et al., 2003). However, in addition to the high efficiency, most of these catalysts suffer from leaching of Mo to the medium, due to which the catalyst loses its activity (Sharipov et al., 2005). Therefore new catalytic materials were sought. Chica, et al., conducted a study on comparative efficiency of Ti/MCM-41 and MoO_3/Al_2O_3 catalyst using TBPH for ODS of DBT in a fixed reactor (Chica, Corma, et al., 2006). The authors shown that Ti/MCM-41 exhibited high desulfurization activity than MoO_3/Al_2O_3 catalyst, as well as no leaching of Ti to the medium was observed. A patent on ODS of distillate fuels using Ti/SiO_2 catalyst in the presence of hydroperoxide oxidation system showed that the catalyst bear high desulfurization efficiency along with high stability in the medium (G. R. a. L. M. Karas LJ, 2008). Similarly, Mo containing kegging type heteropolyacids immobilized on alumina were found to show high efficiency in ODS of hydrotreated diesel in the presence of TBHP with minimal oxidant consumption (Alberto de Angelis et al., 2007).

5.5.4 ODS with H_2O_2- Polyoxometalates (POM)

The cluster of anionic metal oxides containing Mo, W, V, Ge etc. (group VI and V metals) associated with some cation in the form of a salt is termed as Polyoxometalates (POM). In the case that some heteroanions, such as SO_4^{-2} or PO_4^{-2}, are also associated, the POM are called heteropolyoxometalates. Because of their giant molecular structure and large versatile characteristics such as high redox potential, thermal stability, proton acidity and high reactivity of lattice oxygen, POM finds a number of applications ranging from the fields of medicine to catalysis, materials and electronics (Long et al., 2007). As an oxidation catalyst, POM show excellent activity in selective oxidation of sulfur compounds, and are therefore also used in ODS reaction. In ODS processes, these are mostly employed in supported and unsupported forms in the presence of H_2O_2 as oxidant (Gaofei Zhang et al., 2009). In ODS reaction, a highly reactive transient specie, polyoxoperoxo complex is formed by transfer of oxygen from H_2O_2 to the POM molecule. The, the peroxo complex successively oxidizes the sulfur compounds to sulfoxides followed by sulfone. The POM is again re-oxidized by H_2O_2 to form another peroxo complex which is ready for further oxidation (Te et al., 2001).

Since POM salts are soluble in aqueous phase, they are used in biphasic systems in which some polar solvent is added to the non-polar organic phase. During the reaction in the biphasic medium, the sulphur compounds transfer from the non-polar oil phase to the polar phase solvent before being oxidized by POM to the respective sulfones. Acetonitrile and ethanol are the common solvents used for biphasic ODS in the presence of POM. When acetonitrile (at the ratio of 4:1 with oil) is used for the ODS of light oil in the presence of tungstophosphoric acid (TPA) and H_2O_2 at 60 ^{o}C, the amount of sulphur is lowered from 300 ppm to 112 ppm (Yazu et al., 2001). The ODS of model oil has also been investigated with the TPA/H_2O_2 oxidation system comprising of tetradecane-ethanol (Yazu et al., 2003) and octane-acetic acid (Yazu K. et al., 2007). Among various phosphorous and silicon based Keggin type POM catalysts used for ODS of model oil in the presence of H_2O_2, the sulfur removal efficiency was found to be decreased as; phosphotungstic acid > phosphomolybdic acid > silicotungstic acid > silicomolybdic acid (Te et al., 2001). Several phosphorus based keggin type POM salts with W and Mo in different molar ratios have also been used as catalysts for the ODS of diesel oil in biphasic systems with acetonitrile. The POM containing W and Mo in the ratio of 1:1 (i.e. $H_3PW_6Mo_6O_{40}$) showed a desulfurization efficiency of more than 97% in diesel oil (R. Wang et al., 2010).

The reactivity of various sulphur compounds in ODS with POM/H_2O_2 oxidation system has shown to increase as follows:

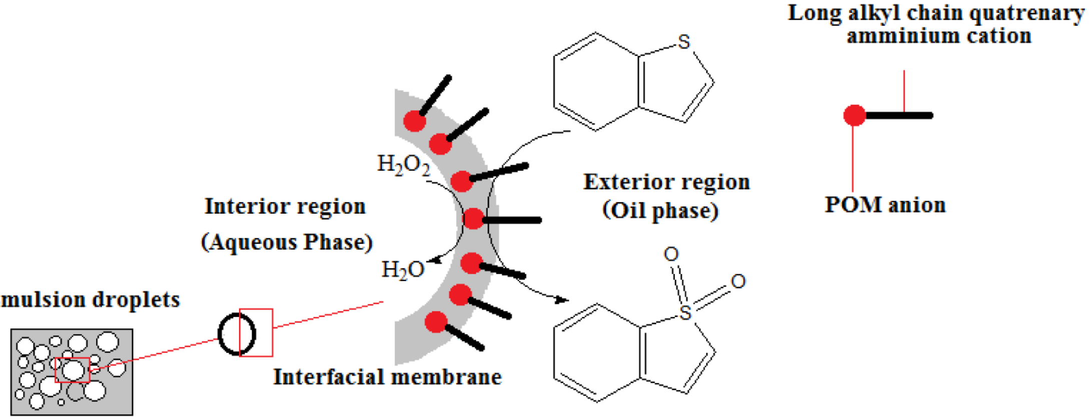
4,6-DMDBT < 4-MDBT < DBT

The reactivity order is similar to that of HDS reactions but opposite to ODS processes without POM catalysts. This is because of the large size and bulky shape of the POM molecules, which produce steric hindrance to alkyl substituent's in the alkylated aromatic sulfur compounds and hence decreases their reactivity.

Several studies have revealed that increasing the surface area of POM by dispersion on a suitable solid support drastically enhances the ODS activity. Various types of material supports have been successfully used for immobilizing POM in ODS reactions, these include different anion exchange resins (AER) (Yazu et al., 2003), SiO_2 (Xue-Min Yan et al., 2007), Al_2O_3 (Zhang Y W et al., 2005,), SBA-15 (L. Yang et al., 2007) etc. As the POM catalyst acts in cyclic mode, it could be used for multiple cycles with negligible loss in activity. It has been observed over a number of studies that POM/H_2O_2 system works well for model oil but not for real fuels without using a polar solvent. Due to phase transfer limitations in real fuels with a complex non-polar nature, the oxidant cannot access the organosulphur compounds completely; hence large quantity of H_2O_2 is consumed. The problem of the phase transfer limitations can be overcome by the application of surfactants in the ODS reaction system. For this purpose different types of surfactants like tertaoctyl-ammonium bromide, hexadecyltrimethyl-ammonium bromide (CTAB), have been used in POM/H_2O_2 oxidation system, which has resulted remarkably high ODS efficiency with low H_2O_2 consumption and shortened reaction time (Collins et al., 1997).

A new approach toward the POM catalysis in ODS is the application of surfactant based POM salts, which consist of a heteropolyoxometalate anion and a quaternary ammonium surfactant cation combined together as a salt and being called emulsion or amphiphilic catalysts. These catalysts in combination with H_2O_2 exhibit remarkable sulfoxidation efficiency with a high selectivity. The amphiphilic or emulsion catalysts circumvent the obstacles of phase transfer limitations and enable an efficient contact between the oxidant aqueous phase and the sulfur compounds in the feed. The catalyst actually produces an emulsion in the reaction medium consisting of tiny bubbles or droplets. For each bubble three distinct regions can be differentiated, the inner regions or interior, the outer continuous region or exterior and the interfacial membrane between these two regions. Likewise the amphiphilic catalyst is also comprised of two parts, a liphophilic part i.e. the alkyl side chains and the hydrophilic part which is the POM cluster. In the reaction medium containing emulsion catalyst and H_2O_2, the liphophilic part of the catalyst disperses at the exterior of the bubble and its hydrophilic part is retained in the interfacial membrane, whereas the H_2O_2 remains in the interior of the bubble. At the interfacial membrane, the contact between the sulphur compounds, the POM catalyst and the oxidant (H_2O_2) occurs before the transfer of oxygen for oxidizing the sulfur. After the reaction is completed, the emulsion is broken and the catalyst is collected at the water-oil interface, dried and then reused (Z. Jiang et al., 2011) (see Figure 12).

Figure 12. Oxidation of DBT in emulsion droplet system



The emulsion or amphiphilic catalysts have shown a remarkable efficiency in the desulfurization of real and model oil samples. The interesting feature of these catalysts is that they can be regenerated and reused for multiple times without losing their activity. Keggin type phosphotungstate based emulsion catalyst i.e. $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$, in combination with H_2O_2 has shown to decrease the level of sulfur to about 1ppm in diesel oil containing 500 ppm sulfur (C. Li et al., 2004). In case of ODS of hydrotreated diesel and straight run diesel, the sulfur content decreased from 500 and 6000 ppm to 1 and 30 ppm respectively, in the presence of quaternary ammonium based sodium phosphotungstate i.e. $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ under mild conditions with O/S=3 (Lü et al., 2006). The ODS of gas oil was studied in the presence of several emulsion catalysts containing tetrabutylammonium cation and different POM anions containing Mo, W and V i.e. $[PV_2Mo_{10}O_{40}]^{4-}$, $[W_6O_{19}]^{2-}$, $[V(VW_{11})O_{40}]^{4-}$ and $[PVW_{11}O_{40}]^{4-}$. The catalysts containing $[V(VW_{11})O_{40}]^{4-}$ showed to be highly active, close to a 90% desulfurization in gas oil after adsorption on silica (Komintarachat et al., 2006).

The emulsion catalysts containing different quaternary ammonium cations lead to the formation of emulsions with different strengths i.e. from weak to strong or very strong. A weak emulsion is unsustainable and hence results in a low ODS yield. However, the emulsion formed might be very stable, being very difficult to break and complicating the removal of the catalyst and the products. As the formation of the emulsion depends on the nature of the quaternary ammonium cation, the amphiphilic catalyst should contain an appropriate cation for producing a suitable emulsion for an efficient ODS process. A variety of quaternary ammonium cations containing alkyl chains of different length have been used in emulsion based POM catalysts for ODS application. Several emulsion catalysts containing decatungstate ($Q_4.W_{12}O_{32}$) POM anions and different quaternary ammonium cations Q^+ including hexadecyltrimethyl ammonium ($C_{16}H_{33}N^+(CH_3)_3$), decyltrimethyl ammonium ($C_{10}H_{21}N^+(CH_3)_3$), dodecyltrimethyl ammonium ($C_{12}H_{25}N^+(CH_3)_3$) and tetradecyltrimethyl ammonium ($C_{14}H_{29}N^+(CH_3)_3$) have been employed for ODS of diesel oil at 60 ^{o}C, showing that a maximum desulfurization (99%) efficiency could be attained with catalysts containing long alkyl chain ammonium cation i.e. hexadecyltrimethyl ammonium ($C_{16}H_{32}N^+(CH_3)_3$) (X. Jiang et al., 2009). For POM based emulsion catalyst used in ODS reaction, the appropriate quaternary ammonium cations have been reported to be di- or tri-methylhexadecyl ammonium cations i.e. $C_{16}H_{33}NH^+(CH_3)_2$ and $C_{16}H_{33}N^+(CH_3)_3$ (J. Gao et al., 2006; C. Li et al., 2005; C. Li et al., 2004; H. Lu et al., 2007; H. Lu et al., 2010; Y. Zhang et al., 2010).

The reactivity of various organosulphur compounds in ODS reactions using emulsion catalysts increases as follows,

BT < 5-MBT < DBT < 4,6-DMDBT

This reactivity trend is similar to that observed in ODS using a H_2O_2/formic acid system (Otsuki et al., 2000), but opposite to that of in the presence of ordinary POM/H_2O_2 system (Collins et al., 1997; Te et al., 2001). This indicates that in the presence of emulsion catalysts, the alkylated aromatic sulfur compounds are more reactive in the emulsion system and the stearic hindrance due to alkyl subtituent is controlled. Furthermore, it has been shown that ODS in the presence of emulsion systems requires a lower amount of H_2O_2 than the ODS using organic peracids and ordinary POM oxidation systems (Z. Jiang et al., 2011).

5.5.6 ODS with Ionic Liquids (IL)

Ionic liquids (IL) are referred to the salts that exist in liquid state at ordinary pressure and temperature. Because of their high chemical and thermal stability, low vapor pressure, non-corrosiveness and non-flammability, ILs are widely used in the fields of synthesis, separation, electrochemistry and catalysis (W. Zhang et al., 2010). In the field of petroleum desulfurization, ILs have been extensively used since the last decade. They are mostly used either directly for selective extraction of organosulphur compounds from liquid fuel, or in ODS process for different purposes like extraction, solvent or catalyst. The application of IL for direct extraction of sulfur compounds has been previously described in the section for extractive desulfurization, therefore the role of IL in ODS reactions is discussed below.

The ILs can extract higher amounts of oxidized sulfur compounds than the organic solvents, hence in ODS process, the desulfurization yield is markedly enhanced when ILs are used for extraction as compared to the use of organic solvents. The ODS of light oil using a H_2O_2/acetic acid oxidation system and 1-butyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate (i.e. [BMIM]PF_6 and [BMIM]BF_4) as ionic liquids showed higher desulfurization yields than the simple extraction process (Lo et al., 2003). Generally, ILs cannot extract sulfur to appreciable levels on their own and the presence of an oxidant enhances the sulfur removal drastically. Thus, [HMIm]BF_4 hardly attains a 6% sulfur removal, however, in the presence of H_2O_2 at 90 °C the sulfur removal increases to 93% (L. Lu et al., 2006). Likewise, the ODS of model oil with H_2O_2 at 60 °C in the presence of N-methyl pyrolidonium tetraflouroborate [HNMp]BF_4 reduced the sulphur level from 1550 ppm to about 1 ppm, in 1 h. The ionic liquid was found to maintain its efficiency to up to 7 times of recycling (WANG Jian-long et al., 2008).

In ODS with ILs, the deep desulfurization of real oil usually requires a high H_2O_2/S ratio, although the use of heterogeneous catalysts allows to reduce the H_2O_2consumption. Some of the common catalysts used include various organic acids (F. T. Li et al., 2009; Dishun Zhao et al., 2007), sodium molybdate (Zhu et al., 2008), vanadiumoxide (Xu et al., 2009), iron based catalyst (H. Li, W. Zhu, et al., 2009; J. Zhang et al., 2009) and POM catalysts (He et al., 2008; H. Li, L. He, et al., 2009; H. Li, X. Jiang, et al., 2009; Zhu et al., 2007). Although the use of ILs in ODS process enables to attain high desulphurization yields, their industrial application is limited by their cost, sensibility to moisture and the high cost of their regeneration. Additionally, because of their high boiling point and high viscosity, IL are not suitable for application with heavy feeds (Javadli & Klerk, 2012).

5.5.7 Photo-Oxidative Desulphurization

In the photo-oxidative desulphurization, the organosulphur compounds in the hydrocarbon stream are photo-chemically oxidized under the influence UV-light. Unlike the ordinary ODS in which the energy required for oxidation is supplied by heat, in photo ODS the energy is supplied by photo irradiation. The process operates under room temperature and atmospheric pressure in a specially designed photo-reactor equipped with a radiation source, usually a high pressure mercury lamp emitting the UV-visible radiations. The oil and a suitable extraction solvent are mixed in a reactor and photo-irradiated for definite time duration, during which the sulfur compounds are photo-chemically oxidized to their respective sulfones. The sulfones subsequently shift from the oil to the solvent phase before being separated.

An experiment on photo-ODS of various model sulfur compounds i.e. DBT, 4-MDBT and 4, 6-DMDBT dissolved in tetradecane solvent, indicated that these compounds are quantitatively decomposed to SO_4^{-2} by photo irradiation under ambient conditions. The trend in reactivity of different the model sulfur compounds was as: DBT < 4-MDBT < 4,6-DMDBT. However, the presence of aromatics have shown to markedly hinder the photoreaction of sulfur compounds, and therefore the desulfurization efficiency in the photo-ODS of commercial oil is very low. For example, in the case of commercial light oil, the sulfur removal was about 20%, even for photo irradiation of 30 h. (Hirai et al., 1996). The application of a triplet photosensitizer such as benzophenone in the photo-oxidation of model oil led to an enhanced desulfurization efficiency (Hirai et al., 1997), but still in the presence of aromatics such as naphthalene the desulphurization yield was low. This revealed that during the photoreaction the triplet energy is probably transferred from photoexited DBT or benzophenone to ground state aromatics i.e. naphthalene, which interferes the oxidation of sulfur compounds. The energy transfer from the photosensitizer or excited DBT in the presence of aromatics can be interrupted by the addition of H_2O_2 as oxidant; in such case the photosensitizer is excited by photo irradiation which further excites thiophenes, the excited thiophenes are then oxidized by H_2O_2. Experiments have shown that using H_2O_2 as oxidant, photo-ODS of commercial and model oil led to high yields of desulfurization, although the feed was rich in aromatics. In case of commercial light oil containing plenty of aromatics, 75% sulfur removal was achieved during photo ODS in the presence of H_2O_2, benzophenone photosensitizer and after 24 hours of photo irradiation (Hirai et al., 1997).

Photo-ODS of light oil by 48 h of photo irradiation ($\lambda > 280$ nm) in the presence of H_2O_2 and benzophenone followed by adsorption over alumina, decreased the sulphur content in light oil from 0.2% to about 0.05% (Shiraishi et al., 1999). The use of some heterogeneous photocatalysts such as Ti containing zeolites in the presence of H_2O_2 was found to sufficiently boost the desulfurization efficiency, close to 90% in the case of model oil (D. Zhao et al., 2009).

Air or molecular oxygen can also be used as oxidants in the photo-oxidative desulfurization of model and commercial oil, exhibiting an improved efficiency. For example, the photo-oxidative desulphurization of thiophene dissolved in octane/water mixture was investigated using air as oxidant and riboflavin as a photosensitizer, and after 3 h of photo irradiation a desulphurization yield of 85% could be achieved for (D. Zhao et al., 2008). Similarly, photo-oxidation of DBT in octane/acetonitrile biphasic system, using molecular oxygen as oxidant and Zeolite adsorbent, resulted in about 96% desulfurization under 5 h photo irradiation ($\lambda = 365$ nm), and during the reaction the DBT was converted to SO_4^{-2} and CO_2 (D. Zhao et al., 2007).

Although photo oxidative desulphurization is an efficient and an economic process for desulphurization, it is not commercially viable as it is also fairly slow in response and requires long photo irradiations (Gaofei Zhang et al., 2009). Furthermore, the process chemistry has not been completely revealed yet, requiring additional research.

5.5.8 Ultrasound Assisted ODS

Ultrasound assisted ODS is a special type of ODS in which the energy required for oxidation of sulfur compounds is provided by ultrasound irradiation, rather than thermal energy as in ordinary ODS. In this process the oil and the oxidant are mixed in the reactor and irradiated by ultrasound for certain time. During the ultrasound irradiation the local temperature and pressure of the reaction medium rises for a short while, leading to the formation of free radicals in the presence of an oxidant that oxidizes the sulphur compounds into the respective sulfones and sometimes to sulfates. The oxidized sulfur compounds can be separated from the oil phase by extraction with a polar solvent (Gaofei Zhang et al., 2009).

A special type of ultrasound assisted ODS process is called UAOD, which involves the ODS of oil by ultrasound irradiation in the presence of emulsion or amphiphilic catalysts. The process is based on the oxidation of the sulfur compounds in the emulsion system with a higher efficiency than ordinary ODS. In the case of diesel oil, the UAOD process using H_2O_2, phosphotungstic acid as catalyst and tetraoctyl ammonium bromide as surfactants to form the emulsion system, achieved a sulfur removal of 99% in 10 min at 75 °C (Mei et al., 2003). In a similar UAOD process for model oil and diesel oil, using POM catalyst and variety of phase transfer agents like tetra-octyl ammounium fluoride, about 99% of conversion of BT and DBT was attained in model oil as well as in diesel (Wan et al., 2007).

The desulfurization efficiency of the ultrasound assisted ODS using other catalysts than emulsion catalyst has also shown to be very high. For example, during the desulfurization of diesel oil spiked with 4,6-DMDBT by ultrasound irradiation using Na_2CO_3 as catalyst and H_2O_2 as oxidant, the concentration of 4,6-DMDBT decreased to up to 90% within 1 h at 60 °C (Deshpande et al., 2004). Similarly, phosphoric acid and formic acid as catalysts were also found to be very efficient when used in the presence of H_2O_2 as oxidants for the ultra sound assisted ODS of commercial diesel oil (Sun M Zh. et al., 2008).

A commercial process based on ultrasound assisted ODS called SulphCo technology uses H_2O_2 as oxidant in water oil emulsion system, and operates at a temperature ranging from 70 to 80 °C, with a residence time of one min in an ultrasound reactor. In this process the desulphurization efficiency for crude oil and diesel oil showed to be 80 and 98% respectively. The first desulfurization unit based on this technology was operated in Italy at IPLOM petroleum refinery, with continuous desulphurization capacity of 350 bbl of diesel oil/day (Babich & Moulijn, 2003).

Generally the efficiency of ultrasound assisted ODS process is very high; however this technique is associated with several problems such as application of ultrasound producing expensive device leads to scale up limitations and consumption of large quantity of H_2O_2 which is also very costly. In addition, mixing of H_2O_2 with oil leads to formation of stable emulsion which requires sufficient time to settle down or break (Gaofei Zhang et al., 2009).

5.6 Desulfurization Using Nanomaterials

The nanomaterials, due to their versatile characteristics find application in petroleum desulfurization as adsorbents and catalysts. Various types of nanomaterials such as TiO_2, Fe_2O_3, zero valent iron nanoparticles, modified single wall and multiwall carbon nanotubes etc. (Deneuve et al., 2011; Saleh et al., 2014; Shang et al., 2004) have been found to efficiently remove sulfur compounds from petroleum by either direct adsorption or being used as catalyst in ODS process. Because of their large surface area, the nanomaterials show high reactivity and therefore exhibit high efficiency in desulfurization. Detailed discussion on this topic is given in the forthcoming chapters.

CONCLUSION

In petroleum, sulfur occurs as H_2S, sulfides, thiophenes, benzothiophenes and dibenzothiophenes. The quantity and structural complexity of the sulfur compounds increases with the increase in the boiling point of the distillate fraction. The compounds of sulfur lead to various detrimental effects in petroleum, such as corrosion problems, catalyst deactivation and environmental deterioration by producing sulfurous emissions, which necessitates their removal from petroleum. Hydrodesulfurization is the only process used for desulfurization in the refineries, which is very expensive and is inadequate to completely desulfurize the feed. Recently, many new desulfurization techniques have emerged, however none of these are mature enough to replace HDS. Adsorptive desulfurization is a simple and cost effective process but the process leads to the removal of aromatic components of the feed. Bio-desulfurization presents minimum requirements of energy; however, the disposal of microbial wastes, storage and handling of bacterial cultures in the industrial environment makes it an industrially unviable process. The side reactions occurring in precipitative desulfurization limits the efficiency of the process. Similarly, oxidative desulfurization seems to hold a promise in substituting HDS, but the removal of the oxidized products in a separate step and the complex chemistry of the process hinder its industrial application. Hopefully these shortcomings could be overcome by the researchers in a near future and the refining industry could find a suitable alternative to HDS.

REFERENCES

Absi Halabi, M., Stanislaus, A., Qamra, A., & Chopra, S. (1996). Effect of presulfiding on the activity and deactivation of hydrotreating catalysts in processing Kuwait vacuum residue. In J. B. M. Absi-Halabi & A. Stanislaus (Eds.), Studies in Surface Science and Catalysis (Vol. 100, pp. 243-251). Elsevier. doi:10.1016/S0167-2991(96)80025-5

Afferden, M., Schacht, S., Klein, J., & Trüper, H. (1990). Degradation of dibenzothiophene by Brevibacterium sp.DO. *Archives of Microbiology*, *153*(4), 324–328. doi:10.1007/BF00249000

Afferden, M., Tappe, D., Beyer, M., Trüper, H. G., & Klein, J. (1993). Biochemical mechanisms for the desulfurization of coal-relevant organic sulfur compounds. *Fuel*, *72*(12), 1635–1643. doi:10.1016/0016-2361(93)90348-6

Agarwal, P., & Sharma, D. K. (2009). Comparative Studies on the Bio-desulfurization of Crude Oil with Other Desulfurization Techniques and Deep Desulfurization through Integrated Processes. *Energy & Fuels*, *24*(1), 518–524. doi:10.1021/ef900876j

Ahmad, W. (2013). *Study on cost effective methodes for desulfurization of kerosene, diesel and furnace oil (PhD)*. Peshawar: University of Peshawar.

Ali, M. F., Al-Malki, A., El-Ali, B., Martinie, G., & Siddiqui, M. N. (2006). Deep desulphurization of gasoline and diesel fuels using non-hydrogen consuming techniques. *Fuel*, *85*(10–11), 1354–1363. doi:10.1016/j.fuel.2005.12.006

Babich, I. V., & Moulijn, J. A. (2003). Science and technology of novel processes for deep desulfurization of oil refinery streams: A review. *Fuel*, *82*(6), 607–631. doi:10.1016/S0016-2361(02)00324-1

Birch, S. F., & Norris, W. S. G. P. (1925). CXXVI.-The chemistry of petroleum. Part I. The occurrence of compounds of sulphur in the light distillate from the crude oil of maidan-i-naftun. *Journal of the Chemical Society Transactions*, *127*(0), 898–907. doi:10.1039/ct9252700898

Braid, C., & Cann, M. (2005). Environmental chemistry. (3rd ed.). New York: W.H Freeman and company.

Brevoord, E., & Gerritsen, L. A., & L., P. F. (2000, November 13–15). Paper presented at The European Refinery Technology Conference, Rome, Italy.

Brieva, GB, Campos-Martin, J M, & Al-Zahrani, S M, & G, F. J. L. (2010). Removal of refractory organic sulphur compounds in fossil fuels using MOF sorbents. *Global NEST Journal*, *12*, 296–304.

Campos-Martin, J. M., Capel-Sanchez, M. C., Perez-Presas, P., & Fierro, J. L. G. (2010). Oxidative processes of desulfurization of liquid fuels. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *85*(7), 879–890. doi:10.1002/jctb.2371

Chang, J., Wang, A., Liu, J., Li, X., & Hu, Y. (2010). Oxidation of dibenzothiophene with cumene hydroperoxide on MoO3/SiO2 modified with alkaline earth metals. *Catalysis Today*, *149*(1–2), 122–126. doi:10.1016/j.cattod.2009.04.026

Chen, L., Guo, S., & Zhao, D.CHEN. (2006). Oxidation of thiophenes over silica gel in hydrogen peroxide/formic acid system. *Chinese Journal of Chemical Engineering*, *14*(6), 835–838. doi:10.1016/S1004-9541(07)60022-6

Chica, A., Corma, A., & Dómine, M. E. (2006). Catalytic oxidative desulfurization (ODS) of diesel fuel on a continuous fixed-bed reactor. *Journal of Catalysis*, *242*(2), 299–308. doi:10.1016/j.jcat.2006.06.013

Chica, A., Gatti, G., Moden, B., Marchese, L., & Iglesia, E. (2006). Selective Catalytic Oxidation of Organosulfur Compounds with tert-Butyl Hydroperoxide. *Chemistry (Weinheim an der Bergstrasse, Germany)*, *12*(7), 1960–1967. doi:10.1002/chem.200500858 PMID:16385590

Collins, F. M., Lucy, A. R., & Sharp, C. (1997). Oxidative desulphurisation of oils via hydrogen peroxide and heteropolyanion catalysis. *Journal of Molecular Catalysis A Chemical*, *117*(1–3), 397–403. doi:10.1016/S1381-1169(96)00251-8

Davis, D. L., Bell, M. L., & Fletcher, T. (2002). A Look Back at the London Smog of 1952 and the Half Century Since. *Environmental Health Perspectives*, *110*(12), A734–A735. doi:10.1289/ehp.110-a734 PMID:12501843 de Angelis, A., Pollesel, P., Molinari, D., O'Neal Parker Jr, W., Frattini, A., Cavani, F., Martins, S., & Perego, C. (2007). Heteropolyacids as effective catalysts to obtain zero sulfur diesel. *Pure and Applied Chemistry*, *79*(11), 1887–1894.

De Filippis, P., Scarsella, M., & Verdone, N. (2010). Oxidative Desulfurization I: Peroxyformic Acid Oxidation of Benzothiophene and Dibenzothiophene. *Industrial & Engineering Chemistry Research*, *49*(10), 4594–4600. doi:10.1021/ie9017622

de Souza, W. F., Guimarães, I. R., Guerreiro, M. C., & Oliveira, L. C. A. (2009). Catalytic oxidation of sulfur and nitrogen compounds from diesel fuel. *Applied Catalysis A, General*, *360*(2), 205–209. doi:10.1016/j.apcata.2009.03.023

Dehkordi, A. M., Sobati, M. A., & Nazem, M. A. (2009). Oxidative Desulfurization of Non-hydrotreated Kerosene Using Hydrogen Peroxide and Acetic Acid. *Chinese Journal of Chemical Engineering*, *17*(5), 869–874. doi:10.1016/S1004-9541(08)60289-X

Deneuve, A., Wang, K., Janowska, I., Chizari, K., Edouard, D., & Ersen, O. et al. (2011). Bucky paper with improved mechanical stability made from vertically aligned carbon nanotubes for desulfurization process. *Applied Catalysis A, General*, *400*(1), 230–237. doi:10.1016/j.apcata.2011.04.042

Denome, S. A., Oldfield, C., Nash, L. J., & Young, K. D. (1994). Characterization of the desulfurization genes from Rhodococcus sp. strain IGTS8. *Journal of Bacteriology*, *176*(21), 6707–6716. PMID:7961424

Denome, S. A., Stanley, D. C., Olson, E. S., & Young, K. D. (1993). Metabolism of dibenzothiophene and naphthalene in Pseudomonas strains: Complete DNA sequence of an upper naphthalene catabolic pathway. *Journal of Bacteriology*, *175*(21), 6890–6901. PMID:8226631

Deshpande, A., Bassi, A., & Prakash, A. (2004). Ultrasound-Assisted, Base-Catalyzed Oxidation of 4,6-Dimethyldibenzothiophene in a Biphasic Diesel−Acetonitrile System. *Energy & Fuels*, *19*(1), 28–34. doi:10.1021/ef0340965

EORC. (2000, June 29-30). Paper presented at the European Oil Refining Conference Exhibition, Berlin, Germany.

Forte, P. (1996). US Patents 5582714.

Froment, G. F., & Delmon, B. (1987). *Catalyst Deactivation 1987*. Elsevier Science.

Funakashi, I., & Aida, T. (2002). EP 711 819 B1.

Funakoshi, I. & Aida, T. (1998). US Patents 5753102. U. Patents.

Furimsky, E. (1996). Spent refinery catalysts: Environment, safety and utilization. *Catalysis Today*, *30*(4), 223–286. doi:10.1016/0920-5861(96)00094-6

Gao, H., Luo, M., Xing, J., Wu, Y., Li, Y., & Li, W. et al. (2008). Desulfurization of Fuel by Extraction with Pyridinium-Based Ionic Liquids. *Industrial & Engineering Chemistry Research*, *47*(21), 8384–8388. doi:10.1021/ie800739w

Gao, J., Wang, S., Jiang, Z., Lu, H., Yang, Y., Jing, F., & Li, C. (2006). Deep desulfurization from fuel oil via selective oxidation using an amphiphilic peroxotungsten catalyst assembled in emulsion droplets. *Journal of Molecular Catalysis A Chemical*, *258*(1–2), 261–266. doi:10.1016/j.molcata.2006.05.058

Gates, B. C., Katzer, J. R., & Schuit, G. C. A. (1979). *Chemistry of catalytic processes*. McGraw-Hill.

Gates, B. C., & Topsøe, H. (1997). Reactivities in deep catalytic hydrodesulfurization: Challenges, opportunities, and the importance of 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene. *Polyhedron*, *16*(18), 3213–3217. doi:10.1016/S0277-5387(97)00074-0

Gray, M. R., Ayasse, A. R., Chan, E. W., & Veljkovic, M. (1995). Kinetics of Hydrodesulfurization of Thiophenic and Sulfide Sulfur in Athabasca Bitumen. *Energy & Fuels*, *9*(3), 500–506. doi:10.1021/ef00051a015

Gruse, W. A., & Stevens, D. R. (1960). Chemical technology of petroleum. (3rd ed.). New York: Mc. Graw Hill.

Guo, W., Wang, C., Lin, P., & Lu, X. (2011). Oxidative desulfurization of diesel with TBHP/isobutyl aldehyde/air oxidation system. *Applied Energy*, *88*(1), 175–179. doi:10.1016/j.apenergy.2010.08.003

Gyanesh, P. Khare, R., D., Engelbert, & Cass, B. W. (2000). US Patents 6056871. U. Patents.

Han Y.-Z., & Leyshon D. W. (2005). U.S Patent No 2005109677.

Hao, L., Benxian, S., & Zhou, X. (2005). An Improved Desulfurization Process Based on H2O2/Formic Acid Oxidation System Followed by Liquid-Liquid Extraction. Part 1. Coker Gas Oil Feedstocks. *Petroleum Science and Technology*, *23*(7-8), 991–999. doi:10.1081/LFT-200034498

Harrison, R. M. (2007). *Principles of Environmental Chemistry*. RSC Publishing. doi:10.1039/9781847557780

He, L., Li, H., Zhu, W., Guo, J., Jiang, X., Lu, J., & Yan, Y. (2008). Deep Oxidative Desulfurization of Fuels Using Peroxophosphomolybdate Catalysts in Ionic Liquids. *Industrial & Engineering Chemistry Research*, *47*(18), 6890–6895. doi:10.1021/ie800857a

Heinrich G, & S, K. (2001). Hydrotreating. In Leprince, P., (Ed), *Petroleum Refining Conversion Processes,* (Vol. 3). Paris: Technip.

Hernández-Maldonado, A. J., Yang, F. H., Qi, G., & Yang, R. T. (2005). Desulfurization of transportation fuels by π-complexation sorbents: Cu(I)-, Ni(II)-, and Zn(II)-zeolites. *Applied Catalysis B: Environmental*, *56*(1–2), 111–126. doi:10.1016/j.apcatb.2004.06.023

Hernández-Maldonado, A. J., & Yang, R. T. (2002). Desulfurization of Liquid Fuels by Adsorption via π Complexation with Cu(I)−Y and Ag−Y Zeolites. *Industrial & Engineering Chemistry Research*, *42*(1), 123–129. doi:10.1021/ie020728j

Hernández-Maldonado, A. J., & Yang, R. T. (2004a). Denitrogenation of Transportation Fuels by Zeolites at Ambient Temperature and Pressure. *Angewandte Chemie International Edition*, *43*(8), 1004–1006. doi:10.1002/anie.200353162 PMID:14966892

Hernández-Maldonado, A. J., & Yang, R. T. (2004b). New sorbents for desulfurization of diesel fuels via π-complexation. *AIChE Journal. American Institute of Chemical Engineers*, *50*(4), 791–801. doi:10.1002/aic.10074

Hirai, T., Ogawa, K., & Komasawa, I. (1996). *Desulfurization process for dibenzothiophenes from light oil by photochemical reaction and liquid-liquid extraction. Journal Name: Industrial and Engineering Chemistry Research; Journal Volume: 35; Journal Issue: 2; Other Information: PBD: Feb 1996, Medium: X* (pp. 586–589). Size.

Hirai, T., Shiraishi, Y., Ogawa, K., & Komasawa, I. (1997). Effect of Photosensitizer and Hydrogen Peroxide on Desulfurization of Light Oil by Photochemical Reaction and Liquid−Liquid Extraction. *Industrial & Engineering Chemistry Research*, *36*(3), 530–533. doi:10.1021/ie960576q

Hobson, G. D., & Petroleum, I. o. (1984). *Modern petroleum technology*. Wiley.

Horii, Y., Onuki, H., Doi, S., Mori, T., Takatori, T., Sato, H., & Ookuro, T. & Sugawara., T. (1996). US Patents 5494572. U. Patents.

Hua, R., Li, Y., Liu, W., Zheng, J., Wei, H., & Wang, J. et al. (2003). Determination of sulfur-containing compounds in diesel oils by comprehensive two-dimensional gas chromatography with a sulfur chemiluminescence detector. *Journal of Chromatography. A*, *1019*(1–2), 101–109. doi:10.1016/j.chroma.2003.08.048 PMID:14650608

Irvine, R. L., & Benson, B. A., & M, V. D. (1999, 21–23 March 1999). *IRVAD™ Process—low cost breakthrough for low sulphur gasoline - paper AM-99-42* Paper presented at the NPRA 1999 Annual Meeting, San Antonio, Texas.

Ishihara, A., Wang, D., Dumeignil, F., Amano, H., Qian, E. W., & Kabe, T. (2005). Oxidative desulfurization and denitrogenation of a light gas oil using an oxidation/adsorption continuous flow process. *Applied Catalysis A, General*, *279*(1–2), 279–287. doi:10.1016/j.apcata.2004.10.037

Javadli, R., & Klerk, A. (2012). Desulfurization of heavy oil. *Applied Petrochemical Research*, *1*(1-4), 3–19. doi:10.1007/s13203-012-0006-6

Jian-long, WANG, & Di-shun, ZHAO, & ZHOU-Er-peng. (2008). Application of Bronsted acidic ionic liquid in extraction and oxidation of dibenzothiophene. [Petroleum Processing Section]. *Acta Petrolei Sinica*, *24*(2), 227–231.

Jiang, X., Li, H., Zhu, W., He, L., Shu, H., & Lu, J. (2009). Deep desulfurization of fuels catalyzed by surfactant-type decatungstates using H2O2 as oxidant. *Fuel*, *88*(3), 431–436. doi:10.1016/j.fuel.2008.11.010

Jiang, Z., Lü, H., Zhang, Y., & Li, C. (2011). Oxidative Desulfurization of Fuel Oils. *Chinese Journal of Catalysis*, *32*(5), 707–715. doi:10.1016/S1872-2067(10)60246-X

Karas, L., Grey, R. & Lynch, M. (2008). US Patent 2008047875.

Karas, L. J., Han, Y.-Z., & Leyshon, D. W. (2004). United States Patent No.

Kaufman, E., Harkins, J., & Borole, A. (1998). Comparison of batchstirred and electrospray reactors for biodesulfurization of dibenzothiophene in crude oil and hydrocarbon feedstocks. *Applied Biochemistry and Biotechnology*, *73*(2-3), 127–144. doi:10.1007/BF02785650

Kent, J. A. (2010). *Kent and Riegel's Handbook of Industrial Chemistry and Biotechnology* (Vol. 1). Springer.

Kilbane, J. J. (1989). Desulfurization of coal: The microbial solution. *Trends in Biotechnology*, *7*(4), 97–101. doi:10.1016/0167-7799(89)90007-3

Kim, B. H., Kim, H. Y., Kim, T. S., & Park, D. H. (1995). Selectivity of desulfurization activity of Desulfovibrio desulfuricans M6 on different petroleum products. *Fuel Processing Technology*, *43*(1), 87–94. doi:10.1016/0378-3820(95)00010-5

Kim, Y., Yeong, H., Kim, T. S., & Kim, B. H. (1990). Degradation of ogranic sulfur compounds and the reduction of dibenzothiophene to biphenyl and hydrogen sulfide by Desulfovibrio desulfuricans M6. *Biotechnology Letters*, *12*(10), 761–764. doi:10.1007/BF01024736

Kirimura, K., Furuya, T., Sato, R., Ishii, Y., Kino, K., & Usami, S. (2002). Biodesulfurization of naphthothiophene and benzothiophene through selective cleavage of carbon-sulfur bonds by Rhodococcus sp. strain WU-K2R. *Applied and Environmental Microbiology*, *68*(8), 3867–3872. doi:10.1128/AEM.68.8.3867-3872.2002 PMID:12147483

Knudsen, K. G., Cooper, B. H., & Topsoe, H. (1999). Catalyst and process technologies for ultra low sulfur diesel. *Applied Catalysis A, General*, *189*(2), 205–215. doi:10.1016/S0926-860X(99)00277-X

Kocal, J. A. (2001). US Patent 6277271.

Kocal, J. A., & Branvold, T. A. (2002). US Patent 6368495.

Komintarachat, C., & Trakarnpruk, W. (2006). Oxidative Desulfurization Using Polyoxometalates. *Industrial & Engineering Chemistry Research*, *45*(6), 1853–1856. doi:10.1021/ie051199x

Krishna, R., Colyar, J. J., Kressmann, S., Boyer, C., Schweitzer, J. M., & Viguie, J. C. (2000). Improvements of Ebullated-Bed Technology for Upgrading Heavy Oils. *Oil & Gas Science and Technology - Rev. IFP*, *55*(4), 397–406.

Lanju, C. H. E. N. (2007). Oxidative desulfurization of simulated gasoline over metal oxide-loaded molecular sieve. *Chinese Journal of Chemical Engineering*, *15*(4), 520–523. doi:10.1016/S1004-9541(07)60118-9

Largeteau, D., Ross, J., Laborde, M., & Wisdom Axens, L. (2012). Challenges and opportunities of 10 ppm sulphur gasoline: Part 2. *Petroleum Technology Quarterly*, *17*(5), 25.

Li, B., Xu, D., Jiang, Z., Zhang, X., Liu, W., & Dong, X. (2008). Pervaporation performance of PDMS-Ni^{2+}Y zeolite hybrid membranes in the desulfurization of gasoline. *Journal of Membrane Science*, *322*(2), 293–301. doi:10.1016/j.memsci.2008.06.015

Li, C., Gao, J., Jiang, Z., Wang, S., Lu, H., Yang, Y., & Jing, F. (2005). Selective Oxidations on Recoverable Catalysts Assembled in Emulsions. *Topics in Catalysis*, *35*(1-2), 169–175. doi:10.1007/s11244-005-3821-5

Li, C., Jiang, Z., Gao, J., Yang, Y., Wang, S., & Tian, F. et al. (2004). Ultra-Deep Desulfurization of Diesel: Oxidation with a Recoverable Catalyst Assembled in Emulsion. *Chemistry (Weinheim an der Bergstrasse, Germany)*, *10*(9), 2277–2280. doi:10.1002/chem.200305679 PMID:15112217

Li, F. T., Liu, R. H., Jin Hhua, W., Zhao, D. S., Sun, Z. M., & Liu, Y. (2009). Desulfurization of dibenzothiophene by chemical oxidation and solvent extraction with $Me_3NCH_2C_6H_5Cl.2ZnCl_2$ ionic liquid. *Green Chemistry*, *11*(6), 883–888. doi:10.1039/b815575e

Li, H., He, L., Lu, J., Zhu, W., Jiang, X., Wang, Y., & Yan, Y. (2009). Deep Oxidative Desulfurization of Fuels Catalyzed by Phosphotungstic Acid in Ionic Liquids at Room Temperature. *Energy & Fuels*, *23*(3), 1354–1357. doi:10.1021/ef800797n

Li, H., Jiang, X., Zhu, W., Lu, J., Shu, H., & Yan, Y. (2009). Deep Oxidative Desulfurization of Fuel Oils Catalyzed by Decatungstates in the Ionic Liquid of [Bmim] PF6. *Industrial & Engineering Chemistry Research*, *48*(19), 9034–9039. doi:10.1021/ie900754f

Li, H., Zhu, W., Wang, Y., Zhang, J., Lu, J., & Yan, Y. (2009). Deep oxidative desulfurization of fuels in redox ionic liquids based on iron chloride. *Green Chemistry*, *11*(6), 810–815. doi:10.1039/b901127g

Li, M. Z., Squires, C. H., Monticello, D. J., & Childs, J. D. (1996). Genetic analysis of the dsz promoter and associated regulatory regions of Rhodococcus erythropolis IGTS8. *Journal of Bacteriology*, *178*(22), 6409–6418. PMID:8932295

Lin, L., Kong, Y., Wang, G., Qu, H., Yang, J., & Shi, D. (2006). Selection and crosslinking modification of membrane material for FCC gasoline desulfurization. *Journal of Membrane Science*, *285*(1–2), 144–151. doi:10.1016/j.memsci.2006.08.016

Lin, L., Kong, Y., Xie, K., Lu, F., Liu, R., & Guo, L. et al. (2008). Polyethylene glycol/polyurethane blend membranes for gasoline desulphurization by pervaporation technique. *Separation and Purification Technology*, *61*(3), 293–300. doi:10.1016/j.seppur.2007.10.020

Lin, L., Zhang, Y., & Kong, Y. (2009). Recent advances in sulfur removal from gasoline by pervaporation. *Fuel*, *88*(10), 1799–1809. doi:10.1016/j.fuel.2009.03.031

Linguist,, L.K., & Pacheco, M. (1999). Enzyme-based diesel desulfurization process offers energy, CO_2 advantages. *Oil & Gas Journal*, *97*(8), 45–48.

Lizama, H., Wilkins, L., & Scott, T. (1995). Dibenzothiophene sulfur can serve as the sole electron acceptor during growth by sulfate-reducing bacteria. *Biotechnology Letters*, *17*(1), 113–116. doi:10.1007/BF00134206

Lo, W. H., Yang, H. Y., & Wei, G.-T. (2003). One-pot desulfurization of light oils by chemical oxidation and solvent extraction with room temperature ionic liquids. *Green Chemistry*, *5*(5), 639–642. doi:10.1039/b305993f

Long, D. L., Burkholder, E., & Cronin, L. (2007). Polyoxometalate clusters, nanostructures and materials: From self assembly to designer materials and devices. *Chemical Society Reviews*, *36*(1), 105–121. doi:10.1039/B502666K PMID:17173149

Lü, H., Gao, J., Jiang, Z., Jing, F., Yang, Y., Wang, G., & Li, C. (2006). Ultra-deep desulfurization of diesel by selective oxidation with $[C_{18}H_{37}N(CH_3)_3]4[H_2NaPW_{10}O_{36}]$ catalyst assembled in emulsion droplets. *Journal of Catalysis*, *239*(2), 369–375. doi:10.1016/j.jcat.2006.01.025

Lu, H., Gao, J., Jiang, Z., Yang, Y., Song, B., & Li, C. (2007). Oxidative desulfurization of dibenzothiophene with molecular oxygen using emulsion catalysis. *Chemical Communications*, *0*(2), 150–152. doi:10.1039/B610504A PMID:17180229

Lu, H., Zhang, Y., Jiang, Z., & Li, C. (2010). Aerobic oxidative desulfurization of benzothiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene using an Anderson-type catalyst $[(C_{18}H_{37})_2N(CH_3)_2]5$ [IMo6O24]. *Green Chemistry*, *12*(11), 1954–1958. doi:10.1039/c0gc00271b

Lu, L., Cheng, S., Gao, J., Gao, G., & He, M.-y. (2006). Deep Oxidative Desulfurization of Fuels Catalyzed by Ionic Liquid in the Presence of H_2O_2. *Energy & Fuels*, *21*(1), 383–384. doi:10.1021/ef060345o

Lu, Y., Wang, Y., Gao, L., Chen, J., Mao, J., Xue, Q., Liu, Y., Wu, H., Gao, G., & He, M. (2008). Aerobic oxidative desulfurization: a promising approach for sulfur removal from fuels. *Chem Sus Chem., 1*(4), 302-306. doi: 3.10.1002/cssc.200700144

Ma, X., Sakanishi, K., & Mochida, I. (1994). Hydrodesulfurization reactivities of various sulfur compounds in diesel fuel. *Industrial & Engineering Chemistry Research*, *33*(2), 218–222. doi:10.1021/ie00026a007

Ma, X., Velu, S., Kim, J. H., & Song, C. (2005). Deep desulfurization of gasoline by selective adsorption over solid adsorbents and impact of analytical methods on ppm-level sulfur quantification for fuel cell applications. *Applied Catalysis B: Environmental*, *56*(1–2), 137–147. doi:10.1016/j.apcatb.2004.08.013

Ma, X., Zhou, A., & Song, C. (2007). A novel method for oxidative desulfurization of liquid hydrocarbon fuels based on catalytic oxidation using molecular oxygen coupled with selective adsorption. *Catalysis Today*, *123*(1–4), 276–284. doi:10.1016/j.cattod.2007.02.036

Magyar, S., Hancsók, J., & Kalló, D. (2005). Hydrodesulfurization and hydroconversion of heavy FCC gasoline on PtPd/H-USY zeolite. *Fuel Processing Technology*, *86*(11), 1151–1164. doi:10.1016/j.fuproc.2004.11.012

Manahan, S. E. (2010). *Environmental Chemistry* (7th ed.). Taylor & Francis.

Martin, R. L., & Grant, J. A. (1965). Determination of Sulfur-Compound Distributions in Petroleum Samples by Gas Chromatography with a Coulometric Detector. *Analytical Chemistry*, *37*(6), 644–649. doi:10.1021/ac60225a005

Mayo S, Plantenga F, Leliveld B, & A., M. Y. (2001, March 18–20). Paper presented at the National Petrochemical & Refiners Association (NPRA) annual meeting, AM-01-09, New Orleans.

McFarland, B. L. (1999). Biodesulf urization. *Current Opinion in Microbiology*, *2*(3), 257–264. doi:10.1016/S1369-5274(99)80045-9 PMID:10383871

McKetta, J. J. (1992). *Petroleum processing hand book*. Taylor & Francis Inc.

McKinley, S. G., & Angelici, R. J. (2003). Deep desulfurization by selective adsorption of dibenzothiophenes on Ag^+/SBA-15 and Ag^+/SiO_2. *Chemical Communications*, (20): 2620–2621. doi:10.1039/b309249f PMID:14594310

Mei, H., Mei, B. W., & Yen, T. F. (2003). A new method for obtaining ultra-low sulfur diesel fuel via ultrasound assisted oxidative desulfurization☆. *Fuel*, *82*(4), 405–414. doi:10.1016/S0016-2361(02)00318-6

Meille, V., Schulz, E., Vrinat, M., & Lemaire, M. (1998). A new route towards deep desulfurization: Selective charge transfer complex formation. *Chemical Communications*, *0*(3), 305–306. doi:10.1039/a706877h

Mikhail, S., Zaki, T., & Khalil, L. (2002). Desulfurization by an economically adsorption technique. *Applied Catalysis A, General*, *227*(1–2), 265–278. doi:10.1016/S0926-860X(01)00937-1

Milenkovic, A., Schulz, E., Meille, V., Loffreda, D., Forissier, M., & Vrinat, M. et al. (1999). Selective Elimination of Alkyldibenzothiophenes from Gas Oil by Formation of Insoluble Charge-Transfer Complexes. *Energy & Fuels*, *13*(4), 881–887. doi:10.1021/ef980262a

Minhas, B. S., & Chuba, M. R. & Saxton., R. J. (2004). Patent US 0026321 A1.

Minhas, B. S., & Saxton, R. J. (2002). Patent WO 02/064529 A1.

Mohebali, G., & Ball, A. S. (2008). Biocatalytic desulfurization (BDS) of petrodiesel fuels. *Microbiology*, *154*(8), 2169–2183. doi:10.1099/mic.0.2008/017608-0 PMID:18667551

Morris, R. (1989). *Acid Toxicity and Aquatic Animals*. Cambridge University Press. doi:10.1017/CBO9780511983344

Murata, S., Murata, K., Kidena, K., & Nomura, M. (2003). A Novel Oxidative Desulfurization System for Diesel Fuels with Molecular Oxygen in the Presence of Cobalt Catalysts and Aldehydes. *Energy & Fuels*, *18*(1), 116–121. doi:10.1021/ef034001z

Nehlsen, J. P., Benziger, J. B., & Kevrekidis, I. G. (2003). Removal of Alkanethiols from a Hydrocarbon Mixture by a Heterogeneous Reaction with Metal Oxides. *Industrial & Engineering Chemistry Research*, *42*(26), 6919–6923. doi:10.1021/ie030665k

Nehlsen, J. P., Benziger, J. B., & Kevrekidis, I. G. (2004). A Process for the Removal of Thiols from a Hydrocarbon Stream by a Heterogeneous Reaction with Lead Oxide. *Energy & Fuels*, *18*(3), 721–726. doi:10.1021/ef034064h

Nie, Y., Li, C.-X., & Wang, Z.-H. (2007). Extractive Desulfurization of Fuel Oil Using Alkylimidazole and Its Mixture with Dialkylphosphate Ionic Liquids. *Industrial & Engineering Chemistry Research*, *46*(15), 5108–5112. doi:10.1021/ie070385v

Nylén, U., Delgado, J. F., Järås, S., & Boutonnet, M. (2004). Characterization of alkylated aromatic sulphur compounds in light cycle oil from hydrotreated vacuum gas oil using GC-SCD. *Fuel Processing Technology*, *86*(2), 223–234. doi:10.1016/j.fuproc.2004.03.001

Oldfield, C., Pogrebinsky, O., Simmonds, J., Olson, E. S., & Kulpa, C. F. (1997). Elucidation of the metabolic pathway for dibenzothiophene desulphurization by Rhodococcus sp. strain IGTS8 (ATCC 53968). *Microbiology*, *143*(9), 2961–2973. doi:10.1099/00221287-143-9-2961 PMID:9308179

Olguin, E., & Vrinat, M., Ceden˜o, L., Ramirez, J., Borque, M., & López-Agudo, A. (. (1997). The use of TiO_2-Al_2O_3 binary oxides as supports for Mo-based catalysts in hydrodesulfurization of thiophene and dibenzothiophene. *Applied Catalysis A, General*, *165*(1–2), 1–13. doi:10.1016/S0926-860X(97)00184-1

Otsuki, S., Nonaka, T., Takashima, N., Qian, W., Ishihara, A., Imai, T., & Kabe, T. (2000). Oxidative desulfurization of light gas oil and vacuum gas oil by oxidation and solvent extraction. *Energy & Fuels*, *14*(6), 1232–1239. doi:10.1021/ef000096i

Pacheco, M. A., Lange, E. A., Pienkos, P. T., & Yu, L. Q., R. M., Lin Q, & LK, L. (1999). *Recent advances in biodesulfurization of diesel fuel.* Paper presented at the National Petrochemical and Refiners Association Annual Meeting NPRA AM-99-27, San Antonio, Texas.

Paybarah, A., Bone, R. L., & Corcoran, W. H. (1982). Selective oxidation of dibenzothiophene by peroxybenzoic acid formed in situ. *Industrial & Engineering Chemistry Process Design and Development*, *21*(3), 426–431. doi:10.1021/i200018a014

Pfüller, O., & Walstra, F. P. (2003). Patent No. DE 102 17 469 C1.

Piddington, C. S., Kovacevich, B. R., & Rambosek, J. (1995). Sequence and molecular characterization of a DNA region encoding the dibenzothiophene desulfurization operon of Rhodococcus sp. strain IGTS8. *Applied and Environmental Microbiology*, *61*(2), 468–475. PMID:7574582

Planeta, J., Karasek, P., & Roth, M. (2006). Distribution of sulfur-containing aromatics between [hmim][Tf_2N] and supercritical CO_2: A case study for deep desulfurization of oil refinery streams by extraction with ionic liquids. *Green Chemistry*, *8*(1), 70–77. doi:10.1039/B511778J

Plummer, M. A., & Bonelli, J. R. F. (2002). Patent US 0139713 A1.

Qi, R., Wang, Y., Chen, J., Li, J., & Zhu, S. (2007a). Pervaporative desulfurization of model gasoline with Ag2O-filled PDMS membranes. *Separation and Purification Technology*, *57*(1), 170–175. doi:10.1016/j.seppur.2007.04.001

Qi, R., Wang, Y., Chen, J., Li, J., & Zhu, S. (2007b). Removing thiophenes from n-octane using PDMS–AgY zeolite mixed matrix membranes. *Journal of Membrane Science*, *295*(1–2), 114–120. doi:10.1016/j.memsci.2007.02.047

Qi, R., Wang, Y., Li, J., Zhao, C., & Zhu, S. (2006). Pervaporation separation of alkane/thiophene mixtures with PDMS membrane. *Journal of Membrane Science*, *280*(1–2), 545–552. doi:10.1016/j.memsci.2006.02.008

Qi, R., Zhao, C., Li, J., Wang, Y., & Zhu, S. (2006). Removal of thiophenes from n-octane/thiophene mixtures by pervaporation. *Journal of Membrane Science*, *269*(1–2), 94–100. doi:10.1016/j.memsci.2005.06.022

Rang, H., Kann, J., & Oja, V. (2006). Advances in desulfurization Research of Liquid Fuel *Oil Shale, 23*(2), 164-176.

Reid, E. E. (1966). *Organic Chemistry of Bivalent Sulfur*. Chemical Pub. Co.

Robert, C. S. (2004 Spring). TransFiningTM – a novel process for low sulfur fuels. Proceedings of the American institute of chemical engineers.

Ron, G., Paul, B., & Visnja, G. (2004). Oxidative desulfurization: A new technology for UISD. *Prepr Pap Am Chem Soc. Div Fuel Chem*, *49*(2), 577–579.

Ryan, J. G. (1942). Influence of Sulfur Compounds on Octane Number and Lead Susceptibility of Gasolines. *Industrial & Engineering Chemistry*, *34*(7), 824–832. doi:10.1021/ie50391a013

Saleh, T. A., Siddiqui, M. N., & Al-Arfaj, A. A. (2014). Synthesis of Multiwalled Carbon Nanotubes-Titania Nanomaterial for Desulfurization of Model Fuel. *Journal of Nanomaterials*, *2014*, 6. doi:10.1155/2014/940639

Salem, A. B. S. H. (1994). Naphtha desulfurization by adsorption. *Industrial & Engineering Chemistry Research*, *33*(2), 336–340. doi:10.1021/ie00026a025

Salem, A. B. S. H., & Hamid, H. S. (1997). Removal of sulfur compounds from naphtha solutions using solid adsorbents. *Chemical Engineering & Technology*, *20*(5), 342–347. doi:10.1002/ceat.270200511

Sampanthar, J. T., Xiao, H., Dou, J., Nah, T. Y., Rong, X., & Kwan, W. P. (2006). A novel oxidative desulfurization process to remove refractory sulfur compounds from diesel fuel. *Applied Catalysis B: Environmental*, *63*(1–2), 85–93. doi:10.1016/j.apcatb.2005.09.007

Saxton, R. J., & Minhas, B. S. (2002). Patent WO 02/053682 A1.

Segawa, K., Takahashi, K., & Satoh, S. (2000). Development of new catalysts for deep hydrodesulfurization of gas oil. *Catalysis Today*, *63*(2–4), 123–131. doi:10.1016/S0920-5861(00)00452-1

Shafi, R., & Hutchings, G. J. (2000). Hydrodesulfurization of hindered dibenzothiophenes: An overview. *Catalysis Today*, *59*(3–4), 423–442. doi:10.1016/S0920-5861(00)00308-4

Shakirullah, M., Ahmad, W., Ahmad, I., & Ishaq, M. (2010). Oxidative desulphurization study of gasoline and kerosene: Role of some organic and inorganic oxidants. *Fuel Processing Technology*, *91*(11), 1736–1741. doi:10.1016/j.fuproc.2010.07.014

Shakirullah, M., & Imtiaz Ahmad, M. (2009). Study on the Role of Metal Oxides in Desulphurization of Some Petroleum Fractions. *Journal of the Chilean Chemical Society*, *56*(1), 107–114. doi:10.1002/jccs.200900015

Shang, H., Liu, C., & Wei, F. (2004). FT-IR study of carbon nanotube supported Co-Mo catalysts. *Journal of Natural Gas Chemistry*, *13*(2), 95–100.

Sharipov, A. K., & Nigmatullin, V. R. (2005). Finishing of Diesel Fuel to Remove Sulfur Compounds after Hydrotreating. *Chemistry and Technology of Fuels and Oils*, *41*(4), 309–312. doi:10.1007/s10553-005-0071-y

Sharma, B. K. (2007). *Environmental Chemistry*. Krishna Prakashan.

Sharma, B. K. *Environmental Chemistry*: Krishna Prakashan.

Shi, Q., Pan, N., Liu, P., Chung, K. H., Zhao, S., Zhang, Y., & Xu, C. (2010). Characterization of Sulfur Compounds in Oilsands Bitumen by Methylation Followed by Positive-Ion Electrospray Ionization and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels*, *24*(5), 3014–3019. doi:10.1021/ef9016174

Shiraishi, Y., Hara, H., Hirai, T., & Komasawa, I. (1999). A Deep Desulfurization Process for Light Oil by Photosensitized Oxidation Using a Triplet Photosensitizer and Hydrogen Peroxide in an Oil/Water Two-Phase Liquid−Liquid Extraction System. *Industrial & Engineering Chemistry Research*, *38*(4), 1589–1595. doi:10.1021/ie980651s

Shiraishi, Y., Tachibana, K., Hirai, T., & Komasawa, I. (2002). Desulfurization and Denitrogenation Process for Light Oils Based on Chemical Oxidation followed by Liquid−Liquid Extraction. *Industrial & Engineering Chemistry Research*, *41*(17), 4362–4375. doi:10.1021/ie010618x

Shiraishi, Y., Tachibana, K., Taki, Y., Hirai, T., & Komasawa, I. (2001). A Novel Desulfurization Process for Fuel Oils Based on the Formation and Subsequent Precipitation of S-Alkylsulfonium Salts. 2. Catalytic-Cracked Gasoline. *Industrial & Engineering Chemistry Research*, *40*(4), 1225–1233. doi:10.1021/ie000548e

Shiraishi, Y., Taki, Y., Hirai, T., & Komasawa, I. (2001). A Novel Desulfurization Process for Fuel Oils Based on the Formation and Subsequent Precipitation of S-Alkylsulfonium Salts. 1. Light Oil Feedstocks. *Industrial & Engineering Chemistry Research*, *40*(4), 1213–1224. doi:10.1021/ie000547m

Singh, A., & Agrawal, M. (2007). Acid rain and its ecological consequences. *Journal of Environmental Biology*, *29*(1), 15. PMID:18831326

Sobati, M. A., Dehkordi, A. M., & Shahrokhi, M. (2010). Extraction of Oxidized Sulfur-Containing Compounds of Non-Hydrotreated Gas Oil. *Chemical Engineering & Technology*, *33*(9), 1515–1524. doi:10.1002/ceat.200900622

Song, C., & Ma, X. (2003). New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization. *Applied Catalysis B: Environmental*, *41*(1), 207–238. doi:10.1016/S0926-3373(02)00212-6

Stanislaus, A., Marafi, A., & Rana, M. S. (2010). Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production. *Catalysis Today*, *153*(1–2), 1–68. doi:10.1016/j.cattod.2010.05.011

Sun, M. Z., Zhao, D. Z., & Sun, W. W. (2008). Study on the oxidative desulfurization of diesel fuel with power ultrasound. . *Chemistry and adhension, 30*(2), 65-68.

Sundararaman, R., Ma, X., & Song, C. (2010). Oxidative Desulfurization of Jet and Diesel Fuels Using Hydroperoxide Generated in Situ by Catalytic Air Oxidation. *Industrial & Engineering Chemistry Research*, *49*(12), 5561–5568. doi:10.1021/ie901812r

Tam, P. S., Kittrell, J. R., & Eldridge, J. W. (1990a). Desulfurization of fuel oil by oxidation and extraction. 1. Enhancement of extraction oil yield. *Industrial & Engineering Chemistry Research*, *29*(3), 321–324. doi:10.1021/ie00099a002

Tam, P. S., Kittrell, J. R., & Eldridge, J. W. (1990b). Desulfurization of fuel oil by oxidation and extraction. 2. Kinetic modeling of oxidation reaction. *Industrial & Engineering Chemistry Research*, *29*(3), 324–329. doi:10.1021/ie00099a003

Tang, X.-, Meng, X., & Shi, L. (2011). Desulfurization of Model Gasoline on Modified Bentonite. *Industrial & Engineering Chemistry Research*, *50*(12), 7527–7533. doi:10.1021/ie200475x

Te, M., Fairbridge, C., & Ring, Z. (2001). Oxidation reactivities of dibenzothiophenes in polyoxometalate/H_2O_2 and formic acid/H_2O_2 systems. *Applied Catalysis A, General*, *219*(1–2), 267–280. doi:10.1016/S0926-860X(01)00699-8

Tian, F., Li, C., Jiang, Z., & Weicheng, W. U. (2005). Adsorption of Sulphur containing compounds from FCC Gasoline on Cerium-Exchanged Y Zeolite. *Chinese Journal of Catalysis*, *26*(9), 734–736.

Tiers, G. V. D., & Brostrom, M. L. (2000). Lead mercaptides: Materials useful as powder secondary standards and internal references for calibration of X-ray diffractometers at small and medium angles. *Journal of Applied Crystallography*, *33*(3 Part 2), 915–920. doi:10.1107/S0021889800002806

Varshney, C. K., Garg, J. K., Lauenroth, W. K., & Heitschmidt, R. K. (1979). Plant responses to sulfur dioxide pollution. *CRC Critical Reviews in Environmental Control*, *9*(1), 27–49. doi:10.1080/10643387909381667

Vasudevan, P. T., & Fierro, J. L. G. (1996). A Review of Deep Hydrodesulfurization Catalysis. *Catalysis Reviews*, *38*(2), 161–188. doi:10.1080/01614949608006457

Velu, S., Ma, X., & Song, C. (2003). Selective Adsorption for Removing Sulfur from Jet Fuel over Zeolite-Based Adsorbents. *Industrial & Engineering Chemistry Research*, *42*(21), 5293–5304. doi:10.1021/ie020995p

Venkateshwar Rao, T., Sain, B., Kafola, S., Nautiyal, B. R., Sharma, Y. K., Nanoti, S. M., & Garg, M. O. (2007). Oxidative Desulfurization of HDS Diesel Using the Aldehyde/Molecular Oxygen Oxidation System. *Energy & Fuels*, *21*(6), 3420–3424. doi:10.1021/ef700245g

W., S. (2001, March 18–20). Paper presented at the National Petrochemical & Refiners Association (NPRA) annual meeting, AM-01-29, New Orleans.

Wan, M.-W., & Yen, T.-F. (2007). Enhance efficiency of tetraoctylammonium fluoride applied to ultrasound-assisted oxidative desulfurization (UAOD) process. *Applied Catalysis A, General*, *319*(0), 237–245. doi:10.1016/j.apcata.2006.12.008

Wang, D., Qian, E. W., Amano, H., Okata, K., Ishihara, A., & Kabe, T. (2003). Oxidative desulfurization of fuel oil: Part I. Oxidation of dibenzothiophenes using tert-butyl hydroperoxide. *Applied Catalysis A, General*, *253*(1), 91–99. doi:10.1016/S0926-860X(03)00528-3

Wang, L., Zhao, Z., Li, J., & Chen, C. (2006). Synthesis and characterization of fluorinated polyimides for pervaporation of n-heptane/thiophene mixtures. *European Polymer Journal*, *42*(6), 1266–1272. doi:10.1016/j.eurpolymj.2005.12.013

Wang, R., Zhang, G., & Zhao, H. (2010). Polyoxometalate as effective catalyst for the deep desulfurization of diesel oil. *Catalysis Today*, *149*(1–2), 117–121. doi:10.1016/j.cattod.2009.03.011

Wasserscheid, P., & Jess, A. (2004). Deep desulfurization of oil refinery streams by extraction with ionic liquids. *Green Chemistry*, *6*(7), 316–322. doi:10.1039/b407028c

White, L. S., Wormsbecher, R. F., & Lesemann, M. (2004). Patent US 0211706 A1.

Willey, C., Iwao, M., Castle, R. N., & Lee, M. L. (1981). Determination of sulfur heterocycles in coal liquids and shale oils. *Analytical Chemistry*, *53*(3), 400–407. doi:10.1021/ac00226a006

Wood, A. E., Sheely, C., & Trusty, A. W. (1925). Corrosion Effect of Naphtha Solutions of Sulfur and Sulfur Compounds. *Industrial & Engineering Chemistry*, *17*(8), 798–802. doi:10.1021/ie50188a008

Xu, D., Zhu, W., Li, H., Zhang, J., Zou, F., Shi, H., & Yan, Y. (2009). Oxidative Desulfurization of Fuels Catalyzed by V2O5 in Ionic Liquids at Room Temperature. *Energy & Fuels*, *23*(12), 5929–5933. doi:10.1021/ef900686q

Yan, X.-M., Lei, J.-H., Liu, D., Wu, Y.-C., & Guo, L.-P.Xue-Min Yan. (2007). Oxidative Desulfurization of Diesel Oil Using Mesoporous Phosphotungstic Acid/SiO2 as Catalyst. *Journal of the Chilean Chemical Society*, *54*(4), 911–916. doi:10.1002/jccs.200700131

Yang, L., Li, J., Yuan, X., Shen, J., & Qi, Y. (2007). One step non-hydrodesulfurization of fuel oil: Catalyzed oxidation adsorption desulfurization over HPWA-SBA-15. *Journal of Molecular Catalysis A Chemical*, *262*(1–2), 114–118. doi:10.1016/j.molcata.2006.08.058

Yang, R. T., Hernández-Maldonado, A. J., & Yang, F. H. (2003). Desulfurization of Transportation Fuels with Zeolites Under Ambient Conditions. *Science*, *301*(5629), 79–81. doi:10.1126/science.1085088 PMID:12843388

Yazu, K., Furuya, T., Miki, K., & Ukegawa, K. (2003). Tungstophosphoric Acid-catalyzed Oxidative Desulfurization of Light Oil with Hydrogen Peroxide in a Light Oil/Acetic Acid Biphasic System. *Chemistry Letters*, *32*(10), 920–921. doi:10.1246/cl.2003.920

Yazu, K., Sato, S., Sugimoto, Y., Matsumura, A., & Saito, I. (2007). Tungstophosphoric acid–catalyzed oxidative desulfuriazation of naphtha with hydrogen peroxide in naphtha/acetic acid biphasic system. *Journal of the Japan Petroleum Institute*, *50*(6), 329–334. doi:10.1627/jpi.50.329

Yazu, K., Yamamoto, Y., Furuya, T., Miki, K., & Ukegawa, K. (2001). Oxidation of Dibenzothiophenes in an Organic Biphasic System and Its Application to Oxidative Desulfurization of Light Oil. *Energy & Fuels*, *15*(6), 1535–1536. doi:10.1021/ef0101412

Yin, C., & Xia, D. (2004). A study of the distribution of sulfur compounds in gasoline produced in China. Part 3. Identification of individual sulfides and thiophenes. *Fuel*, *83*(4–5), 433–441. doi:10.1016/j.fuel.2003.09.003

Yin, C., Zhu, G., & Xia, D. (2002). A study of the distribution of sulfur compounds in gasoline fraction produced in China: Part 2. The distribution of sulfur compounds in full-range FCC and RFCC naphthas. *Fuel Processing Technology*, *79*(2), 135–140. doi:10.1016/S0378-3820(02)00108-X

Yu, G., Lu, S., Chen, H., & Zhu, Z. (2005). Diesel fuel desulfurization with hydrogen peroxide promoted by formic acid and catalyzed by activated carbon. *Carbon*, *43*(11), 2285–2294. doi:10.1016/j.carbon.2005.04.008

Zannikos, F., Lois, E., & Stournas, S. (1995). Desulfurization of petroleum fractions by oxidation and solvent extraction. *Fuel Processing Technology*, *42*(1), 35–45. doi:10.1016/0378-3820(94)00104-2

Zhang, Gaofei, & Yu, Fengli, & Wang., R. (2009). Research advances in oxidative desulphurization technologies for the production of low sulfur fuel oils. *Petroleum and Coal*, *51*(3), 196–207.

Zhang, J., Zhu, W., Li, H., Jiang, W., Jiang, Y., Huang, W., & Yan, Y. (2009). Deep oxidative desulfurization of fuels by Fenton-like reagent in ionic liquids. *Green Chemistry*, *11*(11), 1801–1807. doi:10.1039/b914130h

Zhang, S., & Conrad Zhang, Z. (2002). Novel properties of ionic liquids in selective sulfur removal from fuels at room temperature. *Green Chemistry*, *4*(4), 376–379. doi:10.1039/b205170m

Zhang, W., Xu, K., Zhang, Q., Liu, D., Wu, S., Verpoort, F., & Song, X.-M. (2010). Oxidative Desulfurization of Dibenzothiophene Catalyzed by Ionic Liquid [BMIm]HSO4. *Industrial & Engineering Chemistry Research*, *49*(22), 11760–11763. doi:10.1021/ie100957k

Zhang, Y., Lü, H., Wang, L., Zhang, Y., Liu, P., & Han, H. et al. (2010). The oxidation of benzothiophene using the Keggin-type lacunary polytungstophosphate as catalysts in emulsion. *Journal of Molecular Catalysis A Chemical*, *332*(1–2), 59–64. doi:10.1016/j.molcata.2010.08.021

Zhang Y W, Shen J., & D., Y. X. (2005,). .Desulfurization by catalytic oxidation and adsorption over Ti3(PW12O)4. *Petroleum process and petrochemicals,*, *36*(3), 20-24.

Zhao, D., Li, F., Han, J., & Li, H. (2007). Photochemical oxidation of thiophene by O2 in an organic two-phase liquid-liquid extraction system. *Petroleum Chemistry*, *47*(6), 448–451. doi:10.1134/S0965544107060138

Zhao, D.-, Li, F.-, & Sun, Z.-. (2008). Study on photosensitized oxidative desulfurization of thiophene by riboflavin. *Journal of Fuel Chemistry and Technology*, *36*(2), 161–164. doi:10.1016/S1872-5813(08)60016-X

Zhao, D., Wang, J., & Zhou, E. (2007). Oxidative desulfurization of diesel fuel using a Bronsted acid room temperature ionic liquid in the presence of H2O2. *Green Chemistry*, *9*(11), 1219–1222. doi:10.1039/b706574d

Zhao, D., Zhang, J., Wang, J., Liang, W., & Li, H. (2009). Photocatalytic Oxidation Desulfurization of Diesel Oil Using Ti-containing Zeolite. *Petroleum Science and Technology*, *27*(1), 1–11. doi:10.1080/10916460802108314

Zhao, X., Krishnaiah, G., & Cartwright, T. (2004). S-Brane technology brings flexibility to refiners' clean fuel solutions. *NPRA annual meeting*. San Antonio, TX.

Zhou, M., Ma, , & Song, . (2006). Liquid-Phase Adsorption of Multi-Ring Thiophenic Sulfur Compounds on Carbon Materials with Different Surface Properties. *The Journal of Physical Chemistry B*, *110*(10), 4699–4707. doi:10.1021/jp0550210 PMID:16526705

Zhou, X., Gai, H., Wang, J., Zhang, S., Yang, J., & Zhang, S. (2009). Oxidation of Benzothiophenes Using Tert-amyl Hydroperoxide. *Chinese Journal of Chemical Engineering*, *17*(2), 189–194. doi:10.1016/S1004-9541(08)60192-5

Zhou, X., Li, J., Wang, X., Jin, K., & Ma, W. (2009). Oxidative desulfurization of dibenzothiophene based on molecular oxygen and iron phthalocyanine. *Fuel Processing Technology*, *90*(2), 317–323. doi:10.1016/j.fuproc.2008.09.002

Zhou, X., Zhao, C., Yang, J., & Zhang, S. (2006). Catalytic Oxidation of Dibenzothiophene Using Cyclohexanone Peroxide. *Energy & Fuels*, *21*(1), 7–10. doi:10.1021/ef060441p

Zhu, W., Li, H., Jiang, X., Yan, Y., Lu, J., He, L., & Xia, J. (2008). Commercially available molybdic compound-catalyzed ultra-deep desulfurization of fuels in ionic liquids. *Green Chemistry*, *10*(6), 641–646. doi:10.1039/b801185k

Zhu, W., Li, H., Jiang, X., Yan, Y., Lu, J., & Xia, J. (2007). Oxidative Desulfurization of Fuels Catalyzed by Peroxotungsten and Peroxomolybdenum Complexes in Ionic Liquids. *Energy & Fuels*, *21*(5), 2514–2516. doi:10.1021/ef700310r

ADDITIONAL READING

Babich, I. V., & Moulijn, J. A. (2003). Review. *Fuel*, *82*, 607.

Campos-Martin, J. M., Capel-Sanchez, M. C., Perez-Presas, P., & Fierro, J. L. G. (2010). Review. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *85*, 879.

Hobson, G.D. (1984). Modern petroleum technology.

Javadli, R., & Klerk, A. (2012). Review. *Applied Petrochemical Research*, *1*, 3.

McKetta, J. J. (1992). *Petroleum processing hand book*. Taylor & Francis Inc.

Wiley Ma, X., Zhou, A., & Song, C. (2007). Review. *Catalysis Today*, *123*, 276.

KEY TERMS AND DEFINITIONS

Autoxidation: Oxidation reaction which occur in the presence of air or molecular oxygen and results in formation of peroxides and hydroperoxides.

Deep Desulfurization: Desulfurization of feed to less than 50 ppm sulfur.

Flux: The amount of feed components permeating through the unit area of the membrane in unit time.

Hydrogenolysis: Reaction which involve the cleavage of carbon-carbon or carbon-heteroatom bond by interaction with hydrogen.

Ionic Liquid: Salts which exist in liquid state at ordinary pressure and temperature, and exhibit high chemical and thermal stability.

Mutagenic: A chemical or physical agent causing gene mutation.

Photosensitizer: A molecule which can initiate a photochemical reaction, by first exiting itself and then transfer the energy to the desired reactant.

Refractory Sulfur Compounds: Alkylated benzo- and dibenzo thiophenes which are stable to thermal decomposition at high temperature in the HDS process.

Space Velocity: The quantity of feed entering the reactor per unit weight of catalyst in unit time.

Sulfur Enrichment Factor: The ratio of the amount of sulfur in feed to that in permeate.

Ultra Low Level Sulfur: The amount of sulfur ranging from 20-10 ppm.

APPENDIX: LIST OF ABBREVIATIONS

HDS: Hydrodesulfurization
RFCC: Residue fluid catalytic cracked
FCC: Fluidized catalytic cracked
VGO: Vacuum gas oil
CCG: catalytically cracked gasoline
BDS: Biodesulfurization
PVP: Polyvinylpyrrolidone
CTA: Cellulose triacetate
TBPH: Tertiary butylhydroperoxide
EDS: Extractive desulphurization
DMF: Dimethyl formamide
DMSO: Dimethyl sulfoxide
NMP: N-methylpyrolidone
PV: Pervaporation
IL: Ionic liquid
BDS: Biodesulphurization
PEG: Polethyeneglycol
PDMS: Polydimethylsiloxane
PI: Polyimide
ODS: Oxidative desulphurization
4,6-DMDBT: 4,6-Dimethyldibenzothiophene
4-MDBT: 4-methyldibenzothiophene
DBT: Dibenzothiophene
BT: Benzothiophene
Th: Thiophene
POM: Polyoxometalates
TPA: Tungstophosphoric acid
CTAB: Cetyltrimethyl-ammonium bromide
UAOD: Ultrasound assisted Oxidative desulphurization
HBPS: Hydroxybiphenylsulfinate
HBP: Hydroxybiphenyl

Chapter 2

Sulfur and Nitrogen Chemical Speciation in Crude Oils and Related Carbonaceous Materials

Sudipa Mitra-Kirtley
Rose-Hulman Institute of Technology. USA

Oliver C. Mullins
Schlumberger-Doll Research, USA

Andrew E. Pomerantz
Schlumberger-Doll Research, USA

ABSTRACT

This chapter gives an overview of sulfur x-ray absorption near edge spectroscopy (XANES) studies performed on some carbonaceous materials, viz. crude oil and related materials (asphaltenes, kerogens, bitumens, and resins), and coals. Thiophene, sulfide, sulfoxide, sulfone, pyrite, and sulfate are found in varying amounts in these materials. In source rock bitumens, sulfoxide is more abundant than in the kerogens, while within the kerogens, the less aromatic Type I samples show a smaller ratio of thiophenic/sulfidic sulfur than in Type II samples. Petroleum asphaltenes have a similar sulfur chemistry, regardless of the source or the burial depth. Resins and oil fractions retain the polar sulfoxide species of the parent oil similar to the more polar asphaltenes fractions. More aromatic sulfur species also dominate in the more matured coals than in the younger coals. Studies of nitrogen XANES also reveal that aromatic forms of nitrogen prevail in samples with increased aromatic carbon.

INTRODUCTION

Sulfur has been an age old impediment in the processing and utilization of fossil fuels, such as crude oil. The presence of sulfur in crude oil and its by-products can make refining tasks very difficult, as it reacts with catalysts and produces corrosive poisons. Noble metal catalysts used in refining processes form corrosive agents in the presence of sulfur, as sulfur can bond strongly with the catalysts (Ruiz-

DOI: 10.4018/978-1-4666-9545-0.ch002

Figure 1. Sulfur removal from Athabasca bitumen is stored as elemental sulfur in exposed enormous yellow mounds

Guerrero, 2006), and corrode refining equipment (Manning & Thompson, 1991). Sulfur is sometimes found in the form of H_2S in crude oils, and is lethal even at small concentrations (~100 ppm) and is a major concern in creating extreme brittleness in many metals. In addition, burning of fossil fuels with significant amounts of sulfur releases sulfur dioxide into the atmosphere causing environmental hazards (Orr & White, 1990). The presence of sulfur in fuels serves no useful purpose (Orr, 1990), as some of them contain only minor quantities of sulfur and generally removal of sulfur from fuels is a primary objective in processing. Sulfur removal for Athabasca bitumen has led to storage of elemental sulfur in huge yellow mounds as seen in Figure 1.

Sulfur chemistry also gives us a picture of the geochemical environment of the deposition of the source materials for the fossil fuel energy resources (Orr, 1990). Organo-sulfur compounds in crude oils provides information about the formation, migration, and thermal maturity of the oil. (Hughes, 1989; Lin, 1988; Wang, 2005; Radke, 1982). Sulfur content in kerogen and bitumen is an important indicator of how these fractions ultimately produce oil and gas (Pomerantz, 2013; Lewan, 1985, 1998; Seewald, 1998; Sinninghe, 1989, 1990; Gransch, 1974). The presence of sulfur also affects solubility and other characteristics of the important fractions of crude oils, such as asphaltenes (Mitra-Kirtley, 2007).

Sulfur content in crude oils and bitumens ranges from a fraction of a percent to 14% (Orr 1990), making it generally the most abundant element after carbon and hydrogen. The world reserves of sweet crude oils (crude oils with low sulfur content) are becoming more limited as time progresses, making the refining of more sour (high sulfur content) varieties a necessity (Purcell, 2007; Swain, 1998). Atmospheric and vacuum bottom residues are increasingly converted to lighter products (Purcell, 2007), and desulfurization of these reserves is becoming increasingly favored.

Sulfur in coal also reveals a wealth of information about the depositional environment. Much of the sulfur in low sulfur coals is derived from the deposited plant material. The presence of a brackish environment results in the presence of sulfates; these sulfates can get reduced to H_2S by microbial action, and high sulfur coals derive most of their sulfur from this environment. (Calkins, 1994). Sulfur in coal has also been a major concern in the coal utilization, in particular for electric power generation. The familiar "acid rain" environmental problem is primarily due to production of sulfur oxides in coal combustion. As such, understanding sulfur chemistry in coal has been critical in optimization of resource utilization. Similar methods of sulfur chemical speciation apply to a host of carbonaceous materials such as crude oil, bitumen, kerogen, coal, and related products. (Mitra-Kirtley, 2007; Huffman, 1991; Mullins, 1993; Wiltfong, 2005; Waldo, 1992).

Other light heteroatoms are also of interest in carbonaceous materials, particularly nitrogen and oxygen. In crude oil, many of the sulfur containing moieties are relatively nonpolar, with the exception of occasional occurrence of sulfoxides. In contrast, oxygen and nitrogen often appear in chemical moieties with moderate or large electric dipoles. Nitrogen in fossil fuels can be oxidized in combustion yielding nitric oxide, another major component of acid rain. Nitrogen containing hydrocarbons are also known to be responsible for forming coke on the catalyst surface, making the catalysts less efficient (Rodgers, 2002). In addition, both nitrogen and oxygen containing organics tend to be polar impacting interfacial interactions, an important concern for crude oil production. In particular, rock wettability, thus oil recovery in reservoirs, is dependent on interfacially active components in crude oil. Nitrogen and oxygen can also mediate stronger intermolecular interactions of the heavy ends of crude oil, the asphaltenes, and thereby can impact processing of such resources. Also, naphthenic acids, which are released into wastewaters, can be harmful during petroleum refinery processes (Rodgers, 2002; Kane, 2002; Piehl, 1987).

SULFUR GEOCHEMISTRY IN SOME CARBONACEOUS MATERIALS

Kerogen is the insoluble organic matter in sediments, and bitumen is the solvent extractable organic fraction of sediment. Both kerogen and bitumen are responsible for petroleum generation via diagenesis and catagenesis processes, and the majority of oil production is from kerogen (Orr & Damaste, 1990). Under rapid heating condition, bitumen can serve as an intermediate in the transformation from kerogen to oil and gas (Miknis, 1995).

Sulfur in kerogen and bitumen has attracted much recent attention because of the revolution in oil and gas production from unconventionals (Alexander, 2011). Sulfur geochemistry is relevant to unconventional resources because sulfur impacts many of the processes relevant to petroleum generation and production. Petroleum generation occurs mainly by unimolecular decomposition of larger molecular weight kerogen and bitumen molecules into smaller molecular weight oil and gas. The activation energy of those reactions depends on the composition of the kerogen and bitumen. Sulfide functional groups (sulfur bonded to aliphatic carbon) represent one of the weakest chemical bonds found in kerogen, and the presence of that group can lower the activation energy required to generate petroleum (Lewan, 1998). As a result, kerogens with high sulfur contents (assuming the sulfur is present as sulfides) generate oil and gas at relatively low levels of maturity (Dembicki, 2009).

The recovery of oil and gas from unconventional resources is also impacted by adsorption. Some fraction of the hydrocarbons are physically adsorbed to the rock surface, preventing their released until the reservoir pressure is low (loucks, 2009; Valenza, 2013). Hydrocarbon adsorption is typically mitigated by the polarizability interaction, and thiophene functional groups (sulfur bonded to aromatic carbon) can contribute greatly to the polarizability of kerogen.

Hydrocarbon production from unconventional sources occurs after massive hydraulic fracturing. Efficient production therefore requires that the water introduced during the hydraulic fracturing does not interfere with the flow of hydrocarbons in the oil-wet pore system. Sulfoxide functional groups (sulfur double bonded to one oxygen) represent one of the most polar bonds in kerogen, with a dipole moment double that of water. Kerogens and bitumens comprised mostly of hydrophobic carbon and hydrogen can act as naturally occurring surfactants especially if they also contain a hydrophilic sulfoxide group, impacting the subsurface flow of oil and water (Pomerantz, 2014).

The introduction of sulfur in crude oils can have a number of origins. Sulfurization in the organic matter may happen at different stages of geological progression. Most of the sulfur incorporation can occur at an earlier stage, and the extent of sulfurization also depends on the state of maturation (Grant & Posthuma, 1973; Orr, 1990). Dissolved H_2S and elemental sulfur account for only a small but important fraction of the total sulfur in crude oils, as most of the sulfur is organic in nature, with the highest concentration of organic sulfur found in high molecular weight compounds (Tissot, 1984; Hunt, 1979; Orr, 1975, 1978). Sulfur content in pyrite and sedimentary organic matter is sometimes from H_2S, formed as a result of activities from sulfate reducing bacteria at the surface of water or at shallow depths of sediments rich in organic material (Feux, 1977; Thode, 1965; Krouse, 1977).

Changes in the matured oils depend on other factors such as the degree of migration and reservoir environments (Gransch & Posthuma, 1974).The amount of sulfur in crude oils may depend on the reduction of sulfates by biodegradation in the later stages of maturation (Bailey, 1973, Davis 1967). Nevertheless, it is possible that sulfurization at low temperatures where microbial degradation takes place is not very common (Gransch, 1973). Orr (1990) et al. find that in heavy and asphaltic oils the effect of biodegradation on sulfurization is affected by removal of non-sulfur containing entities rather than addition of sulfur containing compounds.

In recent years heavy oils have been the focus of numerous studies. Heavy oils are often products of extensive biodegradation of lighter oils (Orr, 1990). In addition, heavy oils can form by accumulation of asphaltenes at the base of the oil column by convective currents within the oil (Mullins, 2013). Heavy oils usually have higher sulfur, nitrogen and oxygen content than the lighter kinds. (Purcell, 2007). The sulfur content of the heavier oils is mainly determined from the sulfur content of the un-degraded precursor original oil, with favored removal of non-sulfur components determined by the extent of biodegradation (Orr, 1990) or the extent of asphaltene accumulation (Mullins, 2013; Pomerantz, 2014).

Petroleum usually contains four fractions, viz. saturates, aromatics, resins, and asphaltenes (SARA). Asphaltenes affect the chemical and physical properties of crude oil and also play a significant role in the production, refinement, and transportation processes (Chilingarian, 1978; Bunger, 1981; Speight, 1980; Tissot, 1984). They are defined in terms of their solubility properties. One definition is that asphaltenes are soluble in toluene but insoluble in n-alkanes, such as n-heptane (Pfeiffer, 1950; Sheu, 1995). Resins may be defined as not extractable on an activated alumina column at room temperature in n-heptane and toluene but extractable in a 1/1 (v/v) dichloromethane/methanol solution. The composition of asphaltene molecules and aggregates is described by the Yen-Mullins model (Mullins, 2010, 2012, 2014). Asphaltenes have the appearance of dark friable solids, with a density of about 1.2 g/cm^3 (Akbarzadeh, 2007). They have an average molecular weight of 750 g/mole, with an average of 7 fused aromatic rings generally in a single aromatic core. (Groenzin, 1999, 2000; Pomerantz, 2008, 2009; Sabbah, 2011). The Yen-Mullins model stipulates that in crude oils, asphaltenes can exist as isolated molecules, or in nanoaggregates containing ~6 molecules (Wu, 2014), or clusters containing ~8 nanoaggregates (Mullins, 2013; Dutta Majumdar; 2013; Eyssautier, 2011). Asphaltenes contain a higher heteroatom content than the parent oil, up to 10 wt% (Tissot, 1984; Chilingarian, 1981). The concentration of asphaltene in conventional crude oils varies from 0-30% (Ching, 2010; Mullins 2013), impacted by factors such as maturity (Tissot, 1984; Sheu & Mullins, 1995) and convective currents that concentrate asphaltenes (Mullins, 2013).

Kerogens are generally of higher molecular weight than bitumens. Thermal maturation results in the breaking of the macromolecules typically characteristic in kerogens, resulting in simpler molecules in bitumens (Pomerantz, 2014), making them soluble in some organic solvents. Bitumens in shales are formed before the oil generation, and are found in subsurface environments where, albeit being a reducing environment, oil and organic oxygen are still present (Durand, 1980). The weak carbon-sulfur bonds in kerogens are broken during catagenesis (Lewan, 1998), and the reactive sulfur radicals form sulfoxide groups in the presence of organic oxygen (Pomerantz, 2014) during the formation of bitumens. Similar processes in the laboratory have also resulted in the formation of sulfoxides and sulfones (Lewan, 1997), validating such causes of sulfoxide abundance in the bitumens. Asphaltenes extracted from petroleum, archeological bitumens, and oil seeps have also exhibited large sulfoxide contents (Sarret, 1999; Waldo, 1992). Furthermore, the presence of sulfoxides in bitumens contribute to their solubility properties in polar and polarizable solvents. It is also noteworthy that bitumens act as surfactants, in part as a result of the polar sulfoxide groups; this interfacial activity can influence the flow of hydrocarbons in hydraulically fractured shales. Pyrite and sulfate are also often associated with kerogens due to their acid resistive character, and these minerals can appear in S XANES spectra.

When higher-order plants comprise much of the deposited sediments, then during early diagenesis the transformation usually leads to the formation of peat and brown coal (Killops, 1993). In peat bogs the humic substances transform into humic coals, the deeper layers preserving more of the organic material. With increased diagenesis, less of the cellulose and lignin from the plants are preserved in the peat, increasing the amount of humic substances, which eventually transform into brown coal with a 60-65% of carbon content (Fuchs, 1931). Coals still contain fine grained remains of plant material, called macerals (Teichmuller, 1982), which have distinct physical and chemical properties, and are often characterized by their optical properties. Kerogens are often associated with different coal macerals, and similarities between ratios of H/C and O/C between different kerogen types and coal macerals are observed. Type I kerogens, originating mainly from alginates, particularly lacustrine, in low oxygen environments, are akin to liptinite coal macerals. Type II kerogens primarily originate in marine environments and contain cutinite, sporinite, resinite, and liptinite, all familiar in coal petrography. Type III kerogens originate primarily from vascular plants and are deficient in lipids and waxy material. Type III kerogen has macerals similar to vitrinite coal macerals; this type of kerogen is less likely to produce oil than Types I and II kerogens. High sulfur brown coals have S/C ratios of greater than 0.04, and low (~1.00) H/C and high (>0.20) O/C ratios. With increased thermal and chemical maturation, coals undergo changes in coal ranks, and ultimately can result in the formation of anthracite (Killops, 1993; Tissot, 1984). The increase in coal rank is characterized by an increase in carbon content and a decrease in oxygen content.

HETEROATOM CHARACTERIZATION IN FOSSIL FUELS

Researchers in the fossil fuel field have performed numerous studies to characterize sulfur chemical forms in petroleum, and many review articles have been published on the topic (Dean, 1967; Drushel, 1970; Mehmet, 1971; Gal'pern, 1971). X-ray absorption Near-Edge Structure (XANES) spectroscopy with synchrotron radiation has been very successful in determining the different chemical structures of various solid and liquid phase carbonaceous materials in a non-destructive manner, even when the materials are insoluble in organic solvents and difficult for chemical characterization. This chapter explains some of the various studies that have been performed on these materials. (Mitra-Kirtley, 1993, 1998, 2007; Mullins, 1993; Pomerantz, 2013, 2014; Huffman, 1991; George, 1989). Among other characterization techniques, gas chromatography has been used to separate sulfur compounds in petroleum (Martin, 1965; Garcia, 2002; Depauw, 1997; Stumpf, 1998). Infra-red (IR) techniques have been successful in characterizing chemical forms of oxygen in asphaltene fractions in crude oils (Chiilingarian, 1978; Tissot, 1984). Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) methodology has been successful at analyzing petroleum at the molecular level (Marshall, 2003, 2008; Rodgers, 2005; McLafferty, 2008; Shi, 2010). Electrospray Ionization (ESI) FT-ICR-MS has been used to analyze crude oil components (Purcell, 2007; Hughey, 2002; Wu, 2003; Mueller, 2005) including those components that contain sulfur (Purcell, 2007; Hughey, 2002; Wu, 2003).

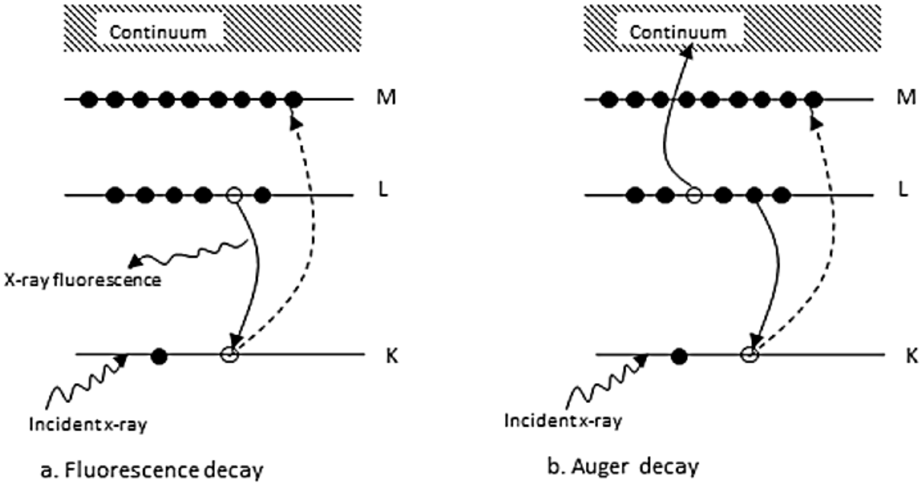
Sulfur characterization of humic substances helps in the understanding of the complex processes of kerogen formation and conversion into oil (Vairavamurthy, 1997; Xia, 1998). Humic acids are regarded as important precursors in the formation of kerogen (Welte, 1974), and it is interesting to follow the chemistry of sulfur from humic substances to the formation of kerogen. Sulfur XANES studies on humic substances have shown that the sulfur content is mainly in many forms, such as sulfide/thiol, sulfoxide, sulfonate, sulfate, and thiophene (Xia, 1998). A separate study found that humic substances have oxidized forms such as sulfonates and reduced forms such as sulfides (Vairavamurthy, 1997). The reduced forms are detected in the layers closer to the surface of the organic matter, and the thiophenic sulfur that is found mostly in deeper layers is a result of increased diagenesis of the organic matter (Vairavamurthy, 1997; Eglington, 1994; Alzenshtat, 1995). While the sulfides may have been produced in these samples by geochemical processes, it is possible that the ester bonded sulfates have been present in the organic matter of the source as a result of bacterial activity.

X-RAY ABSORPTION NEAR EDGE SPECTROSCOPY (XANES)

X-ray Absorption Near-Edge Spectroscopy, or XANES, is a direct, non-destructive, element-specific analysis tool, and successfully identifies the different chemical species of the element. This method is effective even when the element in question is present in very small (in the order of ppm) quantities, irrespective of whether the sample is in a solid or a liquid phase. This method is therefore particularly preferred for identifying chemical structures of elements in complex carbonaceous systems where the element is hard to detect by other characterization techniques. XANES methodology has been very successful in determining heteroatom chemical structures, particularly of sulfur and nitrogen, in many fossil fuel samples. Sulfur XANES methodology has been employed in the study of kerogens (Wiltfong, 2005), bitumens (Pomerantz, 2013; Kasrai, 1994), asphaltenes (George, 1989; Mitra-Kirtley, 1998; Waldo, 1992), as well as coals (Huffman, 1991). Nitrogen XANES has also been used for similar purposes on kerogens and bitumens (Mitra-Kirtley, 1993), and coals (Mullins, 1993).

In the XANES process, the core electron of an atom is excited by the incident x-ray photon, which then makes a transition to a higher energy level. In fluorescence detection of XANES, the de-excitation of the atom is accompanied by an electronic transition from a higher energy to fill the vacant hole (Figure 2). In the Auger process of XANES, as one electron de-excites to a lower energy, another electron is ejected to the continuum (Mitra-Kirtley, 2007). In the case of sulfur K-edge XANES, an atomic picture

Figure 2. Fluorescence decay and Auger decay processes



is sufficient to identify the important resonance. A typical sulfur XANES spectrum is characteristic of a narrow, intense signature resonance, or “white line” (Mitra-Kirtley, 2007), which can be explained with an atomic picture in mind, as the 1s→3p electronic transition.

For thin concentrated samples or in dilute thick samples, the fluorescence intensity, I_F, is linearly proportional to the absorption A and, of course, to the incident intensity, I_o. Thus,

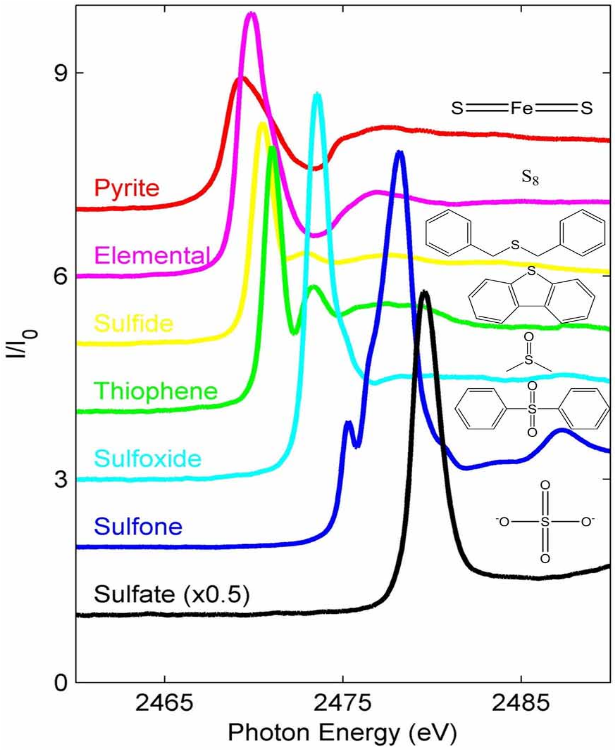
$$\frac{I_F}{I_o} = A\,.$$

The concentration of the element in the sample is, therefore, of large significance, as deviation from the linear behavior in the theory, and consequently distortion in the spectrum, will result if the sample is not diluted enough for the element of study. Details of this theory is given elsewhere (Mitra-Kirtley, 2007; Pomerantz, 2013).

For sulfur K-edge XANES, as the formal oxidation number of sulfur increases in the different chemical structures, the white line peak position shifts to higher energy. The simple atomic picture to explain this is as follows: as the formal oxidation number becomes more positive, the remaining electrons feel a stronger attraction toward the nucleus; thus a higher photon energy is needed to remove the core K-shell electrons. This shift of the white line to higher energy values with increasing formal oxidation numbers is almost linear and spans more than 10 eV. Figure 3 shows a plot of absorption spectra of different sulfur compounds with varying formal oxidation numbers, as a function of incident photon energy.

In the case of nitrogen, the K-edge XANES needs to be explained from a molecular point of view. The white lines can be ascribed to electronic transitions from 1s→π* and 1s→σ*states. Aromatic chemical structures show several π* transitions, while saturated structures show only σ* transitions. Pyridine and pyrrole molecules have the same formal oxidation number for nitrogen; nevertheless, their π*resonances are separated by several electron-volts. The red-shift in the π* transitions in pyridines arises from the fact that the lone pair of electrons in pyridine does not take part in the aromatic bonding, giving the electronegative nitrogen a partial negative charge. In contrast, in pyrrole, the lone pair of electrons on

Figure 3. Sulfur K-edge XANES plot of different chemical structures; as the formal oxidation number of sulfur increases, the 1s→3p peak moves to higher photon energy, almost in a linear fashion.
(Pomerantz, 2014).



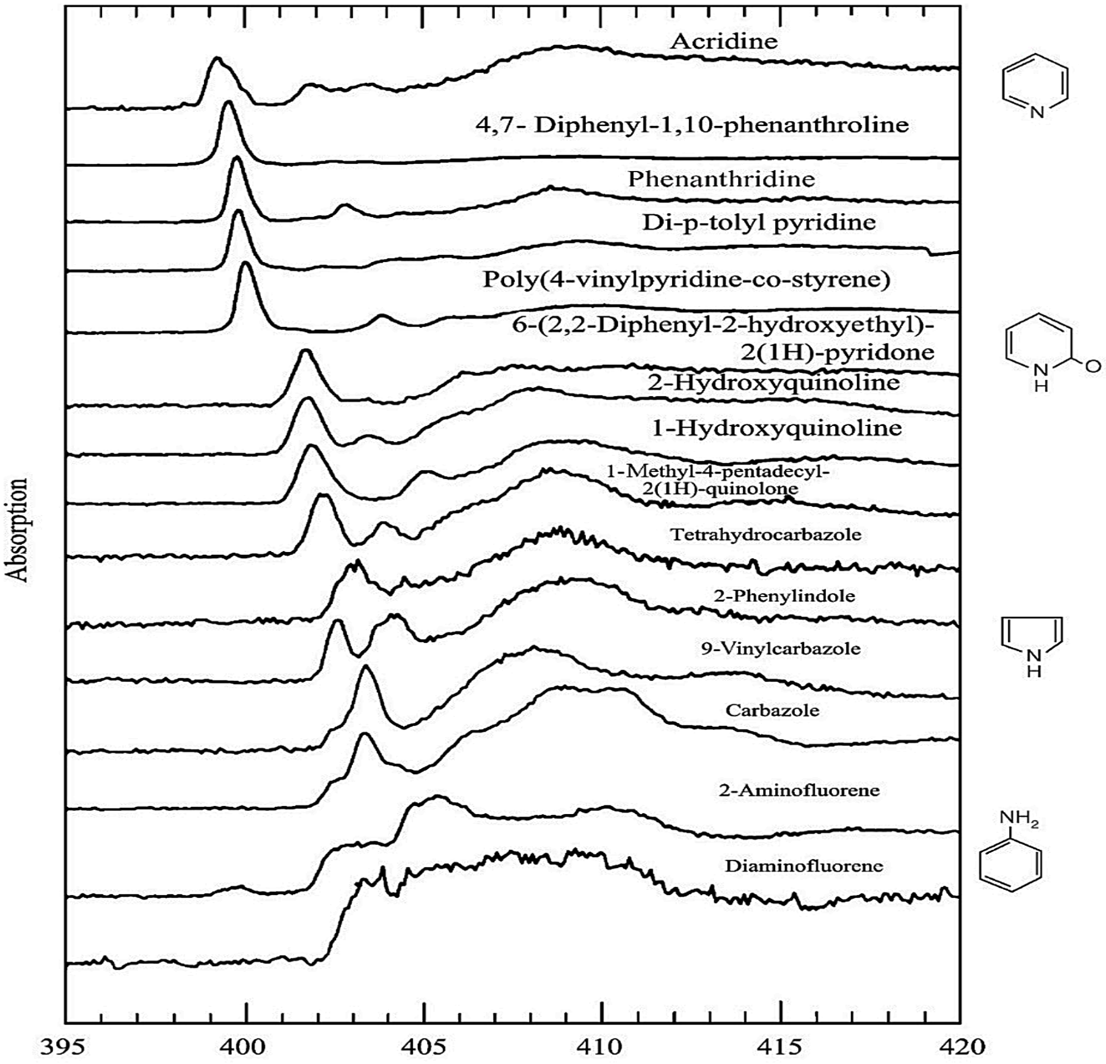
nitrogen both contribute to the aromatic sextet; the five-fold symmetry thereby yielding a partial positive charge on the nitrogen causing a blue shift of the white line. Details of these studies are given elsewhere (Mitra-Kirtley, 1993). Figure 4 shows the distinct energy positions of the white line features of pyridines, pyrroles, and aromatic amines.

XANES EXPERIMENTAL DETAILS

XANES methodology is very powerful when the x-ray source is a synchrotron radiation source. In a synchrotron radiation facility, electrons are accelerated through curved trajectories at relativistic speeds. The resulting electromagnetic radiation is focused in the forward direction, with very intense photon flux. All the XANES studies described here that have been performed by the author(s), have been obtained from National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), and from Advanced Photon Source (APS) at Argonne National Laboratory (ANL). The sulfur data were collected from NSLS and APS, and the nitrogen data were collected at NSLS. Figure 5 shows an aerial view of APS, and Figure 6 shows a schematic diagram of the beamlines inside NSLS.

Synchrotron beamline 9-BM at APS has an energy range of 2.1-24 KeV. It is equipped with Si[111] and Si[220] double crystal monochromators for controlling photon energies, and the sulfur K-edge ex-

Figure 4. Nitrogen K-edge XANES spectra of different nitrogen structures; the spectra of models belonging to different structures are well separated in photon energies.



periment used the former. This beamline operates on a bending magnet principle; a 250 µm Be window separates the high vacuum front end part of the beam from the part entering the sample hutch. The incident photon intensity was measured by an ion chamber, and a Stern Heald, or Lytle detector (Lytle, 1988) (Figure 7) was used for fluorescence data collection. The three sections of the beamline inside the sample hutch, the windows upstream with the incident intensity (Io) detector, the sample chamber, and the fluorescence (I_F) detector were separated from each other by a 5 micron thick polycarbonate membrane, so each of the sections could be purged separately. The Io ion chamber was purged with helium gas, as was the sample chamber; the I_F detector was purged with nitrogen gas.

The sample holder at APS consisted of a Teflon sample holder where solid samples were directly loaded on the face of the holder, and liquid samples were placed inside an indented groove in the holder,

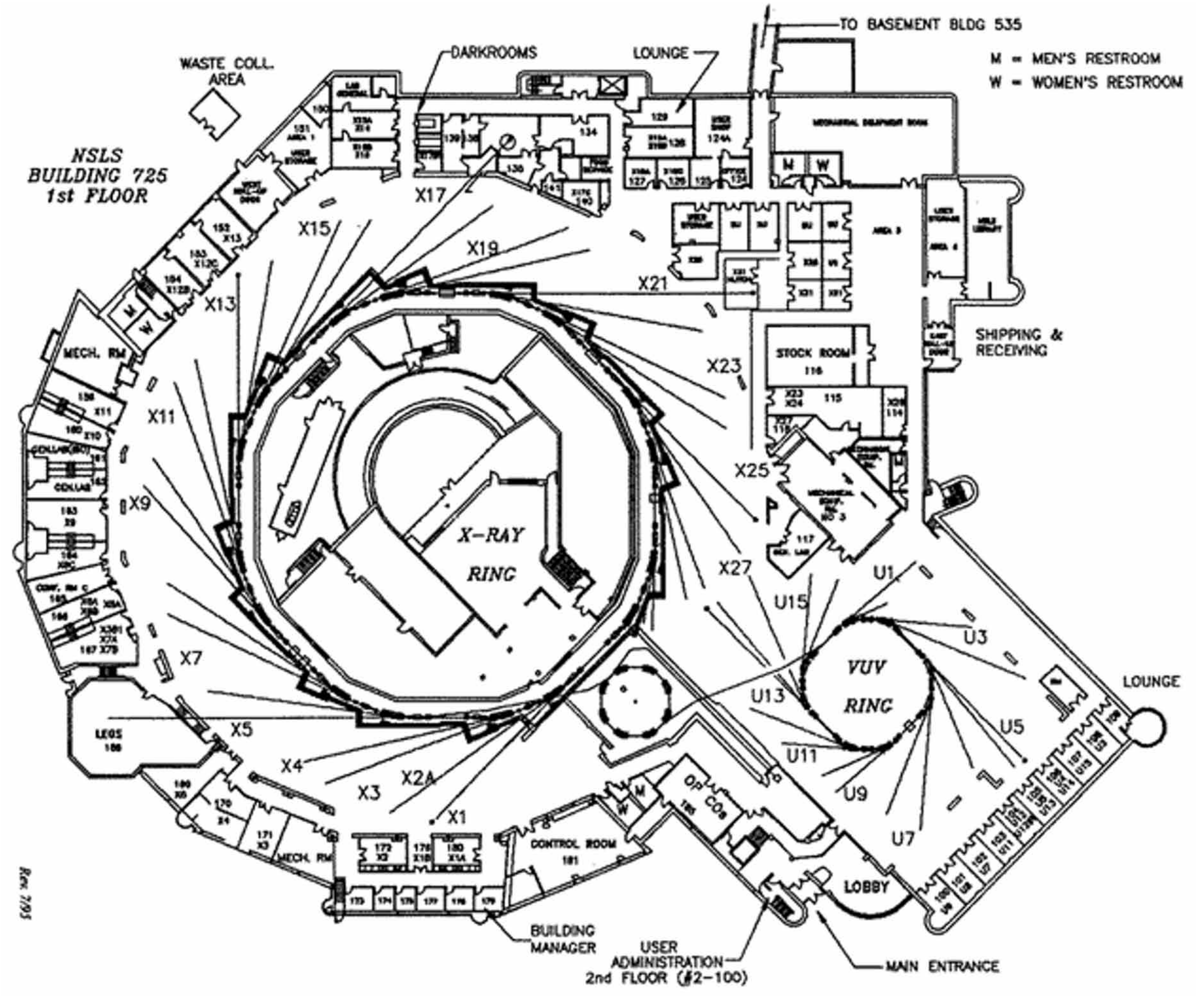
Figure 5. Aerial view of APS at Argonne National Laboratory
(https://www1.aps.anl.gov/Users-Information)

which was sealed with aluminized Mylar. Care was taken so that there were no air bubbles in the path of the beam for the liquid samples. The typical beam size was 0.5 mm^2. The monochromator was detuned to about 30% to mitigate the higher harmonics. A typical energy resolution near the sulfur K-edge energy was about 0.3 eV. The beamline characteristics and data acquisition were performed using Sun UNIX EPICS with VME, SPEC, and LabView programs.

The beamline at NSLS used for sulfur K-edge data collection was X-19 A. The same kind of Si[111] double crystal monochromator was used as at the APS. The sulfur data for kerogens was collected using a Passivated Implanted Planar Silicon (PIPS) detector by Canberra, and the coal data was collected with a Lytle detector. A Pentium PC (Windows OS) was used to monitor beamline characteristics and data collection. Small solid sample pellets were made, or the solid samples were mounted on a parafilm substrates or on Mylar films; liquid samples were held in place inside small Mylar bags (see Figure 8).

Data from the nitrogen samples discussed here (Mitra-Kirtley, 1993, Mullins, 1993) were collected at NSLS, beamline U4B (Chen, 1987). A grating monochromator, with grating of 600 lines/mm, and a multi-element germanium detector from Canberra (Cramer, 1991) in the fluorescent mode were used for the experiment. Details of the experiments are given elsewhere (Mitra-Kirtley, 1993, Mitra-Kirtley, 2007).

Figure 6. A schematic representation of the layout of beamlines at NSLS, Brookhaven National Laboratory (https://cdac.carnegiescience.edu/facilities/hp-nsls-facilities)



XANES ANALYSIS

A number of data analysis software programs were used, including commercially available WinXAS, Kaleidagraph, and a program developed by some of the participants in the project. All the spectra were first calibrated using a standard sulfur model compound (elemental sulfur in the case of some of the kerogens, and coals, and sodium thiosulfate in the case of asphaltenes, kerogens, and bitumens). For each experimental session, all the data of the sulfur model compounds as well as the fossil fuel samples were adjusted to the same photon energy of that calibration model. The background was subtracted, and the spectra were then normalized at the same post-edge photon energy. Figure 9 shows a typical XANES sulfur K-edge spectrum of a sulfur model compound, elemental sulfur, normalized and background corrected.

Figure 7. A fluorescence Lytle detector
(http://www.saga-ls.jp)

Figure 8. X-19A at NSLS, Brookhaven National Laboratory.

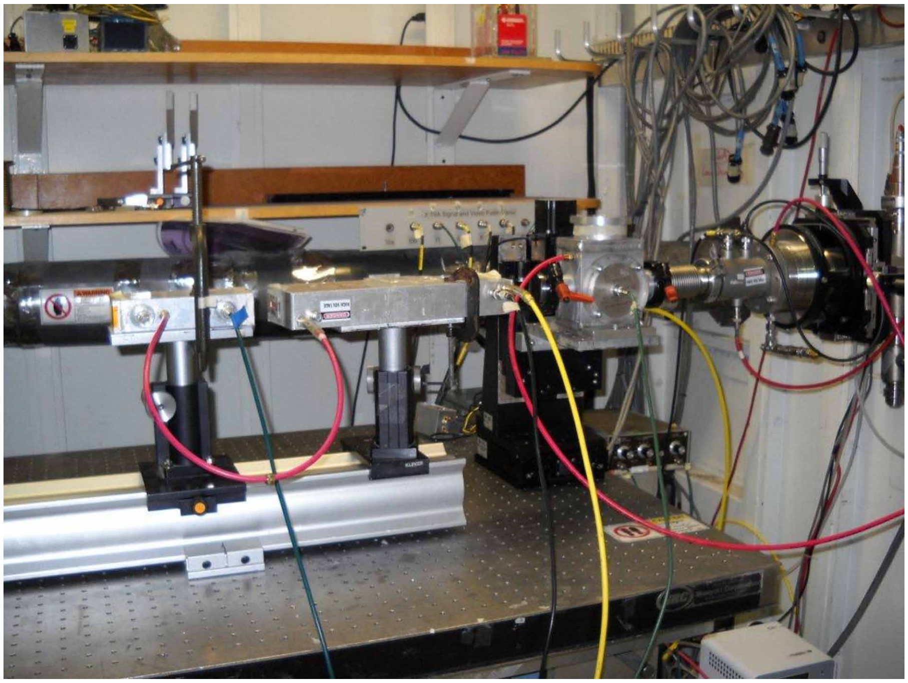
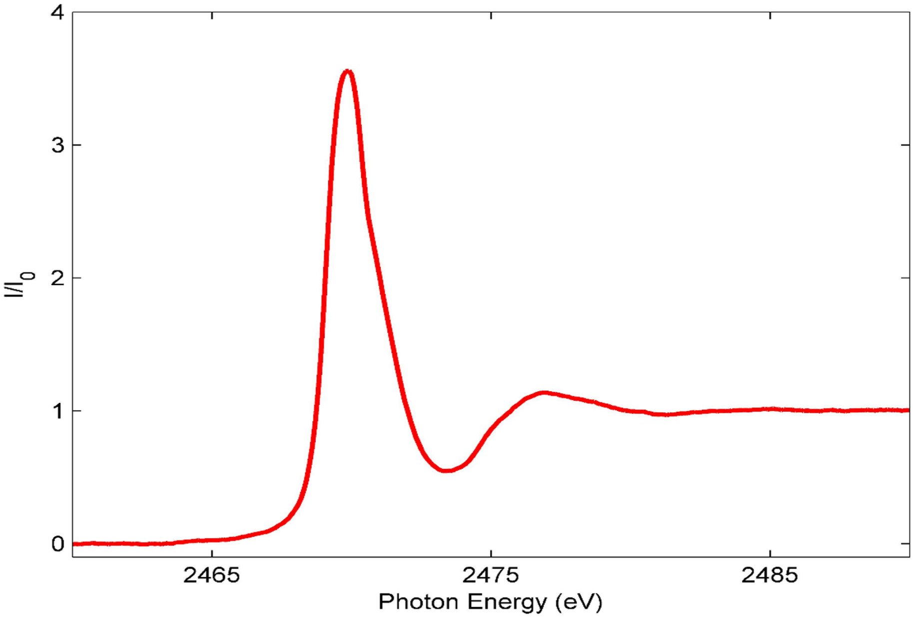


Figure 9. Sulfur K-edge XANES spectrum of elemental sulfur



The fossil fuel spectra were also corrected from the background, and normalized. A deconvolution process of each spectrum was carried out into individual Lorentzian peaks, and an arctangent step representing excitation of the continuum. The near edge peaks were identified to the white lines of the different sulfur model spectra; characteristics of the white lines, such as the height, width, and position were kept at identical values in the fossil fuel spectra as in the model spectra. The arctangent step function, which represented the electronic transition to the continuum, was also kept as the model spectra. Figure 10 shows a figure of a fossil-fuel spectrum that is fitted with a superposition of XANES spectra of sulfur model compounds. The areas under the identified signature Lorentzian peaks were calculated, when needed, and the actual percent compositions of the individual sulfur chemical structures present in the fossil fuel samples were determined. In the different projects described here, many analogues of such analysis software programs were developed and tested, and the results were compared with each other for consistency.

RESULTS AND DISCUSSIONS

Sulfur K-edge XANES studies on the asphaltenes, resins, and oil fractions of crude oil show that the most dominant form of sulfur is in thiophenic form, followed by sulfidic form (Mitra-Kirtley 1998). Figure 11 shows the sulfur K-edge XANES spectra of several asphaltenes, resins, and oil fractions and of sulfur model compounds that are the major contributors to their sulfur content.

Table 1 shows the differences between the different sulfur chemical structures found in these samples. In the CAL sample, there is significant sulfoxide content in all the fractions, probably not a result of atmospheric exposure of the samples. The sulfide content in the oil fractions of both the parent crudes is found to be relatively higher than the corresponding asphaltene. This is consistent with the fact that

Figure 10. Sulfur K-edge XANES spectrum of a fossil fuel spectrum and its deconvolution into constituent spectra, each representing a different sulfur chemical structure. A few standard chemical structures are identified here.

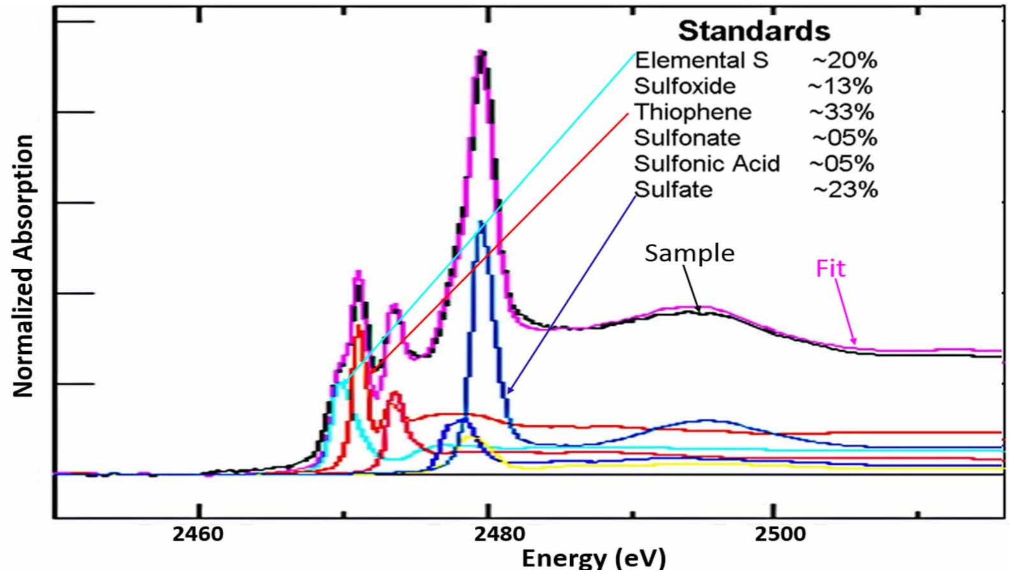


Figure 11. Sulfur K-edge XANES spectra of asphaltene, resin and oil fractions of two crude oils, and of dibenzyl sulfide, dibenzothiophene, and dibenzyl sulfoxide

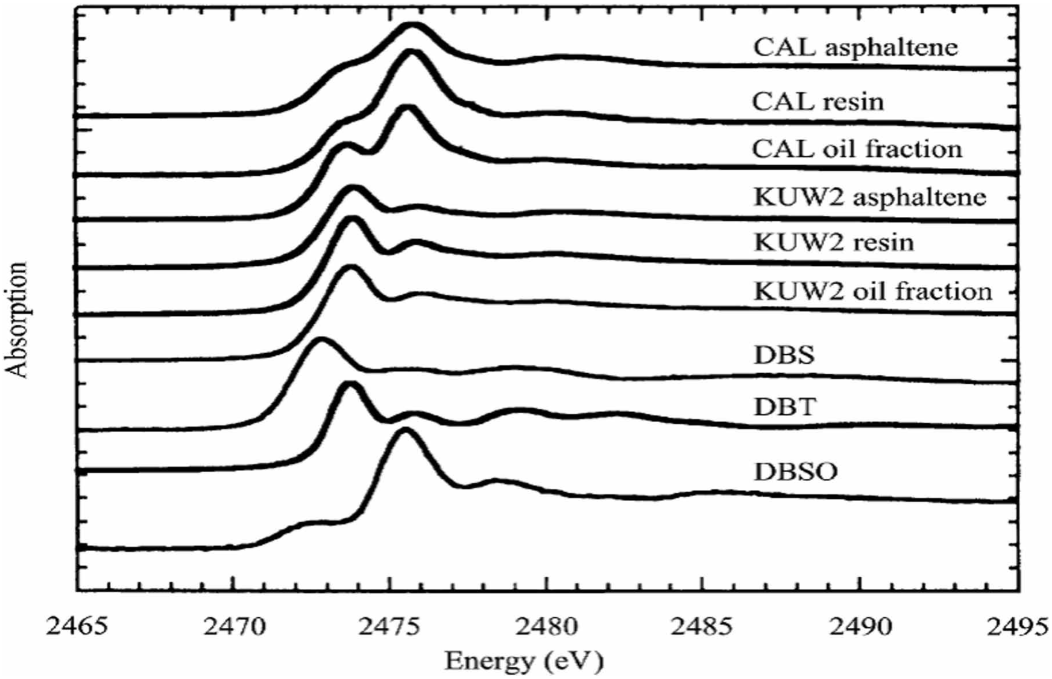


Table 1. Relative abundances of different sulfur chemical forms in asphaltene, resin, and oil fractions of CAL and UG8 crude oils

Samples	Sulfide	Thiophene	Sulfoxide	Sulfone	Sulfate
CAL					
Asphaltene	15	29	50	5	1
Resin	11	27	59	1	1
Oil	24	27	46	1	1
UG8					
Asphaltene	40	55	2	1	1
Resin	40	52	5	1	1
Oil	45	47	5	1	1

the oil fractions tend to be less aromatic than the other fractions (Yen, 1975). CAL crude oil is from shallower depths than UG8, and less mature. Consequently, the thiophene content in all the fractions from CAL is consistently lower than in the fractions from UG8.

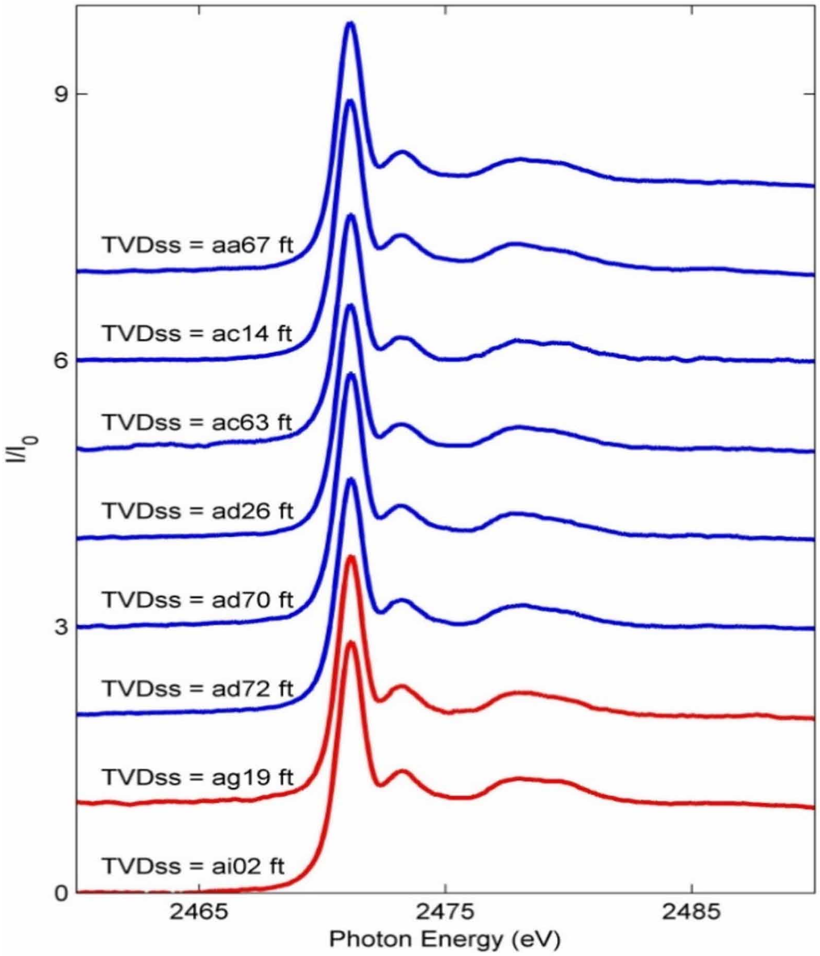
The CAL asphaltene sample studied earlier (Waldo, 1992) yielded the same results as a later study (Mitra-Kirtley, 1998) indicating that atmospheric oxidation of the sample had been insignificant.

A recent study on sulfur chemical speciation was performed on asphaltenes extracted from reservoirs with large asphaltene gradients (Pomerantz, 2013) by XANES methodology. It is found that there is no observable difference in the different sulfur chemical structures in the samples even though the asphaltene gradient among the samples from the same reservoir varied considerably. Eight oils from two stacked reservoirs, each spanning a vertical distance of ~60 meters and a lateral distance of 100 kilometers were used in the study. The six oils from the reservoir had a large asphaltene gradient, with a range of 3% to 31% (Mullins, 2013). Figure 12 shows the sulfur XANES spectra of all the eight asphaltene samples, with the one at the shallowest depth on the top, and the deepest at the bottom. The Flory-Huggins-Zuo (Zuo, 2012, 2013) model of characterizing this gradient showed thee gravity term dominated with asphaltenes in the form of clusters from the Yen-Mullins (Mullins, 2010, 2012, 2013) model. It is evident from this study that the asphaltene sulfur chemistry is invariant; thus the large gradient in this oil column is due to asphaltene concentration differences, not asphaltene compositional differences.

In the suite of samples studied here, thiophene seems to be the most dominant structure; varying small quantities of elemental sulfur, sulfides, and sulfoxides are also found. In some instances, negligible quantities of sulfones and sulfates have been observed, but all the secondary contributions are well within our error bars (~±5%). Similarities of sulfur chemical structures within samples from the same reservoir are noteworthy. All the samples had about 8-10% of sulfur content. Table 2 shows the relative abundances of sulfur chemical structures in all the samples. Earlier studies (Waldo, 1991) performed on oils and oil extracts showed that petroleum samples from similar sources have higher thiophenic content with greater thermal maturity. In addition, the source of the petroleum helps determine the relative concentration of sulfides and thiophenes; some carbonate-rich sources tend to produce thiophene-rich petroleum (Waldo, 1991).

Sulfur K-edge XANES analyses on kerogens and bitumens have been very successful, in spite of the insoluble nature of kerogens. Studies on groups of Type I and II kerogens reveal distinct differences

Figure 12. Sulfur K-edge XANES spectra of eight different asphaltenes extracted from two different reservoirs; the top six spectra (blue) belong to samples from the first, and the bottom two (red) from the second reservoir. The samples are shown to deepest with depth expressed as True Vertical Depth subsea (TVDss). All the samples show similar spectra, with thiophenic signature as the dominant one.



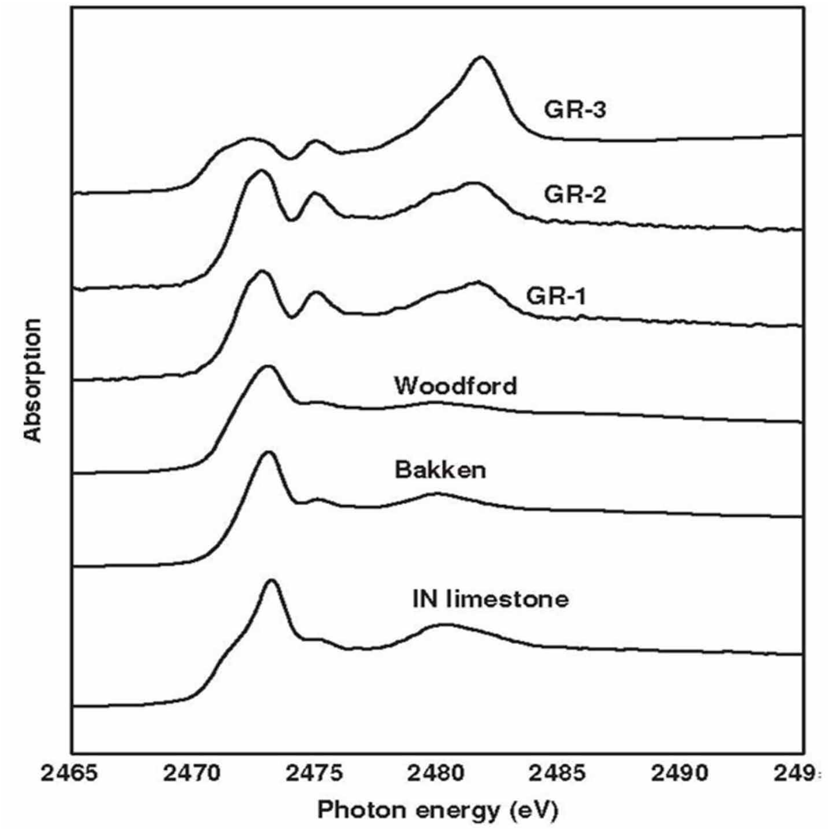
(Wiltfong, 2005). Figure 13 shows the XANES spectra of several kerogens; Type I Green River kerogen samples show smaller thiophene/sulfide ratios than the Type II kerogens such as Woodford, Bakken, and IN limestone kerogens. This mimics the carbon story in that Type I samples have lower aromatic/aliphatic carbon than Type II samples (Tissot, 1984). All of these samples show significant content of elemental sulfur and/or pyrite. The elemental sulfur in kerogens could be a result of oxidation of pyrite, or could be due to thermochemical and biological alteration of sulfates (Vairavamurthy, 1997). Moreover, the Type I samples in general show a larger content of sulfur-oxygen compounds compared to Type II samples, which supports the theory that with increased maturation the oxygen content usually decreases, as is also found elsewhere (Mitra Kirtley, 1993; Mullins, 1993). Table 3 shows the relative percentages of the different sulfur chemical structures found in these samples.

In a more recent study (Pomerantz, 2014), kerogens and bitumens have been isolated and extracted from shales, and analyzed. The kerogen and bitumen samples had three different sources: Green River

Table 2. Relative percentages of abundances of sulfur chemical structures in asphaltene samples extracted from different depths and different reservoirs; the samples are listed shallowest to deepest. The top six samples belong to the same reservoir while the bottom two belong to the second reservoir. The sulfur chemistry of all asphaltenes is quite similar.

Sample	Elemental Sulfur	Sulfide	Thiophene	Sulfoxide	Sulfone	Sulfate
aa67	5	3	89	2	0	1
ac14	3	5	90	2	0	0
ac63	7	0	86	4	1	2
ad26	4	3	88	3	1	1
ad70	5	0	92	3	0	0
ad72	6	0	88	4	1	1
ag19	4	0	92	3	0	1
ai02	5	0	91	3	0	1

Figure 13. Sulfur XANES spectra of several kerogens; Woodford, Bakken, and IN limestone samples belong to Type II and the GR (Green River) samples belong to Type I. The kerogens from each type are similar to each other, but distinct from the other type.



Sulfur K-edge XANES spectra of some kerogen samples

Table 3. Relative percentages of different sulfur chemical forms in Type I and Type II kerogens

Kerogen (Type)	Sulfur	Sulfide	Thiophene	Sulfoxide	Sulfonate	Sulfate
IN limestone (II)	29	2	59	2	9	<1
Bakken (II)	11	8	70	2	0	7
Woodford (II)	19	9	71	0	0	0
GR-1 (I)	9	22	39	8	9	11
GR-2 (I)	14	23	39	12	3	9
GR-3 (I)	31	4	22	7	11	24

from Colorado, USA (Type I), Eagle Ford from Texas, USA (Type II), and Muwaqqar from Jordan (Type III). Analysis of these sulfur K-edge XANES spectra show that the sulfur moieties in kerogens are significantly different from those found in the bitumens (Pomerantz, 2014). Figure 14 shows the sulfur K-edge XANES spectra of several kerogens and bitumens, and it is clear that bitumens possess a huge sulfoxide fraction while the kerogens do not.

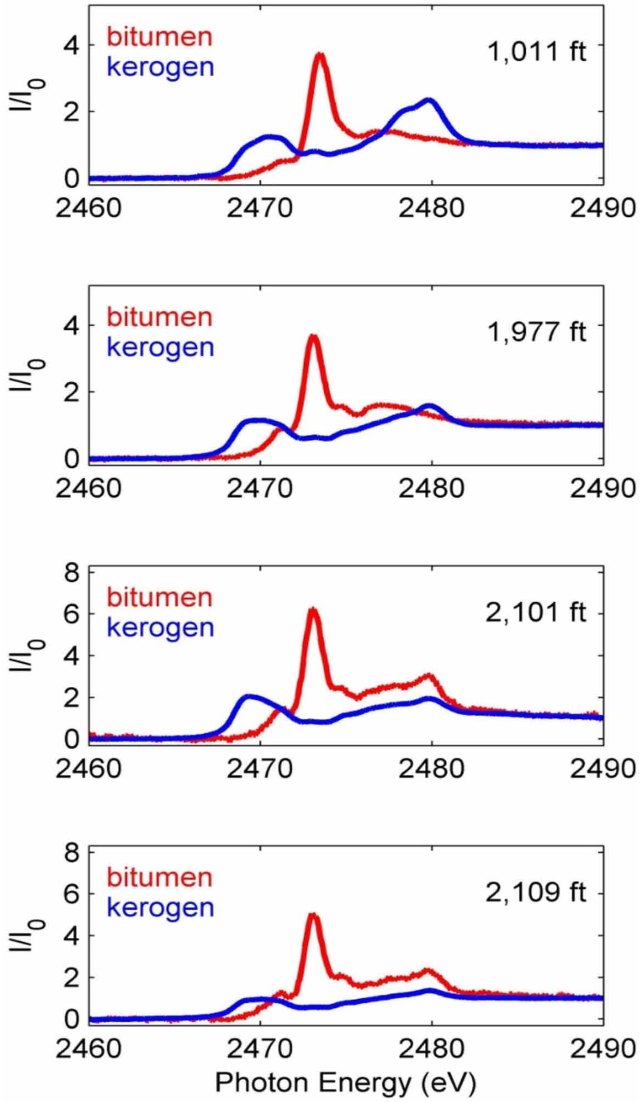
Table 4 tabulates the different sulfur forms in the kerogens and bitumens. The reduced forms of sulfur in the kerogens occur in the forms of elemental sulfur, aliphatic sulfide, and thiophene. In contrast, the bitumens contain significant quantities of sulfoxides. Dilution of the insoluble kerogen samples was samples was solved by diluting the samples in BN in a novel way. The samples were first cooled at liquid nitrogen temperatures, the resulting brittle pieces were then crushed by a wiggle-bug, and diluted in boron nitride. Experiments were performed at different sulfur concentration levels to ensure that the self-absorption effects in the spectra are not present. Naturally, pyrite, elemental sulfur and sulfates are carried with the insoluble kerogens as gleaned in Table 4. In the earlier studies (Wiltfong, 2005) where the kerogens were not separated from the bitumens, the samples showed presence of both the reduced as well as sulfoxide forms of sulfur (Figure 14).

This tendency of kerogens to contain little to no sulfoxides is not restricted to samples with only particular values of total sulfur content. In a separate study, three kerogens with much higher sulfur concentrations (14.6-26.9% by weight) from a US source were analyzed using the same XANES procedures. Appropriate dilution of the samples were carried out carefully to avoid self-absorption effects and

Table 4. Relative percentages of different sulfur chemical forms found in kerogens and bitumens extracted from oil shales

	Depth (ft)	Pyrite	Elemental	Sulfide	Thiophene	Sulfoxide	Sulfone	Sulfate
Kerogen	1011	9	18	7	18	2	16	30
	1977	19	27	0	20	3	9	21
	2101	26	34	1	17	1	7	14
	2101	19	24	0	21	4	10	21
Bitumen	1011	1	2	0	17	68	11	1
	1977	3	0	0	24	57	15	0
	2101	0	0	3	17	61	10	8
	2101	0	0	6	18	61	7	8

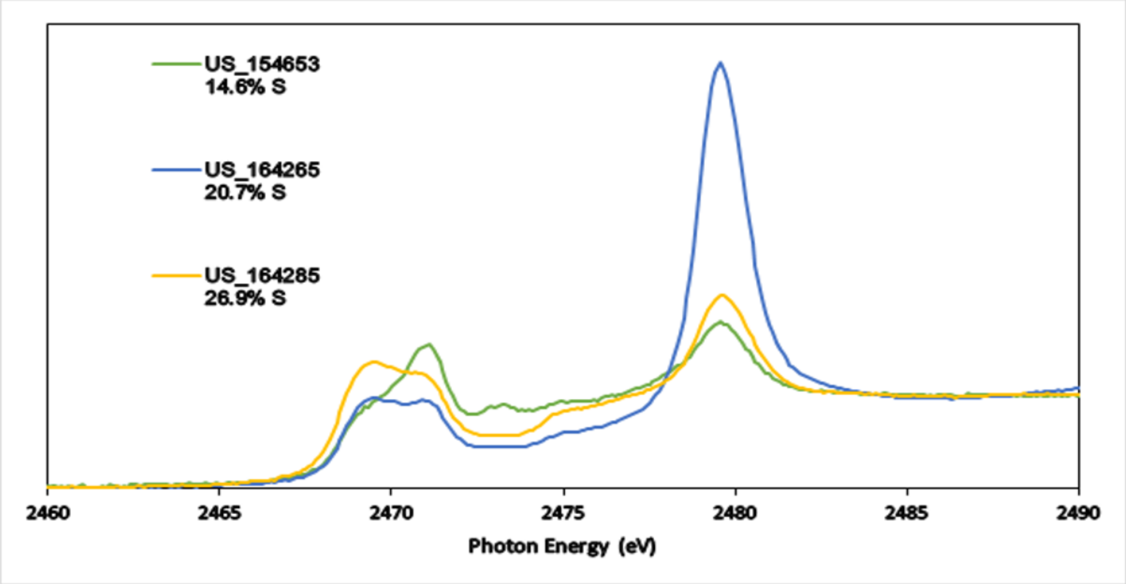
Figure 14. Sulfur XANES spectra of kerogen and bitumen samples extracted from oil shales at different depths; one of the major differences between the kerogen and the bitumen spectra is that the bitumens show a large sulfoxide signature.
(Pomerantz, 2014).



distorted data (Pomerantz, 2014), just as in the previous batch. Figure 15 is a plot of the spectra of these kerogens. Here, only one of the kerogens showed a very small amount (~3%) of sulfoxides, which falls well within the error bar of 5%, but neither of the other two did. In one of these samples the signature sulfate peak at around 2482 eV shows up prominently. It is clear that regardless of the total sulfur content and the occurrence of sulfates in kerogens, the sulfoxide content can be unaffected. The evidence of pyrite and sulfate in these samples is in part due to the presence of acid resistance minerals, as seen before.

Sulfur XANES studies in coal (Huffman, 1991) reveal yet again that the sulfur chemistry mimics the carbon chemistry as coals undergo geochemical transformation. More mature coals have a larger

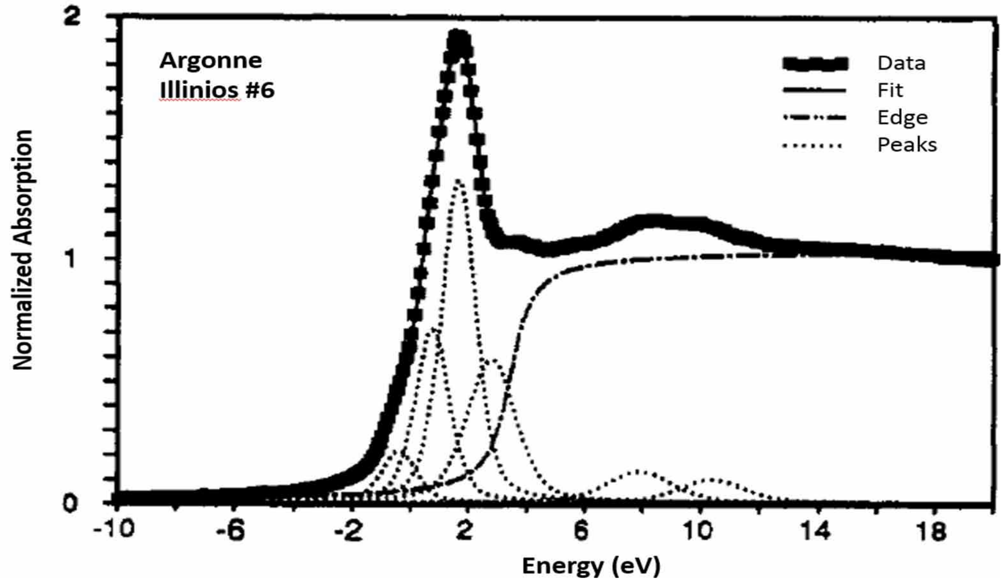
Figure 15. Sulfur XANES of three kerogens with large sulfur content; none of the kerogens show any sulfoxide content. Presence of pyrite and sulfate is in part due to the presence of acid resistant minerals.



thiophenic/sulfidic ratios than less mature coals, supporting the fact that more matured coals are more aromatic. The sulfide to thiophene ratio ranged from 0 in the higher rank coals to 0.93 in the lower rank coals such as lignite. Coals were also found to contain some inorganic sulfur compounds such as pyrite. Figure 16 shows a fitted coal spectrum, showing the constituent peaks, each representative of a different sulfur chemical structure; the zero of the energy scale is taken at the 1s-3p resonance energy of elemental sulfur (Huffman, 1991). Extensive S XANES studies on coal macerals have also been performed. The fraction of sulfides is higher in exinites compared to inertinite and vitrinite consistent with the lower aromaticity of exinites (Huffman, 1991). However, even though inertinites are more aromatic than vitrinites, some inertinites exhibit larger sulfide/thiophene ratios. This could be tied to the high occurrence of pyrite in these samples; the labile nature of inorganic sulfides tend to produce larger quantities of organic sulfides in these samples. Coals also show varying degrees of sulfoxides, sulfones, and sulfates.

Nitrogen XANES studies have been conducted on different types of fossil fuel materials, such as asphaltenes (Mitra-Kirtley, 1993), kerogens and bitumens (Mitra-Kirtley, 1993), and coals (Mullins, 1993). An overview of nitrogen XANES work on carbonaceous materials has been done (Sheu, 1995). Unlike in the sulfur case, the resonances in the nitrogen XANES spectra must be attributed to transitions between molecular orbitals, viz. $1s \rightarrow \pi^*$, and $1s \rightarrow \sigma^*$. The $1s \rightarrow \pi^*$ transitions are the signatures of the aromatic moieties, while $1s \rightarrow \sigma^*$ transitions are prominent in the saturated structures. The pyridine, pyrrole, and aromatic amine signature resonances are well separated, again facilitating the identification and quantification of different nitrogen structures in a complex sample. Even though the nitrogen in pyridine and in pyrrole has the same formal oxidation state, the lone pair of electrons on the pyridinic nitrogen is in an sp^2 orbital and not involved in the aromatic bonding. This localization of the lone pair of electrons, in addition to the high electronegativity of nitrogen, results in a partial negative charge on

Figure 16. A typical fitted sulfur K-edge XANES spectrum of a coal; the zero of energy is at the 1s-3p resonance energy (continuum excitation) of elemental sulfur. The zero of energy is at the sulfur K-edge. (Huffman, 1991).



the nitrogen in the pyridine. In contrast, the lone pair of nitrogen electrons in pyrrole are both involved in the aromatic π-bonding, thus leading to loss of electron density at the nitrogen site. The nitrogen pyrrole hydrogen is acid, and the 1s→π* transition is blue shifted by several eV compared to pyridine.

Figure 17 shows the nitrogen XANES plot of several nitrogen model compounds. In all the samples studied, nitrogen is found to be present in organic forms. In the asphaltenes, virtually all of the nitrogen is found to be aromatic, with pyrrolic nitrogen forms being the most dominant (Mitra-Kirtley, 1993). Figure 18 shows the nitrogen spectra of several asphaltenes. As evident in the raw data, it was found that the pyridinic content in these samples varied significantly, and there were, at most, little quantities of saturated amines. Studies of kerogens and bitumens showed that again, nitrogen exists mostly in aromatic forms in these samples, dominated by pyrrolic forms were more dominant than pyridinic forms. At most, small fractions of aromatic amines are indicated. A few instances of samples containing metallic porphyrin and saturated amine were detected analyzed. The porphyrins contain ½ pyrrolic signatures and ½ pyrridinc signatures; it is not the number of atoms in the aromatic ring but rather the disposition of the nitrogen lone pair that determines the type of 1s→π* resonance. The asphaltenes did not show presence of any pyridone, possibly due to transformation of pyridone to pyridine during extensive maturation leading to the formation of asphaltenes. Eight Argonne coals, ranging in rank from anthracite to lignite were also studied for nitrogen chemical speciation using XANES. Pyrroles, followed by pyridines again dominated the samples. The ratio of pyridone to pyridine decreased with higher rank, consistent with the fact that increased maturation drives away oxygenated molecules. The results did not show any atmospheric oxidation, as these samples were pristine, and not exposed to the atmosphere.

Figure 17. Nitrogen XANES spectra of several model compounds

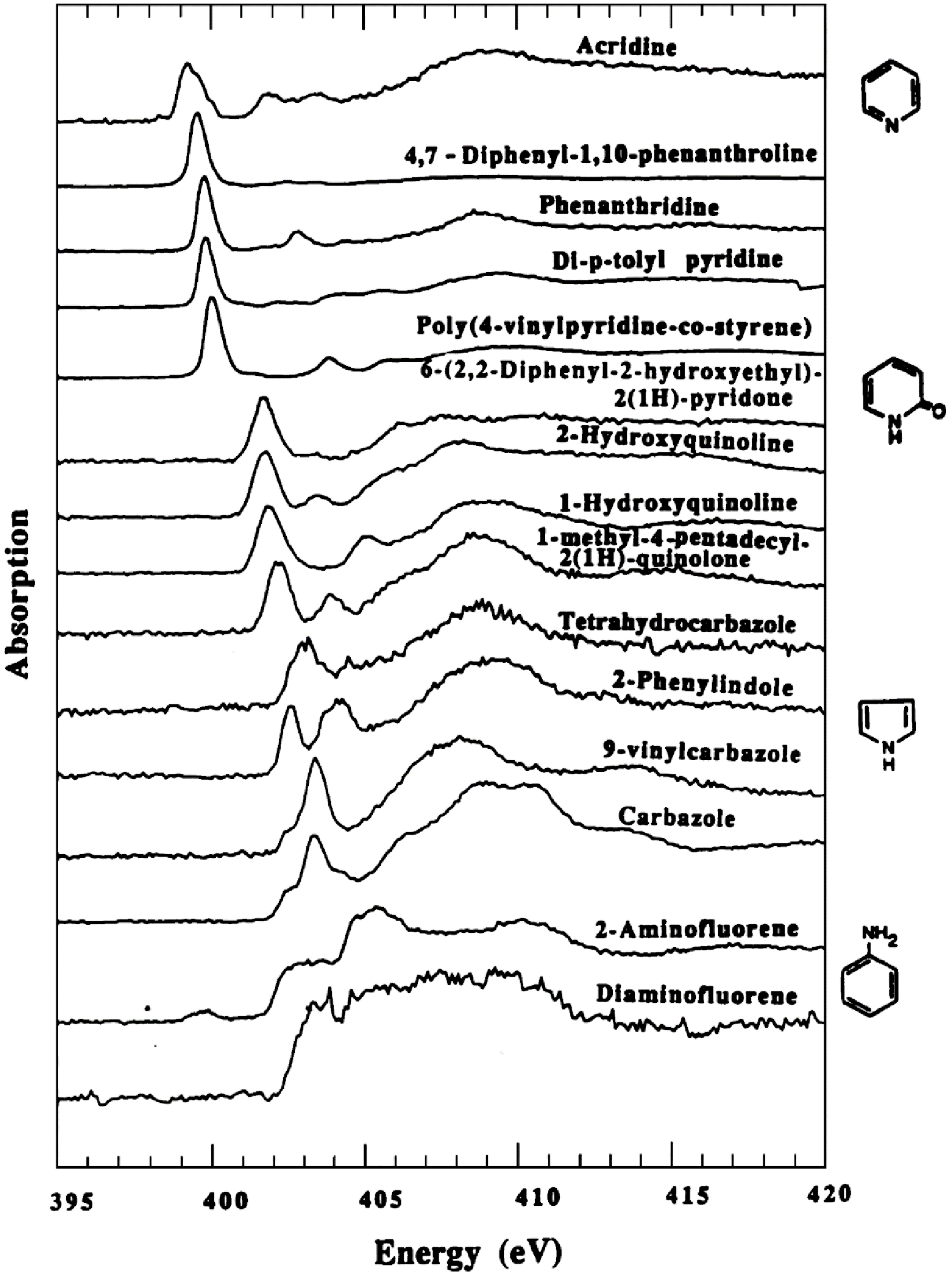
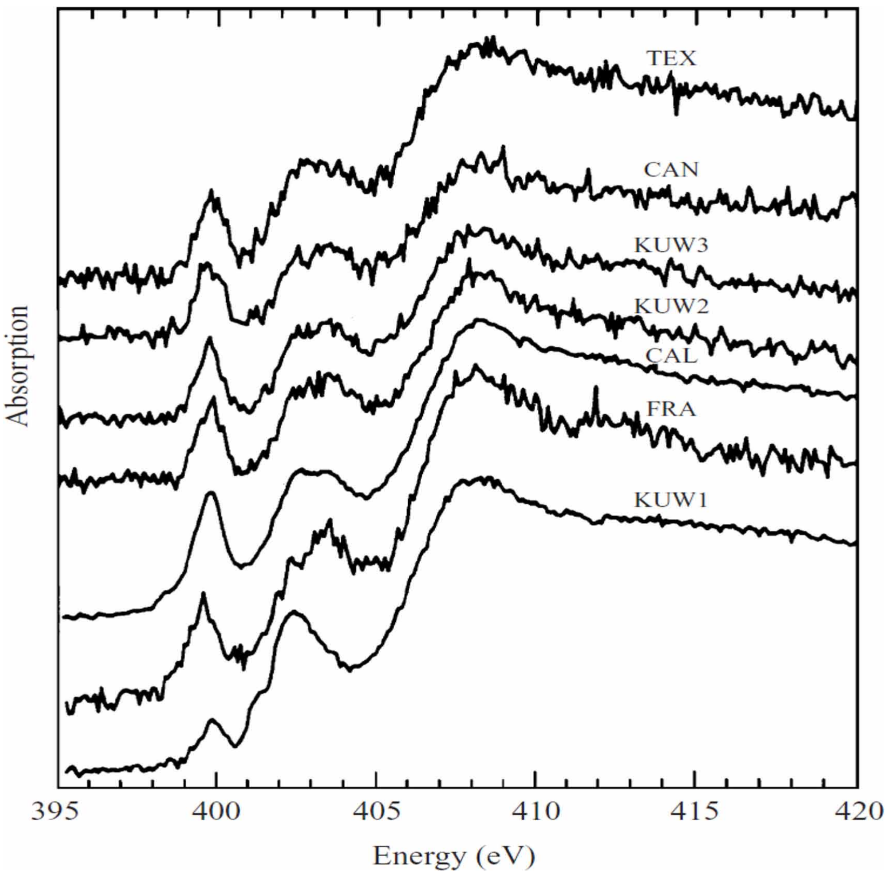


Figure 18. Typical XANES plots of petroleum asphaltenes



CONCLUSION

The formation of carbonaceous materials such as petroleum source rocks, oils, oil extracts and coals over geological time is very complex; nevertheless significant advances are being made understanding the corresponding chemistry. Detailing the chemistry of the heteroatoms sulfur and nitrogen in these materials acts as powerful probes for understanding the intricate geochemical processes that lead to their development. Heteroatoms are also important in the refining and utilization of these energy resources, and often times these heteroatoms are impediments to their effective utilization. Knowledge of the chemical structures of the heteroatoms lead to more effective utilization of these resources. For all these reasons and more, speciation of heteroatom chemistry in these energy resources is very important. XANES methodology is a direct, non-destructive, fast and a robust method of deciphering the sulfur and nitrogen chemistry in fossil fuel materials. Here, an overall account of sulfur and nitrogen K-edge XANES results from different kerogens, bitumens, petroleum asphaltenes, is presented along with S XANES results for coals.

As fossil fuel resources mature with geological time, carbon tends to become more aromatized; this is observed in deposits that are both marine, which mostly end up in petroleum generation, and terrestrial, which are mostly responsible for coal formation. Sulfur chemistry is also found to follow the same path. Sulfur in more matured samples tend to be more aromatic following the carbon chemistry. Specific macerals also show trends, exinite, with its high saturated carbon content, exhibits a high fraction of (reduced) sulfide sulfur, again following the carbon chemistry.

Sulfur in kerogens has a distinct difference from that found in bitumens. Unlike kerogen, bitumen exhibits very high sulfoxide content, the origin of this difference is still under investigation. Possibly, this observation is due to a process where the weaker carbon-sulfur links in kerogens are broken during extensive thermal maturation, producing the reactive sulfur radicals in bitumens that find and react with oxygen. The complex macromolecules of kerogens are substituted by smaller molecules in bitumens, resulting in bitumens having a smaller molecular weight than kerogens. Some amounts of pyrite and sulfate are evident in some kerogens, due to the presence of acid resistive minerals in the deposits. Within the kerogens, Type I show less thiophenic/aliphaltic sulfur than Type II, consistent with the fact that Type I is less aromatic than Type II.

Asphaltenes are important fraction of crude oils, and have been the topic of numerous studies in recent years. As with the other fossil fuel materials discussed here, they are difficult to study because of their complex structures. XANES analysis has been successfully employed to probe into their sulfur and nitrogen chemical structures. Sulfur in petroleum asphaltenes generally have a similar chemistry regardless of the origin and the depth of the samples. Asphaltenes tend to contain large amounts of thiophene, followed by sulfide and elemental sulfur, and (usually) small amounts of oxidized sulfur is also present. Asphaltenes belonging to a connected and equilibrated reservoir tend to have almost exactly the same sulfur structures. Furthermore, asphaltenes, resins, and oil fractions extracted from the same crude oil have similar sulfur chemistry, even though the chemical nature of the fractions is quite different. Nitrogen in asphaltenes also show similar chemistry; pyrrolic nitrogen is generally dominant over pyridinic.

Sulfur and nitrogen studies on coals by XANES analysis also reaffirm the increased aromaticity of the coals with increased maturation. Sulfur in more matured coal is found to be rich in thiophenic content compared to less geochemically matured counterparts. Nitrogen in higher rank coals showed smaller pyridone to pyridine ratios than in low maturity coals.

ACKNOWLEDGMENT

The authors are grateful to an ACS-PRF grant for completion of part of the studies, and to the following students from Rose-Hulman Institute of Technology for their research assistance in the collection and analysis of some of the results: Brian Kodalen, Chung-Hei Lo, Grant Brodnik, Michael Gerhardt, and Eric Kercher. The authors would also like to acknowledge Paul Craddock, Kyle Bake, and Kurt Kurzenhauser from Schlumberger-Doll Research for their hard work in this project.

REFERENCES

Akbarzadeh, K., Ahmed Hammami, A., Abdel Kharrat, A., Dan Zhang, D., Stephan Allenson, S., & Jefferson, C., Creek, S.K., Jamaluddin, A., Marshall, A., Rodgers, R., Mullins, O.C., Solbakken, T. (2007). Asphaltenes-Problematic but Rich in Potential. *Oilfield Review*, *19*(2), 22–43.

Alexander, T. et al. (2011). Shale Gas Revolution. *Oilfield Review 23*, 40-55.

Bailey, N. J. L., Krouse, H. R., Evans C. R., and Rogers, M. A. (1973). *Alteration of crude oil by waters and bacteria-evidence from geochemical and isotope studies*. Am. Assoc. Petrol. Geologists Bull., 57.

Bunger, J. W., & Li, N. C. (Eds.). (1981). *Chemistry of Asphaltenes*. Washington, DC: American Chemical Society.

Calkins, W. H. (1994). Fuel, *The Chemical Forms of Sulfur in Coal. RE:view*, *73*(4), 475–484.

Chen, C. T. (1987). Concept and Design Procedure for Cylindrical Element Monochromators for Synchrotron Radiation. *Nucl. Instrum. Methods Phys. Sec. A*, *256*(3), 595–604. doi:10.1016/0168-9002(87)90307-X

Chilingarian, G. V. (1981). *Chemistry of Asphaltenes* (J. W. Bunger, Ed.). Washington, DC: American Chemical Society.

Chilingarian, G. V., & Yen, T. F. (Eds.). (1978). *Bitumens, Asphalts, and Tar Sands*. Amsterdam: Elsevier Pub. Co.

Cramer, S. P., Tench, O., Yocum, M., Kraner, H., Rogers, L., & Radeka, V. (1991). X-ray absorption fine structure. In S. S. Hassian (Ed.), *Proc. of 6th Intl. XAFS Conf* (p. 640).

Davis, J. B. (1967). *Petroleum Microbiology*. Elsevier Pub. Cr.

Dean, R. A., & Whitehead, E. V. (1967). Proceedings of the 7th World Petroleum Congress, *Panel Discussion 23*, paper 7.

Dembicki, H. Jr. (2009). Three common source rock evaluation errors made by geologists during prospect or play appraisals. *AAPG Bulletin*, *93*(3), 341–356. doi:10.1306/10230808076

Depauw, G. A., & Froment, G. F. (1997). Molecular analysis of the sulphur components in a light cycle oil of a catalytic cracking unit by gas chromatography with mass spectrometric and atomic emission detection. *Journal of Chromatography. A*, *761*(1-2), 231–247. doi:10.1016/S0021-9673(96)00819-9

Drushel, H. V. (1970). Sulfur compounds in petroleum - known and unknown. *ACS Div. of Petroleum Chemistry Preprints*, *15*(2), C12–C42.

Dutta Majumdar, R., Gerken, M., Mikula, R., & Hazendonk, P. (2013). Validation of the Yen–Mullins Model of Athabasca Oil-Sands Asphaltenes using Solution-State1H NMR Relaxation and 2D HSQC Spectroscopy. *Energy & Fuels*, *27*(11), 6528–6537. doi:10.1021/ef401412w

Eglington, T. I., Irvine, J. E., Vairavamurthy, A., Zhou, W., & Manowitz, B. (1994). Formation and diagenesis of macromolecular organic sulfur in Peru margin sediments. *Organic Geochemistry*, *22*(3-5), 781–799. doi:10.1016/0146-6380(94)90139-2

Eyssautier, J., Levitz, P., Espinat, D., Jestin, J., Gummel, J., Grillo, I., & Barre, L. (2011). Insight into asphaltene nanoaggregate structure inferred by small angle neutron and X-ray scattering. *The Journal of Physical Chemistry B*, *115*(21), 6827–6837. doi:10.1021/jp111468d PMID:21553910

Feux, A. N. (1977). The use of stable carbon isotopes in hydrocarbon exploration. *J. Geochem. Res.*, *7*, 155–188. doi:10.1016/0375-6742(77)90080-2

Fuchs, W. (1931). *Die Chemie der Kohle*. Berlin: Springer. doi:10.1007/978-3-642-91582-6

Gal'pern, G. D. (1971). Organic sulfides in petroleum. *Intl. J. Sulfur Chem.*, *6*, 115.

Garcia, C. L., Becchi, M., Grenier-Loustalot, O., & Szymanski, R. (2002). Analysis of aromatic sulfur compounds in gas oils using GC with sulfur chemiluminescence detection and high-resolution MS. *Analytical Chemistry*, *74*(15), 3849–3857. doi:10.1021/ac011190e PMID:12175175

George, G. N., & Gorbaty, M. L. (1989). Sulfur K-edge absorption spectroscopy of petroleum asphaltenes and model compounds. *Journal of the American Chemical Society*, *111*(9), 3182–3186. doi:10.1021/ja00191a012

Gransch, J. A., & Posthuma, J. (1974). *On the oriqin of sulfur in crudes*, Adv. In B. Tissot & F. Bienner (Eds.), *Org. Geochemistry* (Vol. 727). Paris: Editions Technip.

Groenzin, H., & Mullins, O. C. (1999). Asphaltene molecular size and structure. *The Journal of Physical Chemistry A*, *103*(50), 11237–11245. doi:10.1021/jp992609w

Groenzin, H., & Mullins, O. C. (2000). Molecular sizes of asphaltenes from different origin. *Energy & Fuels*, *14*, 677. doi:10.1021/ef990225z

Huffman, G. P., Mitra, S., Huggins, F. E., Shah, N., Vaidya, F., & Lu, F. (1991). Quantitative analysis of all major forms of sulfur in coal by x-ray absorption fine structure spectroscopy. *Energy & Fuels*, *5*(4), 574–581. doi:10.1021/ef00028a008

Hughes, W. B., Holba, A. G., & Dzou, L. (1989). A method for determining the depositional. Soc. environment and lithology of crude oil and source rocks. Proceedings of the 1989 ACS *Meeting*, Honolulu, Hawaii.

Hughey, C. A., Rodgers, R. P., & Marshall, A. G. (2002). Resolution of 11,000 compositionally distinct components in a single electrospray ionization FT-ICR mass spectrum of crude oil. *Analytical Chemistry*, *74*, 4145–4149. doi:10.1021/ac020146b PMID:12199586

Hunt, J. M. (1979). *Petroleum Geochemistry and Geology*, W. H. *The Freeman*, 617.

Kane, R. D., and Cayard, M. S. (2002). *A Comprehensive Study on Naphthenic Acid Corrosion.* NACE Intl., paper 02555.

Kasrai, M., Bancroft, G. M., Brunner, R. W., Jonasson, R. G., Brown, J. R., Tan, K. H., & Feng, X. (1994). Sulfur speciation in bitumens and asphaltenes by x-ray absorption fine structure spectroscopy. *Geochimica et Cosmochimica Acta*, *58*(13), 2865–2872. doi:10.1016/0016-7037(94)90120-1

Killops, S. D., & Killops, V. J. (1993). *An Introduction to Organic Geochemistry* (2nd ed.). Longma Scientific and Technical.

Krouse, H. R. (1977). Sulfur isotope studies and their role in petroleum exploration. *Journal of Geochemical Exploration*, *7*, 189–211. doi:10.1016/0375-6742(77)90081-4

Lewan, M. D. (1998). Sulfur-radical control on petroleum formation rates. *Nature*, *391*(6663), 164–166. doi:10.1038/34391

Lewan, M. D., Spiro, B., Illich, H., Raiswell, R., Mackenzie, A. S., & Durand, B. et al. (1985). Evaluation of petroleum generation by hydrous pyrolysis experimentation. *Philos. Trans. R. Soc. London, A*, *315*(1531), 123–134. doi:10.1098/rsta.1985.0033

Lin, R. Z., & Wang, P. R. (1991). PAH in fossil fuels and their geochemical significance. Journal of Southeast Asian Earth Sciences. *Journal of Southeast Asian Earth Sciences*, *5*(1-4), 257–262. doi:10.1016/0743-9547(91)90034-U

Loucks, R. G., Reed, R. M., Ruppel, S. C., & Jarvie, D. M. (2009). Morphology, Genesis, and Distribution of Nanometer-scale Pores in Siliceous Mudstones of the Mississippian Barnett Shale. *Journal of Sedimentary Research*, *79*(12), 848–861. doi:10.2110/jsr.2009.092

Manning and Thompson. (1991). *Oilfield Processing of Petroleum*. PennWell books.

Marshall, A. G., & Rodgers, R. P. (2003). Petroleomics: The next grand challenge for chemical analysis. *Accounts of Chemical Research*, *37*(1), 53–59. doi:10.1021/ar020177t PMID:14730994

Marshall, A. G., & Rodgers, R. P. (2008). Petroleomics: Chemistry of the underworld. *Proceedings of the National Academy of Sciences of the United States of America*, *105*(47), 18090–18095. doi:10.1073/pnas.0805069105 PMID:18836082

Martin, R. L., & Grant, J. A. (1965). Determination of Thiophenic Compounds by Types in Petroleum Samples. *Analytical Chemistry*, *37*(6), 649–657. doi:10.1021/ac60225a006

McLafferty, F. W. (2008). Mass spectrometry across the sciences. *Proceedings of the National Academy of Sciences of the United States of America*, *105*(47), 18088–18089. doi:10.1073/pnas.0800784105 PMID:18922771

Mehmet, Y. (1971). Alberta Sulfur Research Quart. *Bull*, *6*, 1–17.

Miknis, F. P., & Turner, T. F. (1995). The Bitumen Intermediate in Isothermal and Nonisothermal Decomposition of Oil Shales. In C. Snape (Ed.), *Composition, Geochemistry, and Conversion of Oil Shales* (pp. 295–311). The Netherlands: Kluwer Academic Publishers. doi:10.1007/978-94-011-0317-6_18

Milkins, F. P., Turner, T. F., Berdan, G. L., & Conn, P. J. (1987). Formation of soluble products from thermal decomposition of Colorado and Kentucky oil shales. *Energy & Fuels*, *1*(6), 477–483. doi:10.1021/ef00006a004

Mitra-Kirtley, S., & Mullins, O. C. (2007). *Sulfur Chemical Moieties in Carbonaceous Materials, Asphaltenes, Heavy Oils, and Petroleomics* (O. C. Mullins, E. Sheu, A. Hammami, & A. Marshall, Eds.). Springer.

Mitra-Kirtley, S., Mullins, O. C., Branthaver, J. F., & Cramer, S. P. (1993). Nitrogen chemistry of kerogens from XANES spectroscopy. *Energy & Fuels*, *7*(6), 1128. doi:10.1021/ef00042a062

Mitra-Kirtley, S., Mullins, O. C., Ralston, C. Y., Sellis, D., & Pareis, C. (1998). *Determination of sulfur species in asphaltene, resin, and oil fractions of crude oils,* Appl. *Spec.*, *52*(12), 1522.

Mitra-Kirtley, S., Mullins, O. C., van Elp, J., George, S. J., Chen, J., & Cramer, S. P. (1993). Determination of the Nitrogen Chemical Structures in Petroleum Asphaltenes Using XANES Spectroscopy. *Journal of the American Chemical Society*, *115*(1), 252–258. doi:10.1021/ja00054a036

Mueller, H., Andersson, J. T., & Schrader, W. (2005). Selective characterization of high-molecular weight sulfur containing aromatics in vacuum residues using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Analytical Chemistry*, *77*(8), 2536–2543. doi:10.1021/ac0483522 PMID:15828790

Mullins, O. C. (2010). The Modified Yen Model. *Energy & Fuels*, *24*(4), 2179–2207. doi:10.1021/ef900975e

Mullins, O. C., Mitra-Kirtley, S., van Elp, J., & Cramer, S. P. (1993). Molecular structure of nitrogen in coal from XANES spectroscopy. *Appl*, *47*(Spec.), 1268.

Mullins, O. C.; Pomerantz, A. E.; Zuo, J. Y.; Dong, C. (2014). Downhole fluid analysis and asphaltene science for petroleum reservoir evaluation. *Annual review of chemical and biomolecular engineering*, 5, 325-45.

Mullins, O. C., Sabbah, H., Eyssautier, J., Pomerantz, A. E., Barré, L., & Andrews, A. B. et al. (2012). Advances in asphaltene science and the Yen–Mullins model. *Energy & Fuels*, *26*(7), 3986–4003. doi:10.1021/ef300185p

Mullins, O. C., Seifert, D. J., Zuo, J. Y., & Zeybek, M. (2013). Clusters of Asphaltene Nanoaggregates Observed in Oilfield Reservoirs. *Energy & Fuels*, *27*(4), 1752–1761. doi:10.1021/ef301338q

Orr, W. L. (1975). Sulfur in petroleum and related fossil organic materials. *ACS Div Petr. Chem. Preprints*, *21*, 417–421.

Orr, W. L. (1978). In O. P. Strausz & E. M. Lown (Eds.), *Oil Sand and Oil Shale Chemistry* (pp. 223–243). Verlag Chemie.

Orr, W. L. & White, C.M. (Eds.) (1990). Geochemistry of Sulfur in Fossil Fuels. ACS Books, Washington. doi:10.1021/bk-1990-0429

Pfeiffer, J. P. (1950). *The Properties of Asphaltic Bitumen*. Amsterdam: Elsevier.

Piehl, R. L. (1987). Paper 196, *Naphthenic Acid Corrosion in Crude Distillation Units*. *Corrosion*, 87.

Pomerantz, A. E., Bake, K. D., Craddock, P. R., Kurzenhauser, K., Kodalen, B. G., Mitra-Kirtley, S., & Bolin, T. (2014). Sulfur speciation in kerogen and bitumen from gas and oil shales. *Organic Geochemistry*, *68*, 5–12. doi:10.1016/j.orggeochem.2013.12.011

Pomerantz, A. E., Hammond, M. R., Morrow, A. L., Mullins, O. C., & Zare, R. N. (2008). Two-Step Laser Mass Spectrometry of Asphaltenes. *Journal of the American Chemical Society*, *130*(23), 7216–7217. doi:10.1021/ja801927v PMID:18484722

Pomerantz, A. E., Hammond, M. R., Morrow, A. L., Mullins, O. C., & Zare, R. N. (2009). Asphaltene Molecular-Mass Distribution Determined by Two-Step Laser Mass Spectrometry. *Energy & Fuels*, *23*(3), 1162–1168. doi:10.1021/ef8006239

Pomerantz, A. E., Seifert, D. J., Bake, K. D., Craddock, P. R., Mullins, O. C., & Kodalen, B. G. et al. (2013). Sulfur chemistry of asphaltenes from a highly compositionally graded oil column. *Energy & Fuels*, *27*(8), 4604–4608. doi:10.1021/ef400773f

Purcell, J. M., Juyal, P., Kim, D.-G., Rodgers, R. P., Hendrickson, C. L., & Marshall, A. G. (2007). Sulfur speciation in petroleum: Atmospheric pressure photoionization or chemical derivatization and electrospray ionization fourier transform Ion cyclotron resonance mass spectrometry. *Energy & Fuels*, *21*(5), 2869–2874. doi:10.1021/ef700210q

Radke, M., Welte, D. H., & Wilsch, H. (1982). Geochemical study on a well in the Western Canada Basin: Relation of the aromatic distribution pattern to maturity of organic matter. *Geochimica et Cosmochimica Acta*, *46*(1), 1–10. doi:10.1016/0016-7037(82)90285-X

Rodgers, R. P., Hughey, C. A., Hendrickson, C. L., & Marshall, A. G. (2002). Advanced characterization of petroleum crude and products by high field Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Am. Chem. Soc. Fuel Chemistry Division Preprints*, *47*(2), 636–698.

Rodgers, R. P., & Marshall, A. G. (2005). *Petroleomics: Advanced Characterization of Petroleum-Derived Materials by Fourier Transform Ion-Cyclotron Resonance mass Spectrometry* (pp. 63–93). New York: Springer.

Ruiz-Guerrero, R., Vendeuvre, C., Thiebaut, D., Bertoncini, F., & Espinat, D. (2006). Comparison of comprehensive two-dimensional gas chromatography coupled with sulfur-chemiluminescence detector to standard methods for speciation of sulfur-containing compounds in middle distillates. *Journal of Chromatographic Science*, *44*(9), 566–573. doi:10.1093/chromsci/44.9.566 PMID:17059685

Sabbah, H., Morrow, A. L., Pomerantz, A. E., & Zare, R. N. (2011). Evidence for Island Structures as the Dominant Architecture of Asphaltenes. *Energy & Fuels*, *25*(4), 1597–1604. doi:10.1021/ef101522w

Sarret, G., Conna, J., Kasrai, M., Bancroft, G. M., Charrié-Duhaut, A., & Lemoine, S. et al. (1999). Chemical forms of sulfur in geological and archeological asphaltenes from Middle East, France, and Spain determined by sulfur K- and L-edge X-ray absorption near-edge structure spectroscopy. *Geochimica et Cosmochimica Acta*, *63*(22), 3767–3779. doi:10.1016/S0016-7037(99)00205-7

Seewald, J. S. (1998). Sulfur greases the wheels. *Nature*, *391*(6663), 128–129. doi:10.1038/34301 PMID:9428759

Sheu, Y., & Mullins, O. C. (Eds.). (1995). *Asphaltenes Fundamentals and Applications*. New York, London: Plenum.

Shi, Q., Hou, D., Chung, K. H., Xu, C., Zhao, S., & Zhang, Y. (2010). Distribution of acids and neutral nitrogen compounds in a Chinese crude oil and its fractions: characterized by negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels*, *24*, 2545–2553. doi:10.1021/ef901564e

Sinninghe Damaste, J. S., & de Leeuw, J. W. (1990).. . *Organic Geochemistry*, *16*, 1077–1101.

Sinninghe Damste, J. S., Rijpstra, I. C., Kock-van Dalen, A. C., de Leeuw, J. W., & Schenck, P. A. (1989). Quenching of labile functionalized lipids by inorganic Sulphur species: Evidence for the formation of sedimentary organic sulphur compounds at the early stage of diagenesis. *Geochimica et Cosmochimica Acta*, *53*(6), 1343–1355. doi:10.1016/0016-7037(89)90067-7

Speight, J. G., *The Chemsitry and Technology of Petroleum*, Marcel-Dekker, Inc., New York.

Stumpf, A., Tolvaj, K., & Juhasz, M. (1998). Detailed analysis of sulfur compounds in gasoline range petroleum products with high-resolution gas chromatography–atomic emission detection using group-selective chemical treatment. *Journal of Chromatography. A*, *819*(1-2), 67–74. doi:10.1016/S0021-9673(98)00444-0

Swain, E. J. (1998). US refining crude slates continue towards heavier feeds, high sulfur contents. *Oil & Gas Journal*, *96*(40), 43–48.

Teichmuller, M. (1982). Origin of petrographic constituents of coal. In E. Stach, M-T. Mackowsky, M. Teichmuller, G.H. Taylor, D. Chandra, & R. Teichmuller, (Eds.), Stach's Textbook on Coal Petrology (Trans., English ed. by D.G. Murchison, G.H. Taylor, & F. Zierke). Gebruder Borntraeger, Berlin, Stuttgart.

Thode, H. G. (1965). In A. Young & J. E. Galley (Eds.), *Fluids in Subsurface Environments* (pp. 367–377). AAPG Press.

Tissot, B. P., & Welte, D. H. (1984). *Petroleum Formation and Occurrence* (2nd ed., p. 699). Berlin: Springer-Verlag. doi:10.1007/978-3-642-87813-8

Tsang Mui Ching, M.-J., Pomerantz, A. E., Andrews, A. B., Dryden, P., Schroeder, R., Mullins, O. C., & Harrison, C. (2010). On the nanofiltration of asphaltene solutions, crude oils, and emulsions. *Energy & Fuels*, *24*(9), 5028–5037. doi:10.1021/ef100645b

Vairavamurthy, M. A., Maletic, D., Wang, S., Monowitz, B., Eglington, T., & Lyons, T. (1997). Characterization of Sulfur-Containing Functional Groups in Sedimentary Humic Substances by X-ray Absorption Near-Edge Structure Spectroscopy. *Energy & Fuels*, *11*(3), 546–553. doi:10.1021/ef960212a

Valenza, J. J., Drenzek, N., Marques, F., Pagels, M., & Mastalerz, M. (2013). Geochemical controls on shale microstructure. *Geology*, *41*(5), 611–614. doi:10.1130/G33639.1

Waldo, G. S., Carlson, R. M. K., Moldowan, J. M., Peters, K. E., & Penner-Hahn, J. (1991). Sulfur speciation in heavy petroleums: Information from X-ray absorption near-edge structure. *Geochimica et Cosmochimica Acta*, *55*(3), 801–814. doi:10.1016/0016-7037(91)90343-4

Waldo, G. S., Mullins, O. C., Penner-Hahn, J. E., & Cramer, S. P. (1992). Determination of the chemical environment of sulphur in petroleum asphaltenes by X-ray absorption spectroscopy. *Fuel*, *71*(1), 53–57. doi:10.1016/0016-2361(92)90192-Q

Wang, T. G., He, F. Q., & Li, M. J. (2005). Alkyl dibenzothiophenes: A biomarker tracing petroleum charge. *Science Bulletin*, *50*(2), 176–181.

Welte, D. (1974). *Advances in Organic Geochemistry*, Editions Technip, 3-13.

Wiltfong, R., Mitra-Kirtley, S., Mullins, O. C., Andrews, B., Fujisawa, G., & Larsen, J. (2005). Sulfur speciation in different kerogen by XANES spectroscopy. *Energy & Fuels*, *19*(5), 1971–1976. doi:10.1021/ef049753n

Wu, Q., Pomerantz, A. E., Mullins, O. C., & Zare, R. N. (2014). Laser-Based Mass Spectrometric Determination of Aggregation Numbers for Petroleum- and Coal-Derived Asphaltenes. *Energy & Fuels*, *28*(1), 475–482. doi:10.1021/ef401958n

Wu, Z., Jernström, S., Hughey, C. A., Rodgers, R. P., & Marshall, A. G. (2003). Resolution of 10,000 compositionally distinct components in polar coal extracts by negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels*, *17*(4), 946–953. doi:10.1021/ef030026m

Xia, K., Weesner, F., Bleam, W. F., Bloom, P. R., Skyllberg, U. L., & Helmke, P. A. (1998). XANES studies of oxidation states in aquatic and soil humic substances. *Soil Science Society of America Journal*, *62*(5), 1240–1246. doi:10.2136/sssaj1998.03615995006200050014x

Yen, T. F. (Ed.). (1975). *The Role of Trace Metals in Petroleum*. Michigan: Ann Arbor Science Inc.

Zuo, J. Y., Mullins, O. C., Freed, D., Elshahawi, H., Dong, C., & Seifert, D. J. (2013). Advances in the Flory–Huggins–Zuo Equation of State for Asphaltene Gradients and Formation Evaluation. *Energy & Fuels*, *27*(4), 1722–1735. doi:10.1021/ef301239h

Zuo, J. Y., Mullins, O. C., Mishra, V., Garcia, G., Dong, C., & Zhang, D. (2012). Asphaltene grading and tar mats in oil reservoirs. *Energy & Fuels*, *26*(3), 1670–1680. doi:10.1021/ef201218m

Chapter 3

Cleaner Energy Fuels:

Hydrodesulfurization and Beyond

Neha Sareen
Banaras Hindu University, India

Subrato Bhattacharya
Banaras Hindu University, India

ABSTRACT

Today, SO_2 pollution has become a glaring problem especially in India and China. Thus, desulfurization of fossil fuels has become an essential area of research. Advances in experimental sciences to explain the desulfurization mechanism will be beneficial to the rational designing of more effective HDS catalysts. Several reaction pathways involving desulfurization of thiophene have been compiled. Also, a repertoire of the desulfurization pathways encountered in the author's laboratory has been provided. The results will not only throw light on some unusual mechanisms of desulfurization process but also break the popular belief that desulfurization is limited to C-S bond cleavage only. The reactions may also serve as a basis for engineering optimal catalysts for future applications.

INTRODUCTION

The air that we breathe is precious and life giving. However, we have taken it for granted for too long. In the worldwide zeitgeist of rapid economic growth and technological advancements, we have gambled away our very right to breathe fresh air. Since the beginning of the industrial revolution, widespread combustion of fossil fuels by humans has been adding a noxious cocktail of fumes into the atmosphere. Now, as the industrial setups encroach in our residential and agricultural areas, adverse effects on our environment and health have become evident. The world and specially the developing nations such as India, China and south-east Asia are shrouded in a blanket of smog, struggling for a breath of clean air. A state of emergency was declared during the *Malaysian haze* of 2005 when pollution levels (Air Quality Index (AQI)) sky rocketed beyond the permissible 500 mark. In 2013, the New York Times ran an article on Beijing's air quality describing it as "Crazy Bad". A recent report showed that a third of the urban population in India lives in cities where the PM_{10} (particulate matter less than 10μm in diameter)

DOI: 10.4018/978-1-4666-9545-0.ch003

levels were found to be “critical”. The gravity of the situation can be judged by the number of lives lost and the irreparable damage caused to our ecosystem. In 2008, nearly 3000 people died pre-mature deaths in Canada due to acute short-term exposure to air-pollutants. These excerpts distinctly reverberate the fact that air pollution, and particularly SO_2 pollution is an environmental crisis that demands immediate attention.

SO_x and sulfate aerosols are some of the major air pollutants responsible for incidents of smog. The Indo-Gangetic planes are especially vulnerable to a marked increase in the levels of black carbon and sulfate aerosols every year before monsoons, which adversely affect agriculture in this fertile area (Ramanathan *et al.*, 2005; Ramana *et al.*, 2010). A recent study by Burney and Ramanathan, 2014 showed that short-lived climate pollutants (SLCPs) such as black carbon, surface ozone and sulfate aerosols were responsible for about 36% decline in wheat production in India in 2010. If recent reports are to be believed, SO_2 emissions in India escalated by over 40% during 2005-2010 (Klimont, Smith, & Cofala, 2013). While China continues to be the world’s largest SO_2 emitter, these findings catapult India to a close second.

SO_2 is released into the atmosphere during volcanic eruptions and wild fires (natural sources) and by burning of fossil fuels at large stationary combustion units (anthropogenic sources). Fossil fuels’ combustion in coal-fired electric power and transportation sectors account for maximum anthropogenic SO_2 emissions. Coal burning electric utilities are liable for 73% of the total SO_2 emissions in US. (See US-EPA) The amount of sulfur in coal varies from less than 1% -over 12% (Calkins, 1994). SO_2 gets oxidized to sulphuric acid in the atmosphere which in turn gets deposited as “acid rain” (Ehhalt, 1999). Precipitation can be many times more acidic than natural rain with a *pH* of 3 or less and poses serious environmental and health hazards. SO_2 is also the prime precursor for anthropogenic aerosols. Sulfate aerosols are formed in the atmosphere by nucleation of gas-phase species such as SO_2 and H_2SO_4. In a seminal paper Ward, 2009 shows that scientists may have, until now, underestimated the role of SO_2 in bringing about the climate change. His work, which spans the effect of volcanoes on climate change over the past 46,000 years, shows that each of the episodes of rapid global warming were concomitant with episodes of extreme volcanism (a large number of volcanic eruptions within a short time span). The bulk of the paper is flowing lava of evidence arguing the role of SO_2, opposed to CO_2, as the key initiator of global warming and climate change.

By the turn of the 20th century, anthropogenic SO_2 influx had reached 150Mt of SO_2 per annum. (Smith, Conception, Andres, and Lurz, 2004; Smith, Pitcher, and Wigley, 2001) Eliminating acid rain and curbing sulfur emissions from fossil-fuelled power plants has since then become an environmental goal. The US EPA Clean Air Act had made it mandatory to keep the S levels in gasoline and diesel within 30 to 50 ppm since the year 2005. The permissible limit was further reduced in 2009 to 10 ppm -15 ppm. (Brunet, Mey, Pérot, Bouchy, and Diehl, 2005) For fuel cells, using gasoline as feed the limit is even lower at 1ppmw. (Herna´ndez-Maldonado and Yang, 2004) Stricter environmental regulations to limit the sulfur content in coal, gasoline and diesel are steering us into a world of “zero” sulfur/sulfur free fuels. Traces of sulfur in diesel fuels act as poison for the oxidation catalysts in the emission control system thus reducing their efficiency to oxidize harmful carbon monoxide and hydrocarbons (Corro, 2002). In addition, rapidly declining resources of crude sweet oil makes it even more crucial to tackle the problem of sulfur removal from fuels. A commercially viable desulfurization process must be a catalytic process with a low energy pathway that involves cheaper and reusable catalyst. In order to develop efficient low energy pathways for fuel desulfurization, it is essential to master the underlying science. The reactions of transition metal and organometallic complexes in solution are often reproduced on the catalyst surface, and a detailed study of the mechanism can prove to be fruitful in the synthesis of industrial catalysts. This chapter discusses some reported desulfurization reactions and their possible mechanistic pathways. The goal of this work is to analyse these reactions for their applicability in the ongoing research for S-free fuels and to serve as a guide to investigators exploring potential catalysts. The authors feel that a breakthrough in this field is possible by extensive study of such reactions which can provide new routes to desulfurization, which, in future may be mimicked to develop a catalytic process.

CONVENTIONAL HYDRODESULFURIZTION (HDS)

HDS is one of the most extensively studied and documented reaction, with the first reports dating back to 1970s. Nevertheless, several aspects of this process such as reaction mechanisms, structure of the active sites etc. remain debatable. Without entering into details which are beyond the scope of this chapter, a brief description of the hydrodesulfurization process will be provided. In the sections that follow, we will examine:

1. A brief outline of the hydrodesulfurization process;
2. Limitations of HDS;
3. Oxidative desulfurization and biodesulfurization as non-conventional desulfurization processes.

The Reaction-Overview

Conversion of organosulfur compounds to H_2S and sulfur free hydrocarbons in presence of H_2, over a heterogeneous catalyst, lies at the heart of hydrodesulfurization (HDS) process. At present, hydrotreating is a key step employed in industrial processes for desulfurization of fossil fuels. Sulfur is present most abundantly in the form of thiols, thiophenes (THs), benzothiophenes (BTs) and dibenzothiophenes (DBTs). Some of the organosulfur compounds which are important in hydrotreating process are listed in Table 1. Desulfurization is carried out by metal catalysed hydrogenolysis/hydrogenation (or both) of such organosulfur compounds to yield low-sulfur/sulfur free hydrocarbons and H_2S. H_2S is disposed of by oxidation to elemental sulfur by the Claus process. (Austin, 1984) Catalytic HDS is carried out at elevated temperatures (300-350 °C) and high hydrogen partial pressure 150−1000 psi.

Depending on their structure, the organosulfur compounds differ greatly in their reactivity, though some generalizations can be drawn based on the literature.

1. The reactivity of thiols, sulfides and disulfides is significantly greater than those of thiophenic compounds. In fact, under classic HDS conditions, the aliphatic and alicyclic compounds are conveniently eliminated (Zaczepinski, 1996).
2. Thiophenes and dibenzothiophenes, especially 4,6-dimethyldibenzothiophene are not easily reduced to H_2S under similar reaction conditions. Kinetic studies by Nag and co-workers (Nag, Sapre, Broderick, and Gates, 1979) have shown that the order of reactivity is dependent on the number of rings in the substrate molecule (Table 2). For example, among thiophene, benzothiophene and dibenzothiophene, the order of reactivity was found to be as follows- thiophene > benzothiophene > dibenzothiophene (DBT).

Table 1. Some important organosulfur compounds encountered in HDS reactions

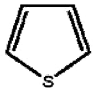
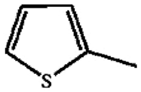
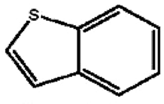
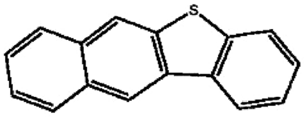
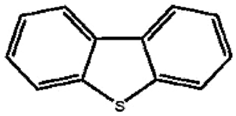
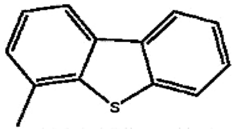
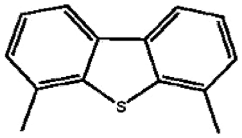
Aliphatic		**Aromatic**	
Class	**Structure**	**Class**	**Structure**
Thiols	R-S-H	Thiophenes	 Thiophene  2-Methyl-thiophene
Sulfides	R-S-R'	Benzothiophenes	 Benzothiophene  Benzo[b]naphtho[2,3-d]thiophene
Disulfides	R-S-S-R	Dibenzothiophenes	 Dibenzothiophene  4-Methyl-Dibenzothiophene  4,6-Dimethyl-dibenzothiophene

Table 2. Reactivity trends in some typical organosulfur compounds

Reactants	***k*, pseudo first order rate constant (L/g of catalyst . s)**
Thiophene	1.38×10^{-3}
Benzothiophene	8.11×10^{-4}
Dibenzothiophene	6.11×10^{-5}

(Nag et al., 1979).

3. The reactivity of alkyl substituted thiophenes and dibenzothiophenes are less than their unsubstituted counterparts. Among the family of thiophenes, the reactivity varies as follows- thiophene > 2-methylthiophene > 2,5-dimethylthiophene (Satterfield, Modell, and Wilkens, 1980).
4. Rate equations determined for different dibenzothiophenes indicates that the reactivity is effected by the number as well as the position of the alkyl substituents (Table 3). Following trend was observed: 2,8-dimethyldibenzothiophene (2,8-DMDBT) > dibenzothiophene (DBT) > 4-methyldibenzothiophene (4-MDBT) > 4,6-dimethyldibenzothiophene (4,6-DMDBT).

Table 3. Reactivity trends in some typical organosulfur compounds showing the effect of alkyl group substitution

Reactants	Pseudo first order rate constant (L/g of catalyst . s)*	Rate constant for reaction catalysed by Co-Mo/Al_2O_3 relative to that catalysed by Ni-Mo/Al_2O_3 **
Dibenzothiophene	7.38×10^{-5}	1.07
4-Methyldibenzothiophene	6.64×10^{-6}	0.90
4,6-Dimethyldibenzothiophene	4.92×10^{-6}	0.75
3,7-Dimethyldibenzothiophene	3.53×10^{-5}	-
2,8-Dimethyldibenzothiophene	6.72×10^{-5}	-

* Houalla et al., 1980; ** Whitehurst, Isoda, and Mochida, 1998.

The presence of methyl groups at 4- and 6- positions sterically hinders the adsorption of these molecules on the catalyst surface. Experimental evidence to support this claim was provided by Ma *et al.* (Ma, Kim, and Song, 2003) who found that the adsorption selectivity of various dibenzothiophenes increased in the order:

4,6-DMDBT < 4-MDBT < DBT. These findings clearly indicate that the presence of alkyl substituents at 4- and 6- position hinders the interaction between the S atom and the active site of the catalyst.

The Reaction Mechanism

The mechanism for hydrodesulfurization of thiophenic compounds has been reviewed by a large number of research groups and the general conclusion drawn is that the reaction proceeds *via* two competing parallel pathways:

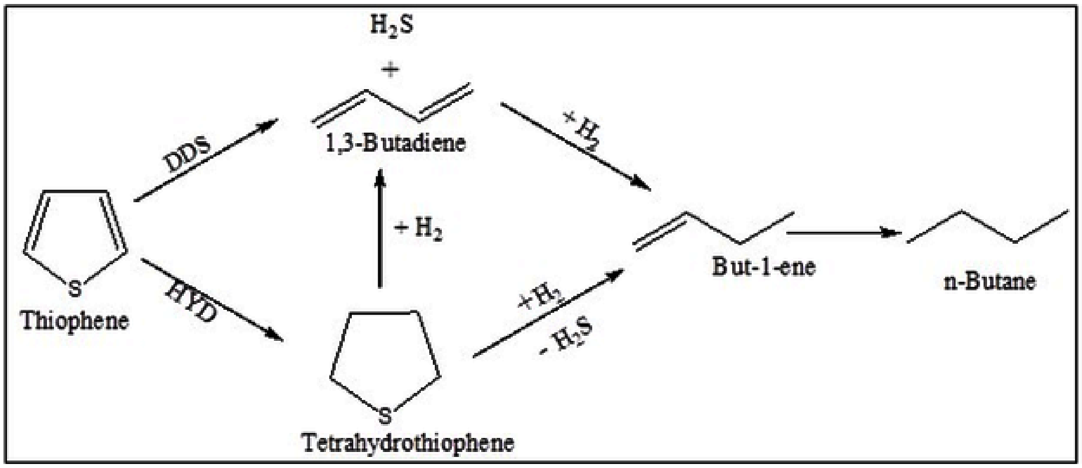
1. Direct desulfurization (DDS) pathway which involves the hydrogenolysis of C-S bond.
2. Hydrogenation (HYD) pathway involving tetra- or hexa-hydro intermediates followed by subsequent desulfurization.

The type of route followed depends on the nature of substrate as well as the chemical composition of the catalyst employed. Figure 1 shows the desulfurization of thiophene as proposed by Topsoe and Gates. (Topsoe, Clausen, and Massoth, 1996; Gates, Katzer, and Schuit, 1979)

Desulfurization of DBT and 4,6-DMDBT also proceeds through two parallels pathways: Direct desulfurization (DDS) and hydrogenation (HYD). Houella and coworkers (Houalla *et al.*, 1980; Houalla, Nag, Sapre, Borderick, and Gates, 1978) proposed a reaction network for desulfurization of dibenzothiophene on Co/Mo/Al_2O_3 catalyst consisting of these two competing pathways. (Figure 2)

The direct desulfurization (DDS) of 4,6-DMDBT leads to the formation of 3,3'-dimethylbiphenyl by cleavage of C-S bond. Hydrogenation (HYD) proceeds *via* saturation of an aromatic ring followed

Figure 1. Popularly accepted pathways for desulfurization of thiophene
Adapted from the work of Topsoe et al., 1996.

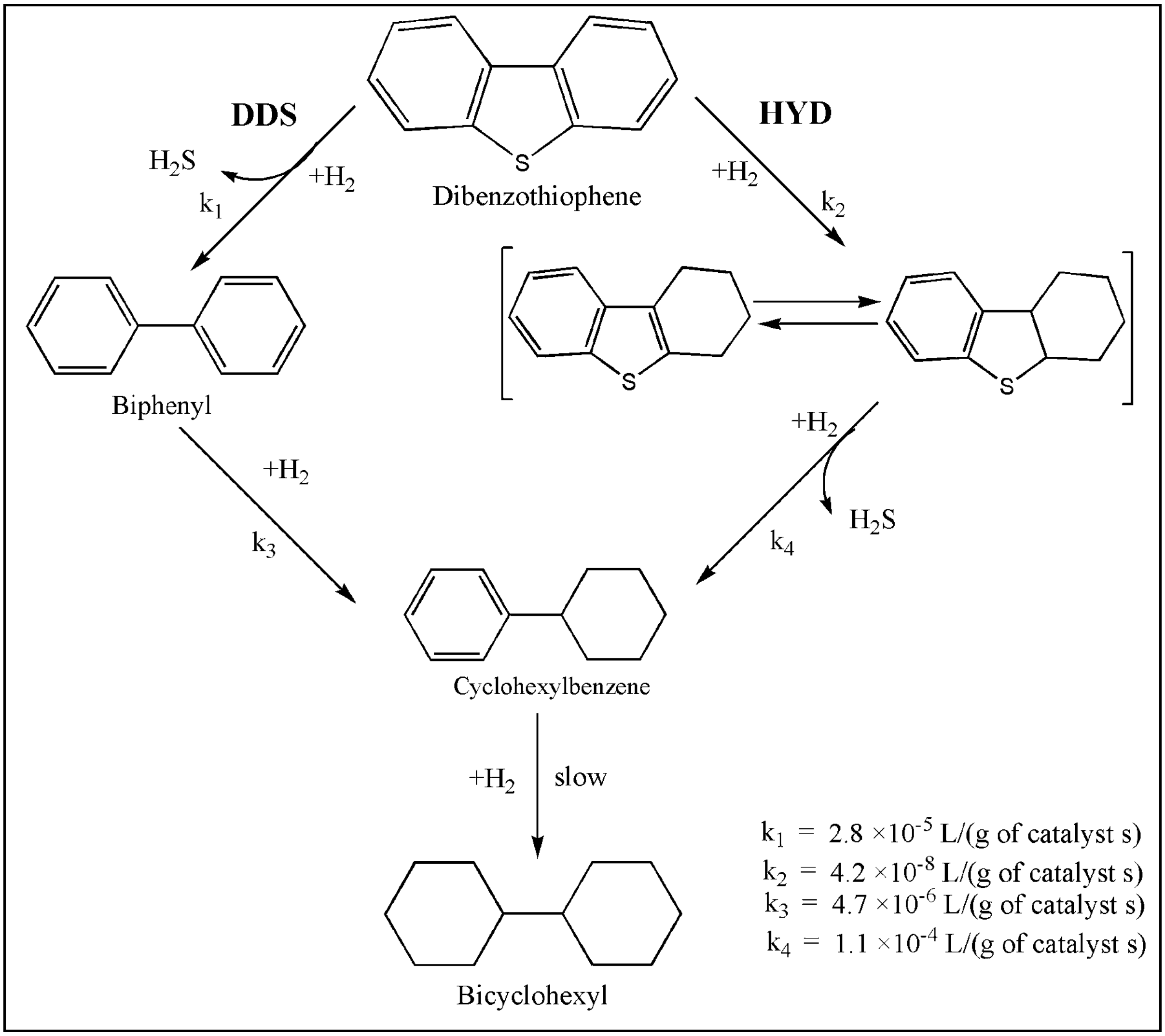


by desulfurization of the hydrogenated intermediates to yield 3.3'-dimethylcyclohexylbenzene and 3,3'-dimethyl-bicyclohexyl (Figure 3) (Bataille *et al.*, 2000; Li, Wang, Egorova, and Prins,2007; Kim, Ma, Song, Lee, and Oyama, 2005).

Kinetic studies on 4-MDBT and 4,6-DMDBT have shown that the relative rate of hydrogenolysis *vs*. hydrogenation is less in the case of former (Houalla *et al.*, 1980; Kilanowski *et al.*, 1978; Kabe, Ishihara, and Tajima, 1992; Kabe, Ishihara, and Zhang, 1993). While dibenzothiophene is desulfurized predominantly by the hydrogenolysis pathway, desulfurization of 4,6-DMDBMT preferentially follows the hydrogenation pathway. Hydrogenation is believed to relieve some of the steric hindrance which makes subsequent sulfur removal easier (Kabe *et al.*, 1993; Isoda, Nagao, Ma, Korai, and Mochida, 1996). The resultant cyclohexyl ring can rotate and adopt such conformations in which the methyl groups are directed away from the sulfur atom, thus increasing the approachability of the S atom to the active site. Computer modeling studies have further revealed that desulfurization of 1,2,3,4,5,6,-hexahydro-4,6-DMDBT is faster that for 4,6-DMDBT. (Landau, Berger, and Herskowitz, 1996) Ni/Mo/Al_2O_3 catalysts are better hydrogenation catalysts as compared to Co/Mo/Al_2O_3which have higher activity in hydrogenolysis reactions. Thus, it is expected that Ni/Mo/Al_2O_3 would turn out to be a better catalyst for the conversion of 4,6-DMDBT. Indeed, Mochida and coworkers compared the reaction pathways on the two catalysts and found the HDS activity of Ni/Mo/Al_2O_3 to be higher for 4,6-DMBMT (Isoda *et al.*, 1996; Ma, Sakanishi, Isoda, and Mochida, 1995).

Three types of metal thiophene complexes have been reported on the basis of their mode of bonding to the metal: C-bonded, S-bonded and π-bonded. Some of the earliest theories in this field are those given by Lipsch and Schuit who suggested an η^1-S type of coordination (Figure 4a) (Lipsch and Schuit, 1969). Later, Kwart *et al.* proposed a model according to which thiophene binds to the catalyst surface through a C=C bond in an η^2 coordination mode. (Kwart, Schuit, and Gates, 1980) Partial hydrogenation of thiophene by surface SH groups weakens the C-S bond leading its cleavage through a β- elimination (Figure 4b). It was shown by Zaera *et al.* (Zaera, Kollin, and Gland, 1987) that thiophene binds on the Mo(100) surface in both η^1-S and η^5 manner.

Figure 2. Reaction network for desulfurization of dibenzothiophene; catalyst used: Co-Mo/γ-Al_2O_3; k values represent pseudo first order rate constants
Adapted from Houalla et al., 1978.

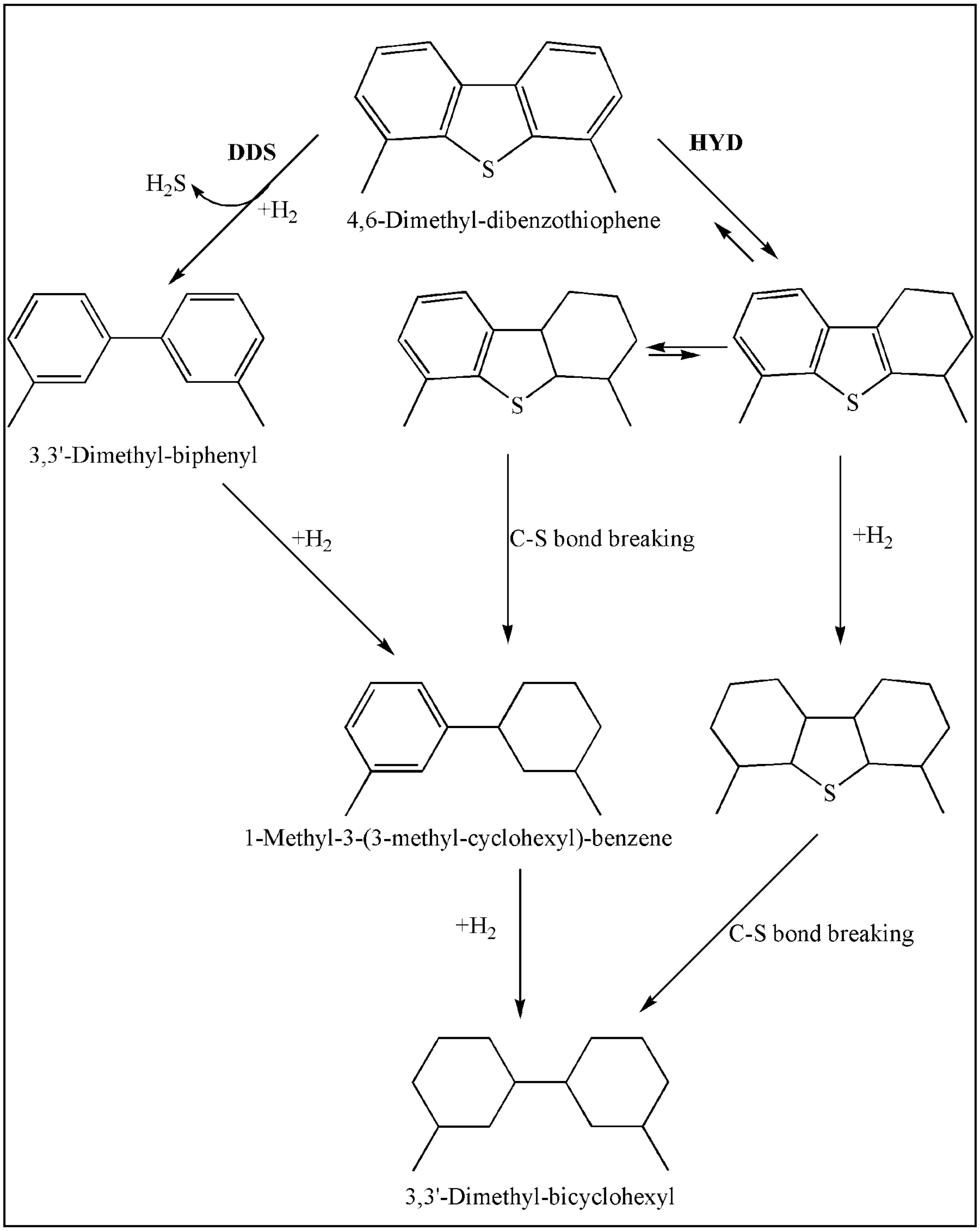


k_1 = 2.8 $\times 10^{-5}$ L/(g of catalyst s)
k_2 = 4.2 $\times 10^{-8}$ L/(g of catalyst s)
k_3 = 4.7 $\times 10^{-6}$ L/(g of catalyst s)
k_4 = 1.1 $\times 10^{-4}$ L/(g of catalyst s)

The Catalysts

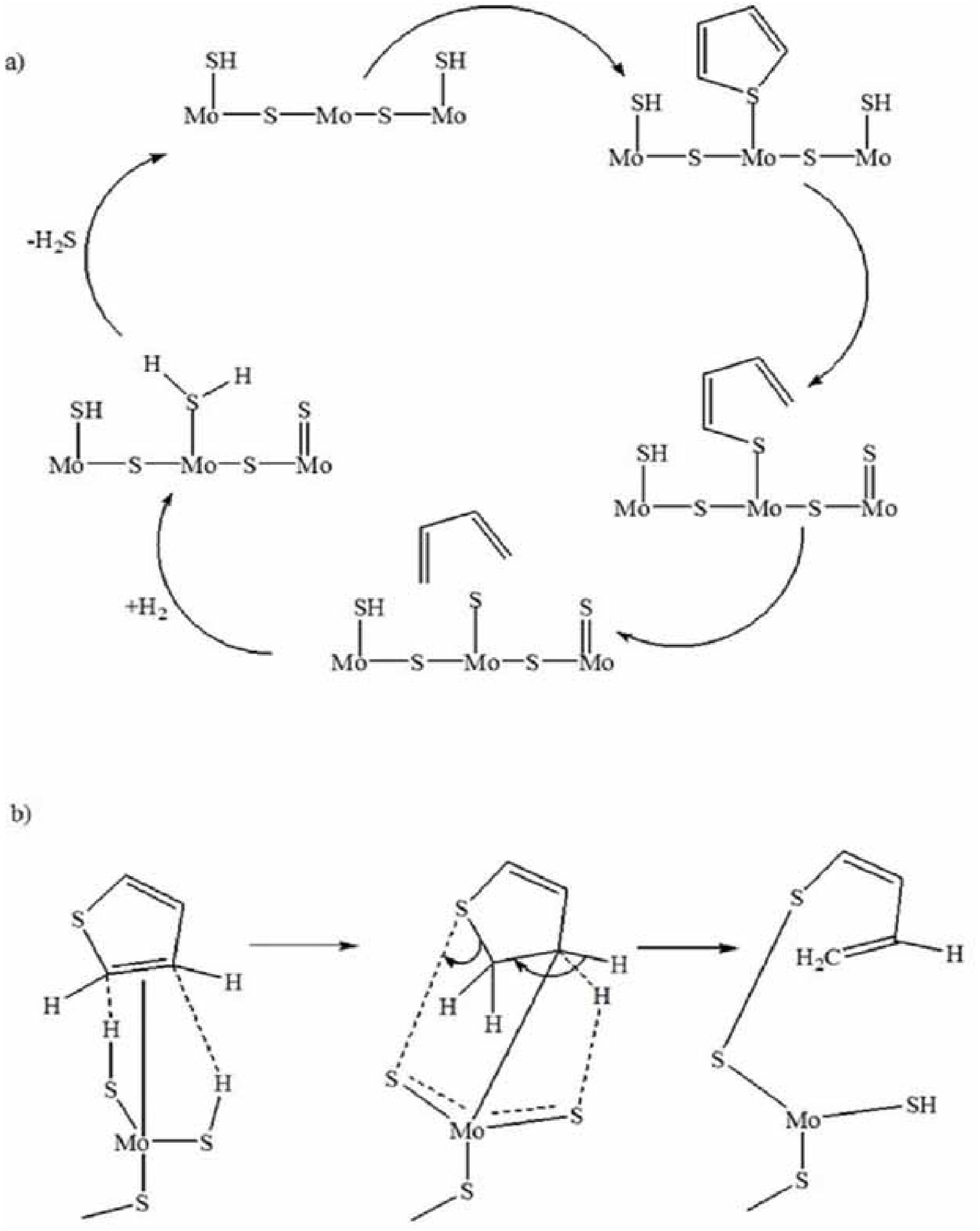
Transition metal sulfide (TMS) catalysts are the cornerstone of hydroprocessing industry due to the innate stability of their catalytically active phases. Since the beginning of the 20th century, TMS have played an important role in fuel upgradation. Ni-or Co- promoted MoS_2 and WS_2 on Al_2O_3 support are the most widely used catalyst systems in conventional HDS. (Whitehurst *et al.*, 1998; Schuit and Gates, 1973; Topsøe and Clausen, 1984; Prins, de Beer, and Somorjai, 1989; Topsøe, Clausen, and Massoth, 1996; Iwata *et al.*, 1998; Alonso and Chianelli, 2004; Song, 2003; Brunet, Mey, Pe´rot, Bouchy, and Diehl, 2005). Mössbauer emission spectroscopy (MES) and EXAFS techniques have enabled scientists to elucidate the complex structures and *in situ* activities of the sulfided Mo/Al_2O_3 catalysts. Various

Figure 3. Course of reaction for the desulfurization of 4,6-DMDBT
Reproduced from Bataille et al., 2000 and Li et al., 2007.



research groups have attempted to characterize the Co/ Mo- Al_2O_3 catalysts. The Co(Ni)-Mo-S structure has been unequivocally recognized as the active structure in the above catalysts. The popular adage “Co-Mo-S” was first used by Topsøe *et al.*, more than 30 years ago when describing the type of Co phases in a series of sulfided Co/Mo- Al_2O_3 catalysts. (Wivel, Candia, Clausen, Mørup and Topsøe, 1981) Three

Figure 4. Schematic representation of η^1 (a) and η^2 (b) mode of bonding of thiophene
Adapted from Dong, Duckett, Ohman and Jones, 1991.



types of Co species were identified in the catalyst, two being the well-known structures- $Co:A1_2O_3$ and Co_9S_8 and a third Co-Mo-S phase. In a study involving HDS of thiophene using different Co/Mo- Al_2O_3 catalysts, Alstrup *et al.*, 1982, established the catalytic significance of "Co-Mo-S" phase. For each series of catalysts, the activity was found to be directly proportional to the amount of Co present in the form of “Co-Mo-S”. (Alstrup, Chorkendoff, Candia, Clausen, and Topsøe, 1982). Several models have been proposed to explain the morphology of MoS_2 catalysts (supported and unsupported) and role of Co- and Ni- promoters in HDS catalysis.

The “Edge Decoration Model”

Structure is composed of MoS_2 crystallites in which Co atoms occupying the edge position (Topsøe *et al.*, 1984; Wivel *et al.*, 1981; N.-Y. Topsøe and H. Topsøe, 1983; Byskov, Hammer, Nørskov, Clausen, and Topsøe, 1997; Smith and Johnson, 1994; Lauritsen, 2001; Miller, Marshall, and Kropf, 2001). The MoS_2 crystals are arranged in layers and are anisotropic in nature. The basal planes are composed of coordinately saturated S atoms and are thus, chemically inert and the active sites are confined to the edge planes. (Sorensen, Clausen, Candia and Topsøe, 1985; Helveg *et al.*, 2000)

The “Rim-Edge” Model

Daage and Chianelli, 1994 developed this model to derive a correlation between the layered structure and the selectivity of MoS_2 catalysts for hydrogenolysis vs. hydrogenation reaction. They identified two different sites for catalysis, the rim sites and the edge sites. According to them, the MoS_2 crystallites could be imagined as a stack of n number of discs, each having diameter d. Located at the top and bottom layers are the “edge” sites which catalysed the hydrogenation of DBT as well as the final C-S bond cleavage to give cyclohexylbenzene. The sites forming the edges of the interior layers (the rim sites) were found to be active, exclusively, for the direct desulfurization of dibenzothiophene i.e. C-S bond cleavage. Selectivity, S ($S=k_{THDBT}/k_{BP}$) is linearly related to 1/h where h is the stacking height. The rim edge model was propounded for unsupported MoS_2 catalysts. Synchrotron X-ray scattering technique was used to determine the morphology of MoS_2 in Co-promoted Mo/Al2O3 catalysts. The results show while Co promoters increase the stacking height of MoS2 phase, the very conditions of HDS, such as high H_2 pressure (Peng *et al.*, 2001), favour the “destocking” of layers. MoS_2 was found to be present in the catalyst, primarily, in single layered form and mostly “rim” sites were present on supported catalysts (Berhault, Dela Rosa, Mehta, Yacaman, and Chanelli, 2008).

It is now well known that the activity of the catalysts emanates from the MoS_2 phase (Topsøe, Clausen, Topsøe, and Pederson, 1986). Studies show that activity of various TMS for HDS of DBT exhibit a typical “volcano” plot depending on their position in the periodic table. (Pecoraro and Chianelli, 1981). Sulfides of Ru, Rh, Os and Ir such as Rh_2S_3, RuS_2, OsS_2, and IrS_2 showed the highest activity. Chianelli *et al.* were the first to relate these findings with the metal-sulfur bond strength, the heat of formation of the metal sulfides and the number of d- electrons in the highest occupied molecular orbital (HOMO) of the transition metals. (Harris and Chianelli, 1984) A comprehensive review on HDS promoters has been provided by Prins, Somorjai and coworkers (Prins *et al.*, 1989) An important phenomenon observed in bimetallic sulfide catalysts is the synergistic or promotion effect. It is measured as the ratio of the activity of the bimetallic catalyst to that of the corresponding Mo catalyst. (Kaluža, Gulková, and Zdražil, 2007) Harris and Chianelli proposed that the promoter atoms increased the electron density on Mo atoms. (Topsøe *et al.*, 1986) Donation of electrons from Co to Mo weakens the metal-sulfur bond which amplified their HDS activity (Harris and Chianelli, 1986; Chianelli *et al.*, 2002). Owing to its thermal and chemical stability, γ-Al_2O_3 is the most commonly used support in industries. (Xia *et al.*, 2003) The morphology of alumina is crucial in determining its physicochemical properties which in turn influence the catalytic behaviour of the catalysts. Surface acidity of alumina (Chen *et al.*, 2013) is the one of the most important features which controls the dispersion of Co-Mo phases and affects the metal-support interaction.

Co-or Ni/MoS_2 catalysts are highly efficient in removing the aliphatic organosulfur species, however, removal of DBT and its alkyl substituents are extremely problematic. The MoS_2 crystals have a layered structure and are anisotropic in nature. As a result, the metal atoms are exposed solely on the edge planes, leading to a low active site density. (Ghenciu, 2002) Thus, researchers are turning attention to new catalytic systems wherein the metal atoms are exposed on all crystallographic faces (isotropic structures). Transition metal phosphates such as Ni_2P, adopt isotropic structures and may replace the conventional TMS in the future due to their enhanced HDS activity (Prins and Bussell, 2012; Savithra *et al.*, 2013). Addition of phosphorus (Poulet, Hubaut, Kasztelan, and Grimblot, 1991; Iwamoto and Grimblot, 2000; Sun, Nicosia, and Prins, 2003; Ramirez, Castano, Leclercq, and Lopez Agudo, 1992) and chelating agents (Sun *et al.*, 2003) have shown to improve the catalytic activity of the Co-Mo-S system. Glasson *et al.* found that incorporation of carbon in CoMo catalysts lead to a positive increase in its HDS activity for thiophene (Glasson, Geantet, Lacroix, Labruyere, and Dufresne,` 2002). Recently, noble-metal-supported catalysts have emerged as ideal candidates (Lin and Song, 1996; Song and Schmitz, 1997; Tang, Yin, Wang, Ji, and Xiao, 2007) since they are much better hydrogenation catalysts than conventional TMS. Hydrogenation, and successive desulfurization is a useful approach in removal of hindered sulfur compounds. Supports other than alumina, such as carbon (Hensen *et al.*, 2000; Farag, Whitehurst, Skanishi and Mochida, 1999; Ledoux, Michaux, Agostini, Panissod, 1986), aluminosilicates (Yue, Sun, and Gao, 1997) mixed oxide supports formed by TiO_2 (Kaluža *et al.*, 2007; Ramı´rez *et al.*, 1989; Okamoto, 1997) and zeolites (Solı´s, Agudo, Ramı´rez, and Klimova, 2006;) are also being explored to study their effect on the desulfurization activity. A new group of catalysts based on Mo-W-Ni, more popularly called the NEBULA are being touted as some of the most efficient next generation catalysts for production of ultra low sulfur diesel. These are known to reduce the sulfur content to 5 ppmw (Chitnis,Novak, Ortelli, and Lewis, 2005; Kerby, Degnan, Marler, and Beck, 2005).

Limitations

Till date, HDS technologies were considered efficient enough for abatement of SOx emissions from gasoline and diesel fuels. HDS and other adjunct technologies are commercially proven technologies, relatively inexpensive and robust. However, with the progressively increasing demand for Ultra-Low Sulfur diesel, the need for alternative solutions is beginning to be felt. In meeting the worldwide demand for ultra-low or zero level sulfur, the efficiency of the hydrotreating process becomes a key issue. As of now, the hydrodesulfurization process cannot produce such zero level sulfur fuels. 4-MDBT and 4,6-DMDBT have been found to be some of the most refractory sulfur compounds present in feedstock which are the major bottle necks in reducing the sulfur content of fossil fuels. The resistance is primarily attributed to the stability of the ring structure as well as the steric inhibition due to the substituents at 4- and 6- positions. There are several other limitations with HDS. It is a high temperature, high pressure process. H_2S produced during desulfurization, inhibits desulfurization of all organosulfur compounds. Both direct desulfurizations as well as the hydrogenation pathways are inhibited; however, the direct desulfurization pathway is inhibited to a much greater extent. (Egorova *et al.*, 2004; Girgis and Gates, 1991) Another challenge when meeting extremely low S content is the selective hydrogenation of organosulfur compounds while maintaining a high octane number of fuels. (Ito and Rob van Veen, 2006) Thus, the classical hydrotreating processes are bound to become extremely expensive in order to meet the future legal specifications.

Unconventional Desulfurization Techniques

Lately, non-HDS based technologies have gained popularity among researchers (Babich and Moulijn, 2003). Two interesting alternatives to HDS, oxidative desulfurization (ODS) and biodesulfuriztion (BDS) will be discussed in this section. Details of oxidative desulfurization and biodesulfurization have been succinctly described by Ito *et al.*, 2006 and Srivastava, 2012. Here, we will only briefly touch the topics focusing on their advantages over hydrodesulfurization.

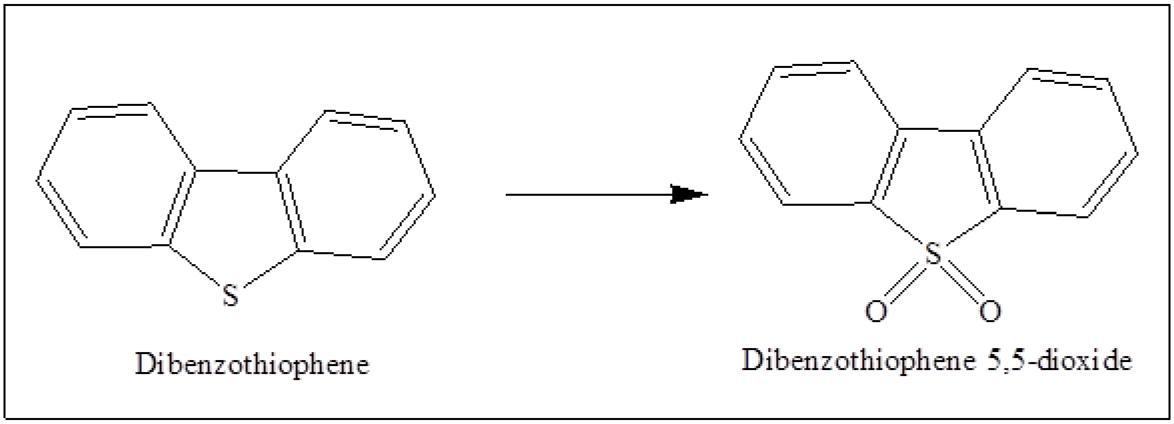
Oxidative Desulfurization

It involves the conversion of organosulfur compounds into corresponding sulfones and sulfoxides which are then removed from the stream by solvent extraction, adsorption and distillation (Tam, Kittrell, and Eldridge, 1990; Aida, Yamamoto, and Sakata, 2000; Dolbear and Skov, 2000). The polarity of sulfones is relatively higher than that of the parent molecules which makes their removal easier. ODS offers several advantages over HDS. ODS is operated under mild conditions (about 50 °C / atmospheric pressure) and in the absence of expensive H_2 (Ali, Al-Maliki, El-Ali, Martinie, and Siddiqui, 2006). The most attractive feature of ODS, is, however, its relatively higher efficiency in converting DBTs, which are among the most recalcitrant compounds towards HDS. The reactivity trends are opposite to those observed for HDS. Thus, where the reactivity of a compound towards HDS decreased with the increase in number of aromatic rings, in ODS, electrophilic attack on S atom is favored by the presence of electron rich aromatic rings. Additionally, electron donating alkyl groups further increase the electron density on S atom, making it susceptible to electrophilic attack. Thus, the reactivity of molecules like 4,6-DMBMT is higher than dibenzothiophene for ODS. Some common oxidizing agents used are inorganic and organic peroxyacids, peroxysalts, catalyzed hydro-peroxides, NO_2, *tert*-butyl-hydroperoxide, etc. (Babich *et al.*, 2003; Ali *et al.*, 2006; Vasile, Francois and Jacques, 2000; R. T. Yang, F. H. Yang, Takahashi, and Maldonado, 2002; Zaykina, Zaykin, Mamaonava, and Nadirov, 2002; H. Mei, B. W. Mei, and Yen, 2003; Yu, Lu, Chen, and Zhu, 2005; Lu *et al.*, 2006; Yang, Li, Yuan, Shen, and Qi, 2007). Oxidative desulfurization of dibenzothiophene can be simply represented as shown in Figure 5. Notably, hydrogen is not used in this reaction.

Biodesulfurization

A much more greener and environmental friendly take on desulfurization is the biodesulfurization. Microbes and bacteria using dibenzothiophenes as S source which metabolize (oxidize) them into water soluble compounds are abounding in nature. Examples include *Pseudomonas, Arthrobacter, and Rhodococcus spp. Pseudomonas and Rhodococcus* are the most widely researched species for oxidative desulfurization. (Grossman, Siskin, Ferrughelli, Lee, and Senius, 1999; Konishi, Yoshitaka, Kouichi and Suzuki, 1999) Soleimani *et al.*(Soleimani, Bassi, and Margaritis, 2007) have reviewed the BDS of refractory organic sulfur compounds in fossil fuels. Recently, it was discovered that a thermophilic bacterium *Mycobacterium goodii* X7B, has exceptional desulfurization characteristics. Li et al have shown

Figure 5. Oxidative desulfurization of Dibenzothiophene into its sulfoxide



that the bacteria brought about an approximate 99% reduction in sulfur content of dibenzothiophene in just 24 hrs. (Li, Zhang, Feng, Cai, and Ping, 2007). The total sulfur content of the crude oil was brought down from 3600 ppm to 1478 ppm in 72 hrs. Studies have demonstrated that BDS of dibenzothiophenes usually occurs along two pathways:

1. The Kodama Pathway (Soleimani *et al.*, 2007; McFarland *et al.*, 1998; Gupta, Roychoudhury, 2005).
2. The 4S Pathway (Monticello, Bakker and Finnerty, 1985).

Though extremely advantageous, none of the above processes are completely devoid of practical or economic problems. Oxidative desulfurization is associated with high cost of solvent extraction, frequent catalyst deactivation and low efficiency of oil recovery. (Zhang, Yu, Wang, 2009) Some major deterrents in commercialization of biodesulfurization is the slow rate of desulfurization (Goubin, Huaiying, Weiquan, Jianmin, and Huizhou, 2005), inhibition in bacterial growth and a lower efficiency (Rath and Upadhyay, 2014). The challenges and limitations linked with engineering advanced catalysts have been reviewed by Bej and co-workers (Bej, 2004; Bej, Maity, and Turaga, 2004).

SCOPE AND SIGNIFICANCE

Inspite of the rapid development of several non-hydrotreating technologies in the past years, HDS continues to remain a key process in every refinery. However, the chemistry of catalytic hydrodesulfurization still remains a subject of debate. Some pertinent questions which need to be answered revolve around the nature of bonding of thiophenes and dibenzothiophenes at the catalyst surface and the C-S bond cleavage step. Benothiophenes and dibenzothiophenes represent a class of compounds which are most averse to desulfurization. Mechanistic insights into the desulfurization of these compounds can, hence, provide plausible reaction sequence for their activation and desulfurization.

By investigating homogeneous desulfurization reactions, it may become possible to procure some insights into the working and improvement of candidate catalysts. Transition metal complexes are excellent stoichiometric reagents to study the desulfurization reactions of thiols, thioethers, thiophene etc. The chapter attempts to describe the progressive research over the years in the area of modelling studies for desulfurization and its mechanism. Features of the desulfurization mechanism which need to be addressed include the binding mode to the catalyst and various reaction pathways adopted. The main motivation behind writing this chapter was to compile the many stoichiometric reactions which demonstrate desulfurization through diverse reaction pathways. Selected studies and some major landmarks have been discussed. One might anticipate that such a study will lead to a better understanding of the desulfurization process and its various facets. Many such reactions show striking similarity.

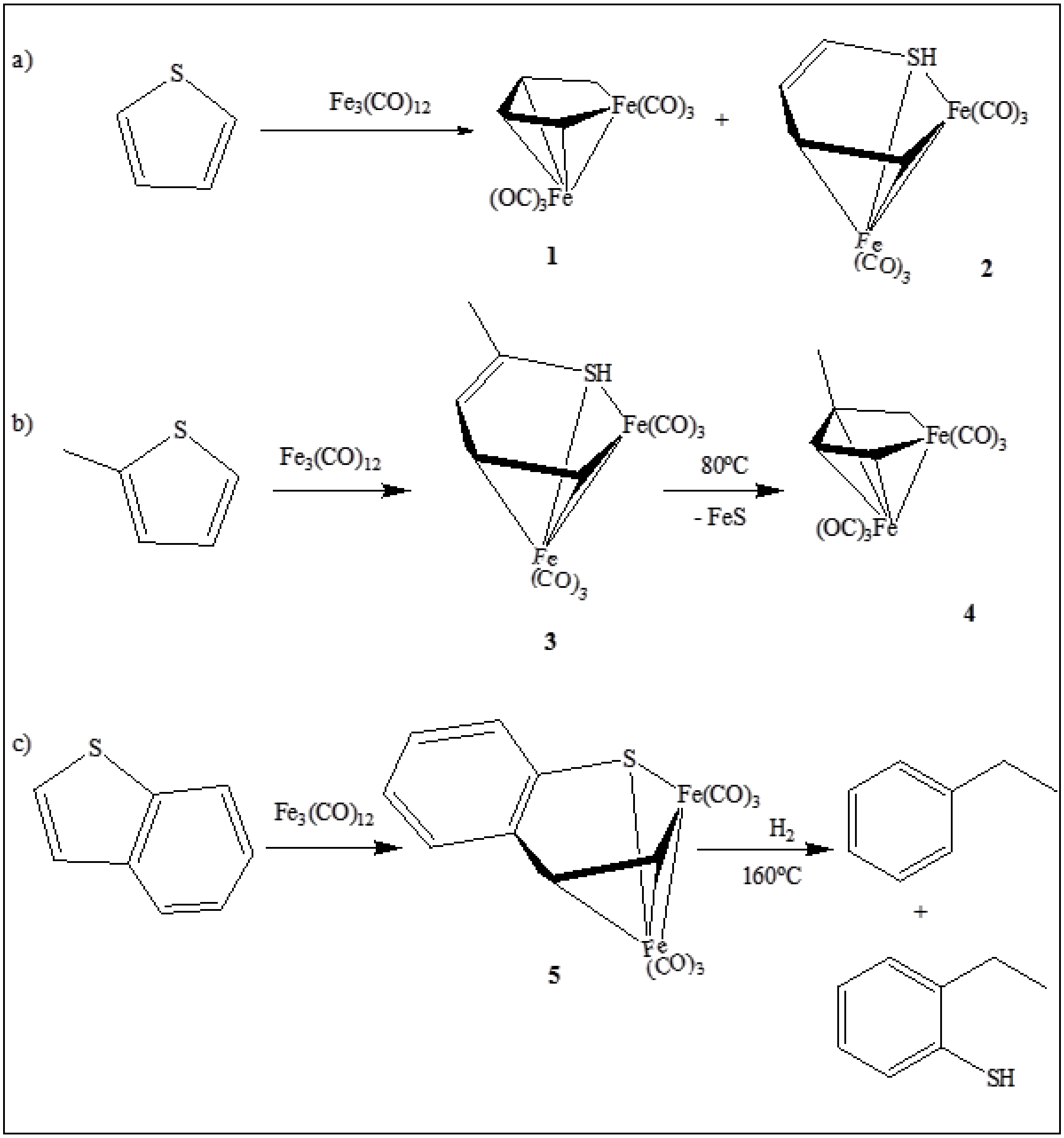
A Review of the Desulfurization Reactions: Mechanisms, Models, and New Routes

Sulfur is abstracted from hydrocarbons on the catalyst surface mainly by the cleavage of C-S bond. The mechanism behind the scissoring of the C-S bond has fruitfully been studied by Ogilvy, Rauchfuss (Ogilvy, Draganjac, Rauchfuss, and Wilson, 1988; Ogilvy, Skaugset, and Rauchfuss, 1989; Feng, Krautscheid, Rauchfuss, Skaugset, and Venturelli, 1995), Curtis (Curtis and Druker, 1997; Riaz, Curnow, and Curtis, 1994), Angelici (Chen, Daniels, and Angelici, 1996) and many others. Thiophene being relatively simple in structure has predominantly featured as substrate in model studies by Rauchfuss and coworkers. Insertion of metal into the C-S bond possibly labilizes the bond and activates it for desulfurization. Homogeneous desulfurization of thiophene and alkyl substituted thiophenes by $Fe_3(CO)_{12}$ gives ferrols (1) and thiaferrols (2) (Ogilvy *et al.*, 1988) (Figure 6 a,b). The thiaferroles, $Fe_2(2\text{-}MeC_4H_3S)(CO)_6$(3) and $Fe_2(2,5\text{-}Me_2C_4H_2S)(CO)_6$ undergo a facile conversion to corresponding ferroles (4) in refluxing benzene solution. Benzothiophene reacts with $Fe_3(CO)_{12}$ yielding bezothiaferrole $Fe_2(C_8H_6S)(CO)_6$ (5) in about 50% yield. Hydrogenation of $Fe_2(C_8H_6S)(CO)_6$ generated ethylbenzene (41%) and substituted ethylbenzenes along with an insoluble iron containing product (Figure 6c). On the contrary, dibenzothiophene was found to be unreactive under similar conditions. The finding offer conclusive proofs for the activation of C-S bond in thiophenic compounds following the insertion of Fe atom.

Reaction of $[(\eta^5\text{-}C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)]$ (7) (formed by two one electron reduction of $[(\eta^5\text{-}C_5Me_5)Rh(\eta^5\text{-}C_4Me_4S)]^{2+}$(6))with $Fe_3(CO)_{12}$ gave $(C_5Me_5)RhC_4Me_4Fe(CO)_3$ (8) with elimination of FeS. The product is analogous to that obtained in the reaction of thiophene with $Fe_3(CO)_{12}$ (Figure 7) It has been invoked that electron transfer leads to a change in the heptacity of the thiophene ligand from η^5 to η^4. Such η^5 to η^4 transformations can be expected to take place on the HDS catalyst surface as possible route in the desulfurization of thiophenes.

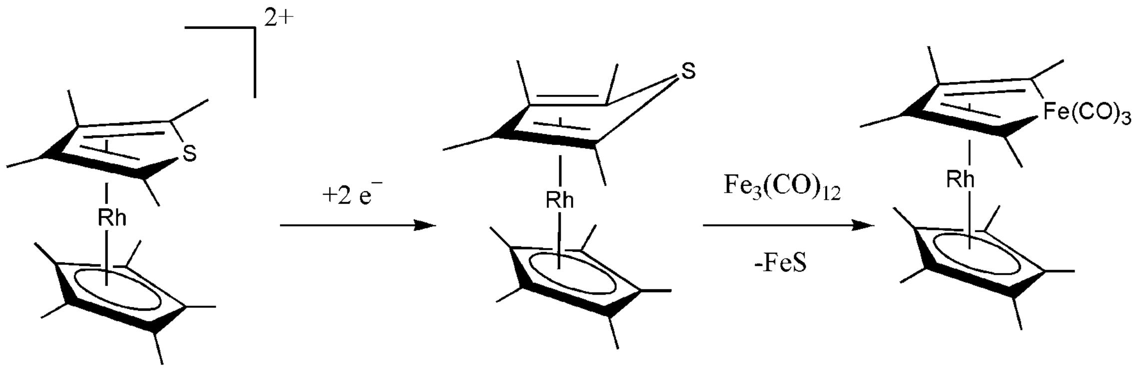
Thermal reaction of cyclic thioethers such as thiirane with a cationic thioether complex $[(CpMo)_2(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]^+$ (9) results in its desulfurization *via* the release of free dimethylsulfide and ethylene by an intramolecular hydrocarbon elimination (Gabay, Dietz, Bernatis, Rakowski and DuBois, 1993) (Figure 8) Similar facile desulfurization reactions have been reported for thietane and 2,5-Dihydrothiohene (2,5-DHT) yielding cyclopropane and butadiene as products respectively. The findings are in agreement with studies of Roberts and Friend who postulated an identical pathway for the desulfurization of thiirane on a Mo(110) surface. (Roberts and Friend, 1987). Thus, the reactions provide a homogeneous model for the formation of anionic vacancies on the sulfided Mo(110) surface (Gabay et al., 1993) It has been proposed that the S atom of the heterocyclic ring initially binds with one or both the Mo atoms followed by the elimination of a hydrocarbon.

Figure 6. Reaction of Thiophenes and Benzothiophenes with $Fe_3(CO)_{12}$
Adapted from the work of Ogilvy et al., 1988.



Adams and co-workers (Adams, Pompeo, Wu, and Yamamoto, 1993) showed that partially hydrogenated thiophenes are possible intermediates in the desulfurization of thiophenes. They proposed a ring opening route for the desulfurization of 2,5-THT on the Mo(110) surface. The mechanism has its roots in the transformations on the osmium carbonyl cluster as shown in Figure 9.

Figure 7. Desulfurization of $[(\eta^5\text{-}C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)]$
Adapted from Ogilvy et al., 1989.

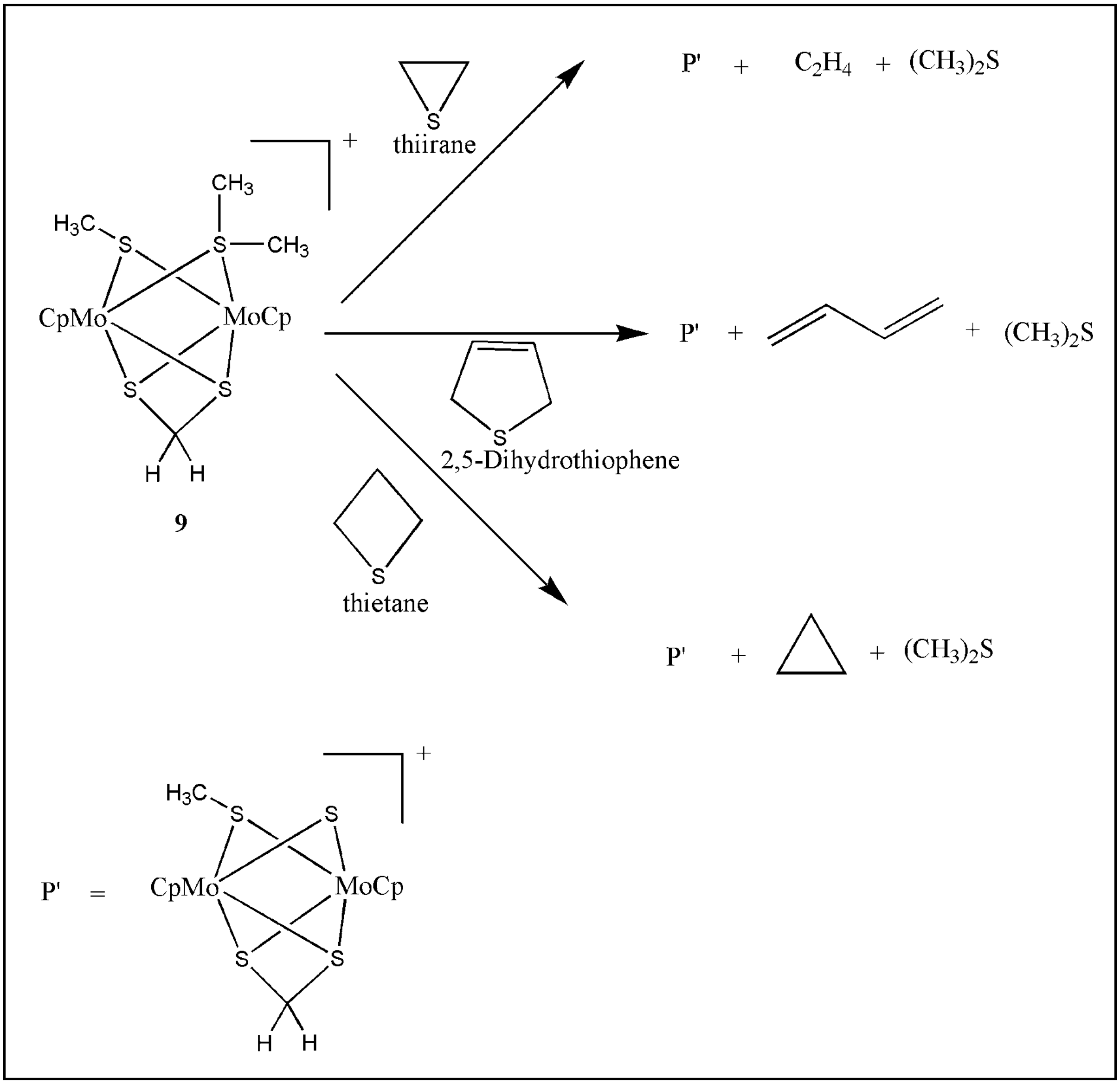


6 **7** **8**

Among one of the earliest most extensive studies of the cleavage of C-S bond is that of Druker and Curtis, 1995. Electron deficient clusters have been presented as models for HDS studies. He showed that the electron deficient $Cp'_2Mo_2Co_2S_3(CO)_4$ (10) ($Cp' = C_5H_4Me$) mediates the homolytic C-S bond cleavage of several organosulfur compounds such as RSH (R= ^{t}Bu, Ph etc) and thiophene. Curtis and Riaz gave the following mechanism for the desulfurization (Figure 10). (Curtis, 1996) This system best resembles the heterogenous catalyst Co-Mo-S. They proposed that the apparent “mobility” of the sulfur atom on the “cluster surface” was responsible for the formation of transient intermediates with open coordination sites for the incoming organosulfur compound.

Discrete metal complexes have proven to be useful in studying the mode of binding of thiophene at the catalyst surface and its reactivity. (Angelici, 1990, 1997, 2001;Rauchfuss, 1991; Sánchez-Delgado, 2002) Both π-bonded metal-thiophene and insertion of metal into the C-S bond have been suggested as probable intermediates in the HDS of thiophene. The DDS pathway takes place primarily through σ- bonding whereas the HYD route is initiated by π- coordination through the aromatic ring, as postulated by Egorova and Prins, 2004. Lesch *et al.* studied the reactions of π-bonded thiophene ligand in a complex, $Mn(CO)_3(thiophene)^+$ (Lesch, Richardson, Jacobson, and Angelici 1984). This complex was highly susceptible to nucleophilic addition reactions. Nucleophilic addition at the C lying adjacent to the S atom of thiophene breaks the aromatic stabilization of the five membered thiophene ring. Under HDS conditions, this step may prove to be critical in decreasing the energy barrier for desulfurization. Li, Carpenter, and Sweigart, 2000 showed that η^6 coordination of $Mn(CO)_3^+$ to benzothiophene as well as dibenzothiphene made them susceptible for nucleophilic attack. Coordination of the electophilic metal fragment to the phenyl ring activates the C(aryl)-S bond in the adjacent heterocylic ring to attack by the nucleophile, $Pt(PPh_3)_2(C_2H_4)$. The reactions provide crucial evidence that η^6 coordination of benzo and dibenzothiophenes promotes insertion of metal in the C-S bond. (Figure 11) It has also been observed that thiophenes undergo C-S bond oxidative addition when heated with a complex, $(C_5Me_5)Rh(PMe_3)(Ph)H$ (11). The reaction involves coordination of metal to S atom in η^1 mode followed by insertion of

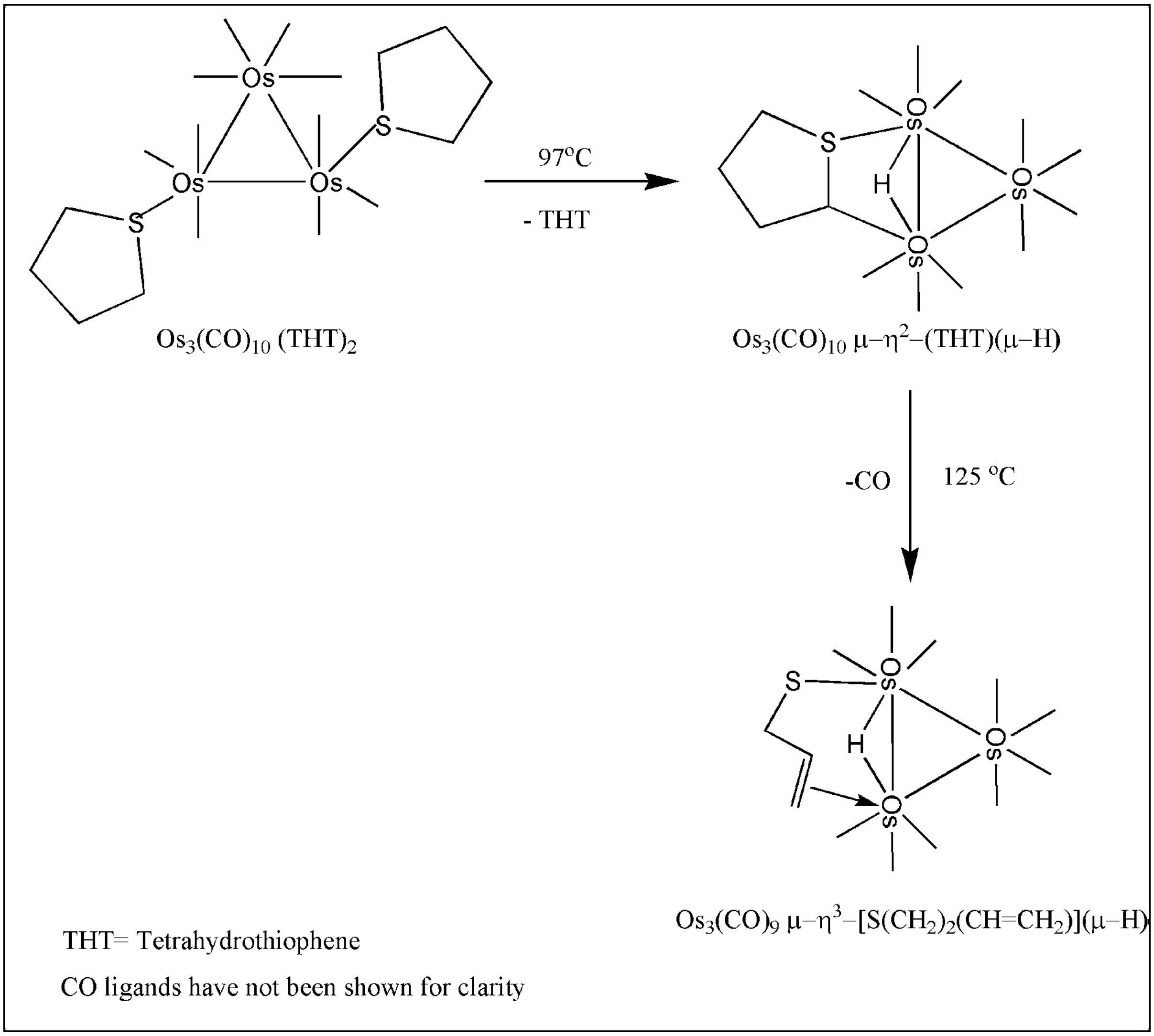
Figure 8. Desulfurization reactions mediated by dinuclear cyclopentadienylmolybdenum complexes



metal into C-S bond of thiophene (Jones and Dong, 1991). Reaction of (C_5Me_5)Rh(PMe_3)(Ph)H with benzothiophenes and dibenzothiophenes also results in formation the C-S inserted products, 12 and 13 respectively. (Angelici, 2001) (Figure 12)

Strained ring thioethers such as thiirane and thietane quintessentially serve as a source of S atoms. Thus, it was expected that a reaction of thiirane with CpRu(PPh_3)$_2$OTf would yield a complex of the type [CpRu(PPh_3)$_2$S]$^{4+}$ after cleavage of C-S bond. Instead, a transition metal analogue of the elusive episulfonium salt with the molecular formula [CpRu(PPh_3)$_2$(SC_2H_4)]OTf (14) was obtained in 80% yield (Figure 13a) (Amarasekera, Rauchfuss, and Wilson, 1988). In this complex, thiirane acts as a ligand and is bound to the central metal through the S atom. As shown earlier heterocyclic compounds may

Figure 9. Ring opening of tetrahyrothiphene by a triosmium cluster
Adapted from Adams et al., 1993.



bind to the metal centre in HDS through S atom. Another study, however, shows the synthesis of a new sulfido metal carbonyl complex, $Mn_2(CO)_7(\mu\text{-}S2)$ (15) by transfer of the sulfur atom of thiirane to the metal atoms of $Mn_2(CO)_9(NCMe)$ (Figure 13b). (Adams, Kwon, and Smith, 2002)

Reaction of a substituted pyrazolyl ligand, bis-(3,5-dimethylpyrazolyl)methylphosphine sulfide, $MeP(S)(3,5\text{-}Me_2Pz)_2$ (16) with cuprous chloride in 1:1 ratio leads to the formation of a tetranuclear copper cluster. It has been proposed that initially, a complex $16.CuCl_2$ is formed. (Figure 14) The five coordinate phosphorus centre in $16.CuCl_2$ is attacked by H_2O molecules giving the species 17. Ready desulfurization of 17 in form of H_2S and a simultaneous hydrolysis of the P-N bond gives the polynuclear complex. (Chandrasekhar, Kingsley, Vij, lam, and Rheingold, 2000)

The 17-electron radical species, $CpCr(CO)_3\bullet$ (Cp= η5-C_5H_5) have been investigated for their role in the facile cleavage of C-S bond. The radical species are extremely thiophilic and have been shown

Figure 10. Mechanism of desulfurization at the catalyst surface; M'= Mo(Cp')
Adapted from Curtis, 1996.

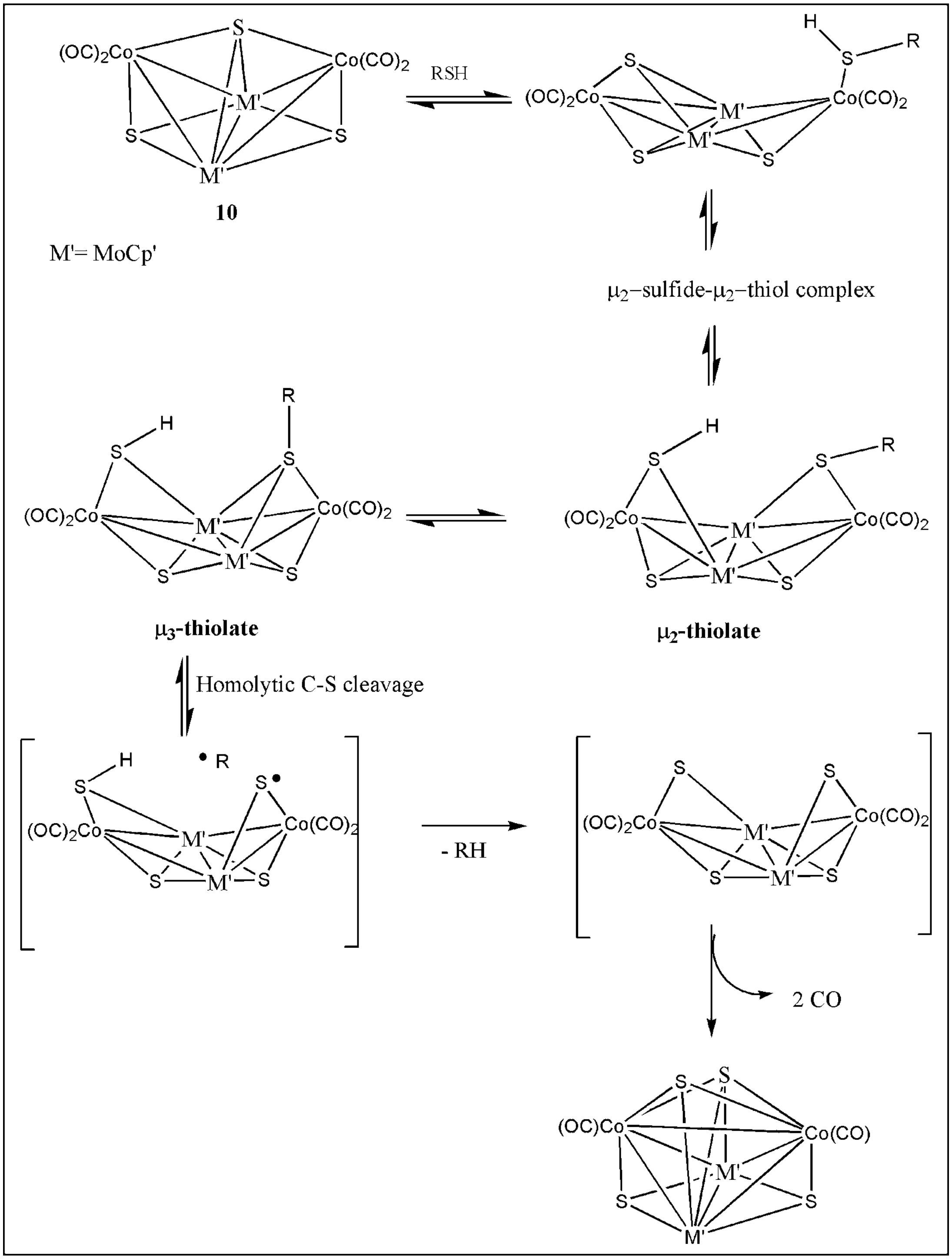


Figure 11. Benzothiophenes and dibenzothiophenes show η^6coordination
Adapted from Li et al., 2000.

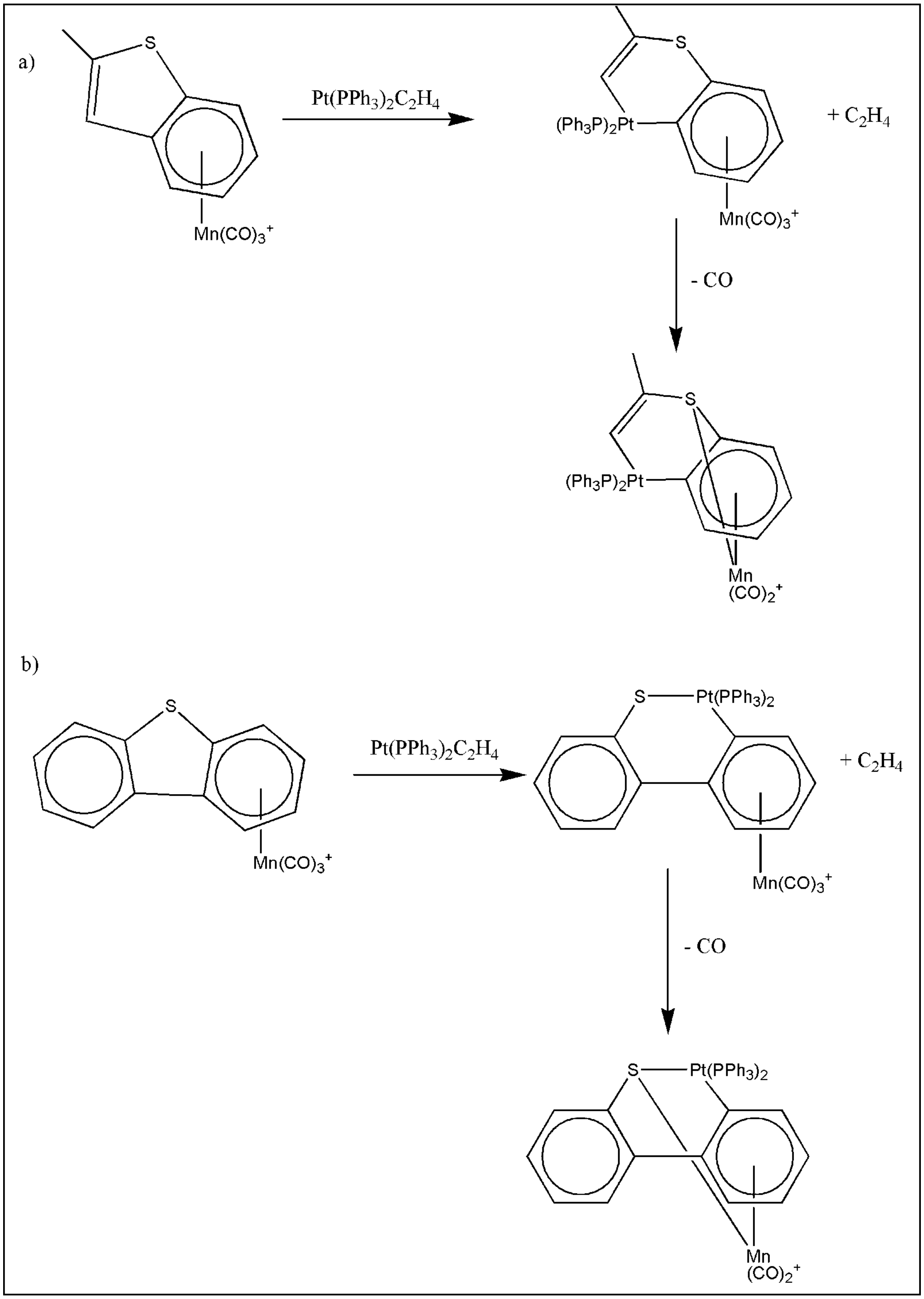
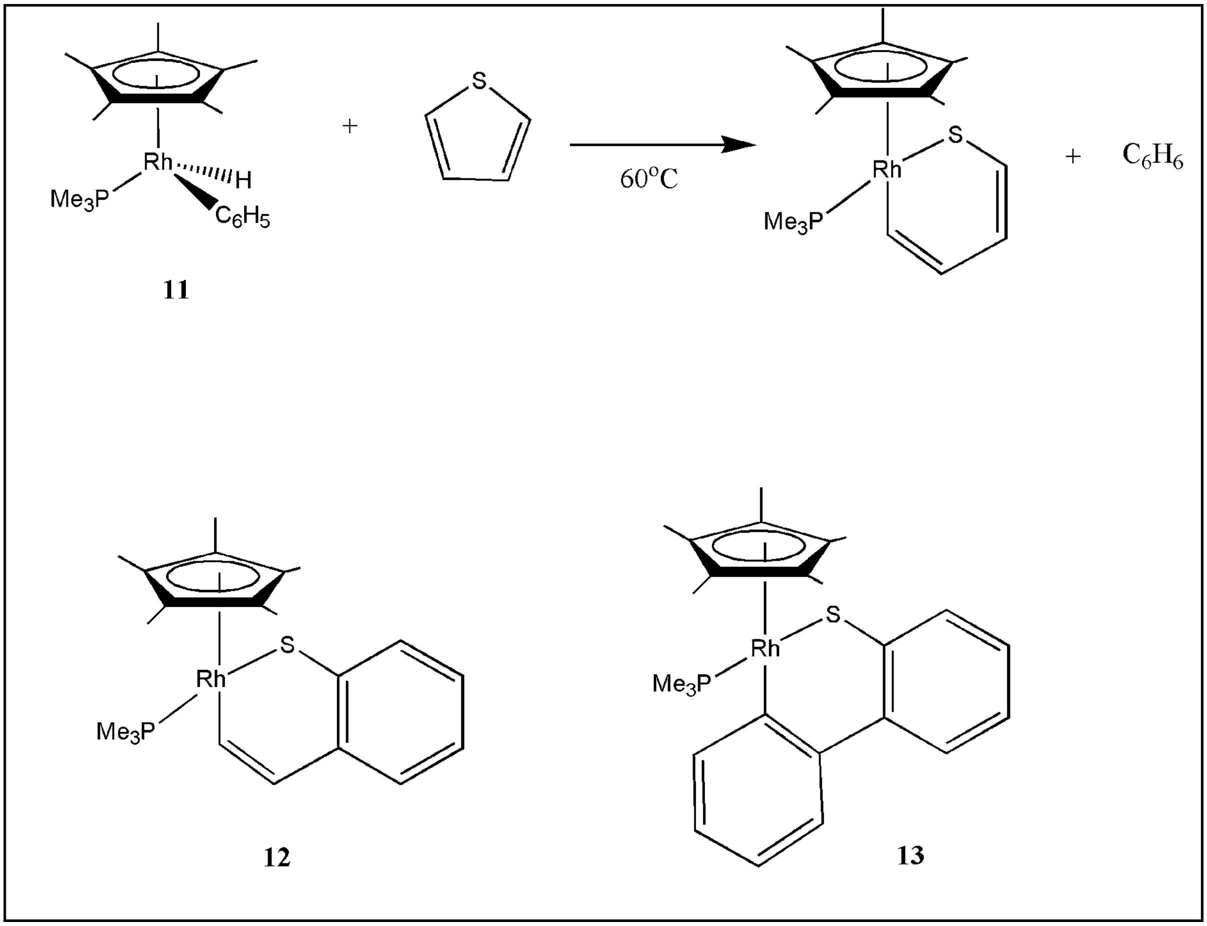


Figure 12. Importance of η^1 coordination in formation of C-S inserted products
Reproduced from Jones et al., 1991.



11

12

13

to promote breaking of C-S in dithiocarbamate ligands. Reaction of [{CpCr(CO)$_3$}$_2$] (18)with 1 mol equivalent of tetraethylthiuram disulfide [Et$_2$NC(S)S]$_2$ at ambient temperature led to the isolation of [CpCr(CO)$_2$(S$_2$CNEt$_2$)] (19) in quantitative yields (Figure 15a). Thermolysis of this complex leads to a mixture of products (Figure 15b). Among them, formation of [CpCr(CO)$_2$(SCNEt$_2$)] (20) is suggestive of the cleavage of a C-S bond in 19. Synchronous cleavage of C-S bond of (19) and intermolecular coupling of C-C bonds between two dithiooxamide ligands gives the double cubane structure of (21) in which the dithiooxamide ligand links the two cubes via μ-η^2,η^4 binding mode (Goh,Weng, Leong, and Leung, 2001).

Analysis of the reactivity of organosulfur compounds towards discrete metal/organometallic complexes having Mo or W as the metal centre is an extremely attractive prospect in view of the fact that most of the HDS catalysts are based on these two metal sulfides. Facile room temperature cleavage of a C-S bond of thiophene byMo(PMe$_3$)$_6$ at room temperature gave two products, the thiophene adduct (η^5-C$_4$H$_4$S)Mo(PMe$_3$)$_3$ (22) and the butadiene-thiolate complex (η^5-C$_4$H$_5$S)Mo(PMe$_3$)$_2$(η^2-CH$_2$PMe$_2$) (23). (Janak, Tanski, Churchill, and Parkin, 2002). Formation of the adduct is attributed to the cleavage of the C-S bond and hydrogenation of thiophene (Figure 16).Hydrogen necessary for this reaction

Figure 13. a) Thiirane as a ligand; b) desulfurization of thiirane

a) Adapted from Amarasekera et al., 1988; b) Reproduced from Adams et al., 2002.

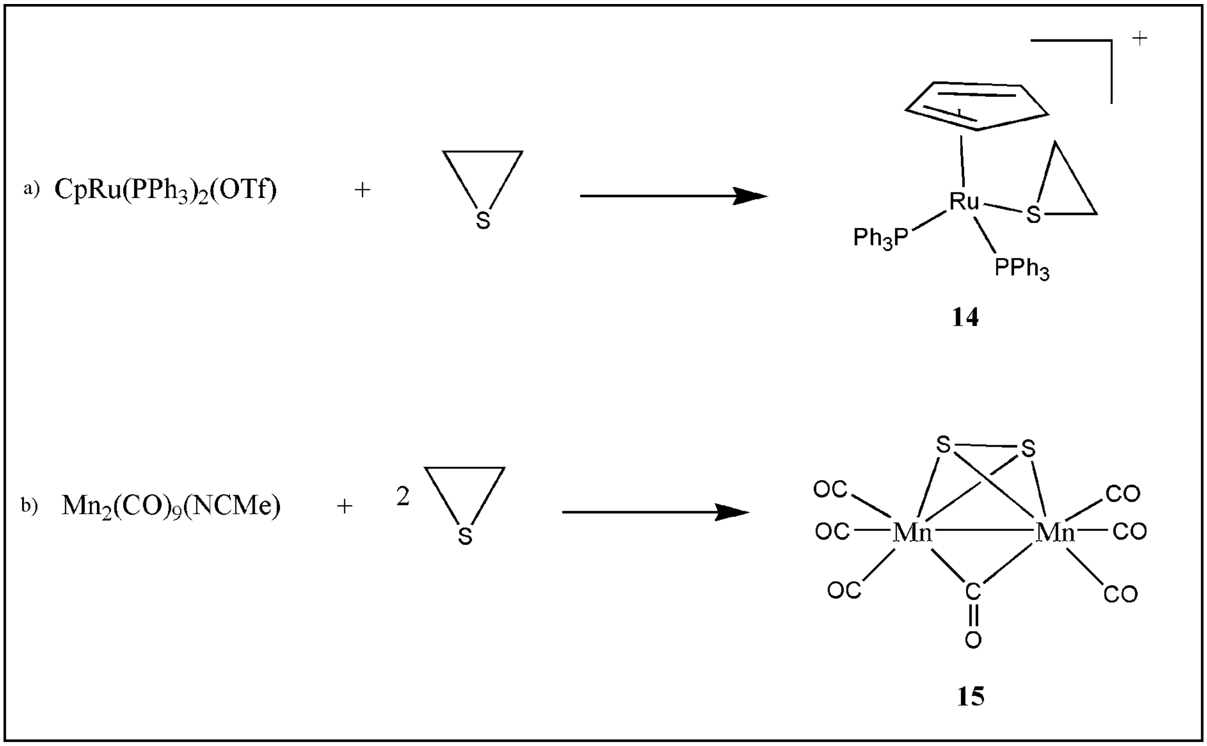


Figure 14. Reaction mechanism for synthesis of polynuclear complex by release of H_2S

Adapted from the work of Chandrashekhar et al., 2000.

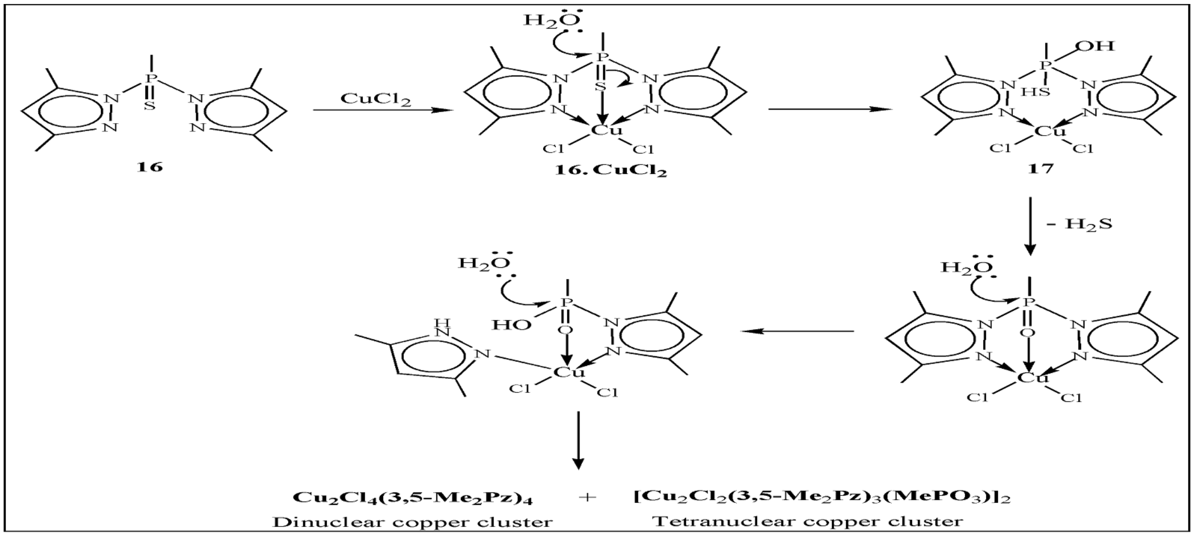
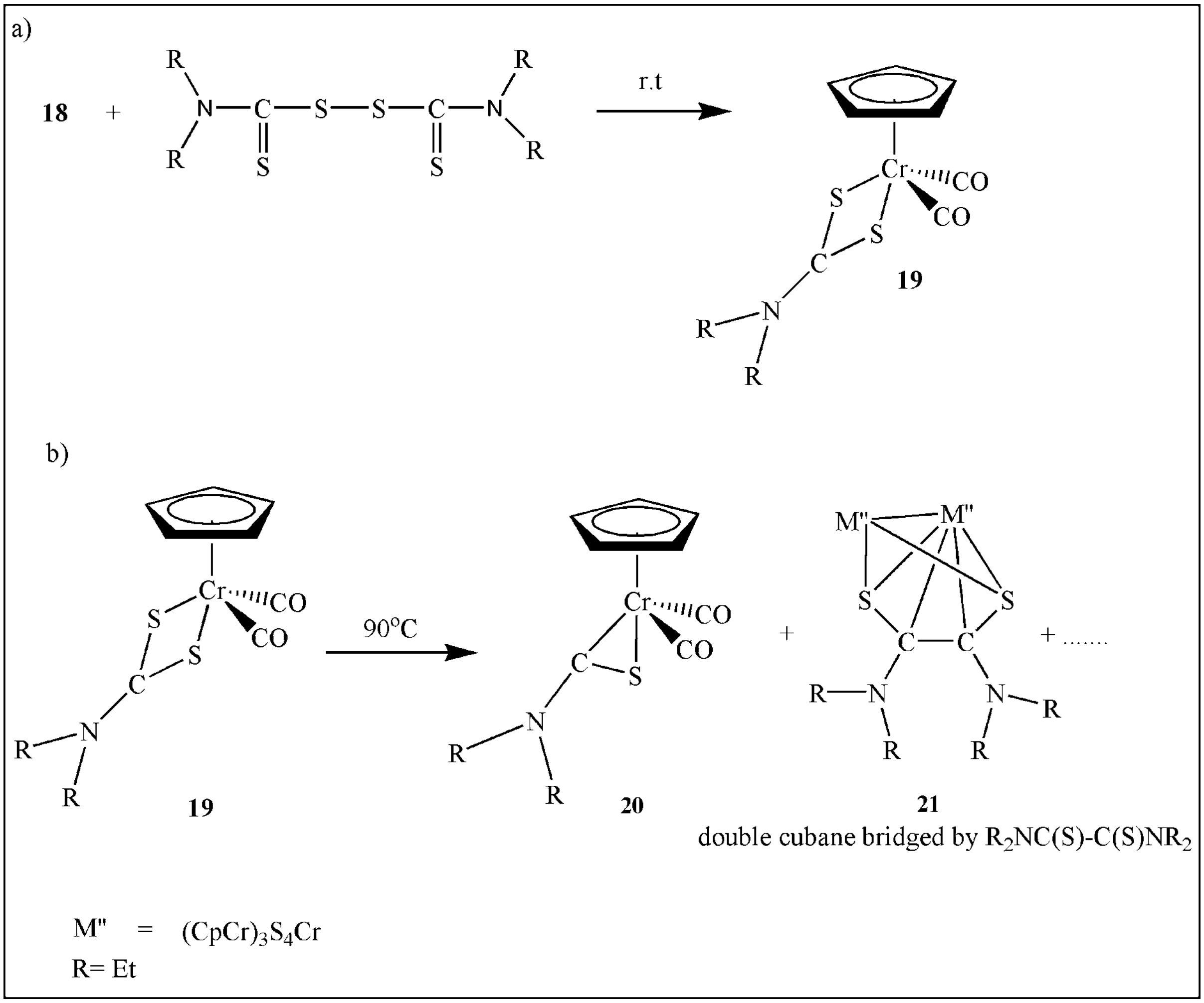


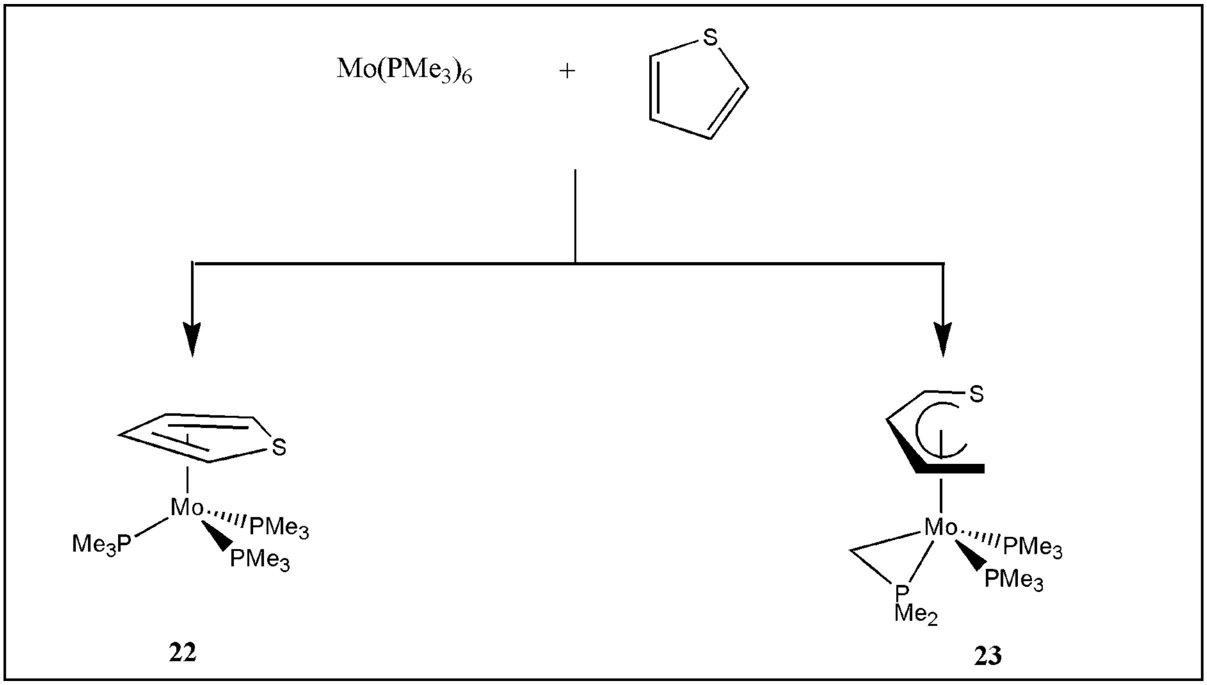
Figure 15. Cleavage of C-S bond and C-C coupling in some chromium complexes
Reproduced from Goh et al., 2001.



is provided by the PMe_3 ligand which itself gets converted to the 'cyclometalated' η^2-CH_2PMe_2 ligand (L). The reaction proceeds via the formation of (κ^2-C,S-C_4H_4S)Mo$(PMe_3)_4$ (24) which readily converts to (23) by the transfer of hydrogen (H*) from PMe_3 to the C of thiophene lying adjacent to the S atom (Figure 17). Both the thiophene adduct as well as the butadiene-thiolate complex have been proposed as possible intermediates in the HDS reaction. The study forms the basis for pursuing reactions which occur on the Mo catalyst surface.

Diffusion of a solution of $CuCl_2$. $2H_2O$ into a solution of 2-mercapto-5-methyl-1,3,4-thiadiazole results in the formation of a one-dimensional polymeric compound, $[Cu(H_4C_3N_2S)Cl_2]_n$. The reaction involves simultaneous desulfurization of the ligand leading to the removal of a side sulfur atom and its subsequent oxidation to sulfate anion (Song *et al.*, 2003). Solvothemal reaction between cupric chloride

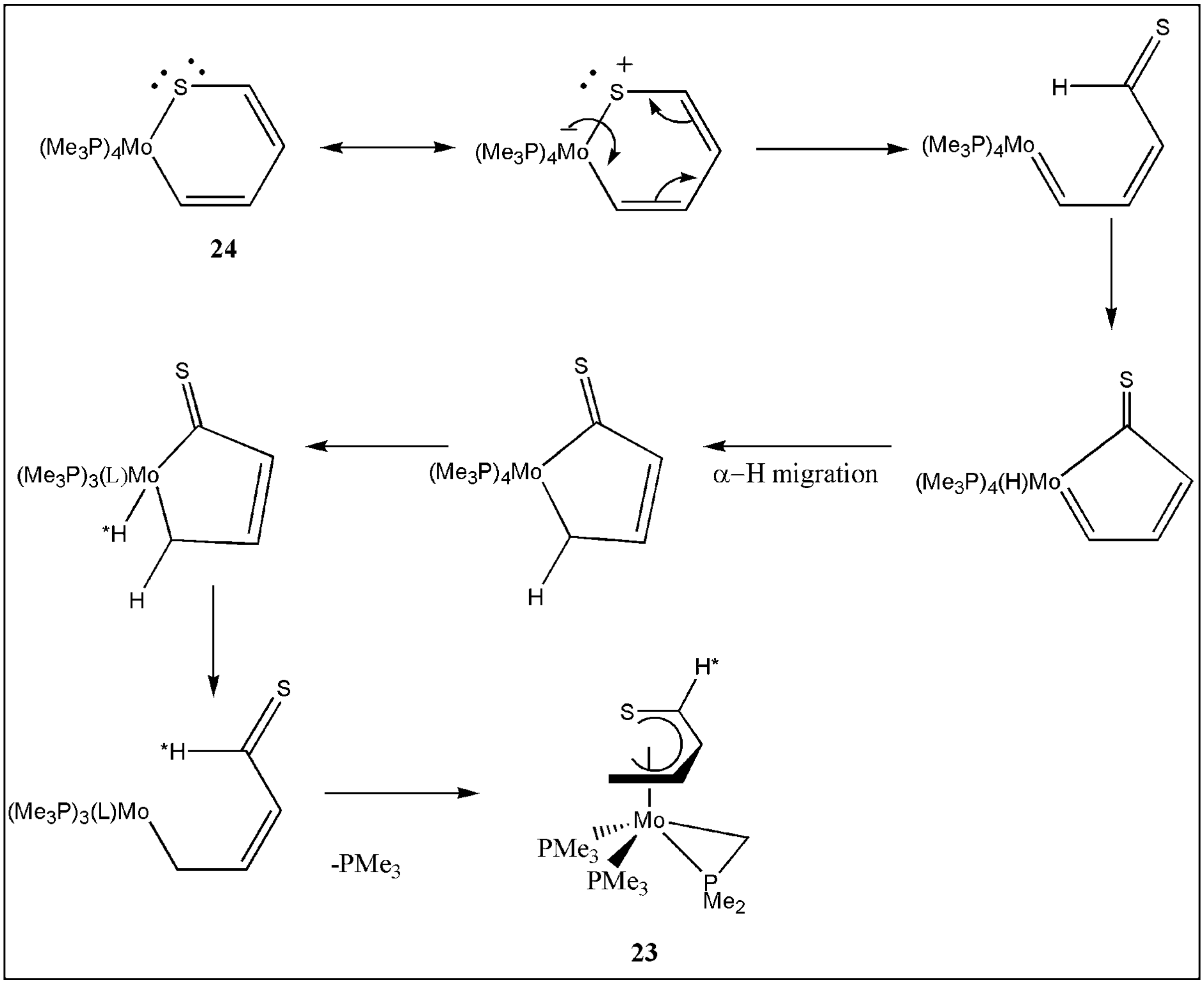
Figure 16. Reaction of $Mo(PMe_3)_6$ *with thiophene*



with pyridine-4-thiol ligand leads to the formation of a decanuclear Cu(I) cluster. Crystals of $CuSO_4.5H_2O$ are procured from the reaction mixture as by-products. The reaction demonstrates an example where an *in-situ* desulfurization of the organosulfur moiety is followed by a redox reaction. S^{2-} is oxidized to S^{6+} while Cu^{2+} reduced to Cu^+. The yield of $CuSO_4.5H_2O$ is, however, low implying that only a small amount of pyridine-4-thiol is desulfurized. (Cheng *et al.*, 2005) Biphenyl-2-thiol is often proposed as an intermediate in the desulfurization of dibenzothiophene. Hence, a reaction involving a facile room temperature desulfurization of biphenyl-2-thiol is extremely significant. Reaction of an equimolar mixture of Nickel (I) dimer $[(dippe)Ni(\mu\text{-}H)]_2$(25) (dippe= 1,2-Bis(diisopropylphosphino)ethane) and biphenyl-2-thiol gives $[(dippe)_2Ni_2(\mu\text{-}S)]$ (26) and biphenyl while a 1:2 ratio yields the a mixture of products, $[(dippe)_2Ni_2(\mu\text{-}S)]$(26), $[(dippe)Ni(\eta^1\text{-S-biphenyl-2-thiolate})_2]$ (27) and complex (28) (Figure 18). Furthermore, when the nickel complex and biphenyl-2-thiol were mixed in a 1:4 ratio respectively, compound 27 was formed as the only product. Variable Temperature NMR analysis of the first reaction in the temperature range of -80°C to 60°C was indicative of the following sequence of events leading to the formation of biphenyl (Figure 19). In the context of industrial HDS processes where Ni is often used as a promoter in catalysts, the compound $[(dippe)_2Ni_2(\mu\text{-}H)(\mu\text{-}S\text{-2-biphenyl})]$ (29) may most likely serve as a model intermediate. (Nieto, Brennessel, Jones, and Gracia, 2009)

Sattler and Parkin, 2011 studied the reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with various thiophenes and compared it with that of the analogous Mo system. It was demonstrated that similar to Mo complexes, tungsten centers also bring about such transformations which are relevant to hydrodesulfuriza-

Figure 17. Formation of metallathiacycle and cleavage of C-S bond
Adapted from Janak et al., 2002.



tion of thiophenes. Cleavage of C-S bond in thiophenes by $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (30) yields the butadiene-thiolate complex $(\eta^5\text{-}C_4H_5S)W(PMe_3)_2(\eta^2\text{-}CH_2PMe_2)$ (31) which on hydrogenation liberates but-1-ene *via* the formation of a butanethiolate complex, $W(PMe_3)_4(SBu^n)H_3$ (32)(Figure 20). Similarly, benzothiophene gets converted to the isomeric forms $(\kappa^1,\eta^2\text{-}CH_2CHC_6H_4S)W(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)$ (33) and $(\kappa^1,\eta^2\text{-}CH_2CC_6H_4S)W(PMe_3)_4$ (34), either of which subsequently get converted to ethylbenzene on hydrogenation followed by heating. Under the above reaction conditions, dibenzothiophene is ultimately transformed to biphenyl.

In the past few years, our research group has investigated several reactions in which the discrete metal complexes underwent desulfurization. As a part of our study on desulfurization processes we have encountered few unprecedented modes of desulfurization. While attempting to synthesise *bis*-dithiocarbamate complexes of Al(III) in our laboratory, cyclic ammonium salts were obtained as products *via* elimination of CS_2 (Figure 21). (Chaturvedi, Bhattacharya, and Nethaji, 2008)

Figure 18. Reactions of Biphenyl-2-thiol with a dimeric nickel complex
Reproduced from the work of Nieto et al., 2009.

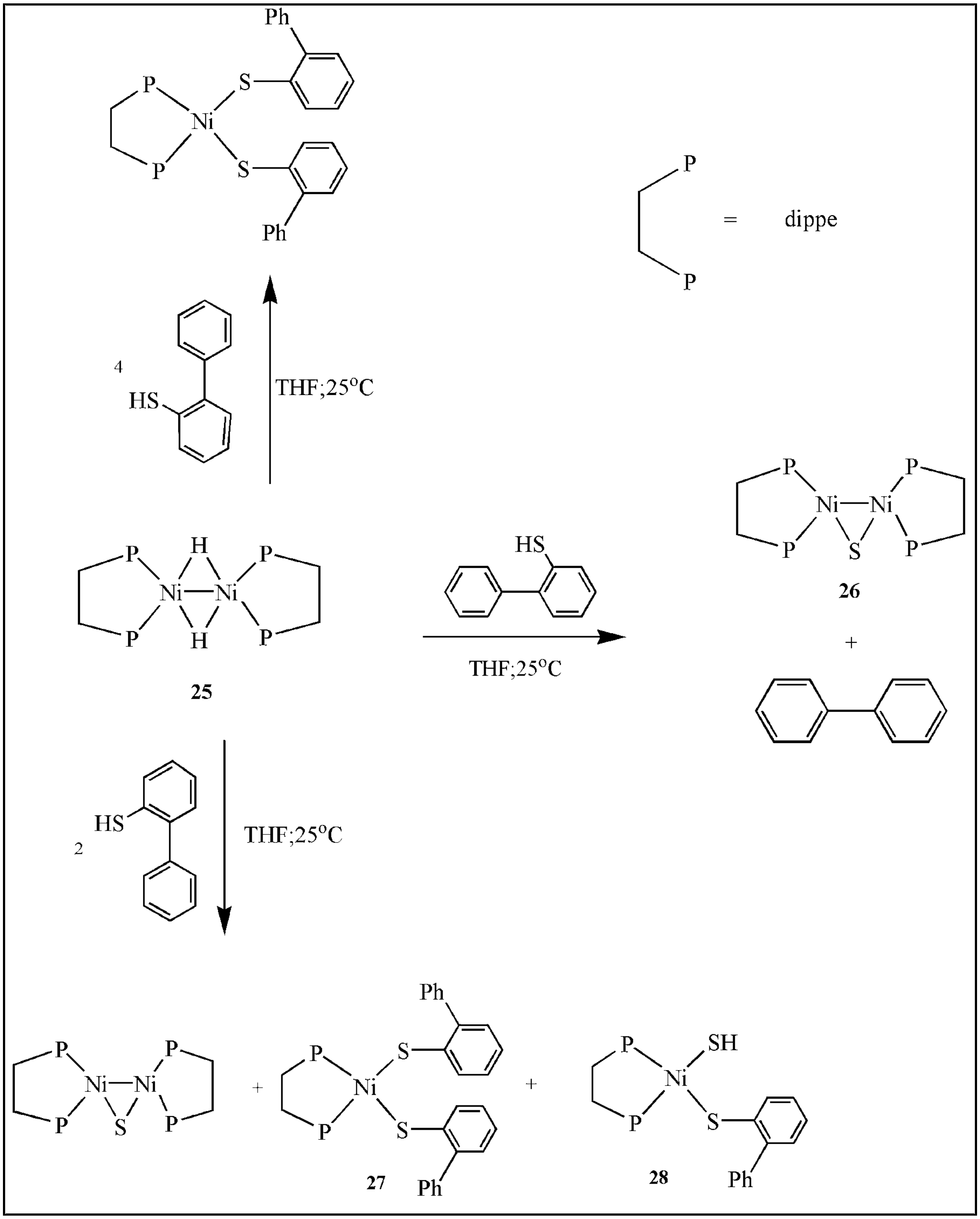
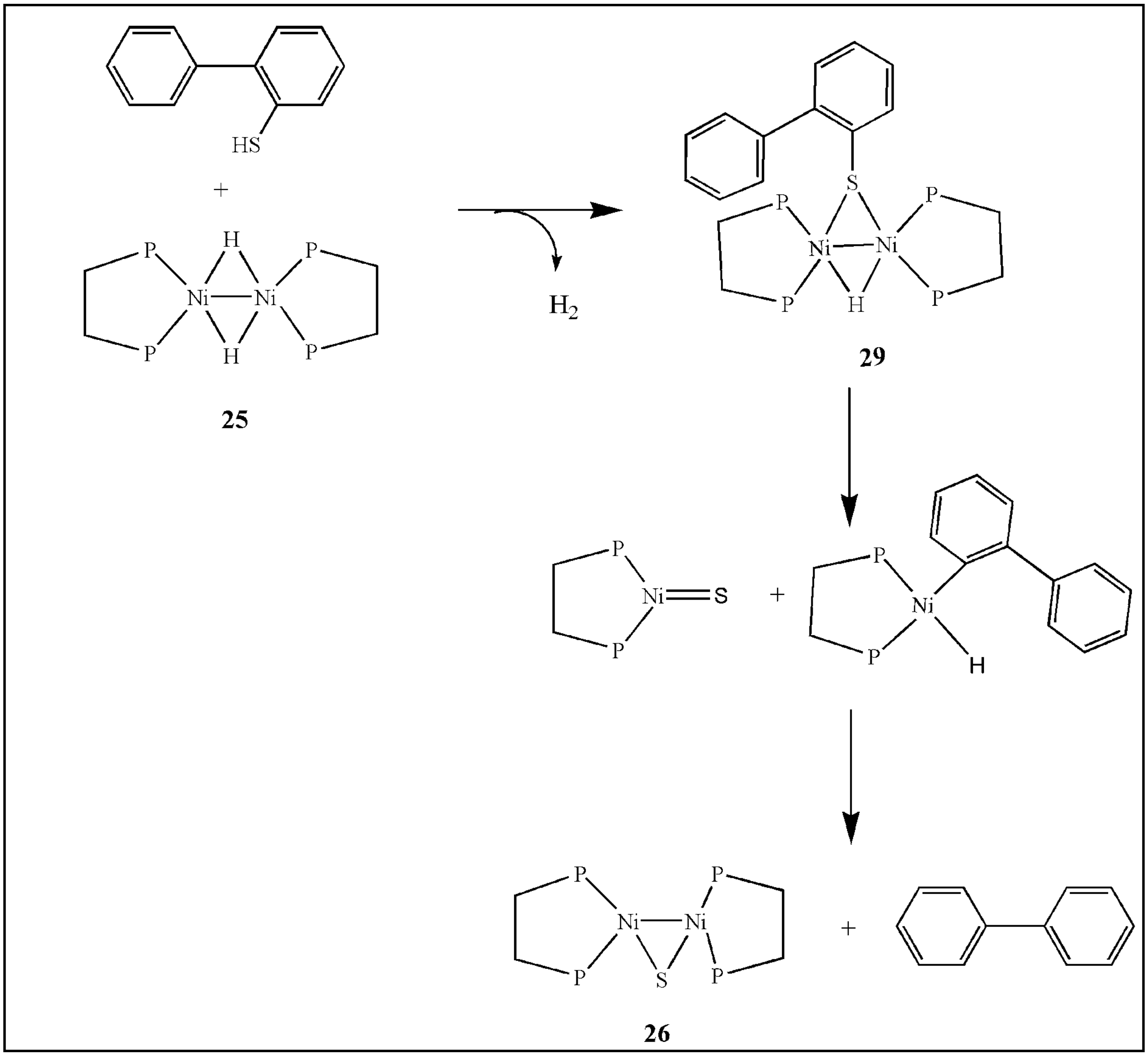


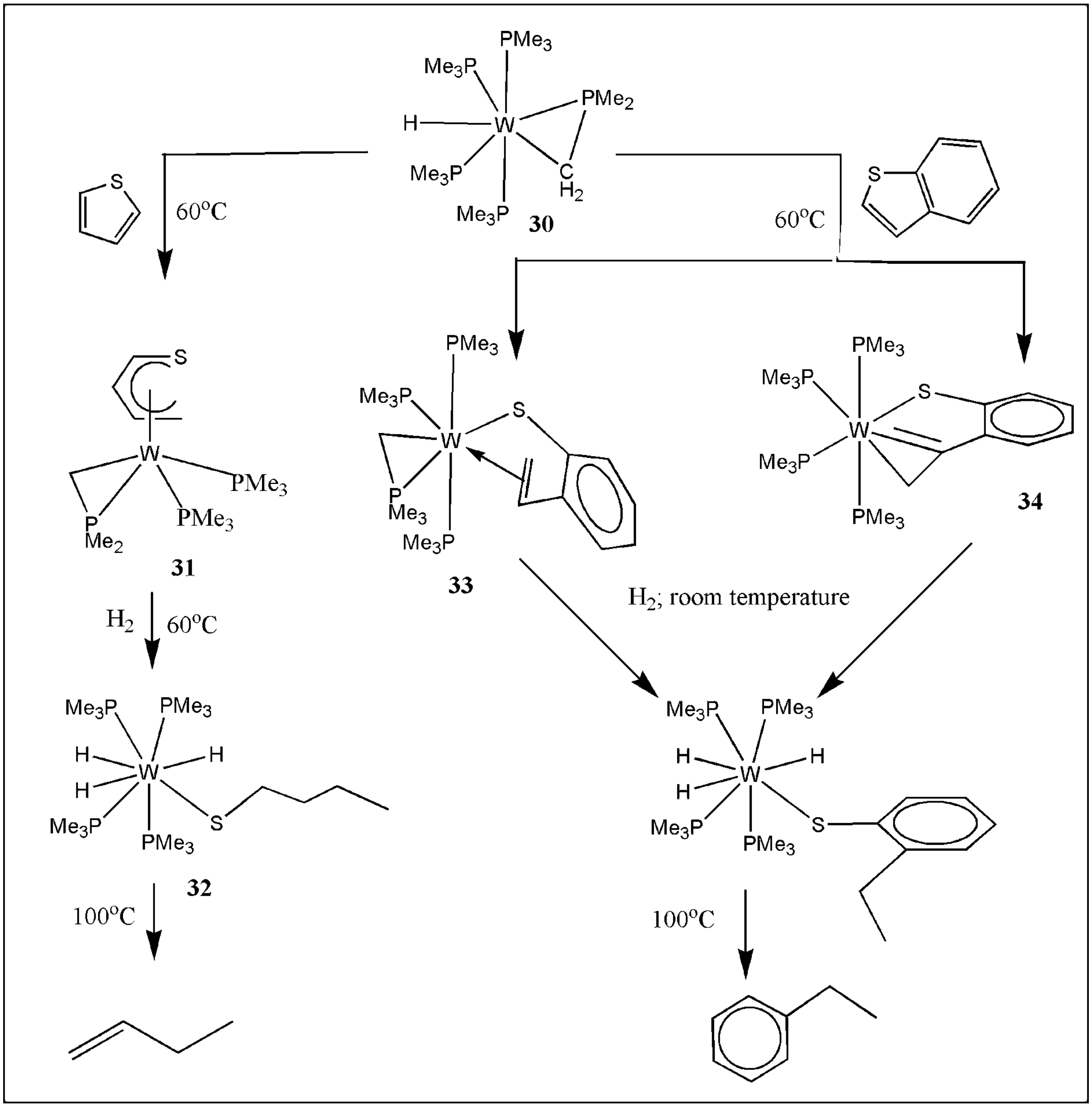
Figure 19. Plausible mechanism of desulfurization leading to formation of biphenyl
Adapted from Nieto et al., 2009.



The reaction was carried out in acetone and its role in cyclization is shown in the following scheme. Protonation of the N atom of dithiocarbamate, makes the cleavage of S_2C-N bond energetically favourable leading to the formation of iminium ion (35). Following this, acetone, in its enol form attacks the iminium ion in a process popularly known as the Mannich Reaction. This electrophilic attack leads to formation of a new C-C bond and ultimate elimination of CS_2 (Figure 22)

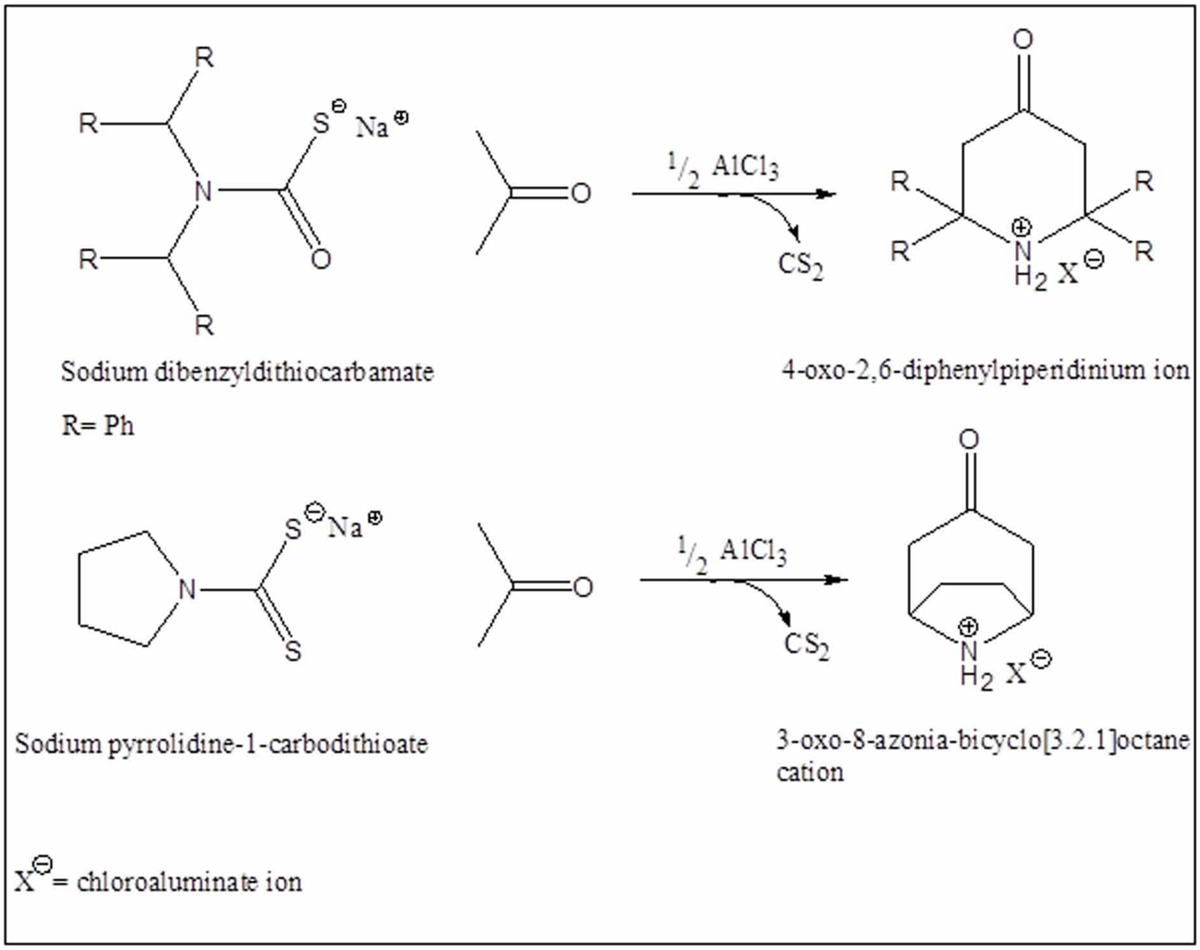
Synthesis and isolation of hydrosulfide complexes such as R_3SnH is extremely difficult due to their easy condensation into corresponding sulfides, $(R_3Sn)_2S$. In this regard, preparation of triphenytin hydride is extremely important in the field of inorganic synthetic chemistry. Moreover, the chemistry

Figure 20. Hydrodesulfurization of Thiophenes via C-S bond cleavage
Adapted from the work of Sattler et al., 2011.



of SH-containing complexes finds relevance in the study of hydrodesulfurization catalysis. (Singh and Bhattacharya, 2011) A novel route to the preparation of Ph_3SnH was discovered in our laboratory *via* desulfurization of thiophosgene. Thiophosgene, a highly toxic liquid was desulfurized in a one pot reaction by treating it with triphenyltinhydroxide in the presence of triethylamine (Figure 23). The reaction proceeds via S_Ni reaction mechanism leading to the formation of a triphenyltin hydride. The side products released are CO_2 and HCl.

Figure 21. Synthesis of cyclic ammonium salts by elimination of CS_2



Singh, Chaturvedi, and Bhattacharya, 2012 reported ready desulfurization of a metal thiocarboxylate, [(Phen)Cu(SCOth)$_2$] (Phen=1,10-phananthroline, th=thiophene) under ambient conditions in the presence of water to give the corresponding carboxylate complex. The reaction proceeds through evolution of H_2S (Figure 24).

As a rule, the C-C bonds are thermodynamically stable and extremely resistant to cleavage by metal complexes. We have successfully designed a reaction in which desulfurization takes place *via* cleavage of a C-C bond, resulting in the removal of thiirane (ethylene sulfide). (Sareen, N., Singh, S., and Bhattacharya S., 2014) Reaction of triethylammonium salt of 2,2'-thiodiacetic acid (H_2tda) with [Cu(TMEDA)(NO$_3$)$_2$] (TMEDA = N,N,N'N'-tetramethyl ethylene-diamine) in a stoichiometric ratio yielded a simple ternary complex {[Cu(TMEDA)(tda)](H_2TMEDA)(NO$_3$)$_2$·H_2O} (36). However, when [Cu(TMEDA)(NO$_3$)$_2$] was added in excess, a μ-oxalato complex {[Cu$_2$(TMEDA)$_2$(μ-ox)(H_2O)$_2$](NO$_3$)$_2$·2CH$_3$CN} (37) was formed (Figure 25). Formation of (37) involved an unusual desulfurization of thiodiacetate moiety

Figure 22. Probable mechanism for elimination of CS_2
Reproduced from Chaturvedi et al., 2008.

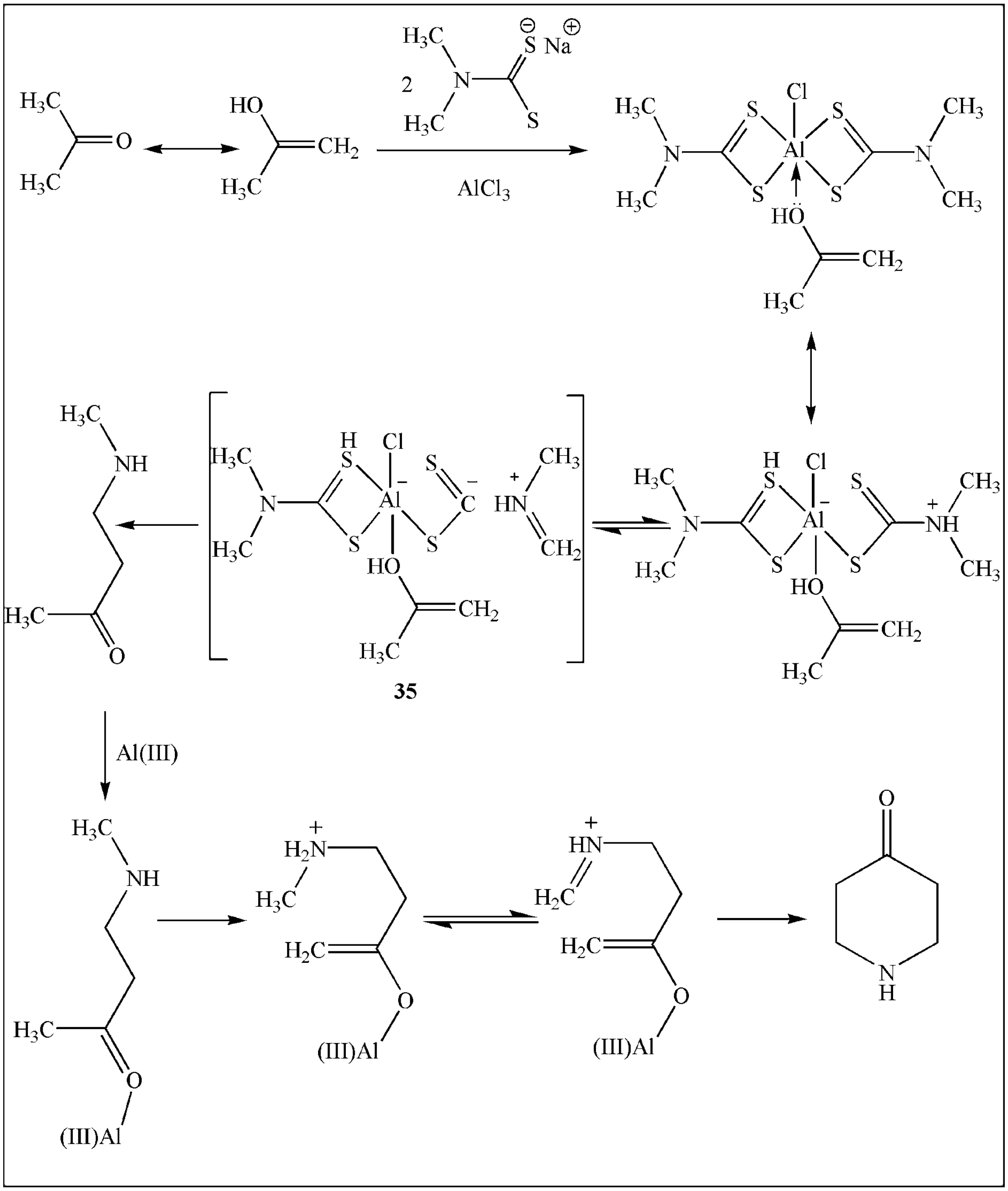
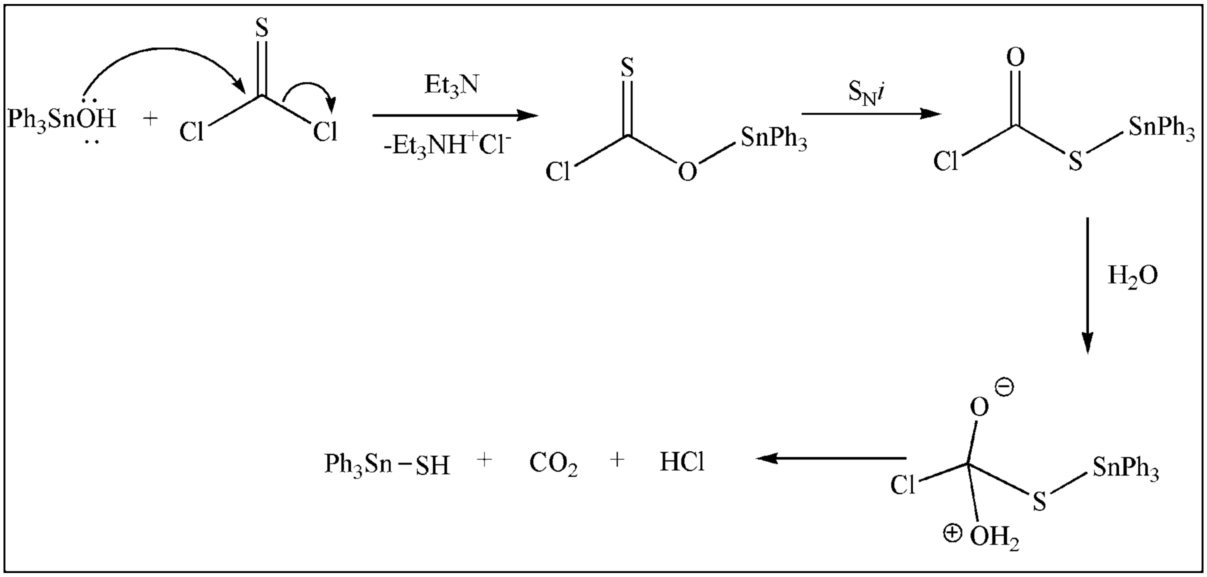


Figure 23. Desulfurization of thiophosgene by triphenyltin hydroxide
Reproduced from the work of Singh et al., 2011.

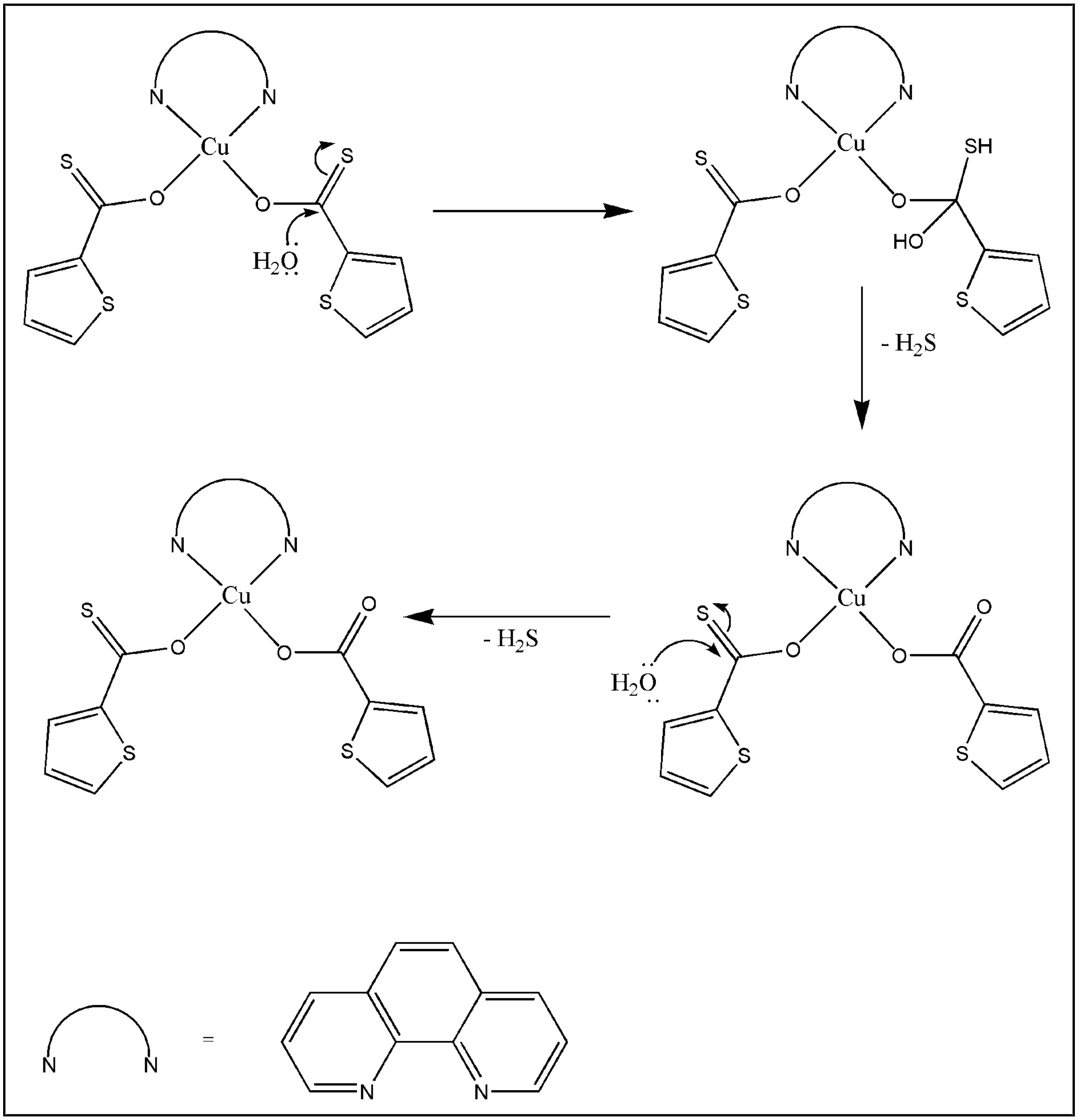


a new mechanism for desulfurization *via* elimination of ethylene sulfide (Figure 26). This reaction is of particular relevance to HDS. Firstly, scission of the C-C single bond in thiophenic compounds has been previously suggested as an alternative non-hydrogenative route for desulfurization (Landau *et al.*, 1996) Secondly, the release of thiirane is also important: Thiiranes can act as ligands through coordination of sulfur atom (Amarasekera *et al.*, 1988). Studies have shown that transfer of the sulfur atom of thiirane to the metal atoms of metal carbonyl complexes yield sulfido metal carbonyl complexes (Adams *et al.*, 2002; Adams, O-Sung, and Smith, 2002). Also, thiiranes can be easily converted to olefins using organometallic (organolithium, Grignard reagents) (Bordwell, Andersen, and Pitt, 1954; Schuetz and Jacobs, 1961) and organophosphorus compounds (Davis, 1958). Former is a synthetically important route for synthesis of certain thiophenols which cannot be prepared easily by standard methods (Bordwell *et al.*, 1954).

CONCLUSION

With the rising concern over the increasing SO_2 pollution levels, demand for sulfur free fuels has escalated. While HDS process is used worldwide to remove sulfur from fossil fuels, it suffers from some serious limitations. The wealth of knowledge that has been collected in the last decade regarding HDS reaction has been provided by applying transition metal complexes. Discrete transition metal/ organometallic complexes serve as excellent models for deciphering the mechanism of desulfurization process.

Figure 24. Room temperature desulfurization by elimination of H_2S
Adapted from Singh et al., 2012.



Moreover, the reactions exhibited by the complexes in solution can be applied to the catalyst surface. Ligand transformations in metal complexes/clusters may be mimicked for catalyst. Study of reaction mechanisms of thiophene and its derivative with organometallic complexes has proved to be extremely useful in uncovering several facts about the mode of binding and C-S bond cleavage mechanism. A

Figure 25. Synthesis of complexes 36 and 37

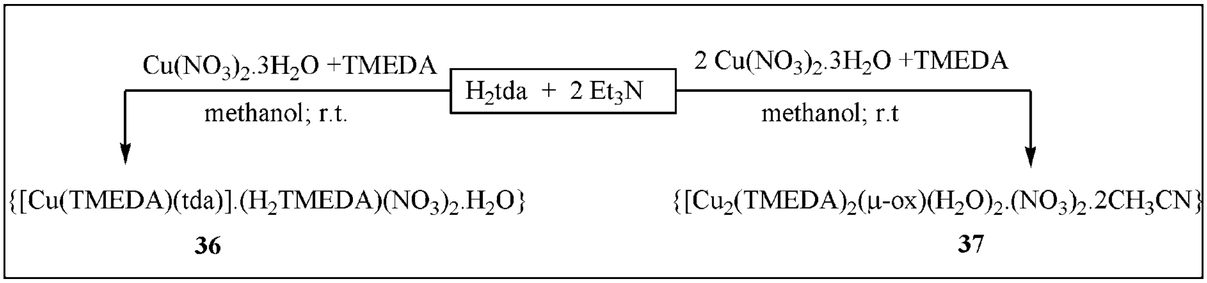
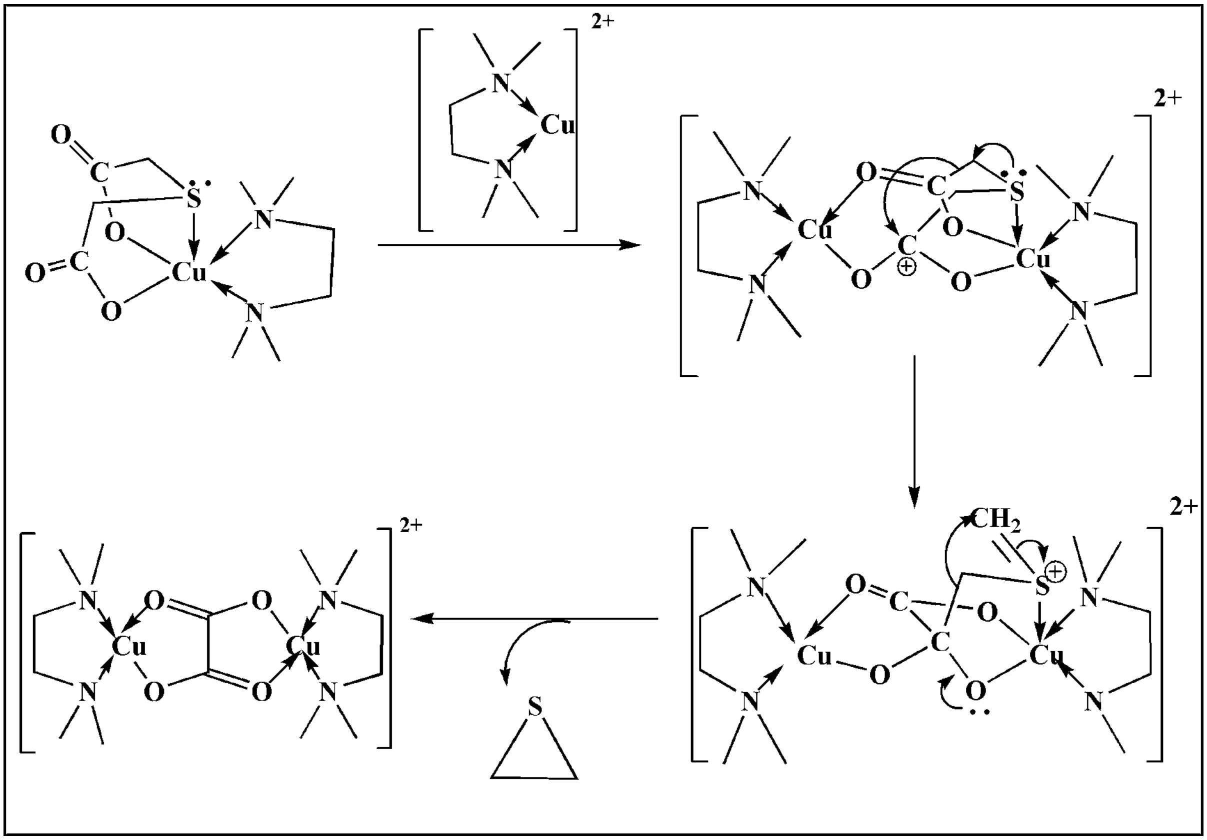


Figure 26. Plausible mechanism for desulfurization of thiodiacetate moiety
Adapted from Sareen et al., 2014.



section of experimental chemists including us has reported several desulfurization reactions which are unique in one way or the other. One of the main highlights of the reactions is that, almost all of them either take place at room temperature or under very mild heating conditions. Though, non-catalytic, these reactions are fascinating from the point of their mechanistic study. It is hoped the reactions emerge as starting points to study modes of desulfurization other than C-S bond cleavage, which may help the design of new and more efficient catalytic systems in future.

REFERENCES

Adams, R. D., Kwon, O.-S., & Smith, M. D. (2002). Disulfides of Manganese Carbonyl. Synthesis of $Mn_2(CO)_7(\mu\text{-}S_2)$ and Its Reactions with Tertiary Phosphines and Arsines. *Inorganic Chemistry*, *41*(24), 6281–6290. doi:10.1021/ic0203670 PMID:12444771

Adams, R. D., Kwon, O.-S., & Smith, M. D. (2002). Insertion of Cyclopentadienylmetal Groups into the S−S Bond of $Mn_2(CO)_7(\mu\text{-}S_2)$. *Organometallics*, *21*(9), 1960–1965. doi:10.1021/om020028e

Adams, R. D., Pompeo, M. P., Wu, W., & Yamamoto, J. H. (1993). Formation of butenethiolate by ring opening of tetrahydrothiphene by a triosmium cluster complex. *Journal of the American Chemical Society*, *115*(18), 8207–8213. doi:10.1021/ja00071a033

Aida, T., Yamamoto, D., & Sakata, K. (2000). Development of Oxidative desulfurization process for diesel fuel. *Reviews on Heteroatom Chemistry*, *22*, 241–256.

Ali, M. H., Al-Maliki, A., El-Ali, B., Martinie, G., & Siddiqui, M. N. (2006). Deep desulphurization of gasoline and diesel fuels using non-hydrogen consuming techniques. *Fuel*, *85*(10-11), 1354–1363. doi:10.1016/j.fuel.2005.12.006

Alonso, G., & Chianelli, R. R. (2004). WS_2 catalysts from tetraalkyl thiotungstate precursors and their concurrent in situ activation during HDS of DBT. *Journal of Catalysis*, *221*(2), 657–661. doi:10.1016/j.jcat.2003.10.003

Alstrup, I., Chorkendoff, I., Candia, R., Clausen, B. S., & Topsse, H. (1982). A combined X-Ray photoelectron and Mössbauer emission spectroscopy study of the state of cobalt in sulfided, supported, and unsupported Co-Mo catalysts. *Journal of Catalysis*, *77*(2), 397–409. doi:10.1016/0021-9517(82)90181-6

Amarasekera, J., Rauchfuss, T. B., & Wilson, S. R. (1988). Synthesis and structure of $[CpRu(PPh_3)_2(SC_2H_4)]OSO_2CF_3$. A transition-metal analog of an episulfonium salt. *Journal of the American Chemical Society*, *110*(7), 2332–2334. doi:10.1021/ja00215a071

Angelici, R. J. (1990). Structural aspects of Thiophene coordination in transition metal complexes. *Coordination Chemistry Reviews*, *105*(1), 61–76. doi:10.1016/0010-8545(90)80018-O

Angelici, R. J. (1997). An overview of modeling studies in HDS, HDN and HDO catalysis. *Polyhedron*, *16*(18), 3073–3088. doi:10.1016/S0277-5387(96)00581-5

Angelici, R. J. (2001). Thiophenes in Organotransition Metal Chemistry: Patterns of Reactivity. *Organometallics*, *20*(7), 1259–1275. doi:10.1021/om010040r

Austin, G. T. (1984). *Shreve's Chemical Process Industries*. New York: McGraw-Hill.

Babich, I. V., & Moulijn, J. A. (2003). Science and technology of novel processes for deep desulfurization of oil refinery streams: A review. *Fuel*, *82*(6), 607–631. doi:10.1016/S0016-2361(02)00324-1

Bataille, F., Lemberton, J., Michaud, P., Pérot, G., Vrinat, M., & Lemaire, M. et al. (2000). Alkyldibenzothiophenes Hydrodesulfurization-Promoter Effect, Reactivity, and Reaction Mechanism. *Journal of Catalysis*, *191*(2), 409–422. doi:10.1006/jcat.1999.2790

Bej, S. K. (2004). Revamping of diesel hydrodesulfurizers: Options available and future research needs. *Fuel Processing Technology*, *85*(13), 1503–1517. doi:10.1016/j.fuproc.2003.07.002

Bej, S. K., Maity, S. K., & Turaga, U. T. (2004). Search for an efficient 4,6-DMDBT hydrodesulphurization catalyst: A review of recent studies. *Energy & Fuels*, *18*(5), 1227–1237. doi:10.1021/ef030179+

Berhault, G., Dela Rosa, M. P., Mehta, A., Yacaman, M. J., & Chanelli, R. R. (2008). The single-layered morphology of supported MoS_2-based catalysts—The role of the cobalt promoter and its effects in the hydrodesulfurization of dibenzothiophene. *Applied Catalysis A, General*, *345*(1), 80–88. doi:10.1016/j.apcata.2008.04.034

Bordwell, F. G., & Andersen, H. M., Pitt, & B. M. (. (1954). The Reaction of Grignard Reagents with 4-Hydroxy- and 4-Ethoxycoumarin. *Journal of the American Chemical Society*, *7*, 1082–1085. doi:10.1021/ja01633a045

Brien, W. X. S. O., Chen, J. W., Nayak, R. V., & Carr, G. S. (1986). Catalytic hydrodesulfurization of dibenzothiophene and a coal-derived liquid. *Industrial & Engineering Chemistry Process Design and Development*, *25*(1), 221–229. doi:10.1021/i200032a036

Brunet, S., Mey, D., Pe'rot, G., Bouchy, C., & Diehl, F. (2005). On the hydrodesulfurization of FCC gasoline: A review. *Applied Catalysis A*, *278*(2), 143–172. doi:10.1016/j.apcata.2004.10.012

Brunet, S., Mey, D., Pérot, G., Bouchy, C., & Diehl, F. (2005). On the Hydrodesulfurization of FCC Gasoline: A Review, *Applied Catalysis, A, 278*, 143.

Burney, J., & Ramanathan, V. (2014). Recent climate and air pollution impacts on Indian Agriculture. *Proceedings of the National Academy of Sciences of the United States of America*, *111*(46), 16319–16324. doi:10.1073/pnas.1317275111 PMID:25368149

Byskov, L. S., Hammer, B., Nørskov, J. K., Clausen, B. S., & Topsoe, H. (1997). Sulfur bonding in MoS_2 and Co-Mo-S structures. *Catalysis Letters*, *47*(3/4), 177–182. doi:10.1023/A:1019009105792

Calkins, W. H. (1994). The chemical forms of sulfur in coal: A review. *Fuel*, *73*(4), 475–484. doi:10.1016/0016-2361(94)90028-0

Chandrasekhar, V., Kingsley, S., Vij, A., Lam, K. C., & Rheingold, A. L. (2000). Formation of a Tetranuclear Copper (II) Cluster Assembled by Metal-Assisted Hydrolysis and Desulfurization of Bis(3,5-dimethylpyrazolyl)methylphosphine Sulfide, $MeP(S)(3,5\text{-}Me_2Pz)_2$. *Inorganic Chemistry*, *39*(15), 3238–3242. doi:10.1021/ic991255k PMID:11196859

Chaturvedi, J., Bhattacharya, S., & Nethaji, M. (2008). A new reaction of dithiocarbamates: CS_2 elimination and two C–C bond formations leading to formation of cyclic ammonium salts. *Inorganic Chemistry Communications*, *11*(7), 720–722. doi:10.1016/j.inoche.2008.03.021

Chen, J., Daniels, L. M., & Angelici, R. J. (1996). Unexpected Reactions of 2,5-Dimethylthiophene ($2,5\text{-}Me_2T$) in $Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)^{2+}$, $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$, and $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$ with Cobaltocene. *Organometallics*, *15*(4), 1223–1229. doi:10.1021/om9505625

Chen, W., Maugé, F., Van Gestel, J., Nie, H., Li, D., & Long, X. (2013). Effect of modification of the alumina acidity on the properties of supported Mo and CoMo sulfide catalysts. *Journal of Catalysis*, *304*, 47–62. doi:10.1016/j.jcat.2013.03.004

Cheng, J.-K., Chen, Y.-B., Wu, L., Zhang, J., Wen, Y.-H., Li, Z.-J., & Yao, Y.-G. (2005). A 3-D Noninterpenetrating Diamondoid Network of a Decanuclear Copper(I) Complex. *Inorganic Chemistry*, *44*(10), 3386–3388. doi:10.1021/ic050301f PMID:15877417

Chianelli, R. R., Berhault, G., Raybaud, P., Kasztelan, S., Hafner, J., & Toulhoat, H. (2002). Periodic trends in hydrodesulfurization: In support of the Sabatier principle. *Applied Catalysis A, General*, *227*(1-2), 83–96. doi:10.1016/S0926-860X(01)00924-3

Chitnis, G. K., Novak, W. J., Ortelli, D. E., & Lewis, E. (2005). *Debottlenecking hydrocrackers with NEBULATM catalyst*. Presented at the 103rd NPRA Annual Meeting, San Francisco, CA.

Clean Air Act Tier 2. (1999). EPA (US).

Corro, G. (2002). Sulfur impact on diesel emission control—a review. *Reaction Kinetics and Catalysis Letters*, *75*, 89–106. doi:10.1023/A:1014853602908

Curtis, M. D. (1996). Electron-Deficient Molybdenum/Cobalt/Sulfido Clusters: Chemistry Related to Hydrodesulfurization. *Journal of Cluster Science*, *7*(3), 247–262. doi:10.1007/BF01171183

Curtis, M. D., & Druker, S. H. (1997). Homolytic C−S Bond Scission in the Desulfurization of Aromatic and Aliphatic Thiols Mediated by a Mo/Co/S Cluster: Mechanistic Aspects Relevant to HDS Catalysis. *Journal of the American Chemical Society*, *119*(5), 1027–1036. doi:10.1021/ja9621096

Daage, M., & Chianelli, R. R. (1994). Structure-Function Relations in Molybdenum Sulfide Catalysts: The "Rim-Edge" Model. *Journal of Catalysis*, *149*(2), 414–427. doi:10.1006/jcat.1994.1308

Davis, R. E. (1958). Cyclic Sulfides. III. The Reaction of Some Ethylene Sulfides with Triphenylphosphine and with Triethyl Phosphite. *The Journal of Organic Chemistry*, *23*(11), 1767–1768. doi:10.1021/jo01105a052

Dolbear, G. E., & Skov, E. R. (2000). Selective Oxidation as a route to petroleum desulfurization. *American Chemical Society Division of Petroleum Chemistry*, *45*, 375–378.

Dong, L., Duckett, S. B., Ohman, K. F., & Jones, W. D. (1992). A Model for Homogeneous Hydrodesulfurization: The importance of η2-Coordination and Sulfur Coordination in C-H and C-S bond Cleavage Reactions of Thiophene. *Journal of the American Chemical Society*, *114*, 151–160.

Druker, S. H., & Curtis, M. D. (1995). Activation of C-S Bond Homolysis by Coordination to a Mo/Co/S-Conatining Cluster. *Journal of the American Chemical Society*, *117*(23), 6366–6367. doi:10.1021/ja00128a030

Egorova, M., & Prins, R. (2004). Hydrodesulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene over sulfided NiMo/γ-Al_2O_3, CoMo/γ-Al_2O_3, and Mo/γ-Al_2O_3 catalysts. *Journal of Catalysis*, *225*(2), 417–427. doi:10.1016/j.jcat.2004.05.002

Ehhalt, D. H. (1999). Photooxidation of trace gases in the troposphere Plenary Lecture. *Physical Chemistry Chemical Physics*, *1*(24), 5401–5408. doi:10.1039/a905097c

Farag, H., Whitehurst, D. D., Skanishi, K., & Mochida, I. (1999). Carbon versus alumina as a support for Co–Mo catalysts reactivity towards HDS of dibenzothiophenes and diesel fuel. *Catalysis Today*, *50*(1), 9–17. doi:10.1016/S0920-5861(98)00476-3

Feng, Q., Krautscheid, H., Rauchfuss, T. B., Skaugset, A. E., & Venturelli, A. (1995). Thermal Fragmentation of Acyl Thiolato Complexes to Reactive Metal Sulfido Intermediates. Structure of Ru (η ^{6}-SC_3Me_3COMe) $(PPh_3)_2$. *Organometallics*, *14*(1), 297–304. doi:10.1021/om00001a043

Gabay, J., Dietz, S., Bernatis, P., & DuBois, M. R. (1993). Dinuclear cyclopentadienylmolybdenum complexes containing thioether ligands. Ligand substitution and desulfurization reactions. *Organometallics*, *12*(9), 3630–3635. doi:10.1021/om00033a040

Gates, B. C., Katzer, J. R., & Schuit, G. C. A. (1979). *Chemistry of Catalytic Processes*. New York: McGraw-Hill.

Ghenciu, A. F. (2002). Review of fuel processing catalysts for hydrogen production in PEM fuel cell systems. *Current Opinion in Solid State and Materials Science*, *6*(5), 389–399. doi:10.1016/S1359-0286(02)00108-0

Girgis, M. J., & Gates, B. C. (1991). Reactivities, reaction networks, and kinetics in high-pressure catalytic hydroprocessing. *Industrial & Engineering Chemistry Research*, *30*(9), 2021–2058. doi:10.1021/ie00057a001

Glasson, C., Geantet, C., Lacroix, M., Labruyere, M., & Dufresne, P. (2002). Beneficial Effect of Carbon on Hydrotreating Catalysts. *Journal of Catalysis*, *212*(1), 76–85. doi:10.1006/jcat.2002.3781

Goh, L. Y., Weng, Z., Leong, W. K., & Leung, P. H. (2001). C−S Bond Cleavage and C−C Coupling in Cyclopentadienylchromium Complexes To Give the First Dithiooxamide-Bridged and Doubly Dithiocarbamate-Bridged Double Cubanes: $[Cp_6Cr_8S_8\{(C(S)NEt_2)_2\}]$ and $[Cp_6Cr_8S_8(S_2CNEt_2)_2]$). *Angewandte Chemie International Edition*, *40*(17), 3236–3239. doi:10.1002/1521-3773(20010903)40:17<3236::AID-ANIE3236>3.0.CO;2-#

Goubin, S., Huaiying, Z., Weiquan, C., Jianmin, X., & Huizhou, L. (2005). Improvement of biodesulfurization rate by assembling nanosorbents on the surfaces of microbial cells. *Biophysical Journal*, *89*(6), L58–L60. doi:10.1529/biophysj.105.073718 PMID:16258046

Grossman, M. J., Siskin, M., Ferrughelli, D. T., Lee, M. K., & Senius, J. D. (1999). *US Patent No. 5910440.*

Gupta, N., Roychoudhury, P. K., & Deb, J. K. (2005). Biotechnology of desulfurization of diesel: Prospects and challenges. *Applied Microbiology and Biotechnology*, *66*(4), 356–366. doi:10.1007/s00253-004-1755-7 PMID:15538557

Harris, S., & Chianelli, R. R. (1984). Catalysis by transition metal sulfides: The relation between calculated electronic trends and HDS activity. *Journal of Catalysis*, *86*(2), 400–412. doi:10.1016/0021-9517(84)90385-3

Harris, S., & Chianelli, R. R. (1986). Catalysis by transition metal sulfides: A theoretical and experimental study of the relation between the synergic systems and the binary transition metal sulfides. *Journal of Catalysis*, *98*(1), 17–31. doi:10.1016/0021-9517(86)90292-7

Helveg, S., Lauritsen, J. V., Laegsgaard, E., Stensgaard, I., Nørskov, J., & Clausen, B. S. et al. (2000). Atomic-Scale Structure of Single-Layer MoS_2 Nanoclusters. *Physical Review Letters*, *84*(5), 951–954. doi:10.1103/PhysRevLett.84.951 PMID:11017413

Hensen, E. J. M., Brans, H. J. A., Lardinois, G. M. H. J., de Beer, V. H. J., Van Veen, J. A. R., & Van Santen, R. A. (2000). Periodic Trends in Hydrotreating Catalysis: Thiophene Hydrodesulfurization over Carbon-Supported 4*d* Transition Metal Sulfides. *Journal of Catalysis*, *192*(1), 98–107. doi:10.1006/jcat.2000.2824

Herna'ndez-Maldonado, A. J., & Yang, R. T. (2004). New sorbents for desulfurization of diesel fuels via π-complexation. *AIChE Journal. American Institute of Chemical Engineers*, *50*(4), 791–80. doi:10.1002/aic.10074

Houalla, M., Broderick, D. H., Sapre, A. V., Nag, N. K., de Beer, V. H. J., Gates, B. C., & Kwart, H. (1980). Hydrodesulfurization of methyl-substituted dibenzothiophenes catalyzed by sulfided Co-Mo/γ-Al_2O_3. *Journal of Catalysis*, *61*(2), 523–527. doi:10.1016/0021-9517(80)90400-5

Houalla, M., Nag, N. K., Sapre, A. V., Borderick, D. H., & Gates, B. C. (1978). Hydrodesulfurization of dibenzothiophene catalyzed by sulfided CoO-$MoO_3\gamma$-Al_2O_3: The reaction network. *AIChE Journal. American Institute of Chemical Engineers*, *24*(6), 1015–1021. doi:10.1002/aic.690240611

Isoda, T., Nagao, S., Ma, X. L., Korai, Y., & Mochida, I. (1996). Hydrodesulfurization of Refractory Sulfur Species. 1. Selective Hydrodesulfurization of 4,6-Dimethyldibenzothiophene in the Major Presence of Naphthalene over CoMo/Al_2O_3 and Ru/Al_2O_3 Blend Catalysts. *Energy & Fuels*, *10*(2), 482–486. doi:10.1021/ef950144c

Ito, E., & Rob van Veen, J. A. (2006). On novel processes for removing sulphur from refinery streams. *Catalysis Today*, *116*(4), 446–460. doi:10.1016/j.cattod.2006.06.040

Iwamoto, R., & Grimblot, J. (2000). Influence of Phosphorus on the Properties of Alumina-Based Hydrotreating Catalysts. *Advances in Catalysis*, *44*, 417–503. doi:10.1016/S0360-0564(08)60516-7

Iwata, Y., Sato, K., Yoneda, T., Miki, Y., Sugimoto, Y., Nishijima, A., & Shimada, H. (1998). Present State of the Art and Future Challenges in the Hydrodesulfurization of Polyaromatic Sulfur Compounds. *Catalysis Today*, *45*, 353–359. doi:10.1016/S0920-5861(98)00262-4

Janak, K. E., Tanski, J. M., Churchill, D. G., & Parkin, G. (2002). Thiophene and Butadiene−Thiolate Complexes of Molybdenum: Observations Relevant to the Mechanism of Hydrodesulfurization. *Journal of the American Chemical Society*, *124*(16), 4182–4183. doi:10.1021/ja012771o PMID:11960426

Jones, W. D., & Dong, L. (1991). Insertion of rhodium into the carbon-sulfur bond of thiophene. Mechanism of a model for the hydrodesulfurization reaction. *Journal of the American Chemical Society*, *113*(2), 559–564. doi:10.1021/ja00002a025

Kabe, T., Ishihara, A., & Tajima, H. (1992). Hydrodesulfurization of sulfur-containing polyaromatic compounds in light oil. *Industrial & Engineering Chemistry Process Design and Development*, *31*, 1577–1580.

Kabe, T., Ishihara, A., & Zhang, Q. (1993). Deep desulfurization of light oil. Part 2: Hydrodesulfurization of dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene. *Applied Catalysis A*, *97*(1), L1–L9. doi:10.1016/0926-860X(93)80059-Y

Kaluzˇa, L., Gulkova´, D., Vı’t, Z., & Zdrazˇil, M. (2007). Effect of support type on the magnitude of synergism and promotion in CoMo sulphide hydrodesulphurisation catalyst. *Applied Catalysis A, General*, *324*, 30–35. doi:10.1016/j.apcata.2007.02.050

Kerby, M., Degnan, T. Jr, Marler, D., & Beck, J. (2005). Advanced catalyst technology and applications for high quality fuels and lubricants. *Catalysis Today*, *104*(1), 55–63. doi:10.1016/j.cattod.2005.03.028

Kilanowski, D. R., Teeuwen, H., Gates, B. C., Beer, V. H. J. D., Schuit, G. C. A., & Kwart, H. (1978). Hydrodesulfurization of thiophene, benzothiophene, dibenzothiophene, and related compounds catalyzed by sulfided CoO-MoO_3/g-Al_2O_3: Low-pressure reactivity studies. *Journal of Catalysis*, *55*(2), 129–137. doi:10.1016/0021-9517(78)90199-9

Kim, J. H., Ma, X., Song, C., Lee, Y., & Oyama, S. T. (2005). Kinetics of Two Pathways for 4,6-Dimethyldibenzothiophene Hydrodesulfurization over NiMo, CoMo Sulfide, and Nickel Phosphide Catalysts. *Energy & Fuels*, *19*(2), 353–364. doi:10.1021/ef049804g

Klimont, Z., Smith, S. J., & Cofala, J. (2013).The last decade of global anthropogenic sulfur dioxide: 2000–2011 emissions. EPA-Environmental Protection Agency *Environmental Research Letters, 8*, 014003. Retrieved from http:// www.epa.gov/air/urbanair; http://www.epa.gov/airquality/sulfurdioxide/implement.html#jan14

Konishi, I., Yoshitaka, I., Kouichi, O., & Suzuki, M. (1999) *US Patent No. 5925560*.

Kwart, H., Schuit, G. C. A., & Gates, B. C. (1980). Hydrodesulfurization of thiophenic compounds: The reaction mechanism. *Journal of Catalysis*, *61*(1), 128–134. doi:10.1016/0021-9517(80)90347-4

Landau, M. V., Berger, D., & Herskowitz, M. (1996). Hydrodesulfurization of Methyl-Substituted Dibenzothiophenes: Fundamental Study of Routes to Deep Desulfurization. *Journal of Catalysis*, *159*(1), 236–245. doi:10.1006/jcat.1996.0083

Lauritsen, J. V., Helveg, S., Lægsgaard, E., Stensgaard, I., Clausen, B. S., Topsøe, H., & Besenbacher, F. (2001). Atomic-Scale Structure of Co–Mo–S Nanoclusters in Hydrotreating Catalysts. *Journal of Catalysis*, *197*(1), 1–5. doi:10.1006/jcat.2000.3088

Ledoux, M. J., Michaux, O., Agostini, G., & Panissod, P. J. (1986). The influence of sulfide structures on the hydrodesulfurization activity of carbon-supported catalysts. *Journal of Catalysis*, *102*(2), 275–288. doi:10.1016/0021-9517(86)90164-8

Lesch, D. A., Richardson, J. W., Jacobson, R. A., & Angelici, R. J. (1984). Reactions of the π-thiophene ligand in $(\eta\text{-}C_4H_4S)Mn(CO)_3{}^+$]. Mechanistic possibilities for catalytic hydrodesulfurization. *Journal of the American Chemical Society*, *106*, 2901–2906. doi:10.1021/ja00322a027

Li, F., Zhang, Z., Feng, J., Cai, X., & Ping, X. (2007). Biodesulfurization of DBT in tetradecane and crude oil by a facultative thermophilic bacterium Mycobacterium goodii X7B. *Journal of Biotechnology*, *127*(2), 222–228. doi:10.1016/j.jbiotec.2006.07.002 PMID:16905217

Li, H., Carpenter, G. B., & Sweigart, D. A. (2000). Models for Homogeneous Deep Hydrodesulfurization. Intramolecular CO Substitution by the Sulfur in $[(\eta^6\text{-2-methylbenzothiophene})Mn(CO)_3]^+$ and $[(\eta^6\text{-dibenzothiophene})Mn(CO)_3]^+$ after Regiospecific Insertion of Platinum into a C-S Bond. *Organometallics*, *19*(10), 1823–1825. doi:10.1021/om000100d

Li, X., Wang, A., Egorova, M., & Prins, R. (2007). Kinetics of the HDS of 4,6-dimethyldibenzothiophene and its hydrogenated intermediates over sulfided Mo and NiMo on γ -Al_2O_3. *Journal of Catalysis*, *250*(2), 283–293. doi:10.1016/j.jcat.2007.06.005

Lin, S. D., & Song, C. (1996). Noble metal catalysts for low-temperature naphthalene hydrogenation in the presence of benzothiophene. *Catalysis Today*, *31*(1-2), 93–104. doi:10.1016/0920-5861(96)00038-7

Lipsch, J. M. J. G., & Schuit, G. C. A. (1969). The $CoO\text{-}MoO_3\text{-}Al_2O_3$ catalyst: III. Catalytic properties. *Journal of Catalysis*, *15*(2), 179–189. doi:10.1016/0021-9517(69)90022-0

Lu, H., Gao, J., Jiang, Z., Jing, F., Yang, Y., Wang, G., & Li, C. (2006). Ultra-deep desulfurization of diesel by selective oxidation with $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ catalyst assembled in emulsion droplets. *Journal of Catalysis*, *239*(2), 369–375. doi:10.1016/j.jcat.2006.01.025

Ma, X., Kim, J. H., & Song, C. (2003). Effect of Methyl Groups at 4- and 6-Positions on Adsorption of Dibenzothiophenes over CoMo and NiMo Sulfide Catalysts. *Fuel Chemistry Division Preprints*, *48*, 135–137.

Ma, X., Sakanishi, K., Isoda, T., & Mochida, I. (1995). Hydrodesulfurization Reactivities of Narrow-Cut Fractions in a Gas Oil. *Industrial & Engineering Chemistry Research*, *34*(3), 748–754. doi:10.1021/ie00042a006

McFarland, B. L., Boron, D. J., Deever, W., Meyer, J. A., Johnson, A. R., & Atlas, R. M. (1998). Biocatalytic Sulfur Removal from Fuels: Applicability for Producing Low Sulfur Gasoline. *Critical Reviews in Microbiology*, *24*(2), 99–147. doi:10.1080/10408419891294208 PMID:9675512

Mei, H., Mei, B. W., & Yen, T. F. (2003). A new method for obtaining ultra-low sulfur diesel fuel via ultrasound assisted oxidative desulfurization. *Fuel*, *82*(4), 405–414. doi:10.1016/S0016-2361(02)00318-6

Miller, J. T., Marshall, C. L., & Kropf, A. J. (2001). (Co)MoS_2/Alumina Hydrotreating Catalysts: An EXAFS Study of the Chemisorption and Partial Oxidation with O_2. *Journal of Catalysis*, *202*(1), 89–99. doi:10.1006/jcat.2001.3273

Monticello, D. J., Bakker, D., & Finnerty, W. R. (1985). Plasmid-mediated degradation of dibenzothiophene by Pseudomonas species. *Applied and Environmental Microbiology*, *49*, 756–760. PMID:4004209

Nag, N. K., Sapre, A. V., Broderick, D. H., & Gates, B. C. (1979). Hydrodesulfurization of polycyclic aromatics catalyzed by sulfided CoO-MoO3γ-Al2O3: The relative reactivities. *Journal of Catalysis*, *57*(3), 509–512. doi:10.1016/0021-9517(79)90016-2

Ogilvy, A. E., Draganjac, M., Rauchfuss, T. B., & Wilson, S. R. (1988). Activation and desulfurization of thiophene and benzothiophene by iron carbonyls. *Organometallics*, *7*(5), 1171–1177. doi:10.1021/om00095a024

Ogilvy, A. E., Skaugset, A. E., & Rauchfuss, T. B. (1989). Electron-transfer activation of coordinated thiophene: Preparation and desulfurization of (η^5-C_5Me_5)Rh(η^4-C_4Me_4S). *Organometallics*, *8*(11), 2739–2741. doi:10.1021/om00113a037

Okamoto, Y. (1997). Preparation and characterization of zeolite-supported molybdenum and cobalt-molybdenum sulfide catalysts. *Catalysis Today*, *39*(1-2), 45–49. doi:10.1016/S0920-5861(97)00087-4

Pecoraro, T. A., & Chianelli, R. R. (1981). Hydrodesulfurization catalysis by transition metal sulphides. *Journal of Catalysis*, *67*(2), 430–445. doi:10.1016/0021-9517(81)90303-1

Peng, Y., Meng, Z., Zhong, C., Lu, J., Yu, W., Yang, Z., & Qian, Y. (2001). Hydrothermal Synthesis of MoS2 and Its Pressure-Related Crystallization. *Journal of Solid State Chemistry*, *159*(1), 170–173. doi:10.1006/jssc.2001.9146

Poulet, O., Hubaut, R., Kasztelan, S., & Grimblot, J. (1991). Experimental Evidences of the Direct Influence of Phosphorus on Activity and Selectivity of a MoS2-γAl2O3 Hydrotreating Catalyst. *Bulletin des Sociétés Chimiques Belges*, *100*(11-12), 857–863. doi:10.1002/bscb.19911001110

Prins, R., & Bussell, M. E. (2012). Metal Phosphides: Preparation, Characterization and Catalytic Reactivity. *Catalysis Letters*, *142*(12), 1413–1436. doi:10.1007/s10562-012-0929-7

Prins, R., de Beer, V. H. J., & Somorjai, G. A. (1989). Structure and Function of the Catalyst and the Promoter in Co—Mo Hydrodesulfurization Catalysts. *Catalysis Reviews. Science and Engineering*, *31*(1-2), 1–41. doi:10.1080/01614948909351347

Ramana, M. V., Ramanathan, V., Feng, Y., Yoon, S.-C., Kim, S.-W., Carmichael, G. R., & Schauer, J. J. (2010). Warming influenced by the ratio of black carbon to sulphate and the black-carbon source. *Nature Geoscience*, *3*(8), 542–545. doi:10.1038/ngeo918

Ramanathan, V., Chung, C., Kim, D., Bettge, T., Buja, L., & Kiehl, J. T. et al. (2005). Atmospheric brown clouds: Impacts on South Asian climate and hydrological cycle. *Proceedings of the National Academy of Sciences of the United States of America*, *102*(15), 5326–5333. doi:10.1073/pnas.0500656102 PMID:15749818

Ramirez, J., Castano, V. M., Leclercq, C., & Lopez, A. (1992). High-resolution electron microscopy study of phosphorus-containing $MoS_2/A1_2O_3$ hydrotreating catalysts. *Applied Catalysis A*, *83*, 251–261. doi:10.1016/0926-860X(92)85038-D

Ramı´rez, J., Fuentes, S., Dı’az, G., Vrinat, M., Breysse, M., & Lacroix, M. (1989). Hydrodesulphurization activity and characterization of sulphided molybdenum and cobalt—molybdenum catalysts: Comparison of Alumina-, Silica-Alumina- and Titania-Supported Catalysts. *Applied Catalysis*, *52*, 211–224.

Rath, K., & Upadhyay, A. (2014). Role of pH in biodesulfurization of dibenzothiophene. *International Journal of Latest Technology in Engineering, Management and Applied Science, 3,* ISSN 2278-2540.

Rauchfuss, T. B. (1991). The Coordination Chemistry of Thiophenes (Vol. 39, pp. 259-329). New York: John Wiley & Sons doi:10.1002/9780470166406.ch5

Riaz, U., Curnow, O. J., & Curtis, M. D. (1994). Desulfurization of Organic Sulfur Compounds Mediated by a Molybdenum /Cobalt / Sulfur Cluster. *Journal of the American Chemical Society*, *116*(10), 4357–4363. doi:10.1021/ja00089a025

Roberts, J. T., & Friend, C. M. (1987). Ring size and strain as a control of reaction selectivity: Ethylene sulfide on molybdenum (110). *Journal of the American Chemical Society*, *109*(25), 7899–7900. doi:10.1021/ja00259a058

Sanchez-Delgado, R. A. (2002). *Organometallic Modeling of the Hydrodesulfurization and Hydrodenitrogenation Reactions*. Boston: Kluwer Academic Publishers. doi:10.1007/0-306-47619-3

Sareen, N., Singh, S., & Bhattacharya, S. (2014). A Cu(II) mediated new desulfurization pathway involving elimination of ethylene sulphide. *Dalton Transactions (Cambridge, England)*, *43*(12), 4635–4638. doi:10.1039/c3dt53395f PMID:24509718

Satterfield, C. N., Modell, M., & Wilkens, J. A. (1980). Simultaneous Catalytic Hydrodenitrogenation of Pyridine and Hydrodesulfurization of Thiophene. *Industrial & Engineering Chemistry Process Design and Development*, *19*(1), 154–160. doi:10.1021/i260073a027

Sattler, A., & Parkin, G. (2011). Carbon−Sulfur Bond Cleavage and Hydrodesulfurization of Thiophenes by Tungsten. *Journal of the American Chemical Society*, *133*(11), 3748–3751. doi:10.1021/ja111034g PMID:21348517

Savithra, G. H. L., Muthuswamy, E., Bowker, R. H., Carrillo, B. A., Bussell, M. E., & Brock, S. L. (2013). Rational Design of Nickel Phosphide Hydrodesulfurization Catalysts: Controlling Particle Size and Preventing Sintering. *Chemistry of Materials*, *25*(6), 825–833. doi:10.1021/cm302680j

Schuetz, R. D., & Jacobs, R. L. (1961). The Preparation and Desulfurization of Some Unsymmetrically Substituted Thiiranes. *The Journal of Organic Chemistry*, *26*(9), 3467–3471. doi:10.1021/jo01067a106

Schuit, G. C. A., & Gates, B. C. (1973). Chemistry and engineering of catalytic hydrodesulfurization. *AIChE Journal. American Institute of Chemical Engineers*, *19*(3), 417–438. doi:10.1002/aic.690190303

Singh, S., & Bhattacharya, S. (2011). Synthesis of triphenyltin(IV) hydrosulfide. *Inorganica Chimica Acta*, *367*(1), 230–232. doi:10.1016/j.ica.2010.12.014

Singh, S., Chaturvedi, J., & Bhattacharya, S. (2012). Studies of synthesis, structural features of Cu(I) thiophene-2-thiocarboxylates and unprecendented desulfurization of Cu(II) thiocarboxylate complexes. *Dalton Transactions (Cambridge, England)*, *41*(2), 424–431. doi:10.1039/C1DT10629E PMID:22024710

Smith, S. J., Conception, E., Andres, R., & Lurz, J. (2004). Historical sulfur dioxide emissions 1850-2000: Methods and results. Pacific Northwest National Laboratory Report PNNL-14537.

Smith, S. J., Pitcher, H., & Wigley, T. M. L. (2001). Global and regional anthropogenic sulfur dioxide emissions. *Global and Planetary Change*, *29*(1-2), 99–119. doi:10.1016/S0921-8181(00)00057-6

Smith, T. S., & Johnson, K. H. (1994). A unified theory of periodic and promotion effects in transition metal sulphide hydrodesulphurization catalysts. *Catalysis Letters*, *28*(2-4), 361–372. doi:10.1007/BF00806067

Soleimani, M., Bassi, A., & Margaritis, A. (2007). Biodesulfurization of refractory organic sulfur compounds in fossil fuels. *Biotechnology Advances*, *25*(6), 570–596. doi:10.1016/j.biotechadv.2007.07.003 PMID:17716849

Solís, D., Agudo, A. L., Ramírez, J., & Klimova, T.Solı's. (2006). Hydrodesulfurization of hindered dibenzothiophenes on bifunctional NiMo catalysts supported on zeolite–alumina composites. *Catalysis Today*, *116*(4), 469–477. doi:10.1016/j.cattod.2006.06.029

Song, C. (2003). An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel. *Catalysis Today*, *86*(1-4), 211–263. doi:10.1016/S0920-5861(03)00412-7

Song, C., & Reddy, K. M. (1999). Mesoporous molecular sieve MCM-41 supported Co–Mo catalyst for hydrodesulfurization of dibenzothiophene in distillate fuels. *Applied Catalysis A, General*, *176*(1), 1–10. doi:10.1016/S0926-860X(98)00230-0

Song, C., & Schmitz, A. D. (1997). Zeolite-Supported Pd and Pt Catalysts for Low-Temperature Hydrogenation of Naphthalene in the Absence and Presence of Benzothiophene. *Energy & Fuels*, *11*(3), 656–661. doi:10.1021/ef960179s

Song, J. L., Dong, Z. C., Zeng, H. Y., Zhou, W. B., Naka, T., & Wei, Q. et al. (2003). [Cu($H_4C_3N_2S$)Cl_2]n, an Unprecedented Diazole-Bridged One-Dimensional Copper Halide: Synthesis, Structure, and Magnetic Properties. *Inorganic Chemistry*, *42*(6), 2136–2140. doi:10.1021/ic025976m PMID:12639152

Sorensen, O., Clausen, B. S., Candia, R., & Topsøe, H. (1985). Hrem and Aem studies of hds catalysts: Direct evidence for the edge location of cobalt in Co-Mo-S. *Applied Catalysis*, *13*(2), 363–372. doi:10.1016/S0166-9834(00)81154-9

Srivastava, V. C. (2012). An evaluation of desulfurization technologies for sulfur removal from liquid fuels. *RSC Advances*, *2*(3), 759–783. doi:10.1039/C1RA00309G

Sun, M., Nicosia, D., & Prins, R. (2003). The effects of fluorine, phosphate and chelating agents on hydrotreating catalysts and catalysis. *Catalysis Today*, *86*(1-4), 173–189. doi:10.1016/S0920-5861(03)00410-3

Tam, P. S., Kittrell, J. R., & Eldridge, J. W. (1990). Desulfurization of fuel oil by oxidation and extraction. 1. Enhancement of extraction oil yield. *Industrial & Engineering Chemistry Research*, *29*(3), 321–324. doi:10.1021/ie00099a002

Tang, T., Yin, C., Wang, L., Ji, Y., & Xiao, F.-S. (2007). Superior performance in deep saturation of bulky aromatic pyrene over acidic mesoporous Beta zeolite-supported palladium catalyst. *Journal of Catalysis*, *249*(1), 111–115. doi:10.1016/j.jcat.2007.03.031

Topsøe, H., & Clausen, B. S. (1984). Importance of Co-Mo-S Type Structures in Hydrodesulfurization. *Catalysis Reviews. Science and Engineering*, *26*, 395–420. doi:10.1080/01614948408064719

Topsoe, H., Clausen, B. S., & Massoth, F. E. (1996). *Hydrotreating Catalysis*. Berlin: Springer. doi:10.1007/978-3-642-61040-0_1

Topsøe, H., Clausen, B. S., & Massoth, F. E. (1996). *Catalysis-Science and Technology* (J. R. Anderson & M. Boudard, Eds.). Vol. 11). Berlin: Springer.

Topsøe, H., Clausen, B. S., Topsøe, N.-Y., & Pederson, E. (1986). Recent basic research in hydrodesulfurization catalysis. *Industrial & Engineering Chemistry Fundamentals*, *25*(1), 25–36. doi:10.1021/i100021a004

Topsøe, N.-Y., & Topsøe, H. (1983). Characterization of the structures and active sites in sulfided Co-Mo/Al2O3 and Ni-Mo/Al2O3 catalysts by NO chemisorption. *Journal of Catalysis*, *84*(2), 386–401. doi:10.1016/0021-9517(83)90010-6

Vasile, H., Francois, F., & Jacques, B. (2000). Mild Oxidation with H_2O_2 over Ti-Containing Molecular Sieves—A very Efficient Method for Removing Aromatic Sulfur Compounds from Fuels. *Journal of Catalysis*, *198*, 179–186.

Ward, P. L. (2009). Sulfur dioxide initiates global climate change in four ways. *Thin Solid Films*, *517*(11), 3188–3203. doi:10.1016/j.tsf.2009.01.005

Whitehurst, D. D., Isoda, T., & Mochida, I. (1998). Present State of the Art and Future Challenges in the Hydrodesulfurization of Polyaromatic Sulfur Compounds. *Advances in Catalysis*, *42*, 345–471. doi:10.1016/S0360-0564(08)60631-8

Wivel, C., Candia, R., Clausen, B. S., Mørup, S., & Topsøe, H. (1981). On the catalytic significance of a Co-Mo-S phase in Co-Mo/Al_2O_3 hydrodesulfurization catalysts: Combined *in situ* Mössbauer emission spectroscopy and activity studies. *Journal of Catalysis*, *68*, 453–463. doi:10.1016/0021-9517(81)90115-9

Xia, Y., Yang, P., Sun, Y., Wu, Y., Mayers, B., & Gates, B. et al. (2003). One-Dimensional Nanostructures: Synthesis, Characterization, and Applications. *Advanced Materials*, *15*(5), 353–389. doi:10.1002/adma.200390087

Yang, L., Li, J., Yuan, X., Shen, J., & Qi, Y. (2007). One step non-hydrodesulfurization of fuel oil: Catalyzed oxidation adsorption desulfurization over HPWA-SBA-15. *Journal of Molecular Catalysis A Chemical*, *262*(1-2), 114–118. doi:10.1016/j.molcata.2006.08.058

Yang, R. T., Yang, F. H., Takahashi, A., & Maldonado, A. J. H. (2002). *US Patent No. 7,029,574*. Washington DC: U.S. Patent and Trademark Office

Yu, G., Lu, S., Chen, H., & Zhu, Z. (2005). Diesel fuel desulfurization with hydrogen peroxide promoted by formic acid and catalyzed by activated carbon. *Carbon*, *43*(11), 2285–2294. doi:10.1016/j.carbon.2005.04.008

Yue, Y., Sun, Y., & Gao, Z. (1997). Disordered mesoporous KIT-1 as a support for hydrodesulfurization catalysts. *Catalysis Letters*, *47*(2), 167–171. doi:10.1023/A:1019084400340

Zaczepinski, S. (1996). Exxon Diesel Oil Deep Desulfurization (DODD). In R. A. Meyers (Ed.), *Handbook of Petroleum Refining Processes*. New York: McGraw-Hill.

Zaera, F., Kollin, E. B., & Gland, J. L. (1987). Vibrational characterization of thiophene decomposition on the Mo(100) surface. *Surface Science*, *184*(1-2), 75–89. doi:10.1016/S0039-6028(87)80273-X

Zang, G., Yu, F., & Wang, R. (2009). Research Advances in Oxidative desulfurization technologies for the production of low sulphur fuel oils. *Petroleum and Coal*, *51*, 196–207.

Zaykina, R. F., Zaykin, Y. A., Mamaonava, T. B., & Nadirov, N. K. (2002). Radiation methods for demercaptanization and desulfurization of oil products. *Radiation Physics and Chemistry*, *63*(3-6), 621–624. doi:10.1016/S0969-806X(01)00654-5

KEY TERMS AND DEFINITIONS

Biodesulfurization: An innovative technology which uses microbes specially, bacteria as biocatalysts to specifically oxidize the refractory sulfur compounds found in crude oil in an enzymatic process.

Oxidative Desulfurization: Technological process which involves low temperature and low pressure removal of sulfur compounds from fuels by their chemical oxidation into sulfones.

Chapter 4

Nanocomposites and Hybrid Materials for Adsorptive Desulfurization

Tawfik A. Saleh
King Fahd University of Petroleum and Minerals, Saudi Arabia

Gaddafi I. Danmaliki
King Fahd University of Petroleum and Minerals, Saudi Arabia

Taye Damola Shuaib
King Fahd University of Petroleum and Minerals, Saudi Arabia

ABSTRACT

Desulfurization (removal of S compounds) of fuels is an important research topic in recent years. Several techniques have been reported to remove the sulfur-containing compounds in fuels. One of these techniques is adsorptive desulfurization (ADS) (removal based on chemisorption and physisorption) which has received much attention because of low energy consumption and facile operation condition. This chapter discusses the methods employed under this technique and the types of nanocomposites and hybrid materials (adsorbents) that have been investigated as potential adsorbents. The strategies to enhance sulfur adsorption capacity and main challenges will be discussed.

1. INTRODUCTION

Fossil fuels are the main source of energy worldwide; crude oil, which occurs naturally and comprises of several organic components (such as diesel, gasoline, jet fuels, kerosene etc.), serves as the major source of energy in the world. Crude oils are usually classified based on density and sulfur content. The lighter the crude oil the better its value and the lower the sulfur content in crude oil the better its profitability. Sulfur is the main important hetero-element found in crude oil and has the most significant effect on refining. It poisons catalyst, corrode refining equipment, and combustion of the products of sulfur from automobiles impair the emission control technology designed to meet the nitrogen oxides (NOx) and

DOI: 10.4018/978-1-4666-9545-0.ch004

particulate emission standards which leads to environmental pollution. It contributes to the deterioration of air quality and affects public health and the ecosystem. The maximum allowable sulfur content in highway diesel fuel in the US was 15 ppmw in 2006 and it will be less than 10 ppmw by 2017. Sulfur compounds found in crude oil are divided into aliphatic (mercaptans, sulfides, disulfides) and aromatic refractory group (thiophenes derivatives). The methods in use for the removal of sulfur compounds in fuels are either pre-combustion techniques or the post combustion techniques. The pre-combustion techniques are the best methods and they involve the decomposition of sulfur compounds, removal of the compounds without decomposition and final separation of the compounds followed by decomposition (Babich et al., 2003). The conventional method used by refineries for the removal of sulfur from the fuel is hydrodesulphurization (HDS) (Bej 2004). It is efficient in the removal of most aliphatic sulfur compounds from fuels e.g. thiols. However, it is not efficient in the removal of aromatic refractory sulfur compounds e.g. thiophene derivatives (dibenzothiophene (DBT) and 4, 6 dimethyl dibenzothiophene (DMDBT)) which are the least reactive and pose more serious danger to the environment. In addition, it requires high temperature, pressure and high dosage of catalyst before achieving the desired objective which is uneconomical (Ali et al., 2006).

Other methods of desulfurization in use to provide solutions to the problems of HDS include: Oxidative desulfurization (ODS), ionic liquids desulfurization (ILD) (Prashant et al., 2010), bio-desulfurization and ADS (Mohammad et al., 2006; Guoxian et al., 2005; Soleimani et al 2007; Isam et al., 2013; Celia et al., 2010). Most of these methods utilize a catalyst to speed up the rate of sulfur removal and they are considered viable alternatives in desulfurization. In ODS, all refractory sulfur compounds are oxidized by oxidants (such as H_2O_2, H_2SO_4, tBuOOH, O_3 and NO_2) to less harmful polar derivatives (sulfoxides and sulfones) that can be easily isolated by adsorption or extraction at room temperature and pressure. Most petroleum refineries use solvent extraction to extract the sulfur compounds from fuels, thereby recovering the solvent by distillation (Babich et al., 2003). The major disadvantages of ODS are: one, in appropriate oxidant may cause unwanted side reactions with other components in the fuel that are of interest and second, solvent selection is critical because undesirable solvents may extract other components of the fuel that will affect overall quality of the product. The use of IL in extractive and oxidative-extractive desulfurization started in 2001 (Bösmann *et a*l., 2001) and it has become an area of interesting research since then. IL are organic salts composed of anions and cations and they have a low melting temperature. They are nonvolatile, nonflammable, chemically and thermally stable and they are easily regenerated due to their negligible vapor pressure. Different types of anions and cations have been used in this process such as: $[BF4]^-$, $[PF6]^-$, alkylsulfates, thiocyanate or bis(trifluoromethylsulfonyl)imide, acetate, dialkylphosphate, alkylpyridinium, pyridinium, imidazolium, pyrrolidinium etc. Varying degrees of affinity and selectivity to sulfur compounds by different ionic IL have been noticed. Cost, lack of thermodynamic data, regeneration of the IL, effect of the liquids to other fuel constituents and corrosion related problems are the major drawbacks of this technology. (Zhang et al., 2002, 2004; Eber et al., 2004; Mochizuki et al., 2008; Cheruku et al., 2012; Holbrey et al., 2008; Borja et al., 2014). Biodesulfurization serves as an alternative to HDS due to its specificity, selectivity to sulfur compounds and mild operating conditions. In BDS, microbial species are used to consume sulfur compounds in fuels as their main energy source. They may either oxidize or reduce the sulfur compounds to sulfate or hydrogen sulfide respectively. Oxidizing the sulfur compounds is the most desirable pathway due to the fact that there will be no further treatment unlike the reduction pathway that requires further treatment of hydrogen sulfide through Clauss process to elemental sulfur. Various strains of microbes have been studied to increase desulfurization activity such as: *Rhodocuccus, desulfovibrio desulfuricans, Arthrobacter, Brevibacterium*

Pseudomonas, and Gordona spp. Slow reaction rate, cost and inability to recover biocatalyst, isolation of the microbial specie after the reaction, emulsion formation, and complex reactor design are the major problems limiting the commercialization of this technology (Srivastava 2012).

The use of nanomaterials and nanocomposites as adsorbents in ADS will be the main aim of this chapter. Variety of adsorbents are currently used in desulfurization for the selective removal of sulfur from petroleum products. It has advantages over other methods of desulfurization because of mild operating conditions, less expensive and does not have scaling or corrosion problems. It has ease of application, and some of the adsorbents have efficient sulfur removal and excellent regenerative ability (Kostas et al., 2014). The known adsorbent materials in use are: nickel based sorbents, zeolites based sorbents, alumina based sorbents, silica, activated carbon (AC), metal oxides, metal sulfide and reduced metals based sorbents (Ma et al., 2003; Fukunaga et al., 2003; Vinay et al., 2006; Hernandez et al., 2010). Current area of research in ADS focuses on the development of cost effective, efficient and reliable adsorbent materials that will have high sorption capacity and selectivity to reduce the sulfur content of fuel to minimal concentrations and to be easily regenerated to minimize environmental disposal impacts.

Principles of Adsorption

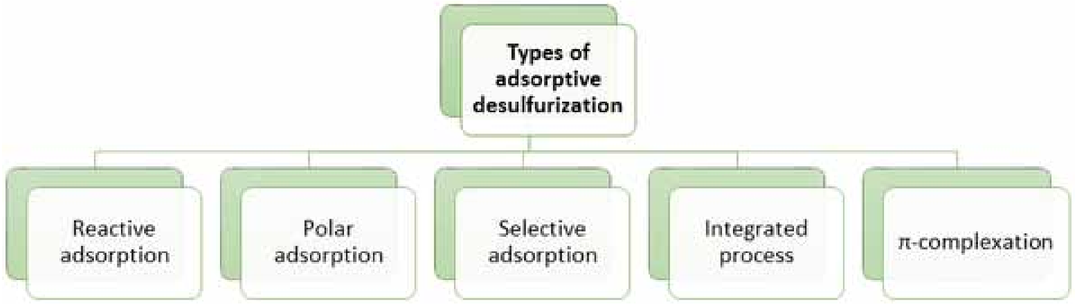
Adsorption is defined as the increase in the density of a fluid within the vicinity of an interface. Adsorption occur when a solid surface is exposed to a liquid or a gas, the gasses and liquids tend to adhere to the unoccupied spaces in solid particles due to the presence of unsaturated molecular forces within a solid material. The principle of adsorption is based on the removal of certain substances called adsorbate (liquid or gas) by an adsorbent (solid material). It can further be defined as the adherence of substances to solid materials. Nearly all substances may have trace capability for adsorption but depending on some favorable characteristics like surface area, active sites, pore size and volume, some materials are far better than others in the way and manner they adsorb particles.

Adsorption involves two types of forces viz: physical forces which may include dispersive forces, polarization forces, or dipole and chemical forces due to the interaction of electrons between solid particles and the atoms of liquids or vapor phase (Roop et al., 2005). There are three principal forces responsible for adsorption which include: van der Waal's forces, chemical affinity and electrostatic attraction. There are two different types of adsorption: physiosorption, which is reversible, and chemiosorption that is irreversible (Zeki 2013). The adsorption process is primarily studied based on certain types of equations and models. The most widely used equations are: Freundlich which is based on empirical equations that describe the adsorption characteristics on heterogeneous surface (Freundlich 1906), Langmuir equation which is based on monolayer adsorption process on energetically homogeneous surface (Langmuir 1918) and Brunauer-Emmett-Teller (BET) equation which is mostly used in gas phase adsorption and it is based on statistical analysis of adsorption sites occupied during a multi-layer adsorption of gasses (Brunauer et al., 1938).

2. TYPES OF ADSORPTIVE DESULFURIZATION

There are various forms of adsorptive desulfurization which will be discussed in this section and these include: reactive adsorption, polar adsorption, selective adsorption, integrated adsorption, π-complexation. The schematic showing different forms of desulfurization is given in Figure 1.

Figure 1. Types of adsorptive desulfurization

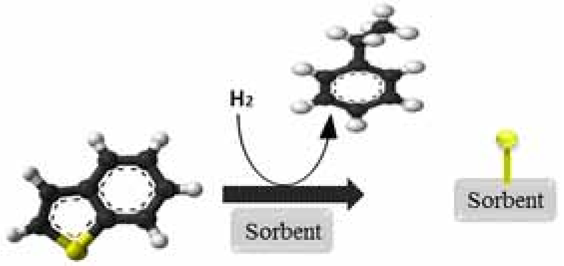


Reactive Adsorption

Reactive adsorption is a form of ADS whereby the sulfur compounds in fuel are removed by chemical interaction between the fuel and the sorbent material. The reaction involves removal or transfer of the sulfur compounds from the fuel followed by attachment of the compounds to the sorbent material which will allow the sulfur free fuel to be collected in the main stream. The process uses metal-based sorbent for sulfur removal to form metal sulfide. The sorbent material can be regenerated by disposing off the sulfur compounds in the form of SO_2, H_2S, or elemental sulfur depending on the method employed. Reactive adsorption can be carried out at ambient conditions, at elevated temperatures and with the aid of hydrogen at elevated temperatures. The efficiency of reactive adsorption depends on the adsorption capacity of the sorbent material, its affinity to the sulfur compounds, its thermal and mechanical stability and its ability to be regenerated. The overall mechanism of the process is outlined in Figure 2.

This process is widely used in the US as the S Zorb process developed by Philips Petroleum for efficient desulfurization at higher temperatures of between 340 -410°C and lower pressure of H_2 between 2-20 bars. Reactive ADS combines the advantages of both the catalytic HDS and adsorption desulfurization and thus highly efficient for deep desulfurization. Research Triangle Institute (RTI) has developed a technology called TReND based on reactive adsorption desulfurization that utilizes metal oxides as sorbents materials to effectively remove sulfur compounds from fuels in the presence of hydrogen at a temperature of 426-535°C. Mercaptans are completely removed from fuels in this process in the absence of hydrogen but thiophenes requires considerable amount of hydrogen for its successful removal (Turk

Figure 2. Reactive adsorption of benzothiophene (BT) on sorbent material in the presence of hydrogen



et al., 2001). Reactive adsorption can be aided with hydrogen at elevated temperatures using selective adsorbents. ZnO has been reported and industrially applied as a promising adsorbent for desulfurization processes. Addition of hydrogen in the process helps in the complete removal of thiophene in fuel.

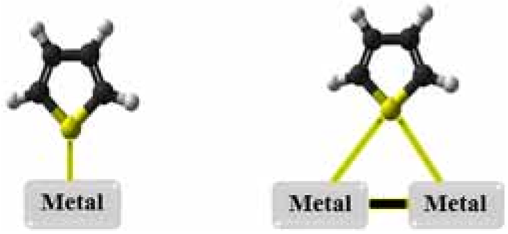
Polar Adsorption

Polar adsorption (IRVAD process) is a less expensive method of providing low sulfur gasoline and it was developed and commercialized by Black and Veatch Pritchard and Alcoa Industrial chemicals to address even low concentrations of sulfur compounds in fuels. Activated alumina in particular Alcoa Selexsorb is widely used as the sorbent material for the removal of polar compounds. The adsorption process is performed in a counter-current moving bed with alumina adsorbent in contact with liquid hydrocarbon in a multi stage adsorber. The adsorbent is normally regenerated using hydrogen at various temperatures due to its heat capacity, thermal conductivity and its availability. The regenerated adsorbent is then recycled for another round of the reaction. The process operates at lower pressures and does not consume high amount of hydrogen. The mechanism is based on the polarity of sulfur in gasoline and it is known to reduce sulfur from fuels to as low as 0.5ppmw.

Selective Adsorption for Removal of Sulfur Compounds (SARS)

The idea behind SARS is to remove sulfur compounds from fuels which constitute only less than 1% of the fuels at ambient conditions without hydrogen and to leave behind the remaining hydrocarbon contents of fuels which can be used as ultra-low sulfur fuels. This process was first demonstrated by Pennsylvania state university (Song et al., 2003) and if fully developed can be used in refinery operations and other mobile/stationary applications. The prime goal of SARS is to design appropriate adsorbents with surface sites having high affinity for sulfur compounds in the presence of aromatics. The adsorbents need to be effective, selective and apt for sulfur removal. Nickel based sorbents and air regenerable metal oxide based sorbents are the most common adsorbent materials used in this process. The basis for the SARS technology is that there is site specific interaction between sulfur and metal species that is possible with selected organometallic complexes. The likely adsorption configurations of thiophenic compounds on adsorbents used in SARS process can be explained from the known coordination geometries that thiophene exerted upon contact with organometallic complexes. Examples of coordination geometries are given in Figure 3. It is a known fact that both thiophenic sulfur compounds and non-sulfur aromatic compounds in fuels can interact with metal species by pi-electrons which is why the likely coordinating

Figure 3. Coordination geometries of thiophene in organometallic complexes



geometries that will best explain the interaction of sulfur atom of the thiophenic compounds with the adsorbent used in SARS are: η^1S (sulfur atom of thiophenes and a metal relation) and S-μ3 (sulfur atom of thiophenes and two metal species).

Integrated Process Adsorption

This is a recent technology that combines selective adsorption with HDS technology using highly efficient catalysts for effective removal of sulfur compounds from fuels. It has added advantages like reduction in cost, better efficiency, faster desulfurization rates and reduction in reactor volumes than using single processes alone. The schematic diagram for the technology is outlined elsewhere by (Chunshan et al., 2003).

ADS by π-Complexation

Adsorption by chemical complexation (π-complexation) has been reported by Yang group of researchers (Yang et al., 2001; Arturo et al., 2004; Yuesong et al., 2012). Cations such as Na^+, Zn^{2+}, Ni^{2+}, Cu^+, Ag^+, Fe^{2+}, Ce^{4+} are used mostly on zeolites due to their larger pores and pore volumes to adsorb large quantities of thiophene, BT and DBT from diesel, gasoline and jet fuels by forming π-complexes between the metals and the compounds of interest. The cations form σ-bonds with free s-orbitals and the d-orbitals will back-donate electron density to the antibonding π-orbitals in the sulfur containing ring of thiophenes. Bonds formed due to this interaction are stronger and yet easily broken by alternating the temperature or pressure which enhances the capacity and selectivity to sulfur compounds. ADS by *π-complexation* yields better results compared to the normal vanderwaals interactions occurring in adsorption studies. Aside from desulfurization, different sorbents have been developed based on this mechanism for aliphatic, olefins and aromatics separation (Takahashi et al., 2001). The mechanism is shown in Figure 4.

3. NANOMATERIALS AND HYBRID MATERIALS PREPARATION

A nanomaterial is a broad name given to all types of materials found at the nanoscale; it is a material that has a unit size between the ranges of 1-100 nm. They can be naturally occurring or chemically/mechanically synthesized with zero dimension (0-D), one dimension (1-D), two dimensions (2-D) or three dimensions (3-D). They have a wide range of both structural and non-structural industrial appli-

Figure 4. ADS of DBT by π-complexation

cations due to their sizes, shapes, chemistry and high surface area. They are applied in most industrial applications to improve performance because their surface properties far exceed their bulk properties. Nano-materials such as alumina, zirconia, silica, and AC have been the subject of research recently due to their promise in adsorption desulfurization. Adsorbents are generally classified into organic sources and inorganic sources. Adsorption on commercial and industrial scale depends solely on the type, quantity, economic cost and effectiveness of adsorbent material. This is why studies on adsorption studies currently focus on the development of better adsorbent materials for large scale industrial applications. Most materials used as adsorbents are relatively porous and have a wide surface area with pore diameter of tens of angstroms.

The most widely used adsorbents are: AC, silica gel, zeolites, molecular sieve carbon, activated alumina, polymers and nanocomposites. Each of these materials has distinct physical and chemical characteristics such as pore sizes and structure, porosity and nature of the adsorbing surface that are different from other materials. The materials that can be used as adsorbent should be thermally and mechanically stable, highly porous with balance between micro and macro-pores with high surface area, high affinity for the adsorbate and should be cheap and be easily regenerated. Table 1 outlines the classes and the applications of the major adsorbents.

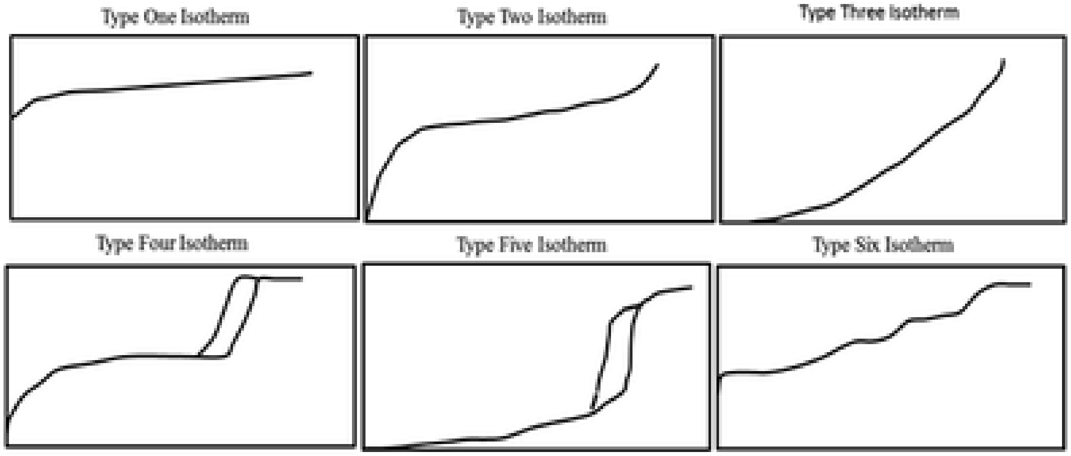
The adsorptive capacity of any adsorbent material depends on the number of pores in the internal area relative to the number of pores on the outer surface. The internal area is much higher than the outer surface area which is the major reason why adsorbent materials adsorb large quantity of the adsorbate. These materials are further classified based on their pore sizes which determines which material they can adsorb into three classes *viz*: Micro porous adsorbents (between 2A° to 20A°), Meso porous adsorbents (between 20 A° to 500 A°) and Macro porous adsorbents (>500 A°). Where A° = Angstrom which is equivalent to 10^{-10} meters = 0.1 nm. Adsorption capacity or otherwise adsorption isotherm depends upon temperature and vapor pressure which help us to classify different forms of adsorbent. Adsorption isotherms are classified into six different classes (Sing 1982). The graphical illustration of the isotherms is shown in Figure 5.

- **Type One Isotherms:** They consist mostly of micro porous adsorbents. E.g. Silica gel and most carbons fall in this category
- **Type Two Isotherms:** They consist of non-porous surfaces and macro porous adsorbents. E.g. Graphitized carbon and some hardened powders of silica.

Table 1. Classes and applications of adsorbents

Adsorbent	Applications
Carbons	Widely used in the removal of hydrogen, nitrogen, odors, vinyl chloride, desulfurization of SOx and denitrogenation of NOx from gasses, in water treatment, and in the treatment of nuclear waste.
Alumina	It is mostly used in drying of gasses (as a desiccant) and adsorption of fluoride, chromium, arsenic and selenium in water treatment. It is also used in desulfurization.
Silica	It is used as a desiccant in drying of gasses, maintenance of relative humidity, and in desulfurization.
Zeolites Zirconia	• Helps in drying of gasses, water treatment, sweetening of gasses and liquids, aids in pollution control of SOx and NOx through desulfurization and denitrogenation, recovery of CO_2, and in the separation of aromatics from paraffins etc. • Desulfurization, adsorption of gasses such as: CO, $CO_{2,}$ $NH_{3,}$ dentistry, biomedical, ceramics, and sometimes used as an alloying agent.

Figure 5. Graphical illustration of different isotherms models



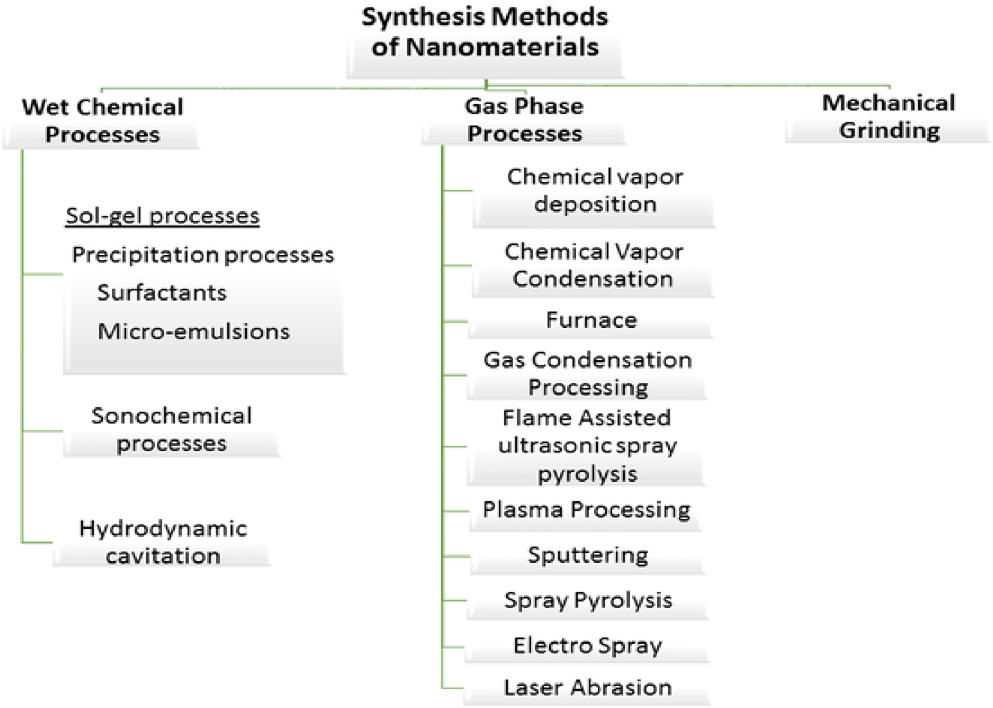
- **Type Three Isotherms:** They consist of non-porous and macro porous solids. E.g. synthetic polymers used as adsorbent materials
- **Type Four Isotherms:** This class exhibit special attribute of hysteresis which means capillary condensation showed by the mesoporous adsorbents. E.g. Low density silica gel
- **Type Five Isotherms:** This class exhibit hysteresis as well but they show similar characteristics to Type three isotherms.
- **Type Six Isotherms:** This isotherm share similar characteristics to type two isotherms but however, the adsorbent belonging to this class adsorb in a multilayered passion.

3.1. Synthesis Methods

Nanomaterials are synthesized using two different approaches viz; bottom-up approach and top-down approach. In the bottom-up approach, the nanoparticles are first obtained at the atomic level and later integrated into the desired material e.g. is the formation of nanoparticle from colloidal dispersion or the formation of powders from sol-gel method followed by a later stage of integration. The top-down approach starts with a bulk material at the macroscopic level followed by trimming of the material to the desired nanoparticles e.g. etching and ball milling. Schematic illustrations of the synthesis methods are provided in Figures 6 and 7.

Figure 6. Synthesis of Nanomaterial

Figure 7. Synthesis routes of nanomaterials



The general outline for the production of nanomaterials involves three different processes; grinding, wet chemical processes otherwise called liquid phase processes and lastly the gas phase processes of producing nanomaterials. These processes are outlined below:

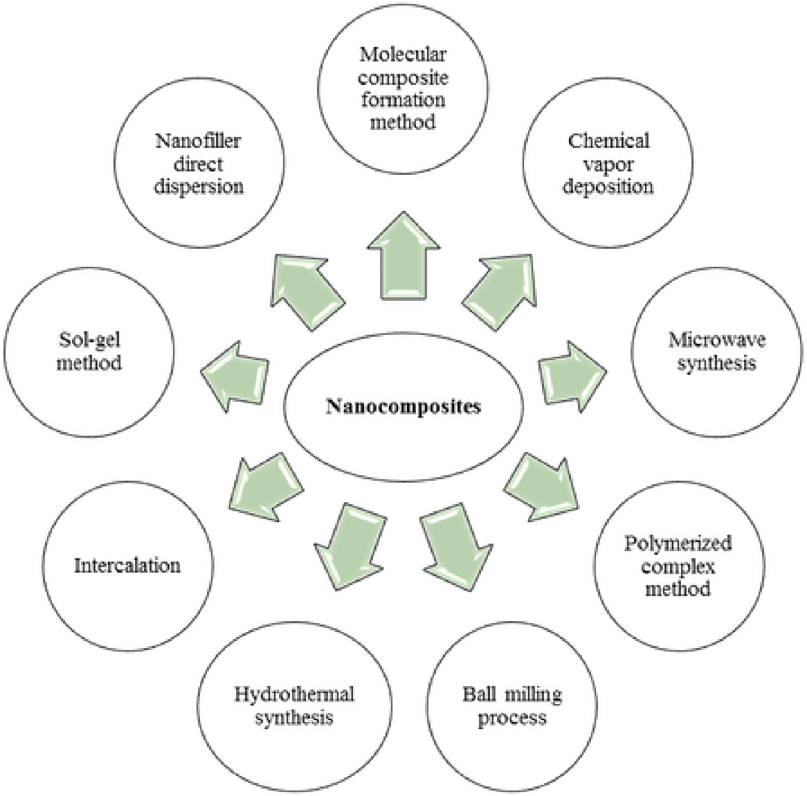
Synthesis of Nanocomposites

Nanocomposites are special classes of materials formed by combining two phases of different materials and they tend to retain the properties of each material used in their formation. A matrix (filler and resin) and a reinforcement (mostly fibers) are required for the formation of a composite. Properties of composites depends on the properties of each material, their relative amounts and overall geometry. In essence, nanocomposites are materials having one or more of their phases in the nanoscale size embedded in a polymer matrix, ceramic matrix or metal matrix. They have nanoparticle properties, high thermal and mechanical stability, multifunctional capabilities, chemical functionalization and huge interphase zone. The combination confer added advantage to them which is why they are currently utilized in various fields of science and technology. They are widely used in catalysis, nanosensors and nanoprobes production, sorption process, chemical and biological applications, fuel cells, non-linear optics, bio-ceramics, batteries with greater power output, environmental protection, anti-corrosion agents, drug delivery, UV protection gels, as fire retardant material, in the production of lubricant and scratch free paints and in adsorptive studies with clear application in desulfurization.

There are various ways of synthesizing nanocomposites which will be outlined in this section. The processes do not take a specific method; the synthesis may involve combining two different methods or even more for the production. The mostly widely used methods are: Intercalation, sol-gel method, molecular composite formation method, high energy sonication, nanofiller direct dispersion method, hydrothermal synthesis, polymerized complex method, surfactant assisted processing, solution-evaporation methods, electrochemical synthesis of polymers, chemical vapor deposition, microwave synthesis, and ball milling process. Figure 8 outlines the methods involved in the synthesis.

- **Sol-Gel Synthesis:** This is the most effective and cost reliable method of producing nanomaterial, nanocomposites and powders recently. Earlier it was widely used in glass and ceramic industries. It involves hydrolysis of the alkoxides by water, alcohol, ammonia, or acid followed by condensation of the products formed to produce a glass like material. It is utilized when forming inorganic or hybrid composites at low temperatures and pressures. The factors affecting this method include: pH, starting material, and solvent to be used.
- **Hydrothermal Synthesis:** This involves combining the starting materials intended for composites synthesis with certain amount of water followed by acid digestion in a reactor at high temperature and pressure. The reactants may not dissolve completely using this method.
- **Chemical Vapor Synthesis:** This is a modification of the chemical vapor deposition where the process is directed towards the synthesis of nanomaterials instead of films. The whole idea of chemical vapor deposition is the attachment of solids produced from chemical reactions in the vapor phase to a heated surface. The energy needed for complete conversion of starting materi-

Figure 8. Synthesis routes of nanocomposites



als to nanoparticles is provided by hot walls, plasma, flame and laser reactors. The availability of appropriate starting material is the major limitation of this technology. It is currently used in the production of monoliths, powders and films.

- **Microwave Synthesis:** Microwave synthesis technique has been used in organic synthesis since time immemorial. More than 2000 papers have been published relating to the application of this technique (Kappe 2004). It is in use in pharmaceutical, biochemical, medical, food, ceramic industries and academic institutions. Use of microwave synthesis in the production of nanocomposites entails combining starting materials by microwave irradiation to yield desired nanomaterial. It is fast, economical and generate less by products.
- **Solution-Evaporation Method:** This is a method of composites formation which involves mixing of nanotubes dispersion with a solution solely made up polymers that dissolves in solvents or thermoplastic polymers followed by evaporating the solvent. This will allow the nanotubes to move freely within the polymer matrix. The mixture can then be subjected to mixing and molding till desired shape is achieved. The mixing intensity and its duration will determine the distribution of the nanoparticles within the polymer. The major drawbacks of this technique is that the polymer has to be soluble in the same solvent used to disperse nanoparticles and the problem of solvent removal limits the application of this technique in major industries.
- **Ball Milling Process:** This is a technique that has been used in almost all industries for size reduction of materials. Nanocomposites production is no exception considering the recent utilization of high energy ball milling process for the production. Powdered materials are normally immersed for ball milling in the appropriate machine through movement of the balls, collision to the supporting disc and centrifugal force exerted nanomaterials are easily formed. Mechanical alloying, mechanical milling and mechanochemical synthesis are the terms mostly used relating to the production of materials by ball milling. This method is perfect for the production of nanomaterials because it is efficient, and cost effective.
- **Intercalation Method:** This is the most widely known method for the synthesis of polymer nanocomposites. The desired outcome depends on whether an intercalated or exfoliated hybrid is required. The process involves combining a starting material (a polymer) within layers of clay of material. When intercalate is required the organic material is immersed within the layers of the clay such that there will be expansion within the component mixtures. While in exfoliated mixture, the whole layers of the clay material will be separated from each other but tied within the matrix of the organic component.
- **Nanoparticle Direct Dispersion Method:** This is a method of producing nanocomposites by chemically modifying nanoparticle to increase compatibility with polymers. The advantage of using this method is that total homogeneity is achieved without compaction. Zinc oxide nanoparticles were prepared by combining zinc sulfate and ammonium bicarbonate in the study conducted by (Yujun et al., 2010).
- **Molecular Composite Formation:** This is a method of producing nanocomposites that have extra mechanical stability due to the reinforcement provided by molecular rods. A strong and durable polymer is normally combined with a malleable polymer matrix at molecular dimension with a solvent that will later be precipitated. An equilibrium compound is required as the third component for this method which will aid in the formation and dispersing of fibrils within the composite.

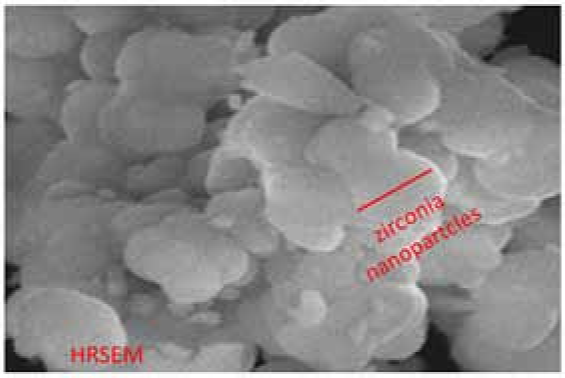
4. APPLICATIONS OF NANOCOMPOSITES AND HYBRID MATERIALS IN DESULFURIZATION

Significant number of papers have been published on the applications of nanomaterials and nanocomposites in adsorptive desulfurization. This section will discuss the use of zirconia, alumina silica and zeolite loaded with metals and metal oxides in desulfurization.

- Zirconia in Desulfurization.

Zirconia has a great promise in adsorption studies due to its moderate surface area, good structure and morphology, good thermal stability, possess both reducing and oxidizing properties and it has bi functional properties (acid/base). It is mostly synthesized through the sol-gel process using metal organic precursors. The particle size of zirconia is from 50-80nm and its crystallite size ranges from 2-10nm. It has good ADS properties; ODS of thiophene from n-octane and n-heptane using zirconia showed great promise (Wang et al., 2009). Adsorption by π-complexation of copper loaded on zirconia was demonstrated by (Baeza et al., 2008) for the removal of thiophene from n-octane at room temperature and pressure; the adsorption capacity increased simultaneously with increase in copper concentration. ODS of BT and DBT from model oil by chromium promoted sulfated zirconia prepared by wetness impregnation showed a good performance, however the reaction rate was very slow with optimum reaction time, dosage, activation energy and surface area of 6h, 5g/l, 3.8kj/mol and 116.2m^2/g respectively (Sachin et al., 2012). Different forms of zirconia viz: zirconia, calcined zirconia and calcined sulfated zirconia were used in the removal of thiophene derivatives from different solvents. The desulfurization process using zirconia is exothermic and its isotherm model best fit BET (Sachin et al., 2011). Zirconia is mostly used as a catalyst support in desulfurization according to the existing literature (Yatsuka et al., 2002). WOx/ZrO$_2$ after calcination at different temperatures was used as catalyst for the oxidative removal of BT and thiophenes from model fuels and it showed promising result (Zubair et al., 2012). The optimum calcination temperature of the catalyst was around 700°C and the catalyst was reussed in ODS. Low selectivity of using Pt/ZrO$_2$ catalyst for oxidizing SO$_2$ from exhaust gas was demonstrated by (Yatsuka et al., 2002). Variety of equipment such as: X-ray photoelectron spectroscopy (XPS), FT-IR, XRD, SEM, TEM, EPMA and BET are used for characterization of zirconia used in desulfurization. A representative SEM image of zirconia is depicted in Figure 9.

Figure 9. SEM image of zirconia



- Alumina in Desulfurization.

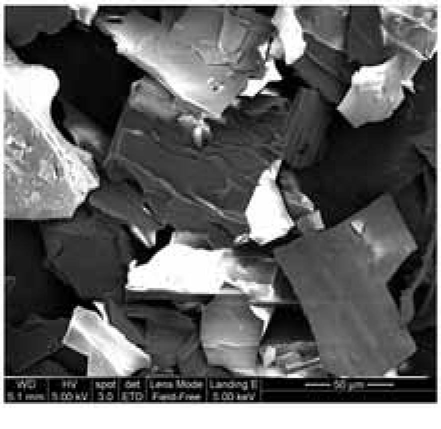
The principle of ADS which allows an adsorbent material that is porous and has high surface area to be placed in contact with the aromatic sulfur compounds in fuels as the substrates has received a considerable attention in recent years. Reports have tried to use alumina for ADS due to its better adsorptive characteristics and chemical stability. It has high surface area for adsorption, high thermal conductivity and highly insoluble in water. The major components in alumina are aluminum oxide and boehmite. Activated alumina have been used in ADS and denitrogenation though the result was not so successful in removing the sulfur compounds due to steric effect but it revealed that the selectivity of the adsorption depends on the acidic-basic interaction and the molecular electrostatic potential (Jae et al., 2006). On the contrary, reports showed how alumina can be used as a strong adsorbent in ADS of thiophene derivatives due to the presence of Lewis sites and carbon-oxygen functional groups on the surface of the adsorbent (Maria et al., 2002; Ankur et al., 2009). Alumina has been synthesized from array of sources for desulfurization. Alumina sorbents were prepared using cationic surfactants and microwave irradiation for the removal of sulfur from petroleum products (Zaki et al., 2013).

Impregnation of silver on nanocrystalline aluminum oxide and nanocrystalline metal oxides to adsorb thiophenes out of hydrocarbons showed a better performance. Nanocrystalline aluminum oxide was more effective compared to the nanocrystalline metal oxides in the desulfurization (Jeevanandam et al., 2005). The adsorbent has regenerative ability after heating at moderate temperature. Impregnated nanoparticles on alumina reduces DBT concentration in n-hexadecane from 250 ppmw to 0 ppmw in the absence of hydrogen after regeneration (Ali et al., 2014). XRD, FT-IR, and SEM are used to understand the mechanism of thiophene derivatives adsorption on alumina and Langmuir isotherm best fit the adsorption pattern. The SEM image of blank alumina is given in Figure 10.

- Silica in Desulfurization.

Silica is a widely used adsorbent and it surface can be modified to desired form. Reports show the suitability of using silica in desulfurization. Mesoporous silica is effective in ODS, the adsorbent has high affinity for sulfur compounds, and high regeneration potential (Paolo et al., 2008). Mesoporous silica

Figure 10. SEM image of blank alumina



have been used in ADS and denitrogenation of refinery fuels. A report indicates the feasibility of using plain mesoporous silica (high surface area) and zirconia combined with mesoporous silica (lower surface area) in desulfurization. SEM images of the samples reveals both samples having diameter between 2-4 μm. In addition, both adsorbent show effective desulfurization, denitrogenation and regenerative ability. However, the structure of the plain mesoporous silica collapses after treatment with deionized water (Jun-Mi et al., 2008). Mesoporous silica nanoparticles are also effective in desulfurization of DMDBT and can perform better than other adsorbents (Jessica et al., 2014). Lead loaded on mesoporous silica reduces 1000 ppm sulfur containing gasoline to 50 ppm in three rounds of adsorption/desorption cycle (Anne et al., 2014). Lithium modified mesoporous silica is also effective in desulfurization of natural gas (Anton et al., 2012).

- Zeolite in Desulfurization.

Using zeolites as adsorbents for sulfur removal has been reported by many workers. Weitkamp et al. examined the removal of thiophene from benzene under dynamic condition using ZSM-5 and the adsorption capacity was 15-17 mg thiophene per gram zeolite (Weitkamp et al., 1991). Zeolite 13X reduced the sulfur level in non- HDS treated naphtha solution from 36.62 (mg S\L) to 0.74 (mg S\L) and a non- HDS treated naphtha solution from 412.2 (mg S\L) to 287.3 (mg S\L), but this sulfur level does not meet environmental regulation (Salem *e*t *a*l., 1994). Hu et al. used a combination of ZSM-5/13X zeolites to extend the life of a reforming catalyst designed for portable power applications. The zeolite combination provided almost an additional 1 hr of life to the catalyst at 80% or better conversion. It shows that molecular sieves are promising options for onboard applications, particularly for unexploited options like the π-complexation adsorbents (Hu *e*t *a*l., 2003). Gongshin prepared sorbents using ion-exchange techniques to introduce d-block metals like Ag^+, Cu^+, Ni^{2+} and Zn^{2+} into zeolites (Gongshin 2006). Zeolites synthesized using coal fly ash were used for adsorption of TH and BTH in n-hexane solution. It was shown that the introduction of different heteroatoms into the framework of zeolites leads to different catalytic and adsorption properties (Ngamcharussrivichai *e*t *a*l., 2008). Gallium atoms introduced into the framework of Y zeolite was employed for desulfurization of various model fuels containing about 500 mg sulfur/g. At ambient conditions, the breakthrough capacity for the adsorption of TH, THT and 4,6-DMDBT were found to be 7.0, 17.4 and 14.5 mg of sulfur/g of adsorbent, respectively (Tang et al., 2008). The removal of dibenzothiophene from model fuel was investigated by adsorption on commercially available adsorbents including an aluminum oxide, 13X and Y zeolite. The evaluation of the tested adsorbents showed that the best adsorptive performance was achieved by the Y zeolite (Muzic et al., 2012).

- Nanocomposites in Desulfurization.

Doping of adsorbents with metals and metal oxides is known to enhance selectivity, reactivity and capacity for the sulfur compounds. Solid metal thiolates that are insoluble in hydrocarbons are formed when metal oxides react with thiophene derivatives; this allows there removal by filtration. Various nanocomposites have been reported of having potentials in ADS such as alkaline and alkaline earth metals, CuO, Cr_2O_3, NiO, $Fe_2O_{3,}$ CeO_2, ZnO etc (Saha et al., 1995; Ramaswamy et al., 2004). Most of the adsorbents adsorbs at ambient conditions and the desulfurization efficiency is dependent on the amount of metals and the type of sorbents used. Varying the nickel/cupper loadings on Ni/Alumina and Ni/Aluminosilicate-5 in ODS using hydrogen peroxide as the oxidant shows a dramatic change in the desulfurization. Loading Ni on Alumina can completely treat sulfur in oil from 350 ppmw to 0 ppmw (Sarda et al., 2012). Dispersion of metals and metal oxides on adsorbents increases adsorption efficiency. Ag/TiOx–Al_2O_3 and Ag/TiO_x–SiO_2 have been used as remarkable adsorbents for the ADS of jet and diesel fuels at ambient conditions. Dispersion of TiOx and loading of Ag on alumina or silica increases desulfurization performance. Ag/TiOx–Al_2O_3 has greatest affinity to BT and it reduces the sulfur content of ULSD from 1170 ppmw to 75 ppmw. It is equally regenerable (Shahadat et al., 2013). A high performance sulfur adsorbent (NiO–CeO_2/Al_2O_3–SiO_2) has been used for the desulfurization of Jet A fuels at ambient conditions. The composite reduces the sulfur content from 1140 ppmw to as low as 10 ppmw; it has sulfur adsorption capacity of 1.4 and 3.22 mg-S/g-ads at breakthrough points of 10 and 50 ppmw respectively. The adsorbent was regenerated four times by calcinating helium gas for a short time before reaching half-life (Xinhai et al., 2014).

NiMCM-41 and NiY adsorbents have been used in vapor phase ADS of diesel under controlled condition. 1g of NiMCM-41 treated 20 ml of diesel and the sulfur concentration was reduced from 450 ppm to 50ppm while 1g of NiY treated 25 ml of diesel and the sulfur concentration was reduced to <50 ppm. Both composites were regenerated under controlled oxidation at approximately 450°C (Soumen et al., 2013). Zeolite-TiO_2 have been tested for the photodegradation of DBT in fuels, β-zeolite adsorbed almost all the degradation product while TiO_2 was used as a photo catalyst in the reaction. Over 88% of DBT was degraded (Faghihian et al., 2013).

π-complexation a form of a ADS using copper species on nanomaterials such as zeolites, AC, silica and alumina or nanocomposites to selectively remove thiophenic compounds in fuels at room temperature and pressure proves to be a promising approach in desulfurization (Yang et al., 2006; Wen-Hang et al., 2010). Complexes are formed between the bulk materials and the cuprous ions which is an essential step in the removal of sulfur compounds from fuels. The extent of removal depends on the amount of the copper species and the limit of dispersion of the species on the nanomaterials. The cuprous species for ADS can be directly introduced or formed from the reduction of cupric species.

An area of interesting research currently focuses on the utilization of membranes for efficient desulfurization. Oleophilic polymer-inorganic nanocomposites are used for the pervaporative removal of organosulfur compounds from gasoline. The inorganic component (silica nanoparticles) can be synthesized in-situ through biomimetic mineralization in confined space using an alkaline inducer catalyst. The membrane has a good performance permeation flux of 7.36 kg/ (m^2h) and a selectivity of 4.98 to thiophene in gasoline (Ben et al., 2012).

5. MECHANISMS OF ADSORPTIVE DESULFURIZATION

ADS is based on physisorption or chemisorption process of organosulfur compounds on solid sorbents. The mechanism of desulfurization in general has not been extensively studied in full details. Most of the reports on this field proposed the mechanism theoretically or experimentally without proper insight into the subject. However, the studies of (Liang et al., 2010; Duan et al., 2014; Lichun et al., 2011) have outlined some of the mechanisms involved in ADS.

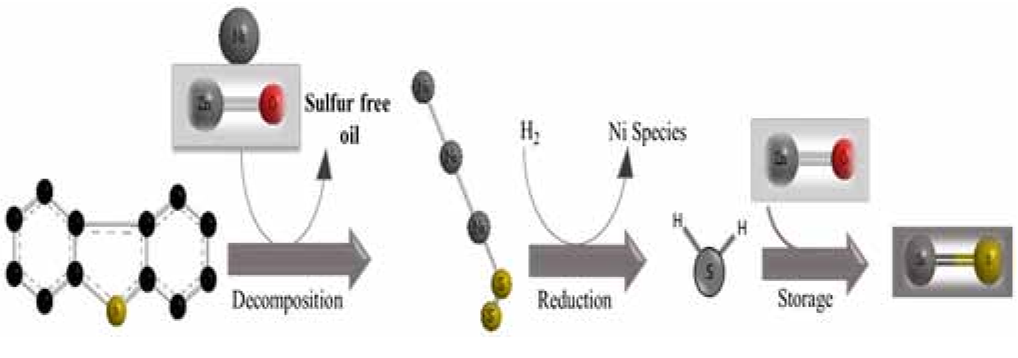
The mechanism of ADS based on the idea to regenerate sulfur-poisoned Ni catalyst in reduced atmosphere has been studied by (Tawara et al., 2000). Ni/ZnO and Ni/Al_2O_3 were utilized as catalysts for adsorptive ultra-deep hydro desulfurization of kerosene using hydrogen at 600K. The idea is based on the fact that sulfur poisoned nickel catalyst particles will be combined with ZnO or Al_2O_3 particles in the presence of hydrogen, then each poisoned catalyst will release a few ppb of H_2S which will be attached to the ZnO or Al_2O_3 particles. This process in turn will allow the effective regeneration of sulfur poisoned nickel catalyst. Residual sulfur was not detected in the treated kerosene with Ni/ZnO. The catalyst completely remove residual sulfur even after 800 h of operation and no methane was produced in contrast to the other materials used. Following the results outlined above, (Babich et al., 2003) further illustrates the mechanism. ZnO/Al_2O_3 was used as the main component of the sorbent while Ni was used as the main site for the hydro desulfurization. Thiophene in the second step of the reaction was decomposed on the Ni site after reacting with hydrogen. Further reaction with hydrogen lead to the removal and transfer of hydrogen sulfide to ZnO surface. Subsequent reactions with thiophene further converts ZnO completely to ZnS which may later be regenerated or discarded.

Reactive adsorption desulfurization of model oil containing DBT over a Ni/ZnO adsorbent has been outlined by (Lichun et al., 2011). The reaction mechanism under different atmospheres has been investigated. The result indicates different mechanisms when nitrogen and hydrogen were used respectively. Desulfurization over Ni/ZnO using nitrogen was achieved based on physical and chemical adsorption but the rate was very slow. However, the desulfurization under hydrogen turns out to be based on reactive adsorption desulfurization and the rate was very fast. Hydrogen is very important in reactive adsorption desulfurization when Ni/ZnO adsorbent is used, it aids in the decomposition of DBT on Ni species and in the formation of Ni_3S_2 and the transfer of sulfur moieties to ZnO. The kinetics of thiophene reactive adsorption on Ni/SiO_2 and Ni/ZnO via thermal gravimetric analysis at 280–360°C under 5–40 mbar of thiophene in H_2 was illustrated by (Bezeverkhyy et al., 2008). The interaction of Ni/SiO_2 with thiophene followed a two-step reactions: surface reaction followed by bulk transformation into Ni_3S_2 (nickel sulfidation). The interaction of Ni/ZnO with thiophene is similar to Ni/SiO_2 interaction, a surface reaction was noticed due to increase in weight but there was no nickel sulfidation transformation instead a nucleation-controlled ZnO surface transformation was noticed followed by complete particle sulfidation.

The sulfur transfer mechanism in the presence of hydrogen involves three step reactions: first step involves the decomposition of DBT in the model oil on Ni surface of Ni/ZnO to form Ni_3S_2, the second step involves the reduction of Ni_3S_2 in the presence of hydrogen to form H_2S followed by the release of active nickel species from Ni_3S_2. The final step involves the storage of H_2S in the adsorbent followed by the final conversion of ZnO into ZnS. The mechanism is illustrated in Figure 11.

The mechanism involved in the removal of thiophene by reactive ADS from model fuels is illustrated by (Xuan et al., 2013). Reduced $NiZnO/Al_2O_3$-diatomite was used as the adsorbent in the studies and

Figure 11. Mechanism of reactive ADS of DBT containing model oil over adsorbent of Ni/ZnO in hydrogen.



the result indicated that S-M bonding of thiophene to Ni sites of the adsorbent was decomposed to form Ni_3S_2 and C4 olefins formed were further saturated by hydrogen to CH_4 which was released back to the stream. The final step involves the transfer of sulfur from Ni_3S_2 to ZnO in a reduced atmosphere which will yield ZnS and a free Ni specie ready for another round of the reaction.

Zeolites are acid catalyst used in olefin hydroforming and aromatic conversion. They are also used in HDS and as bi-functional catalyst. Zeolites contains both acidic and a basic site. The lewis basic site on zeolites is responsible for the catalytic hydrogen desulphurization of most sulfur compounds in fuels; the bronsted acidic site has little or no role to play in the catalysis. Thiophenic ring cracking is the rate determining step in HDS of thiophene and DBT (Rozanska et al., 2003). A periodic density functional theory study of the thiophenic derivative cracking catalyzed by proton or lithium exchanged modernite (zeolite) can be a good method to prove the cracking of thiophene derivatives; benzothiothiophene is cracked by a catalyst where one of the oxygen atoms in the catalyst is the catalytic center for the reaction. The mechanism of benzothiophene cracking is illustrated in Figure 12.

Mechanism of adsorption of DMDBT from solutions in hexadecane on three different nanopourous AC has been illustrated by (Kostas et al., 2014). Each of the nonporous carbons has microporous or combined micropores and mesopores structures. The capacity for 4, 6-DMDBT adsorption increases with increase in the volume of pores. The pores with diameter lower than 10 Å are said to adsorb better because the diameter is similar to that of 4, 6 DMDBT molecule. Acidic functional groups on the surfaces of the larger pores are said to contribute to the adsorption via polar interactions. Most noticeable functional groups are carboxylic acids because they interact with the oxidation products of 4, 6 DMDBT (sulfoxides, sulfones, and sulfonic acids) via hydrogen bond. Dispersive interactions between the delocalized π-electrons within the benzene rings of 4, 6 DMDBT and the electron rich region on the nanoporous carbon aromatic ring also plays a major role in the adsorption. Figure 13 illustrates the mechanism.

Molecular simulation techniques are used for the illustration of reaction mechanisms involved in desulfurization using density functional theory. These techniques are reported by (Hideo et al., 2004; Shengli et al., 2012) and they provide useful information for better optimization and improvement of materials used in the desulfurization technology. The reactive adsorption desulfurization mechanism of thiophene over Zn_3NiO_4 (bimetallic oxide adsorbent) is illustrated using density functional theory. The gas phase thiophene molecule is adsorbed on the Ni site instead of the Zn-site on the adsorbent. Hydrogen

Figure 12. Mechanism of BT cracking by zeolites

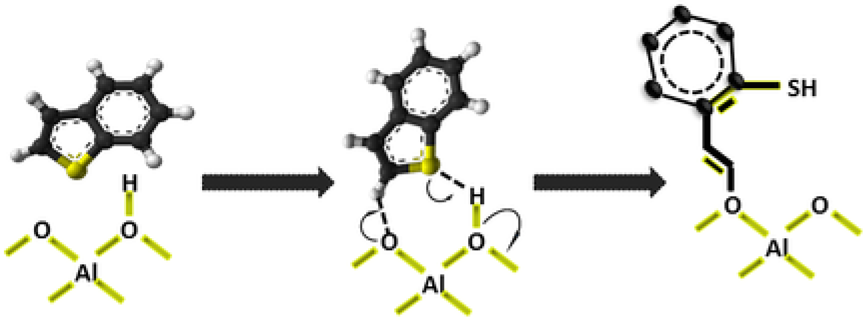
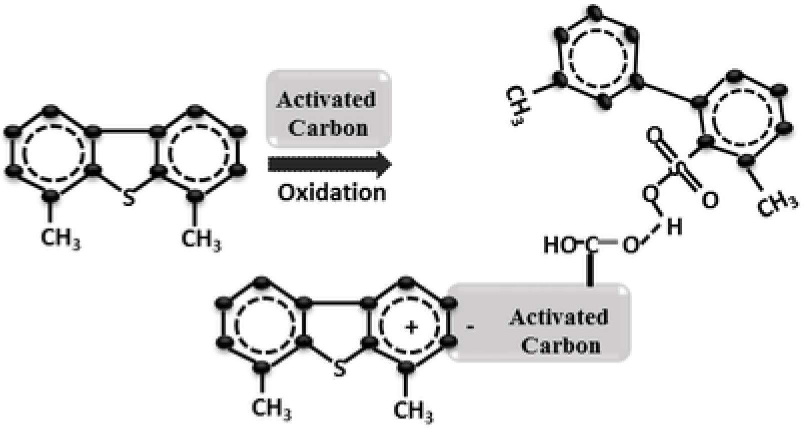


Figure 13. The possible adsorption mechanism of 4,6 DMDBT on AC



plays a fundamental role in the cleavage of the C-S bond of the sulfur compound. The result indicates that thiophene is first decomposed on the Ni site of the adsorbent followed by reduction to nickel sulfide via two pathways. The first pathway is that nickel sulfide is reduced to H_2S in the presence of H_2 while the second pathway allows the transfer of sulfur from nickel site of the adsorbent to zinc site. A further illustration on the adsorption of thiophene on icosahedral Ni_{13} and Zn doped Ni_{13} clusters ($Zn@Ni_{13}$ and Ni@Ni11Zn1) is shown using density functional theory by (Ping et al., 2013). The results indicates that thiophene is preferentially adsorbed on Ni_{13} and $Zn@Ni_{12}$ clusters with the whole ring π-bond to the hollow site (η5 bonding model) and the introduction of Zn to Ni_{13} leads to a small decrease in the bonding energy. Thiophene is preferred to be adsorbed on the Ni rather than on the Zn site.

6. SUMMARY AND OUTLOOK

The chapter discusses the synthesis and applications of nanomaterials and nanocomposites in ADS. Major effects of sulfur to the environment, health, economy and refining equipment have been discussed. The regulation set by USEPA on the level of sulfur in diesel and gasoline is currently 15ppm and various technologies are currently in use to achieve the set standard *viz*: HDS, ODS, BDS, ILE, and ADS. ADS is the most promising approach because it requires no hydrogen, oxidants or solvents and it operates at ambient conditions. It major drawback is lack of selective and regenerable adsorbents. The principle of adsorption that relies on chemiosorption and physisorption is based on the increase in the density of a fluid within the vicinity of an interface. The types of ADS have been discussed which include: reactive, polar, selective, integrated process adsorptions and an adsorption by π-complexation. Various classes of the adsorbents (AC, alumina, zirconia, zeolite, silica etc.) and their applications have been discussed however for efficient adsorption, the material should possess the following properties: high surface area, porosity, affinity to the adsorbate and they should be cheap with thermal and mechanical stability. The synthesis routes of nanomaterials and nanocomposites with their applications in desulfurization have been extensively discussed. The chapter concludes with possible mechanisms of ADS on various adsorbents.

ACKNOWLEDGMENT

The authors would like to acknowledge the support provided by King Abdulaziz City for Science and Technology (KACST) through the Science & Technology Unit at King Fahd University of Petroleum & Minerals (KFUPM) for funding this work through project No. 13-PET393-04 as part of the National Science, Technology and Innovation Plan.

REFERENCES

Aijun, D., Peng, Z., Liang, Z., Jingjing, J., & Zhen, Z. (2014, August 22-24). Computational simulation application in the research of desulfurization mechanism. Proceedings of the 9th International conference on computer science & education (ICCSE 2014), Vancouver, Canada.

Al Zubaidy, I. A. H., Tarsh, F. B., Darwish, N. N., Majeed, B. S. S. A., Al Sharafi, A., & Abu Chacra, L. (2013).. . *Adsorption Process of Sulfur Removal from Diesel Oil Using Sorbent Materials*, *1*(1), 66–68.

Ali, M. F., Al-Malki, A., El-Ali, B., Martinie, G., & Siddiqui, M. N. (2006). Deep desulphurization of gasoline and diesel fuels using non-hydrogen consuming techniques. *Fuel*, *85*(10-11), 1354–1363. doi:10.1016/j.fuel.2005.12.006

Anne Rodrigues, K. O., Ramos, J. E. T., Cavalcante, C. L., Rodriguez-Castellon, E., & Azevedo, D. C. S. (2014). Pd-loaded mesoporous silica as a robust adsorbent in adsorption/desorption desulfurization cycles. *Fuel*, *126*, 96–103. doi:10.1016/j.fuel.2014.02.019

Babich, I. V., & Moulijin, J. A. (2003). Science and technology of novel processes for deep desulfurization of oil refinery streams: A review. *Fuel*, *82*(6), 607–631. doi:10.1016/S0016-2361(02)00324-1

Baeza p, G. Aguila, F. Gracia, P. Araya (2008): Desulfurization by adsorption with copper supported on zirconia. *Catalysis Communications,* 9, 751-755.

Bansel, R. C., & Goyal, M. (2005). *Activated Carbon Adsorption*. USA: Taylor and Francis Group. doi:10.1201/9781420028812

Bej Shyamal, K. (n. d.). Revamping of diesel hydro-desulfurizers: Options available and future research needs. *Fuel Process. Technol,* 85(13), 1503–1517.

Ben Li, W. L., Wu, H., Yu, S., Cao, R., & Jiang, Z. (2012). Desulfurization of model gasoline by bioinspired oleophilic nanocomposite membranes. *Journal of Membrane Science*, *415–416*, 278–287.

Berk, Z. (2013). Food Process Engineering and Technology (Ch. 12) (2nd ed.). Food science and technology.

Bezeverkhyy, I., Ryzhikov, A., Gadacz, G., & Bellat, J. P. (2008). Kinetics of thiophene reactive adsorption on Ni/SiO_2 and Ni/ZnO. *Catalysis Today*, *130*(1), 199–205. doi:10.1016/j.cattod.2007.06.038

Bhandari, V.M., Hyun Ko, C., Geun Park, J., Han, S.-S., Cho, S.-H., Kim, J.-N. (2006). Desulfurization of diesel using ion-exchanged zeolites. *Chemical Engineering Science*, *61*, 2599–2608.

Bösmann, A., Datsevich, L., Jess, A., Lauter, A., Schmitz, C., & Wasserscheid, P. (2001). Deep desulfurization of diesel fuel by extraction with ionic liquids. *Chemical Communications (Cambridge)*, *23*(23), 2494–2495. doi:10.1039/b108411a PMID:12240031

Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gasses in multimolecular layer. *Journal of the American Chemical Society*, *60*(2), 309–319. doi:10.1021/ja01269a023

Cheng, P., Zhang, S., Wang, P., Huang, S., & Tian, H. (2013). First-principles investigation of thiophene adsorption on Ni13 and Zn@Ni12 nanoclusters. *Computational and Theoretical Chemistry*, *1020*, 136–142. doi:10.1016/j.comptc.2013.07.044

Cheruku, S. K., & Banerjee, T. (2012). Liquid–liquid equilibrium data for 1-ethyl-3-methylimidazolium acetate–thiophene–diesel compound: Experiments and correlations. *Journal of Solution Chemistry*, *41*(5), 898–913. doi:10.1007/s10953-012-9840-5

Dasgupta, S., Gupta, P., Aarti, A. N., Goswami, A. N., Garg, M. O., & Tangstad, E. et al. (2013). Adsorptive desulfurization of diesel by regenerable nickel based adsorbents. *Fuel*, *108*, 184–189. doi:10.1016/j.fuel.2012.12.060

De Filippis, P., & Scarsella, M. (2008). Functionalized hexagonal mesoporous silica as an oxidizing agent for the oxidative desulfurization of organosulfur compounds. *Industrial & Engineering Chemistry Research*, *47*(3), 973–975. doi:10.1021/ie071057y

Eber, J., Wasserscheid, P., & Jess, A. (2004). Deep desulfurization of oil refinery streams by extraction with ionic liquids. *Green Chemistry*, *6*, 316–322. doi:10.1039/b407028c

Faghihian, H., & Naeemi, S. (2013). Application of a Novel Nanocomposite for Desulfurization of a Typical Organo Sulfur Compound. *Iran. J. Chem. Chem. Eng.,* 32(3).

Freundlich, H. M. F. (1906). Over the adsorption in solution. *Journal of Physical Chemistry*, *57*, 385–471.

Fukunaga, T., Katsuno, H., Matsumoto, H., Takahashi, O., & Akai, Y. (2003). Development of kerosene fuel processing system for PEFC. *Catalysis Today*, *84*(3-4), 197–200. doi:10.1016/S0920-5861(03)00274-8

Gongshin, Q. (2006). Ph.D. Dissertation, University of Michigan.

Hasan, Z., Jeon, J., Hwa Jhung, S. (2012). Oxidative desulfurization of benzothiophene and thiophene with WOx/ZrO2 catalysts: Effect of calcination temperature of catalysts. *Journal of Hazardous Materials,* 205–206, 216–221.

Herna'ndez-Maldonado, A. J., & Yang, R. T. (2004). New Sorbents for Desulfurization of Diesel Fuels via π-Complexation. *AIChE Journal. American Institute of Chemical Engineers*, *50*(4).

Hernandez, S. P., Fino, D., & Russo, N. (2010). High performance sorbents for diesel oil desulfurization. *Chemical Engineering Science*, *65*(1), 603–609. doi:10.1016/j.ces.2009.06.050

Holbrey, J. D., López-Martín, I., Rothenberg, G., Seddon, K. R., Silveiro, G., & Zheng, X. (2008). Desulfurisation of oils using ionic liquids: Selection of cationic and anionic components to enhance extraction efficiency. *Green Chemistry*, *10*(1), 87–92. doi:10.1039/B710651C

Hu, J., Wang, Y., Vander Wiel, D., Chin, C., Palo, D., & Rozmiarek, R. et al. (2003). Fuel processing for portable power applications. *Chemical Engineering Journal*, *93*(1), 55–60. doi:10.1016/S1385-8947(02)00108-0

Huang, L., Wang, G., Qin, Z., Dong, M., Du, M., & Ge, H. et al. (2011). In situ XAS study on the mechanism of reactive adsorption desulfurization of oil product over Ni/ZnO. *Applied Catalysis B: Environmental*, *106*, 26–38.

Jeevanandam, P., Klabunde, K. J., & Tetzler, S. H. (2005). Adsorption of thiophenes out of hydrocarbons using metal impregnated nanocrystalline aluminum oxide. *Microporous and Mesoporous Materials*, *79*(1-3), 101–110. doi:10.1016/j.micromeso.2004.10.029

Kappe, C. (2012). Controlled Microwave Heating in Modern Organic Synthesis. *Angewandte Chemie International Edition*, *43*, 6250–6284.

Khan, A. (2004). The theory of adsorption equilibria analysis based on general equilibrium constant expression. *Turkish Journal of Chemistry*, *36*, 219–231.

Kim, J. H., Ma, X., Zhou, A., & Song, C. (2006). Ultra-deep desulfurization and denitrogenation of diesel fuel by selective adsorption over three different adsorbents: A study on adsorptive selectivity and mechanism. *Catalysis Today*, *111*(1-2), 74–83. doi:10.1016/j.cattod.2005.10.017

Koriakin, A., Kim, Y.-H., & Lee, C.-H. (2012). Adsorptive Desulfurization of Natural Gas Using Lithium-Modified Mesoporous Silica. *Industrial & Engineering Chemistry Research*, *51*(44), 14489–14495. doi:10.1021/ie301066n

Kulkarni, P.S., & Afonso, C.A.M. (2010). Deep desulfurization of diesel fuel using ionic liquids: current status and future challenges. *Green Chem.*, 12, 1139-1149.

Kumar, S., Srivastava, V. C., & Badoni, R. P. (2011). Studies on adsorptive desulfurization by zirconia based adsorbents. *Fuel*, *90*(11), 3209–3216. doi:10.1016/j.fuel.2011.06.029

Kumar, S., Srivastava, V. C., & Badoni, R. P. (2012). Oxidative desulfurization by chromium promoted sulfated zirconia. *Fuel Processing Technology*, *93*(1), 18–25. doi:10.1016/j.fuproc.2011.08.017

Kwon, J.-M., Moon, J.-H., Bae, Y.-S., Lee, D.-G., Sohn, H.-C., & Lee, C.-H. (2008). Adsorptive desulfurization and denitrogenation of refinery fuels using mesopourous silica adsorbents. *ChemSusChem*, *1*(4), 307–309. doi:10.1002/cssc.200700011 PMID:18605095

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, *40*(9), 1361–1403. doi:10.1021/ja02242a004

Larrubia, M. A., A`ıda, G.-A., Ram`ırez, J., & Busca, G. (2002). A FT-IR study of the adsorption of indole, carbazole, benzothiophene, dibenzothiophene and 4,6-dibenzothiophene over solid adsorbents and catalysts. *Applied Catalysis A, General*, *224*(1-2), 167–178. doi:10.1016/S0926-860X(01)00769-4

Liu, G., Rodriguez, J. A., Chang, Z., Hrbek, J., & Gonzalez, L. J. (2002). Chemistry of sulfur-containing molecules on Au(1 1 1): Thiophene, sulfur dioxide, and methanethiol adsorption. *Surface Science*, *505*(1-3), 295–307. doi:10.1016/S0039-6028(02)01377-8

Ma, X . & Velu, V.& Sun, L.& Song, C., "Adsorptive desulfurization of diesel fuel over a metal sulfide-based adsorbent", Prepr. Pap.-Am. Chem. Soc., Div. Pet. Chem., vol. 48, 2, (2003), p.522-523

Mansouri, A., Khodadadi, A. A., & Mortazavi, Y. (2014). Ultra-deep adsorptive desulfurization of a model diesel fuel on regenerable Ni–Cu/-Al2O3 at low temperatures in absence of hydrogen. *Journal of Hazardous Materials*, *271*, 120–130. doi:10.1016/j.jhazmat.2014.02.006 PMID:24632365

Marín-Rosas, C., Ramírez-Verduzco, L. F., Murrieta-Guevara, F. R., Hernández-Tapia, G., & Rodrı'guez-Otal, L. M. (2010). Desulfurization of Low Sulfur Diesel by Adsorption Using Activated Carbon: Adsorption Isotherms. *Industrial & Engineering Chemistry Research*, *49*(9), 4372–4376. doi:10.1021/ie901756b

Meng, X., Huang, H., & Shi, L. (2013). Reactive Mechanism and Regeneration Performance of NiZnO/Al_2O_3-Diatomite Adsorbent by Reactive Adsorption Desulfurization. *Industrial & Engineering Chemistry Research*, *52*(18), 6092–6100. doi:10.1021/ie303514y

Mochizuki, Y., & Sugawara, K. (2008). Removal of organic sulfur from hydrocarbon resources using ionic liquids. *Energy & Fuels*, *22*(5), 3303–3307. doi:10.1021/ef800400k

Muzic, M., Sertic-Bionda, K., & Adzamic, T. (2012). Evaluation of Commercial adsorbents and their application for desulfurization of model fuel. *Clean Techn Environ Policy*, *14*(2), 283–290. doi:10.1007/s10098-011-0399-4

Ngamcharussrivichai, C., Chatratananon, C., Nuntang, S., & Prasassarakich, P. (2008). Adsorptive removal of thiophene and benzothiophene over zeolites from Mae Moh coal fly ash. *Fuel*, *87*(10-11), 2347–2351. doi:10.1016/j.fuel.2007.10.003

Orita, H., Uchida, K., & Itoh, N. (2004). A volcano-type relationship between the adsorption energy of thiophene on promoted MoS2 cluster-model catalysts and the experimental HDS activity: Ab initio density functional study. *Applied Catalysis A, General*, *258*(1), 115–120. doi:10.1016/j.apcata.2003.08.016

Palomino, J. M., Tran, D. T., Hausser, J. L., Dong, H., & Oliver, S. R. J. (2014). Mesopourous Silica nanoparticles for high Capacity adsorptive desulfurization. *J. Matter. Chem A*, *2*(36), 14890. doi:10.1039/C4TA02570A

Ralph, Y. T., Takahashi, A., & Yang, F. H. (2001). New Sorbents for Desulfurization of Liquid Fuels by π –Complexation. *Industrial & Engineering Chemistry Research*, *40*(26), 6236–6239. doi:10.1021/ie010729w

Ramaswamy, V., Bhagwat, M., Srinivas, D., & Ramaswamy, A. V. (2004). Structural and spectral features of nano-crystalline copper-stabilized zirconia. *Catalysis Today*, *97*(1), 63–70. doi:10.1016/j.cattod.2004.06.141

Rodríguez-Cabo, B., Rodríguez, H., Rodil, E., Arce, A., & Soto, A. (2014). Extractive and oxidative-extractive desulfurization of fuels with ionic liquids. *Fuel*, *117A*, 882–889.

Roquero, F. J., Roquerol K. S., W. Sing, P. Llewellyn, & Maurin, G. (2014). Adsorption by powders and porous solids: Principles, Methodology and Applications (2nd Edition). Elsevier UK.

Rozanska, X., van Santen, R. A., Hutschka, F., & Hafner, J. (2003). A periodic density functional theory study of thiophenic derivative cracking catalyzed by mordenite. *Journal of Catalysis*, *215*(1), 20–29. doi:10.1016/S0021-9517(02)00148-3

Saha, S. K., & Pramanik, P. (1995). Aqueous sol-gel synthesis of cordierite and cordierite-zirconia composite powders. *Journal of Materials Science*, *30*(11), 2855–2858. doi:10.1007/BF00349655

Salem, A. S. H. (1994). Naphtha desulfurization by adsorption. *Industrial & Engineering Chemistry Research*, *33*(2), 336–340. doi:10.1021/ie00026a025

Sarda, K. K., Bhandari, A., Pant, K. K., & Jain, S. (2012). Deep desulfurization of diesel fuel by selective adsorption over Ni/Al_2O_3 and Ni/ZSM-5 extrudates. *Fuel*, *93*, 86–91. doi:10.1016/j.fuel.2011.10.020

Shahadat, H. A. M. H., & Tatarchuk, B. J. (2013). Adsorptive desulfurization of jet and diesel fuels using Ag/TiOx–Al_2O_3 and Ag/TiOx–SiO_2 adsorbents. *Fuel*, *107*, 465–473. doi:10.1016/j.fuel.2012.11.030

Shen, Y., Li, P., Xu, X., & Liu, H. (2012). Selective adsorption for removing sulfur: A potential ultra-deep desulfurization approach of jet fuels. *RSC Advances*, *2*(5), 1700–1711. doi:10.1039/C1RA00944C

Sing, K.S.W. (1982). Reporting Physiosorption Data Gas/Solid systems. *Pure and Applied Chemistry*, *54*(11), 2201–2218.

Soleimani, M., Bassi, A., & Margaritis, A. (2007). Biodesulfurization of refractory organic sulfur compounds in fossil fuels. *Biotechnology Advances*, *25*(6), 570–596. doi:10.1016/j.biotechadv.2007.07.003 PMID:17716849

Song, C. (2003). An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel. *Catalysis Today*, *86*(1-4), 211–263. doi:10.1016/S0920-5861(03)00412-7

Song, C., & Ma, X. (2003). New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization. *Applied Catalysis B: Environmental*, *41*(1-2), 207–238. doi:10.1016/S0926-3373(02)00212-6

Srivastav, A., & Srivastava, V. C. (2009). Adsorptive desulfurization by activated alumina. *Journal of Hazardous Materials*, *170*(2-3), 1133–1140. doi:10.1016/j.jhazmat.2009.05.088 PMID:19523762

Takahashi, A., Yang, R. T., Munson, C. L., & Chinn, D. (2001). Cu(I)−Y-Zeolite as a Superior Adsorbent for Diene/Olefin Separation. *Langmuir*, *17*(26), 8405–8413. doi:10.1021/la011196z

Tang, K., Song, K. L., Duan, L., Li, X., Gui, J., & Sun, Z. (2008). Deep desulfurization by selective adsorption on a heteroatoms zeolite prepared by secondary synthesis. *Fuel Processing Technology*, *89*(1), 1–6. doi:10.1016/j.fuproc.2007.06.002

Tawara, K., Nishimura, T., & Iwanami, H. (2000). Ultra-deep hydrodesulfurization of kerosene for fuel cell system (Part 2) regeneration of sulfurpoisoned nickel catalyst in hydrogen and finding of autoregenerative nickel catalyst. Sekiyu Gakkaishi. *Journal of the Japan Petroleum Institute*, *43*(2), 114–120. doi:10.1627/jpi1958.43.114

Tian, W.-H., Sun, L.-B., Song, X.-L., Liu, X.-Q., Yin, Y., & He, G.-S. (2010). Adsorptive Desulfurization by Copper Species within Confined Space. *Langmuir*, *26*(22), 17398–17404. doi:10.1021/la101856d PMID:20882950

Triantafyllidis, K. S., & Deliyanni, E. A. (2014). Desulfurization of diesel fuels: Adsorption of 4, 6-DMDBT on different origin and surface chemistry nanoporous activated carbons. *Chemical Engineering Journal*, *236*, 406–414. doi:10.1016/j.cej.2013.09.099

Turk, B. S., & Gupta, R. P. (2001). RTI's TReND Process for deep desulfurization of naphtha, Am. Chem. Soc. *Div. Fuel Chem. Prepr.*, *46*, 392.

Wang, B., Zhu, J., & Ma, H. (2009). Desulfurization from thiophene by SO $^{(4)\,(2-)}$/ZrO_2 catalytic oxidation at room temperature & atmospheric pressure. *Journal of Hazardous Materials*, *164*(1), 256–264. doi:10.1016/j.jhazmat.2008.08.003 PMID:18799257

Wang, Y., Zhang, C., Bi, S., & Luo, G. (2010). Preparation of ZnO nanoparticles using the direct precipitation method in a membrane dispersion micro-structured reactor. *Powder Technology*, *202*(1-3), 130–136. doi:10.1016/j.powtec.2010.04.027

Weitkamp, J., Schwark, M., & Ernst, S. (1991). Removal of thiophene impurities from benzene by selective adsorption in zeolite ZSM-5. *Chem. Soc. Chemical Communications*, (16): 1133–1134. doi:10.1039/c39910001133

Xu, X., Zhang, S., Li, P., & Shen, Y. (2014). Adsorptive desulfurization of liquid Jet-A fuel at ambient conditions with an improved adsorbent for on-board fuel treatment for SOFC applications. *Fuel Processing Technology*, *124*, 140–146. doi:10.1016/j.fuproc.2014.03.001

Yang, X., Erickson, L. E., Hohn, K. L., Jeevanandam, P., & Klabunde, K. J. (2006). Sol-Gel Cu-Al_2O_3 Adsorbents for Selective Adsorption of Thiophene out of Hydro carbon. *Industrial & Engineering Chemistry Research*, *45*(18), 6169–6174. doi:10.1021/ie060559t

Yu, G., Lu, S., Chen, H., & Zhu, Z. (2005). Oxidative Desulfurization of Diesel Fuels with Hydrogen Peroxide in the Presence of Activated Carbon and Formic Acid. *Energy & Fuels*, *19*(2), 447–452. doi:10.1021/ef049760b

Zaki, T., Mohamed, N.H., Nessim, M.I., Abd El Salam, H. (2013). Characterization and application of nano-alumina sorbents for desulfurization and dearomatization of Suez crude petrolatum. *Fuel Processing Technology*, *106*, 625–630. doi:10.1016/j.fuproc.2012.09.055

Zhang, S., Zhang, Q., & Zhang, Z. C. (2004). Extractive desulfurization and denitrogenation of fuels using ionic liquids. *Industrial & Engineering Chemistry Research*, *43*(2), 614–622. doi:10.1021/ie030561+

Zhang, S., Zhang, Y., Huang, S., Wang, P., & Tian, H. (2012). Mechanistic investigations on the adsorption of thiophene over Zn3NiO4 bimetallic oxide cluster. *Applied Surface Science*, *258*(24), 10148–10153. doi:10.1016/j.apsusc.2012.06.096

Zhang, S., & Zhang, Z. C. (2002). Novel properties of ionic liquids in selective sulfur removal from fuels at room temperature. *Green Chemistry*, *4*(4), 376–379. doi:10.1039/b205170m

Zhao, L., Chen, Y., Gao, J., & Chen, Y. (2010). Jinsen GAO, Yu Chen "Desulfurization mechanism of FCC gasoline: A review". *Chem. Eng. China*, *4*(3), 314–321. doi:10.1007/s11705-009-0271-9

Chapter 5

Carbon-Based Nanomaterials for Desulfurization:

Classification, Preparation, and Evaluation

Tawfik A. Saleh
King Fahd University of Petroleum and Minerals, Saudi Arabia

Gaddafi Ibrahim Danmaliki
King Fahd University of Petroleum and Minerals, Saudi Arabia

Taye Damola Shuaib
King Fahd University of Petroleum and Minerals, Saudi Arabia

Mohammed A. Al-Daous
Saudi Aramco, Saudi Arabia

ABSTRACT

The special interest in ultra-low sulfur diesel (ULSD) is informed by the need to comply with the strict government policy on low sulfur content of transportation fuels. Better knowledge of different factors that concern deep desulfurization of fuels is important to achieve ultra-low sulfur fuels and cheaper way of producing ULSD. Both the capital and operating cost of the adsorptive desulfurization process is cheaper compare to the conventional hydroprocessing. The need to produce more volume of fuel such as diesel with very low sulfur content from low grade feed stocks like heavy oil and light cycle oil (LCO) in order to meet up with the global demand for sulfur-free fuels is pertinent. Several on-going researches are pointing to the use of adsorbents for removal of sulfur compounds from the hydrocarbon refining stream. In this chapter, varieties of carbon nanomaterials suitable for adsorptive desulfurization are discussed. The approach is feasible for commercial applications with any adsorbent of an adequate lifetime of activity as well as high capacity.

1. INTRODUCTION

Desulfurization is a vital unit operation in petroleum refining since the combustion products of sulfur compounds are the main reason for acid rain and environmental pollution. In addition, sulfur is also a catalyst poison during industrial processes. Compounds with sulfur are removed catalytically at high temperature and pressure. Desulfurization is gaining a lot of attention and efforts have been channeled towards investigating several methods that are effective and economically viable. The attention is warranted

DOI: 10.4018/978-1-4666-9545-0.ch005

by stricter environmental regulations on the amount of sulfur that should be present in transportation fuels (Song, 2003; Yang et al., 2004). Sulfur limit (mass percent) of 0.015, 0.035, and 0.2 for gasoline, diesel fuel and light fuel oil, respectively has been set. A new and more stringent limit of 0.003-0.005 mass percent (30-50 ppm) is imminent for transportation fuels in Europe and United States of America (Song, 2003; State Announcer, 2001; Babich and Monlijn, 2003). It's worthy to note also that; desulfurization processes have found applications in converting used tires and shale oil to fuel oils. Using calcium oxide in binding up sulfur oxide in emissions has been achieved for stationary applications in the desulfurization of non-transportation fuels, but the use of the harmful compounds still a challenge (Svobodal et al., 1994). Therefore, the need to innovate effective technologies for desulfurization processes is paramount.

Several methods of desulfurization processes have been investigated for many years. The need to achieve a lower level of sulfur in fuel oils has also called for different innovative ways of achieving deep desulfurization where the synergy of methods yielding better results (Agarwal and Sharma, 2010; Sundaraman et al., 2009). Hydrodesulfurization (HDS) is a popular process, but there is wide variation in reactivity of sulfur-containing heterocyclic compounds. Alkyl-substituted derivatives of dibenzothiophene like 4-methyldibenzothiophene and 4, 6-dimethyldibenzothiophene from fuel oils have been reported to be relatively unreactive towards hydroprocessing (Gate and Tropsoe, 1997). In order to achieve deep-desulfurization and take care of attending challenges of hydrodesulfurization that include high hydrogen consumption, energy (heat) cost, catalyst volume etc. Many other methods are combined with HDS for better results (Rana et al., 2007). In recent years, efforts are being directed to other methods, including; adsorptive desulfurization, oxidative desulfurization where different catalysts are used (Kumar et al., 2012) extractive desulfurization involving ionic liquids, photochemical activation, bio-desulfurization, ultrasonic-desulfurization, microwave desulfurization and electrochemical approach (Bhatia and Sharma, 2006; Lam et al., 2012).

Adsorptive desulfurization where adsorbents are used to remove sulfur-containing compounds in fuel oils is holding future promise of ultra-clean sulfur-free fuel oils. Adsorption processes can be performed at ambient temperature and pressure, thus saving a lot of energy as compared to other methods of desulfurization (Seredych et al., 2009). Therefore, intensive research is ongoing to produce new adsorbents with great emphasis on good selectivity, high capacity for adsorption and regeneration of the adsorbents with special attention to the mechanism of adsorption (Yang et al., 2007). Various materials have been reported to be good adsorbents for different adsorption processes. These materials include; different types of zeolites and metal-impregnated zeolites such as MCM-22 zeolites (Delitata et al., 2008), MCM-41 (lanthanum loaded, sorbents for diesel fuel) (Subhan et al., 2012), Y-zeolites with exchanged cation (NaY) and carbon nanotubes (CNT) as a template, Ag- and Cu-beta zeolites among others. A deep desulfurization method was presented by Daimler-Chrysler AG (2000) where the adsorption process is used for engine fuel with $TiO_{2,}$ MgO, Al_2O_3 or SiO_2 (with metal additives) as adsorption materials. Dibenzothiophene (DBT) and 4, 6-dimethyldibenzothiophene (4, 6-DMDBT) can also be removed from diesel by using mesoporous carbon synthesized from silica HMS (template) and phenolic resins (sources of carbon) (Zhou et al., 2009). Due to high thermal stability, large surface area and well-arranged mesoporous structure (Arbia and Parvin, 2011) of carbon molecular sieves (CMK-1, 3 and 5), they have been implicated as promising adsorbents of DBT in petroleum fuels.

The following sections will highlight a general classification of carbon materials based on their constituents; discuss major techniques commonly used in their preparation and evaluation of these valuable materials towards desulfurization.

2. CLASSIFICATION OF CARBON-BASED MATERIALS

This section discuses carbon-based materials and their classification based on constituents (Figure 1).

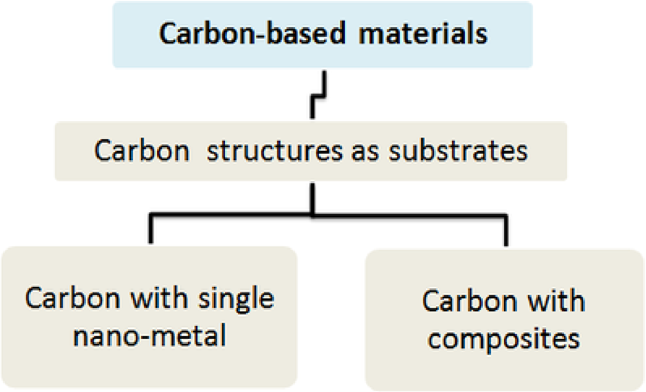
2.1 Carbon Structures as Substrates

Structure indeed determines properties. Different allotropes of low dimension can be formed from carbon, such as; graphene, CNT and C-60. The superiority in properties exhibited by CNT among other 1-D nanomaterials can be traced to its special stereogenic structure. Several attentions have been paid to CNTs over the past two decades; this is due to nothing but unique mechanical, thermal, electrical properties among other key applications in many fields of science and technology (De Volder, et al., 2013; McEuen, et al. 2002; Terrones, 2003; Zhang, 2013).

Over the years, carbon has been used as catalyst support employed for different applications in the chemical industry owing to its fascinating surface nature. The orientation of graphene layers can be varied with respect to the axes of carbon nanofibres (CNFs) giving different morphologies, which make available different pores for catalysts' nanoparticles (Salernitano et al., 2014). Carbon paper substrate with 3-D fibre network is appropriate in fuel cells with Silicon-Carbon composite deposited alongside the fibre network on the electrode (Matsiu et al., 2013). Carbon blacks and typically, acetylene black, have been deeply investigated electrochemically (Kinoshita and Bett, 1973) and gained applications in many areas, like catalysis, energy storage and fuel cell technology (Zhang, et al., 2010). An effective interaction (oxidation-reduction active species) is owned to a large surface area of carbon (particle size 1-50 nm, commercially available).

Although carbon black is not well defined structurally like CNT, graphene materials or nano-onions but their activities in carbon-based nano-sensor, polymer nanocomposites (selective shape sensing), fuel cell and energy storage are very excellent (Iijima, 1991; Molina-Ontoria, et al.,2013; Novoselov, et al., 2014 ; Loo, et al., 2013; Li, 2009; Blanco-L_pez, et al., 2004). Correct choice of nanocarbon substrate is very vital in electrocatalysis and fuel cells, the effects of this have been critically reviewed (Dribinskii, et al., 1989). Pt– carbon nanomaterial composites have found application in fuel cells that is characterized by CO_2 reduction (Perathoner, et al., 2007). With adequate optimization for stable operational conditions, carbon blacks give allowance for gas flow into catalysts' reactive layers.

Figure 1. Classification of carbon-based materials



2.2 Carbon with Single Nano-Metal

Carbon possesses ordered structure which provides its framework with good porosity. However, their uses are limited due to poor solubility, thus limited functionalized nanocomposites of metals and CNTs can be achieved (Ebbesen et al., 1996). However, the increasing development of CNTs chemistry makes possible the preparation of hybrid materials (metals and CNT) with enhanced performance (Ding et al., 2012; Li et al., 2011). These hybrid materials can function as chemical sensors due to their high conductive (electrical) power and selective chemical nature. Another vital property they possess is reasonably large surface area, which provide them with good catalyst, sites in reaction catalysis (Ding et al., 2012). Nanomaterials of low dimension can now be used for electronic applications, chemical sensors, adsorption (desulfurization) e.t.c (Geim AK, 2009). In the same manner, graphene supported metal nanoparticles also performs well (Huang et al., 2012; Bai and Shen, 2012).

Metal-carbon interactions play critical roles in catalytically growing carbon nanotubes and graphene via CVD as well as in controlling the structures of these carbon allotropes and, consequently, have been intensively investigated in order to elucidate the catalytic mechanisms(Jourdain and Bichara, 2013; Mattevi, 2011; Li, 2010; Ding, 2008; Edwards, 2013; Seah, 2014; Cheng and Guo, 2002). Fe and Cu are two metal systems exhibiting distinct interactions with carbon (Naidich, 1981). With partially filled 3d-orbitals, Fe exhibits a high affinity for carbon. Carbon has a finite solubility in Fe at high temperatures (0.022% carbon by weight in α-Fe at 727 ° C and 2.14% carbon by weight in γ-Fe at 1147 °C) and forms metastable iron carbide (Fe_3C, 6.67% carbon by weight) with Fe (Jourdain and Bichara, 2013; Mattevi, 2011).

Due to its strong interactions with carbon, Fe was among the first catalysts and has been most intensively used for CVD growth of single-wall carbon nanotubes (SWCNTs). In contrast, with completely filled d-orbitals, Cu displays a low affinity for carbon. The carbon solubility in Cu is much lower than in Fe (~ 0.008% carbon in Cu by weight at 1085 °C) and there is no carbide formation (Jourdain and Bichara, 2013; Mattevi, 2011). Due to the weak Cu-C interactions, Cu was once considered unsuitable for CVD growth of carbon nanotubes (Deck and Vecchio, 2006). However, this notion did not stop the exploration of using Cu as the catalyst. In fact, it has been demonstrated that Cu can catalyze the growth of SWCNTs (Yoshida et al., 2009; Zhou, 2006) and, furthermore, it is a better catalyst for developing SWCNT system using quartz and silicon as substrates (Li et al., 2010 and Cui et al., 2010). In terms of the metal-catalyzed CVD growth of graphene, the different interactions with carbon between Fe and Cu result in the formation of few-layer graphene (FLG) on Fe foil (Xue et al., 2011) and monolayer graphene on Cu foil (Li et al., 2009). With the formation of methane, carbon hydrogenation reverses the reaction for CVD growth of carbon nanotubes and graphene using methane as the carbon source. It was demonstrated that Fe is an active catalyst in producing methane and in etching channels in graphite. Though an initial study showed that Cu was inactive in catalyzing the hydrogenation of graphite, Cu was later found to be active in catalytic etching channels in graphite (Baker, 1981 and 1995).

Metals of transition series are good options for growing graphene or CNTs. The metal-carbon system can be built by performing the growth and contacting in a single step with the same metal. However, a pressing challenge here is oxide layer formation on exposure of nanoparticles of metal to air as it tarnishes and form oxide coating. The formation of the oxide coatings is largely due to large surface-volume ratio, which translates to high oxidation process. The oxidation process at the metal surface can, however, is prevented in the procedure (Geim AK, 2009). Scanning electron microscope (SEM) reveals the porosity of carbons is paramount to their adsorptive properties. Figure 2 shows SEM images of different carbon structures such as activated carbon (AC), CNT and graphene.

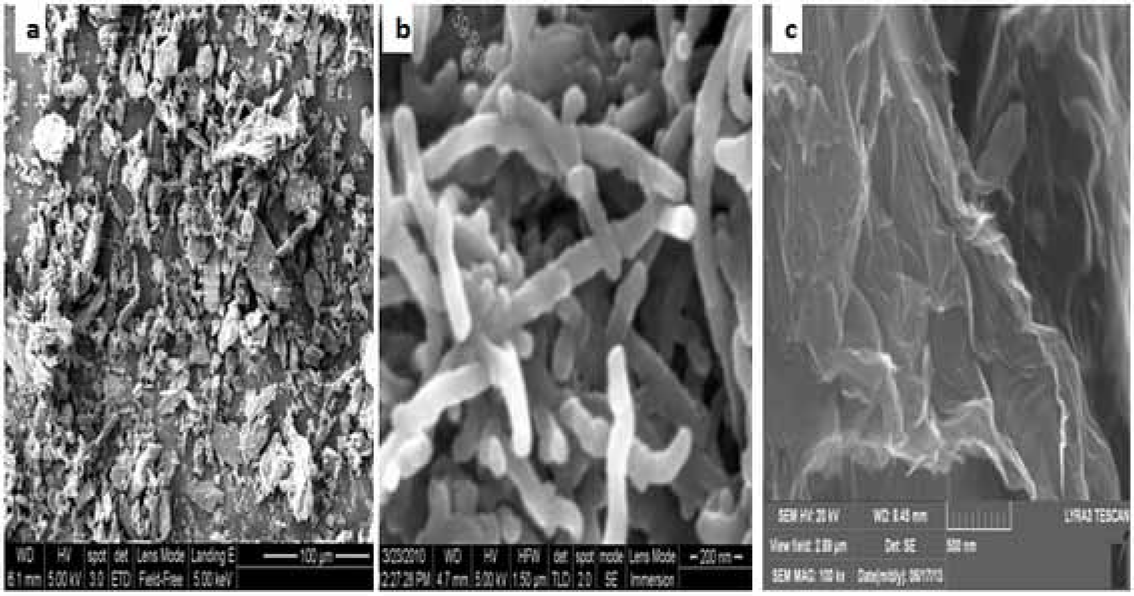
2.3 Carbon-Based Composites

The good surface chemistry, stable structure and very large surface area are factors enabling the fine surface templating property of graphitic supports (carbon nanospheres (CNSs), CNT, and graphene) and their decoration with metal nanoparticles (Iwamoto and Grimblot, 1997). The composites formed show **enhanced or even synergistic activity in their** applications (Salem and Hamid, 1997). The surface chemistry of the composites, however, is not fully established and still open to further studies (Nagai et al., 2000).

Carbon nanomaterial composites made by decorating carbon (graphene, carbon nanospheres, and carbon nanotubes) with transition metals (oxides or salts) are receiving great attention. Carbon-supported metal nanoparticles (MNPs) for example; cobalt, iron, or nickel based nanoparticles (CoOx–CoP/C or FeOx–CoP/C) have been confirmed to be catalytically active for oxygen reduction reaction (ORR); this is due to the nature of the transition metals oxide nanoparticles (Stephanie, et al., 2010). The confirmation of this great activity is shown in the less activity of cobalt porphyrin (CoP/C) when it is adsorbed on unmodified carbon. Sometimes a synergistic activity is observed (Salem, 1997).

In the investigation of the potency of activated carbon materials for desulfurization and denitrogenation gas oils, MAXSORB-II adsorbent, is an effective adsorbent for organosulfur compounds' adsorption at ambient temperature (Mochida et al, 2004a and 2003c). This material can be prepared by activating carbon prepared from petroleum coke with KOH. Oxidizing agents as HNO_3 and H_2O_2 were also used

Figure 2. SEM images of nano-structured carbons of AC (a), CNT (b) and graphene (c)



to further enhance the adsorptive power of commercially available activated carbon, which is then heat –treated (Mochida et al., 2004b, 2003d). These oxidizing agents aid the release of CO (600-800 ^{0}C) at the carbon surface, which thus enhances the absorption power.

3. PREPARATION OF CARBON STRUCTURES

There are three main techniques of preparing carbon nanomaterials such as CNT, CNS, CNF, graphene etc.(Iijima, 1991; Yudasaka et al., 1997; Li et al., 1996). These techniques are listed in Figure 3. Other techniques that are commercially less developed compare to the above-mentioned three which involve the use of flame, solar, electrolysis in their syntheses (Yuan et al., 2001; Hsu et al.,1996; Laplaze et al., 1998).

In the arc discharge technique (Figure 4), with a space of less than 1 mm between graphite electrodes, a direct current is passed under inert environment argon at a low pressure. An illustration of arc discharge technique is depicted in Figure 3. The carbon anode vaporizes on generation of plasma of very high temperature on the application of current and the carbon material is deposited alongside other by-products of carbon at the cathode (Popov et al., 2004; Journet et al., 1998). The production of MWNTs with diameters ranging from 2 to 20 nm and micrometer-scaled lenght can be achieved (Ebbesen and Ajayan, 1992). Similarly, SWNTs of above 70% yield and diameter of close to 1.4 nm can be prepared (Journet et al., 1997).

In the laser ablation technique, the principle is not so different from the arc discharge. The heating is done in a furnace with the aid of pulsed laser source under inert surrounding. In this technique, high temperature carbon vapor is generated from the surface of the graphite as illustrated in the Figure 5 (Journet et al., 1997). The carbon vapor is transported by the flowing helium or argon and then collected on copper-collector as illustrated in Figure 3.

These first two techniques produce high quality carbon nanomaterials in a large amount. However, some shortcomings have been identified; the reliance on high temperature graphitic surface evaporation

Figure 3. Techniques used in preparation of carbon structures

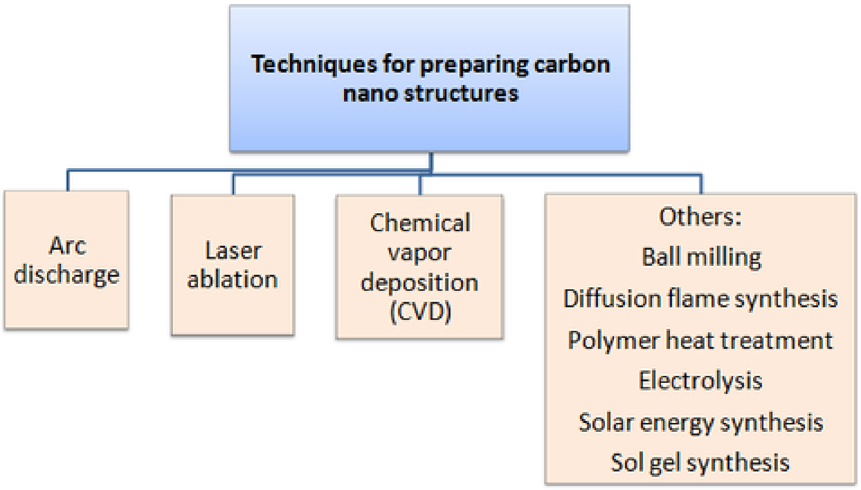


Figure 4. Schematic representation of arc discharge technique for synthesis of carbon nanomaterials

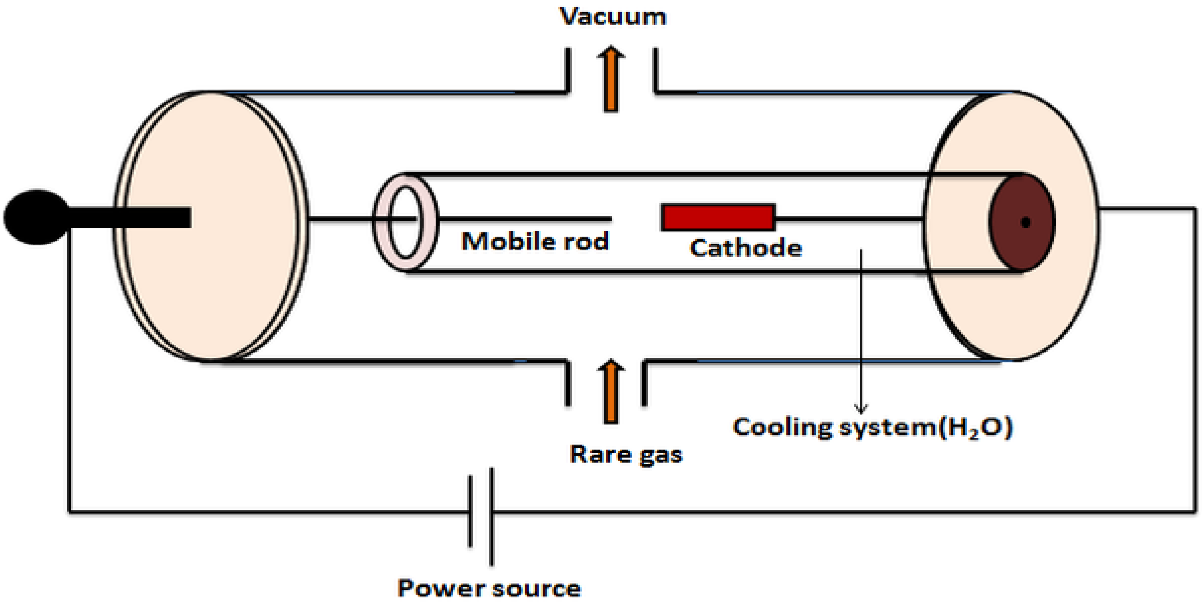
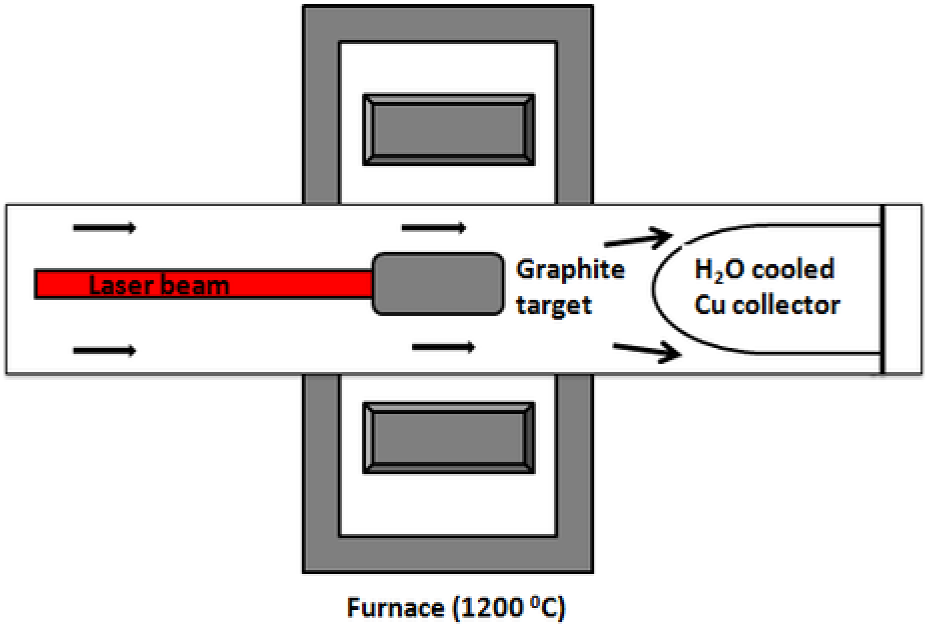


Figure 5. Schematic representation of laser ablation technique for carbon synthesis



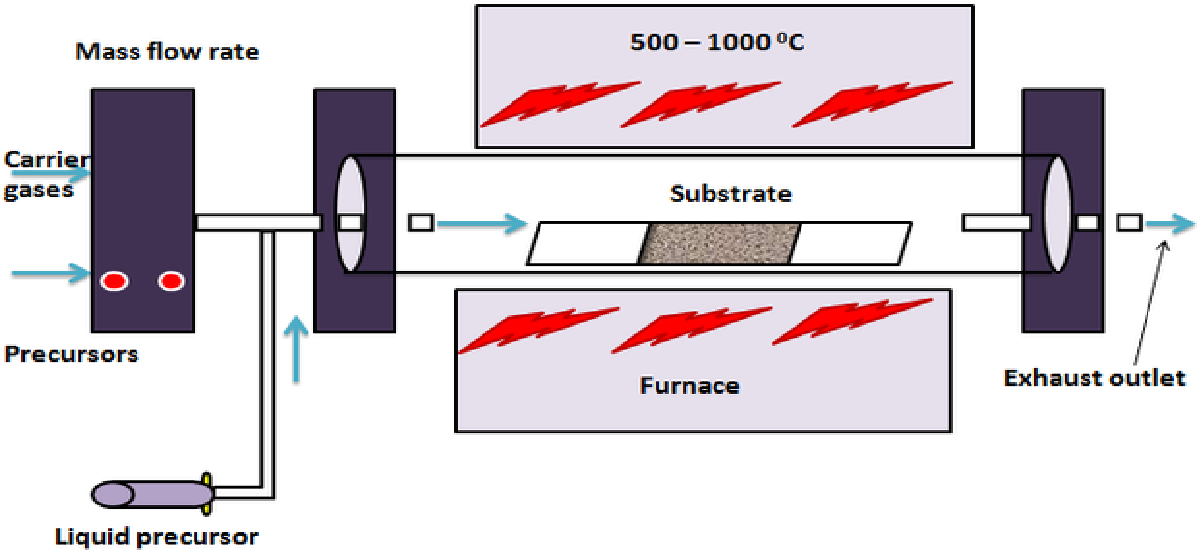
of carbon that is not cost effective as this leads to high-energy consumption and the adhering impurities, which will require further purification of the carbon nanomaterials produced by such methods (Popov et al., 2004).

In view of the above challenges of the two techniques mentioned previously, chemical vapor deposition (Figure 6) is the most commonly used technique. CVD ensure a better control of carbon (e.g. CNT) growth than laser ablation and arc discharge, this makes it a more feasible method (Dai, 2002). It makes use of hydrocarbons as precursors in the presence of metal catalysts at temperature ranging from 500 to 1000 ^{0}C. The hydrocarbons get decomposed at this relatively low temperature and thus the growth of CNTs as the system cools. This techniques is simpler in that lower temperature is involved because the precursor is not solid thus consumes less energy (Journet, 1998). Of a vital advantage of CVD worthy of mentioning is that, it is very versatile. Virtually all the major components involved in the growth can be switched; catalyst and precursor can be in liquid or solid form, the particular precursor to be used, possibility of incorporating other materials like nitrogen, temperature and pressure of the reaction etc. (Nikolav et al., 1999). The choice of catalyst plays important role in decomposition and dispersion of liquid hydrocarbon as precursor to allow in situ decomposition. It allows for better dispersion if liquid hydrocarbon is used or in solid form for large-scale synthesis if loaded on large surface area template as well as a well-patterned growth with nanoparticles (Allen et al., 2009; Hart and Slocum, 2006).

Graphene is commonly prepared by four techniques (Anton et al., 2007; EMTSEV, 2009; Reina, 2009; Lomeda, 2008) listed below:

- Direct sonication of graphite or scoth tape approach (known as mechanical cleavage of graphite);
- Growth on SiC (epitaxial);
- Metal substrates CVD;
- Graphite oxide reduction.

Figure 6. Schematic illustration of carbon vapor deposition (CVD)



Some other approaches being reported are; electrochemical process using graphite electrode and unwrapping of carbon nanotubes (Kosynkin et al., 2009; Liu et al., 2008). The most common approach for large-scale preparation is the reduction of graphite oxide by, firstly, oxidize graphite with acids then convert the oxide formed to graphene by reduction. The reduction process can be carried out thermally, chemically or photo catalytically (McAllister et al., 2007**;** Lomeda et al., 2008; Williams et al., 2008).

4. EVALUATION

4.1 Properties

Carbon nanomaterial, graphene for example, is a monoatomic layer of carbon atoms that is sp^2 hybridized (Geim and Novoselov, 2007). The good electrical properties in ballistic transport of electrons can be traced to its 2D pattern (Novoselov et al., 2004). Graphene also possesses large surface-volume ratio, fast electron transfer mechanism, good tensile strength and very interesting elastic character (Park and Ruoff, 2009; Rao et al., 2009; Yang et al., 2010). A very good stacking is possible with graphene, thus, layers can be varied from single to many of up to 10 layers and the resulting materials are equally interesting.

Multi-walled carbon nanotubes (MWNTs) comprise of several single-walled nanotubes Single-walled carbon nanotubes (SWNTs). The one dimensional SWNTs like graphene sheet (0.4 to 2.0 nm diameter) are rolled-up to form MWNTs (2 to 100 nm diameter) (Baughman et al., 2002; Yang et al., 2010). Largely, MWNTs can possess several surface morphologies such as hollow tubes, stacked cups, carbon filaments etc (Kiselev et al.,1998; Iijima, 1991; Delgado et al., 2008; Allen et al., 2008). The classification of SWNTs can be done based on chiral vectors ($c_h = na_1 + ma_2 = (n, m)$) where n and m are integers that correspond to the two graphene vectors (Figure 7) (Avouris, 2002) as shown in Figure 6. The following are few classes:

- Zigzag ($m = 0$);
- Arm-chair ($n = m$);
- Chiral ($n \neq m$).

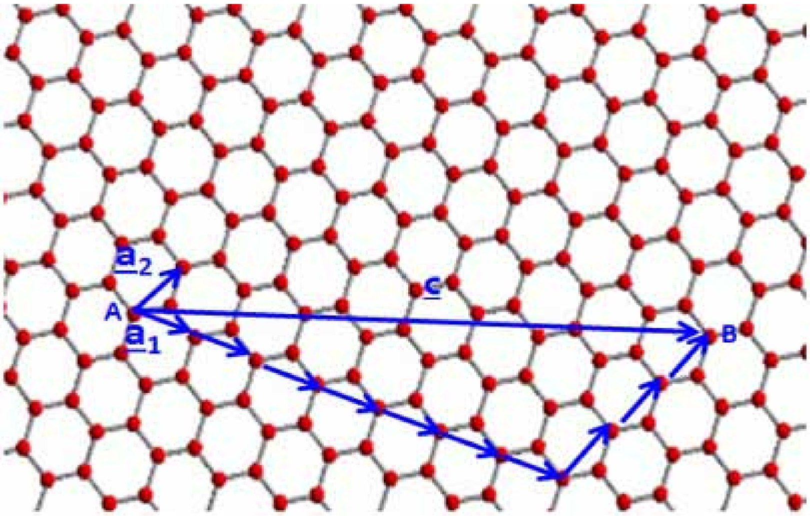
The particular class and vectors provide information about electronic properties; if ($n – m$) gives a multiple of 3, then the SWNTs of arm-chair type is metallic.

Depending on the diameter of SWNTs, which have inverse proportionality with band gap, SWNTs are good semiconductors and have metallic character. Normally, MWNTs also have similar characteristics with SWNTS because the effect of a cylinder on its adjacent cylinder is very minute (Baughman et al., 2002; Charlier, 2002). However, the lack of definite control of chiralities for individual nano-cylinders results into MWNTs with SWNTs of different chiralities, thus a metallic properties similar to graphite (turbostratic) will be observed (Cao, 2004).

4.2 Applications towards Desulfurization

The very unique dimensions of CNTs (1-D) and graphene (2-D) are enabling features for their outstanding electrical conductivity and stability. They are of good surface chemistry for easy decoration with desired functionalities, which in turn guaranteed their use in adsorption (desulfurization), electrochemical and

Figure 7. Schematic representation of a graphene sheet with unit hexagonal lattice vectors (a_1 and a_2)



other applications. This include energy generation via fuel cells and photovoltaic (Brandon et al., 2003; Kauffman et al., 2010), energy storage (batteries, super-capacitors, hydrogen storage) (An et al., 2001) field-effect transistors (Katz, 2004; Kruger et al., 2010) sensors and biosensors (Kauffman and Star, 2008; Ronkainen et al., 2010; Yang et al., 2010). However, there are challenges, like the non-uniformity of materials and their hybids (Jacobs et al., 2010), lack detailed understanding of structure as related to property and possible contaminants from synthetic precursors/catalysts (Dai, 2002; Kruusma, 2007; Pumera and Miyahara, 2009). These are tasking challenges **but provide an avenue for further detailed** studies. In the following sections, the systems and processes used for desulfurization by carbon-based materials are highlighted.

Graphene and carbon nanotubes are considered good candidates for the removal of liquid phase aromatic sulfur compounds and of gas phase hydrogen sulfide through the adsorption method by metal oxide/graphene or nanotube composites. More specifically, the effects of their oxides as substrates are promising for liquid phase sulfur removal. Their structures that possesses π orbitals can adsorb aromatic sulfur compounds through π-π interactions.

4.2.1 Testing Systems

- **Batch System:** Adsorptive desulfurization studies of organosulfur compound removal from naphtha (550 ppmS) feed stocks can be carried out in a batch system. The use of adsorbents such as zeolites (5A and 13X) and activated carbon is effective. These two adsorbents (carbon and zeolites) demonstrated a unique performance in their adsorption capabilities; activated carbon has larger capacity but the percentage of sulfur removal (65% at 80 0C) is lower compare to the zeolitic adsorbent with relatively smaller capacity but a larger percentage of sulfur (100% at room temperature and 800g adsorbent/L feed) can be removed. In line with these observations and for industrial application, a two-bed approach gives a better desulfurization process (Salem and Hamid, 1997).

- **Fixed Bed System:** Adsorption studies in a fixed bed set-up can be achieved also with the use of different adsorbents. Alumina, carbon-supported nickel as well as activated carbon can to a large extent remove sulfur and nitrogen from diesel feed with aromatics, nitrogen and sulfur compounds. Activated carbon shows better selectivity in removing refractory sulfur and nitrogen compounds especially with alkylated dibenzothiophene (4, 6-DMDBT) (Kim et al., 2006; Ko et al., 2007). A superior selectivity for nitrogen removal is observed with alumina as compare to the other two adsorbents. This selectivity with alumina is great when basic nitrogen compound is involved hydrocarbon streams.

4.2.2 Types of Desulfurization Process

There is no generalized classification for desulfurization techniques. However, some classification can be made based on the involvement of hydrogen, what happened to sulfur compound during desulfurization and whether desulfurization occurs physically or chemically or both. Considering the change that happened to sulfur compounds; three situations are possible; either the sulfur compounds get decomposed and removed, removed from process stream without decomposing or decomposed only. From the perspective of the hydrogen involvement; a broad classification desulfurization process can be made; hydrodesulfurization (HDS)-based and non HDS-based groups (Babich and Moulijn, 2003). Hydrogen is involved in the decomposition of sulfur compounds for all HDS-based processes while the non HDS-based processes do not involve hydrogen for desulfurization to occur. However, to eliminate sulfur, in most cases, hydrogen is involved with few exceptions as in the case of selective oxidation. Catalytic conversion of sulfur compounds and subsequent removal of sulfur is a well-established desulfurization process. Such processes are hydroprocessing, distillation, extraction, adsorption, oxidation, precipitation, etc. (Figure 8). Their different combinations have been identified as promising.

During the process of desulfurization, sulfur compounds, for instance, benzothiophene or dibenzothiophene can be removed from the stream and then decomposed separately in a vessel. A very low level of sulfur in transportation fuels can be achieved through this process. This process provides an insight for removing sulfur compounds in fuels through distillation with the help of catalysts. It's also possible that some sulfur products (solid or gas) are generated with just decomposition of of organosulfur compounds with only the hydrocarbons (without sulfur) remaining in the process stream (example is hydro desulfurization). The last class is just a simple removal of organosulfur compounds from process stream. This can be done by conversion of the organosulfur compounds to different compounds that can be removed easily if direct removal is difficult or impossible; however, disposal of the removed sulfur compounds becomes a great challenge for this type of class. This classification is depicted in Figure 9.

- **Extractive Desulfurization:** Extractive desulfurization employs the use of solubility as the key factor for organosulfur removal. Organosulfur compounds tend to be more soluble in some specific solvents. The sulfur compounds, due to this reason, are transferred from oil feed into the solvent and therefore hydrocarbons are easily separated with the aid of a separator. The sulfur compound free hydrocarbons can now be further charged for the next process or discharged as final product. The mixture of organo-sulfur compounds and the solvent used for it extraction will then be subjected to distillation thus solvent is recovered and can be re-used.

Figure 8. Classification of desulfurization processes base on the nature of the process

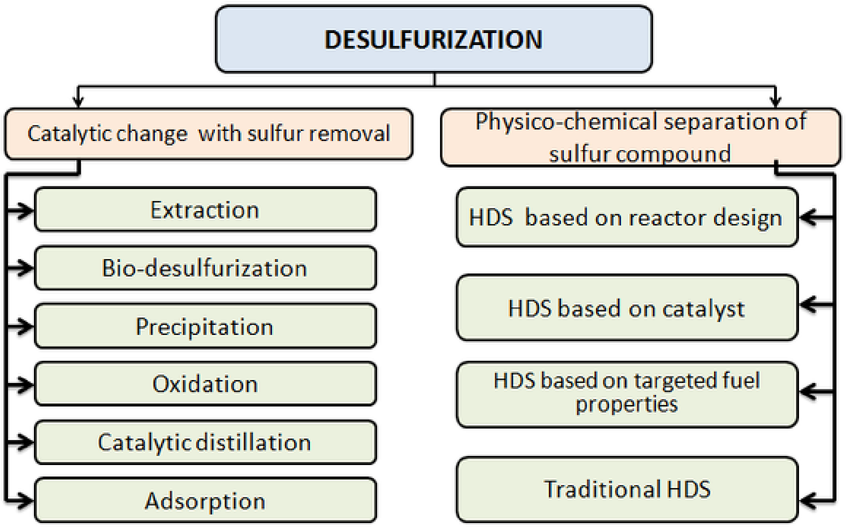
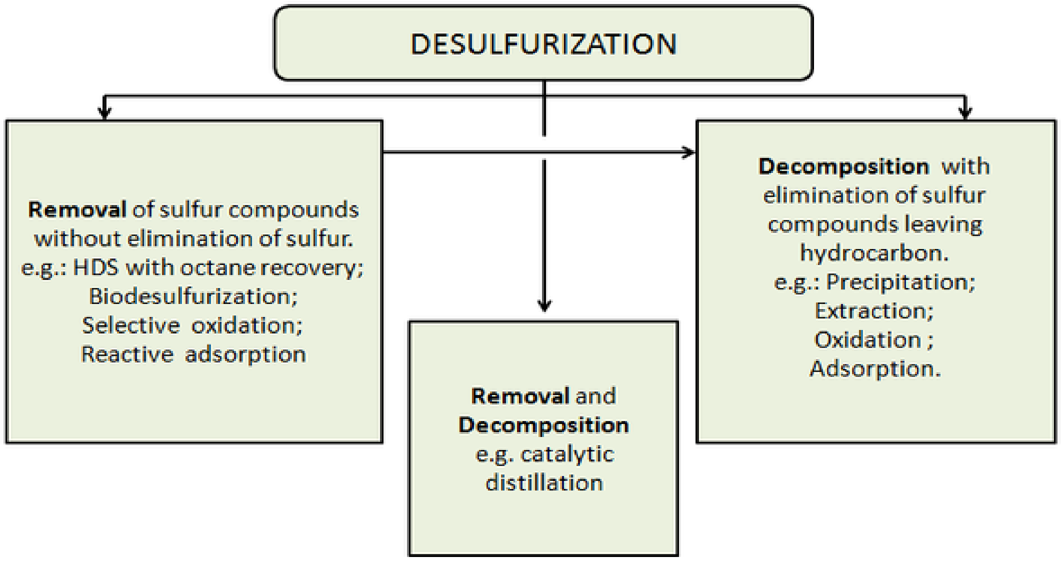


Figure 9. Classification of desulfurization process according to the changes that occur with sulfur compounds



Depending on the number of extraction cycles, several solvents have been identified to be suitable for this purpose with sulfur compound removal of up to 90%. Acetone, glycols, nitrogenous-solvent (Horri, 1996), ethanol are good solvents for extractive desulfurization because they have their boiling points different from those of organo-sulfur compounds and relatively cheap (Forte, 1996; Funakoshi and Aida, 1998).

- **Desulfurization by Precipitation:** Desulfurization can also be achieved via precipitation by forming an insoluble complex of organosulfur compounds and then eliminating them. When a pi acceptor (e.g. tetranitro fluorine) is missed with alkylated-DBT (e.g.4, 6-DMDBT) in fuels, an insoluble complex is formed which can be conveniently removed by filtration and the tetranitro fluorine is recovered by adsorption process with the aid of suitable adsorbent (Meille et al., 1997; Milenkovic et al., 1999). This approach does not remove a significant amount of sulfur (< 25%) as some other hydrocarbons in the feed compete in complex formation (Hernandez-Maldonado and Yang, 2004a; 2004b; 2004c).
- **Bio-Desulfurization (BDS):** This process involves the use of micro-organisms (e.g. bacteria) for removal of organosulfur compound. In this process, the sulfur is removed from its parent compound under mild condition and with availability of oxygen and water without degradation of carbon structure present. One very vital feature of this process is that it does not require hydrogen thus a cheaper process than HDS.
- **Selective Oxidative Desulfurization:** Desulfurization by selective oxidation involves oxidation of organosulfur compounds and then purification (Aida et al., 2000). Processes like sulphCo and photochemical desulfurization employ oxidation as a vital operation. Organosulfur compound can be oxidized selectively and processes like adsorption, distillation or decomposition by heating can subsequently be used to separate the oxidized oganosulfur compounds from the process stream.

The combination of distillation with selective oxidation is not reported in any literature until date. Considering the principle involved, the approach is promising since sulfones, sulfuroxides are the products of oxidation of organosulfur compounds, and they increase their boiling points. (Ford et al., 1997). This process can therefore be likened to the conventional distillation process provided that only separation of organosulfur compounds is desired and subsequent treatment will be done separately. However, the formation of carbonmonoxide and carbon (IV) oxide as by-products and process safety are major issues.

- **Adsorptive Desulfurization:** This is the use of adsorbents for removing sulfur compounds in the fuels. The efficiency of this process lies in the ability of the adsorbents to selectively remove the target sulfur compounds from oil processing stream, durability and regenerability of adsorbent and capacity for adsorption. Desulfurization via adsorption (ADS) can be broadly classified into two based on the nature of interaction of the sulfur compounds and the adsorbent: physical and chemical adsorption. These two classes are briefly explained below.
- **Physical Adsorption (Physisorption):** In physical adsorptive desulfurization, organosulfur compounds adhere to the surface of the solid adsorbent without chemical reaction thus the hydrocarbon refining stream is free of sulfur. Adsorbent regeneration is done by passing suitable solvent on the adsorbent or heating to get rid of adhered sulfur compounds. Several good materials have been used as adsorbents, namely; activated carbon, transition metals supported on zeolites and different metal oxides supported on carbon structures (Ma et al., 2002 and 2005; Velu et al., 2003; Kim et al., 2006). Both denitrogenation and desulfurization can be done simultaneously using activated carbon for adsorption process. For every 1 gram of adsorbent, 0.04 g and 0.1 g of nitrogen and sulfur can be removed from fuel respectively at a temperature close to the room (Sano et al., 2004a; 2004b). Nitrogen and organosulfur compounds are removed in the first stage of the two-step pro-

cess shown in Figure 8. Only very little amount of sulfur is removed at this stage but nitrogen is removed to a large extent. The HDS step removes most of the sulfur and the final adsorption step get rid of remnant nitrogen and sulfur present.

Adsorptive desulfurization processes only decrease the concentration of organosulfur compounds in. Further downstream operation, like hydro processing, needs to be performed at high pressure in order to remove sulfur to achieve ultra-low diesel fuel. For commercial application, certain process parameters have to be set at optimum points. These parameters include but not limited to; fuel feed to adsorbent ratio, particle size of the adsorbent, adsorption cycles, temperature of reactivation etc. To further enhance desulfurization process, a combined adsorption and HDS (Landau et al., 2008) for denitrogenation and desulfurization can be performed as illustrated in Figure 10.

- **Chemical Adsorption (Chemisorptions):** In chemical (reactive) adsorption desulfurization process, the sulfur in the fuel feed combines and reacts to form compound such as hydrogen sulfide (H_2S) which is then adsorbed on the surface of the adsorbent (Figure 9). For diesel fuel desulfurization, the reaction to form H_2S can occur at temperature of 500-700K and pressure of 19-35 bars in the presence of transition metal catalyst. In view of this, many hybrid materials of transition metals supported on carbon, zeolites and several other solid porous materials have been prepared (Slater et al., 2002; Park et al., 2008; Landau et al., 2008). A simple adsorption scheme together with reactivation of spent adsorbent is as illustrated in Figure 11.

SUMMARY AND OUTLOOK

Recently, there has been a remarkable growth in research on achieving ultra-low sulfur level in transportation fuels. Several research groups from different academic institutions and industrial research

Figure 10. An illustration of combined adsorption and hydrodesulfurization (two-step) process

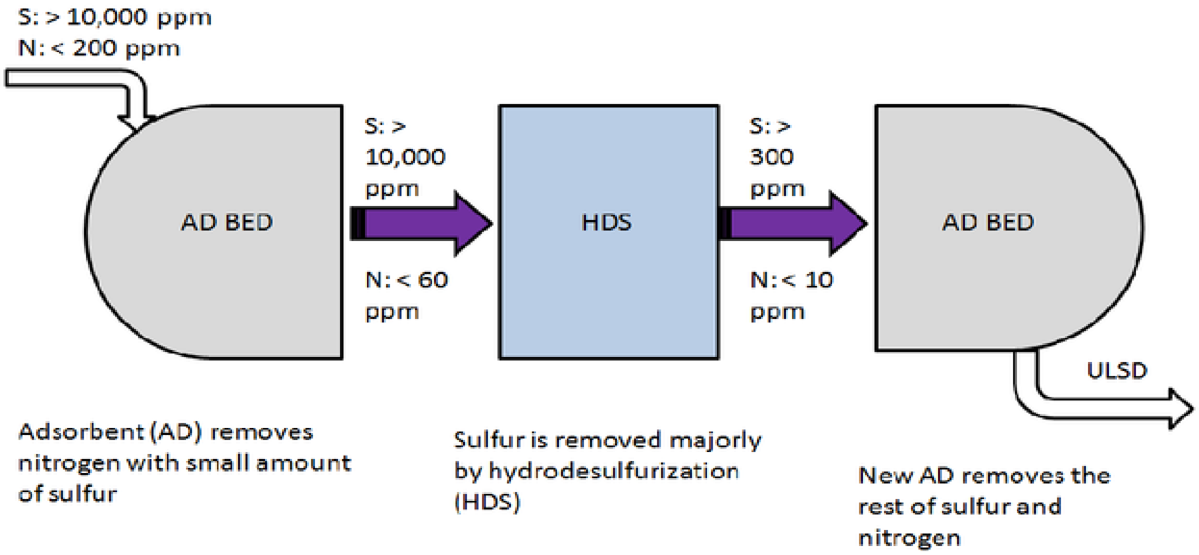
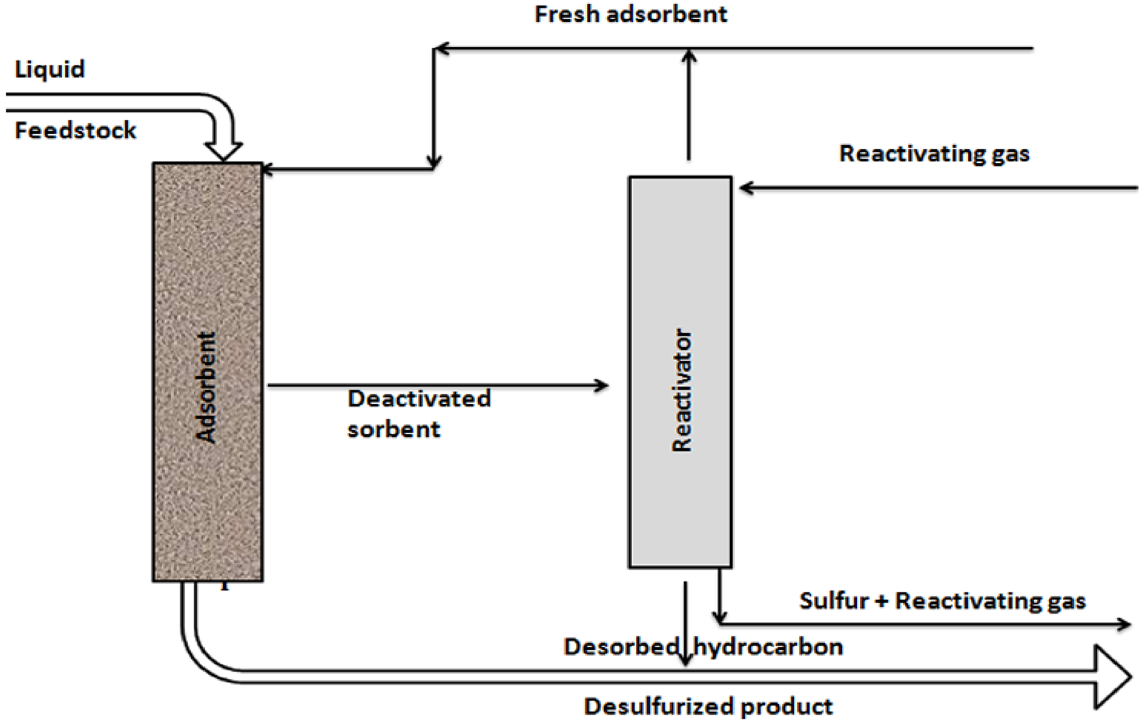


Figure 11. Simplified adsorptive desulfurization process flow



laboratories have published a great number of rich scientific papers. Lower harmful exhaust emissions can easily be achieved with ULSD thereby enhancing air quality. The desulfurization of least active dibenzothiophene (DBT) derivative like 4, 6-DMDBT (sterically hindered) can now be easily achieved by optimizing certain factors such as; kinetics and thermodynamics, feed quality, inhibitory effects, catalytic sites, etc. In the future, the need to produce more volume ULSD from low grade feed stocks like heavy oil and LCO to meet up with the global ULSD demand is pertinent. Other needs like better calorific value, reduced aromatics content and density are also worthy of expectation. These, are challenging, but with enormous economic gain. In order to achieve this great milestone, adsorptive method of desulfurization can play a very big role. ADS does not require hydrogen so it is cheap. It is capable of desulfurizing organ-sulfur compound (e.g. DBT) preferentially. The ADS can be used to achieve a sulfur level of less than 10ppm from the initial sulfur content of 500ppm in diesel fuel.

ACKNOWLEDGMENT

The authors would like to acknowledge the support provided by King Abdulaziz City for Science and Technology (KACST) through the Science & Technology Unit at King Fahd University of Petroleum & Minerals (KFUPM) for funding this work through project No. 13-PET393-04 as part of the National Science, Technology and Innovation Plan.

REFERENCES

Agarwal, P., & Sharma, D. K. (2010). Comparative studies on the biodesulfurization of crude oil with other desulfurization techniques and deep desulfurization through integrated processes. *Energy & Fuels*, *24*(1), 518–524. doi:10.1021/ef900876j

Aida, T., Yamamoto, D., Iwata, M., & Sakata, K. (2000). Development of oxidative desulfurization process for diesel. *Review on Heteroatom Chemistry*, *22*, 241–256.

Allen, B. L., Kichambare, P. D., & Star, A. (2008). Synthesis, characterization, and manipulation of nitrogen-doped carbon nanotube cups. *ACS Nano*, *2*(9), 1914–1920. doi:10.1021/nn800355v PMID:19206432

Allen, B. L., Shade, C. M., Yingling, A. M., Petoud, S., & Star, A. (2009). Graphitic nanocapsules. *Advanced Materials*, *21*, 4692–4695.

An, K. H., Kim, W. S., Park, Y. S., Moon, J.-M., Bae, D. J., & Lim, S. C. et al. (2001). Electrochemical Properties of High-Power Supercapacitors Using Single-Walled Carbon Nanotube Electrodes. *Journal of Advanced Functional. Materials (Basel)*, *11*, 387–392.

Anbia, M., & Parvin, Z. (2011). Desulfurization of fuels by means of a nanoporous carbon adsorbent. *Chemical Engineering Research & Design*, *89*(66A), 641–647. doi:10.1016/j.cherd.2010.09.014

Anton, N. S., Mehdi, M. Y., Romaneh, J., Ouseph, P. J., Cohn, R. W., & Sumanasekera, G. U. (2007). Electrostatic deposition of graphene. *Nanotechnology*, *18*, 13530–13534. PMID:21730375

Atanasova, P., Vladov, Ch., Halachev, T., Fierro, J. L. G., & López, A. A. (1995). Influence on the phosphorus concentration and the method of preparation on the hydrodesulfurization activity of P-Ni-W/alumina catalysts. *Bulletin des Sociétés Chimiques Belges*, *104*(4), 219–223.

Avouris, P. (2002). Molecular electronics with carbon nanotubes. *Accounts of Chemical Research*, *35*(12), 1026–1034. doi:10.1021/ar010152e PMID:12484790

Babich, I. V., & Moulijn, J. A. (2003). Science and technology of novel processes for deep desulfurization of oil refinery streams: A review. *Fuel*, *82*(6), 607–631. doi:10.1016/S0016-2361(02)00324-1

Babich, I. V., & Moulijn, J. V. (2003). Science and technology of novel processes for deep desulfurization of oil refinery streams: A review. *Fuel*, *82*(6), 607–631. doi:10.1016/S0016-2361(02)00324-1

Bai, S., & Shen, X. (2012). Graphene-inorganic nanocomposites. *Royal Society of Chemistry Advances*, *2*, 64–98.

Baker, R. T. K. (1995). A review of in-situ electron microscopy studies of metal/metal oxide graphite interactions. *Journal of Adhesion and Adhensives*, *52*(1-4), 13–40.

Baker, R. T. K., & Chludzinski, J. J. Jr. (1981). Catalytic gasification of graphite by chromium and copper in oxygen, steam and hydrogen. *Carbon*, *19*(2), 75–82. doi:10.1016/0008-6223(81)90110-X

Baughman, R. H., Zakhidov, A. A., & de Heer, W. A. (2002). Carbon nanotubes--the route towards applications. *Science*, *297*(5582), 787–792. doi:10.1126/science.1060928 PMID:12161643

Bernier, P., & Ajayan, P. M. (1994). Application of Carbon Nanotubes as Supports in Heterogeneous Catalysis. *Journal of the American Chemical Society*, *116*(17), 7935–7936. doi:10.1021/ja00096a076

Bhatia, S., & Sharma, D. K. (2006). Emerging role of bio-refining of heavier crude oils and integration of bio-refining with petroleum refineries in the future. *Petroleum Science and Technology*, *24*(10), 1125–1159. doi:10.1080/10916460600817447

Blanco-López, M. C., Gutiérrez-Fernández, C., Lobo-Castañón, M. J., Miranda-Ordieres, A. J., Tuñón-Blanco, P. (2004). Electrochemical sensing with electrodes modified with molecularly imprinted polymer films. *Analytical and Bioanalytical Chemistry*, 378(8), 1922 –1928.

Brandon, N. P., Skinner, S., & Steele, B. C. (2003). Recent advances in materials for fuel cells. *Annual Review of Materials Research*, *33*(1), 183–213. doi:10.1146/annurev.matsci.33.022802.094122

Cao, G. (2004). *Nanostructures and Nanomaterials: Synthesis, properties and applications*. United Kingdom: Imperial College. doi:10.1142/p305

Charlier, J. C. (2002). Defects in carbon nano tubes. *Accounts of Chemical Research*, *35*(12), 1063–1069. doi:10.1021/ar010166k PMID:12484794

Cheng, G., & Guo, T. (2002). Surface segregation in Ni/Co bimetallic nanoparticles produced in single-walled carbon nanotube synthesis. *The Journal of Physical Chemistry B*, *106*(23), 5833–5839. doi:10.1021/jp025530r

Cui, R. L., Zhang, Y., Wang, J. Y., Zhou, W. W., & Li, Y. (2010). Comparison between copper and iron as catalyst for chemical vapor deposition of horizontally aligned ultralong single-walled carbon nanotubes on silicon substrates. *Journal of Physical Chemistry*, *114*(37), 15547–15552.

Daenen, M., De Fouw, R., Hamers, B., Janssen, P., Schouteden, K., & Veld, M. (2003). The Wondrous World of Carbon Nanotubes. A Review of Current Carbon Nanotube Technologies. Eindhoven University of Technology, 89.

Dai, H. (2002). Carbon nanotubes: Opportunities and challenges. *Surface Science*, *500*(1-3), 218–241. doi:10.1016/S0039-6028(01)01558-8

Daimler–Chrysler AG. (2000). Method for desulfurization engine fuel on board a motor vehicle // W.O 2000/20531.

De Volder, M. F. L., Tawfick, S. H., Baughman, R. H., & Hart, A. J. (2013). Carbon nanotubes: Present and future commercial applications. *Science*, *339*(6119), 535–539. doi:10.1126/science.1222453 PMID:23372006

Deck, C. P., & Vecchio, K. (2006). Prediction of carbon nanotube growth success by the analysis of carbon-catalyst binary phase diagrams. *Carbon*, *44*(2), 267–275. doi:10.1016/j.carbon.2005.07.023

Delgado, J. L., Herranz, M. A., & Martin, N. (2008). The nano-forms of carbon. *Journal of Materials Chemistry*, *18*(13), 1417–1426. doi:10.1039/b717218d

Delitala, C., Cadoni, E., Delpiano, D., Meloni, D., Melis, S., & Ferino, I. (2008). Liquid-phase thiophene adsorption on MCM-22 zeolite and activated carbon. *Microporous and Mesoporous Materials*, *110*(2-3), 197–215. doi:10.1016/j.micromeso.2007.06.018

Ding, F., Larsson, P., Larsson, J. A., Ahuja, R., Duan, H. M., Rosen, A., & Bolton, K. (2008). The importance of strong carbon-metal adhesion for catalytic nucleation of single-walled carbon nanotubes. *Nano Letters*, *8*(2), 63–68. doi:10.1021/nl072431m PMID:18162001

Ding, M., Tang, Y., & Star, A. (2012). Understanding Interfaces in Metal–Graphitic Hybrid Nanostructures. *The Journal of Physical Chemistry Letters*, *4*(1), 147–160. doi:10.1021/jz301711a

Dribinskii, A. V., Tarasevich, M. R., & Kazarinov, V. E. (1989). Electrocatalysis on carbon materials. *Materials Chemistry and Physics*, *22*(3-4), 377–400. doi:10.1016/0254-0584(89)90006-0

Ebbesen, T. W., & Ajayan, P. M. (1992). Large scale synthesis of carbon nanotubes. *Nature*, *358*(6383), 220–222. doi:10.1038/358220a0

Ebbesen, T. W., Hiura, H., Bisher, M. E., Treacy, M. M. J., Shreeve-Keyer, J. L., & Haushalter, R. C. (1996). Decoration of carbon nano tubes. *Advanced Materials*, *8*(2), 155–157. doi:10.1002/adma.19960080212

Edwards, R. S., & Coleman, K. S. (2013). Graphene film growth on polycrystalline metals. *Accounts of Chemical Research*, *46*(1), 23–30. doi:10.1021/ar3001266 PMID:22891883

Emtsev, K. V., Bostwick, A., Horn, K., Jobst, J., Kellogg, G. L., & Ley, L. et al. (2009). Towards wafer-size graphene layers by atmospheric pressure graphitization ofsilicon carbide. *Nature Materials*, *8*(3), 203–207. doi:10.1038/nmat2382 PMID:19202545

Ford, J. F., Rayne, T. A., & Adlington, D. G. (1967). Desulfurization of hydrocarbons using oxidative and hydro-treatments. *US Patent*, 3341448.

Forte, P. (1996). Process for the Removal of Sulfur from Petroleum Fractions. *US Patent*, 5582714.

Funakoshi, I., & Aida, T. (1998). Process for recovering organic sulfur compounds from fuel oil. *US Patent,* 5753102.

Gates, B. C., & Tropsoe, H. (1997). Reactivity in deep catalytic hydro-desulfurization: Challenges, opportunities, and the importance of 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene. *Polyhedron*, *16*(18), 3213–3217. doi:10.1016/S0277-5387(97)00074-0

Geim, A. K. (2009). Graphene: Status and prospects. *Science*, *324*(5934), 1530–1534. doi:10.1126/science.1158877 PMID:19541989

Geim, A. K., & Novoselov, K. S. (2007). The rise of graphene. *Nature Materials*, *6*(3), 183–191. doi:10.1038/nmat1849 PMID:17330084

Hart, A. J., & Slocum, A. H. (2006). Rapid growth and flow-mediated nucleation of millimeter-scale aligned carbon nanotube structures from a thin-film catalyst. *The Journal of Physical Chemistry B*, *110*(16), 8250–8257. doi:10.1021/jp055498b PMID:16623503

Hernandez, Y., Nicolosi, V., Lotya, M., Blighe, F. M., Sun, Z., & De, S. et al. (2008). High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature Nanotechnology*, *3*(9), 563–568. doi:10.1038/nnano.2008.215 PMID:18772919

Hernandez-Maldonado, A. J., Stamatis, S. D., Yang, R. T., He, A. Z., & Cannella, W. (2004). New sorbents for desulfurization of diesel fuels via pi-complexation: Layered beds and regeneration. *Industrial & Engineering Chemistry Research*, *43*(3), 769–776. doi:10.1021/ie034108+

Hernandez-Maldonado, A. J., & Yang, R. T. (2003). Desulfurization of commercial liquid fuels by selective adsorption via pi-complexation with Cu(I)-Y zeolite. *Industrial & Engineering Chemistry Research*, 423103–423110.

Hernandez-Maldonado, A. J., & Yang, R. T. (2004a). Desulfurization of diesel fuels by adsorption via pi-complexation with vapor phase exchanged (VPIE) Cu(I)-Y zeolites. *Journal of the American Chemical Society*, *126*(4), 992–993. doi:10.1021/ja039304m PMID:14746446

Hernandez-Maldonado, A. J., & Yang, R. T. (2004b). Desulfurization of diesel fuels via pi-complexation with nickel(JI)-exchanged X- and Y-zeolites. *Industrial & Engineering Chemistry Research*, *43*(4), 1081–1089. doi:10.1021/ie034206v

Hernandez-Maldonado, A. J., & Yang, R. T. (2004c). New sorbents for desulfurization of diesel fuels via pi-complexation. *The American Institute of Chemical Engineers Journal*, *50*, 791–801. doi:10.1002/aic.10074

Horii, Y., Onuki, H., Doi, S., Mori, T., Takatori, T., Sato, H., et al. (1996). Desulfurization and denitration of light oil by extraction. *US Patent*, 5494572.

Hsu, W. K.; Terrones, M.; Hare, J. P.; Terrones, H.; Kroto, H. W.; Walton, D. R. M. Electrochemical formation of carbon nanostructures. *Chemical Physics Lettters,* 262, 161-166.

Huang, X., Qi, X., Boey, F., & Zhang, H. (2012). Graphene-based composites. *Chemical Society Reviews*, *41*(2), 666–686. doi:10.1039/C1CS15078B PMID:21796314

Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature*, *354*(6348), 56–58. doi:10.1038/354056a0

Irvine, R. L. (1998). Process for desulfurizing gasoline and hydrocarbon feedstocks. *US Patent*, 5730860.

Irvine, R. L., Benson, B. A., Varraveto, D. M., & Frye, R. A. NPRA (1999, March 21-23). Proceedings of the *Annual Meeting*, *AM-99-42*, San Antonio, Texas.

Irvine, R. L., Varraveto, D. M. (1999). Adsorption process for nitrogen and sulfur. *Petroleum Technology Quarter Summer* 3, 37- 40.

Ivanov, V., Fonseca, A., Nagy, J. B., Lucas, A., Lambin, P., Bernaerts, D., & Zhang, X. B. (1995). Catalytic production and purification of nanotubulles having fullerene-scale diameters. *Carbon*, *33*(12), 1727–1738. doi:10.1016/0008-6223(95)00132-1

Iwamoto, R., & Grimblot, J. (1997). Acidity and hydrogenation properties of Mo-P-alumina catalysts prepared by a sol-gel method. *Journal of Catalysis*, *172*(1), 252–255. doi:10.1006/jcat.1997.1855

Jacobs, C. B., Peairs, M. J., & Venton, B. J. (2010). Carbon nanotubes electrochemical sensors for biomolecules. *Analytica Chimica Acta*, *662*(2), 105–127. doi:10.1016/j.aca.2010.01.009 PMID:20171310

Jourdain, V., & Bichara, C. (2013). Current understanding of the growth of carbon nanotubes in catalytic chemical vapour deposition. *Carbon*, *58*, 2–39. doi:10.1016/j.carbon.2013.02.046

Journet, C., Bernier, P. (n. d.). Production of carbon nanotubes. *Journal of Applied Physics A,* 67, 1-9.

Journet, C., Maser, W. K., Bernier, P., Loiseau, A., de la Chapelle, M. L., & Lefrant, S. et al. (1997). Large-scale production of single-walled carbon nanotubes by the electric-arc technique. *Nature*, *388*(6644), 756–758. doi:10.1038/41972

Katz, H. E. (2004). Chemically Sensitive Field-Effect Transistors and Chemiresistors: New Materials and Device. Structures. *Journal of Electroanalytical Chemistry*, *16*(22), 1837–1842. doi:10.1002/elan.200403071

Kauffman, D. R., Shade, C. M., Uh, H., Petoud, S., & Star, A. (2009). Decorated carbon nanotubes with unique oxygen sensitivity. *Nature Chemistry*, *1*(6), 500–506. doi:10.1038/nchem.323 PMID:21378918

Kauffman, D. R., & Star, A. (2008). Carbon Nanotube Gas and Vapor Sensors. Angewandte Chemmie International Edition, 47(35), 6550-6570.

Kauffman, D. R., Tang, Y., Kichambare, P. D., Jackovitz, J. F., & Star, A. (2010). Long-Term Performance of Pt-Decorated Carbon Nanotube Cathodes in Phosphoric Acid Fuel Cells. *Energy & Fuels*, *24*(3), 1877–1881. doi:10.1021/ef100013v

Kim, J. H., Ma, X., Zhou, A., & Song, C. (2006). Ultra clean desulfurization and denitrogenation of diesel fuel by selective adsorption over three different adsorbents: A study on adsorptive selectivity and mechanism. *Catalysis Today*, *111*(1-2), 74–83. doi:10.1016/j.cattod.2005.10.017

Kinoshita, K., & Bett, J. A. S. (1973). Potentiodynamic analysis of surface oxides on carbon blacks. *Carbon*, *11*(4), 403–411. doi:10.1016/0008-6223(73)90080-8

Kiselev, N. A., Sloan, J., Zakharov, D. N., Kukovitskii, E. F., Hutchison, J. L., Hammer, J., & Kotosonov, A. S. (1998). Carbon nanotubes from polyethylene precursors: Structure and structural changes as revealed by HREM. *Carbon*, *36*, 1149–1157. doi:10.1016/S0008-6223(98)00092-X

Kongkanand, A., Martínez Domínguez, R., & Kamat, P. V. (2007). Single wall carbon nanotube scaffolds for photoelectrochemical solar cells. capture and transport of photogenerated electrons. *Nano Letters*, *7*(3), 676–680. doi:10.1021/nl0627238 PMID:17309316

Kosynkin, D. V., Higginbotham, A. L., Sinitskii, A., Lomeda, J. R., Dimiev, A., Price, B. K., & Tour, J. M. (2009). Mechanically Assisted Exfoliation and Functionalization of Thermally Converted Graphene Sheets. *Nature*, *458*, 872–876. doi:10.1038/nature07872 PMID:19370030

Kruger, M., Buitelaar, M. R., Nussbaumer, T., Schonenberger, C., & Forro, L. (2001). Electrochemical carbon nanotube field-effect transistor. *Applied Physics Letters*, *78*(9), 1291–1293. doi:10.1063/1.1350427

Kruusma, J., Mould, N., Jurkschat, K., Crossley, A., & Banks, C. E. (2007). Single walled carbon nanotubes contain residual iron oxide impurities which can dominate their electrochemical activity. *Electrochemistry Communications*, *9*(9), 2330–2333. doi:10.1016/j.elecom.2007.06.024

Kumar, S., Srivastava, V. C., & Badoni, R. P. (2012). Oxidative desulfurization by chromium promoted sulfated zirconia. *Fuel Processing Technology*, *93*(1), 18–25. doi:10.1016/j.fuproc.2011.08.017

Kymakis, E., & Amaratunga, G. (2007). Single-wall carbon nanotube/conjugated polymer photovoltaic devices. *Applied Physics Letters*, *80*(1), 112–114. doi:10.1063/1.1428416

Lam, V., Li, G., Song, C., Chen, J., Fairbridge, C., Hui, R., & Zhang, J. (2012). A review of electrochemicaldesulfurization technologies for fossil fuels. *Fuel Processing Technology*, *98*, 30–38. doi:10.1016/j.fuproc.2012.01.022

Laplaze, D., Bernier, P., Maser, W. K., Flamant, G., Guillard, T., & Loiseau, A. (1998, January). Carbon nanotubes: The solar approach. *Carbon*, *36*(5-6), 685–688. doi:10.1016/S0008-6223(98)00025-6

Lee, C., Wei, X., Kysar, J. W., & Hone, J. (2008). Measurement of the elastic properties and intrinsic Strength of monolayer graphene. *Science*, *321*(5887), 385–388. doi:10.1126/science.1157996 PMID:18635798

Lemaire, M. (1999). *Energy & Fuels*, *13*, 881. doi:10.1021/ef980262a

Li, D.-C., Dai, L., Huang, S., Mau, A. W. H., & Wang, Z. L. (2000). Structure and growth of aligned carbon nanotube films by pyrolysis. *Chemical Physics Letters*, *316*(5-6), 349–355. doi:10.1016/S0009-2614(99)01334-2

Li, J. (2009). In P. Serp & J. L. Figueiredo (Eds.), *Carbon Materials for Catalysis* (pp. 507–533).

Li, W. Z., Xie, S. S., Qian, L. X., Chang, B. H., Zou, B. S., & Zhou, W. Y. et al. (1996). Large scale synthesis of aligned carbon nanotubes. *Science*, *274*(5293), 1701–1703. doi:10.1126/science.274.5293.1701 PMID:8939858

Li, X., Cai, W., An, J., Kim, S., Nah, J., & Yang, D. et al. (2009). Large-area synthesis of high-quality anduniform graphene films on copper foils. *Science*, *324*(5932), 1312–1314. doi:10.1126/science.1171245 PMID:19423775

Li, X., Qin, Y., Picraux, S. T., & Guo, Z.-X. (2011). Noncovalent assembly of carbon nanotube-inorganic hybrids. *Journal of Materials Chemistry*, *21*(21), 7527–7547. doi:10.1039/c1jm10516g

Li, Y., Cui, R. L., Ding, L., Liu, Y., Zhou, W. W., & Zhang, Y. et al. (2010). How catalysts affect the growth of single-walled carbon nanotubes on substrates. *Advanced Materials*, *22*(13), 1508–1515. doi:10.1002/adma.200904366 PMID:20437500

Liu, N., Luo, F., Wu, H., Liu, Y., Zhang, C., & Chen, J. (2008). One-step ionic-liquid-assisted electrochemical synthesis of ionic-liquid-functionalized graphene sheets directly from graphite. *Advanced Functional Materials*, *18*(10), 1518–1525. doi:10.1002/adfm.200700797

Lomeda, J. R., Doyle, C. D., Kosynkin, D. V., Hwang, W. F., & Tour, J. M. (2008). Diazonium functionalization of surfactant-wrapped chemically converted graphene sheets. *Journal of the American Chemical Society*, *130*(48), 16201–16206. doi:10.1021/ja806499w PMID:18998637

Loo, A. H., Bonanni, A., & Pumera, M. (2013). Biorecognition on graphene: Physical, covalent, and affinity immobilization methods exhibiting dramatic differences. *Asian Journal of Chemistry*, *8*(1), 198–203. doi:10.1002/asia.201200756 PMID:23090869

Ma, X., & Schobert, H. H. (2000). Molecular simulation on hydrodesulfurization of Thiophenic compounds over MoS_2 using ZINDO. *Journal of Molecular Catalysis A Chemical*, *160*(2), 409–427. doi:10.1016/S1381-1169(00)00278-8

Ma, X., Sun, L., & Song, C. (2002). A new approach to deep desulfurization of gasoline, diesel fuel and jet fuel by selective adsorption for ultra-clean fuels and for fuel cell applications. *Catalysis Today*, *77*(1-2), 107–116. doi:10.1016/S0920-5861(02)00237-7

Ma, X., Velu, S., Kim, J. H., & Song, C. (2005). Deep desulfurization of gasoline by selective adsorption over solid adsorbents and impact of analytical methods on ppm level sulfur quantification for fuel cell applications. *Applied Catalysis B: Environmental*, *56*(1-2), 137–147. doi:10.1016/j.apcatb.2004.08.013

Matsui, M., Horiba, T., Yamamoto, O., Takeda, Y., Seki, N., & Imanishi, N. (2013). Carbon paper substrate for silicon-carbon composite anodes in lithium-ion batteries. *Journal of Power Sources*, *241*, 744–750. doi:10.1016/j.jpowsour.2013.05.090

Mattevi, C., Kim, H., & Chhowalla, M. (2011). A review of chemical vapour deposition of grapheme on copper. *Journal of Materials Chemistry*, *21*(10), 3324–3334. doi:10.1039/C0JM02126A

Mc Allister, M. J., Li, J.-L., Adamson, D. H., Schniepp, H. C., Abdala, A. A., & Liu, J. et al. (2007). Single sheet functionalized graphene by oxidation and thermal expansion of graphite. *Chemistry of Materials*, *19*(18), 4396–4404. doi:10.1021/cm0630800

McEuen, P. L., Fuhrer, M. S., & Park, H. K. (2002). Single-walled carbon nanotube electronics. *IEEE Transactions on Nanotechnology*, *1*(1), 78–85. doi:10.1109/TNANO.2002.1005429

Meille, V., Shulz, E., Vrinat, M., & Lemaire, M. (1997). Hydrodesulfurization of alkyldibenzothiophenes over a NiMo/Al_2O_3 catalyst: Kinetics and mechanism. *Journal of Catalysis*, *170*(1), 29–36. doi:10.1006/jcat.1997.1732

Milenkovic, A., Shulz, E., Meille, V., Lofferda, D., Forissier, M., Vrinat, M., & Sautet, P. (2004). Charge transfer complexes between tetranitrofluorenone and polyaromatic compounds from gasoil: A combined DFT and experimental study. *Physical Chemistry*, *6*, 1169–1180.

Molina-Ontoria, A., Chaur, M. N., Plonska-Brzezinska, M. E., & Echegoyen, L. (2013a). Preparation and characterization of soluble carbon nano-onions by covalent functionalization, employing a Na-K alloy. *Chemical Communications (Cambridge)*, *49*(24), 2406–2408. doi:10.1039/c3cc39077b PMID:23411670

Nagai, M., Goto, Y., Ishii, H., & Omi, S. (2000). XPS and TPSR study of nitrided molybdena-alumina catalyst for the hydrodesulfurization of dibenzothiophene. *Applied Catalysis A, General*, *192*(2), 189–199. doi:10.1016/S0926-860X(99)00341-5

Naidich, J. V. (1981). The wettability of solids by liquid metals. *Progress in Surface Membrane Science*, *14*, 353–484. doi:10.1016/B978-0-12-571814-1.50011-7

Nikolaev, P., Smalley, R. E., Bronikowski, M. J., Bradley, R. K., Rohmund, F., Colbert, D. T., & Smith, K. A. (1999). Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide. *Chemical Physics Letters*, *313*(1-2), 91–97. doi:10.1016/S0009-2614(99)01029-5

Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., & Dubonos, S. V. (2004). Electric field effect in atomically thin carbon films. *Science*, *306*(5696), 666–669. doi:10.1126/science.1102896 PMID:15499015

Park, J. G., Ko, C. H., Yi, K. B., Park, J. H., Han, S. S., Cho, S. H., & Kim, J. N. (2008). Reactive adsorption of sulfur compounds in diesel on nickel supported on mesoporous silica. *Applied Catalysis B: Environmental*, *81*(3-4), 244–250. doi:10.1016/j.apcatb.2007.12.014

Park, S., & Ruoff, R. S. (2009). Chemical methods for the production of graphenes. *Nature Nanotechnology*, *4*(4), 217–224. doi:10.1038/nnano.2009.58 PMID:19350030

Perathoner, S., Gangeri, M., Lanzafame, P., & Centi, G. (2007). Nanostructured electrocatalytic Pt-carbon materials for fuel cells and CO_2conversion. *Kinetics and Catalysis*, *48*(6), 877–883. doi:10.1134/S0023158407060171

Popov, V. N. (2004). Carbon nanotubes: Properties and applications. *Materials Science and Engineering R Reports*, *43*(3), 61–102. doi:10.1016/j.mser.2003.10.001

(2001). Quality requirements for liquid fuels [in Estonian]. *State Announcer. App.*, *66*, 2765–2775.

Rana, M. S., Sa'mano, V., Ancheyta, J., & Diaz, J. A. I. (2007). A review of recent advances on processing technologies for upgrading of heavy oils and residual. *Fuel*, *86*(9), 1216–1231. doi:10.1016/j.fuel.2006.08.004

Rao, C. N. R., Sood, A. K., Subrahmanyam, K. S., & Govindaraj, A. (2009). Graphene: The new two-dimensional nanomaterial. *Angewandte Chemie International Edition*, *48*(42), 7752–7777. doi:10.1002/anie.200901678 PMID:19784976

Reina, A., Jia, X., Ho, J., Nezich, D., Son, H., & Bulovic, V. et al. (2009). Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. *Nano Letters*, *9*(1), 30–35. doi:10.1021/nl801827v PMID:19046078

Ronkainen, N. J., Halsall, H. B., & Heineman, W. R. (2010). Electrochemical biosensors. *Chemical Society Reviews*, *39*(5), 1747–1763. doi:10.1039/b714449k PMID:20419217

Salem, A. B. S. H. (1994). Naphtha desulfurization by adsorption. *Industrial & Engineering Chemistry Research*, *33*(2), 336–340. doi:10.1021/ie00026a025

Salem, A. B. S. H., & Hamid, H. S. (1997). Removal of sulfur compounds from naphtha solutions using solid adsorbents. *Chemical Engineering & Technology*, *20*(5), 342–347. doi:10.1002/ceat.270200511

Salernitanoa, E., Giorgi, L., & Dikonimos, M. (2014). Direct growth of carbon nanofibers on carbon-based substrates as integrated gas diffusion and catalysts layer for polymer electrolytes fuel cells. *International Journal of Hydrogen Energy*, *39*(27), 15005–15016. doi:10.1016/j.ijhydene.2014.07.060

Sano, Y. (2004a). Adsorptive removal of sulfur and nitrogen species from a straight run gas oil over activated carbons for its deep hydrodesulfurization. *Applied Catalysis B: Environmental*, *49*(4), 219–225. doi:10.1016/j.apcatb.2003.12.007

Sano, Y., Choi, K. K., Korai, Y., & Mochida, I. (2004b). Selection further activation of activated carbons for removal of nitrogen species in gas oil as a pretreatment for its deep hydrodesulfurization. *Energy & Fuels*, *18*(3), 644–651. doi:10.1021/ef034080e

Sano, Y., Sugahara, K., Choi, K. H., Korai, Y., & Mochida, I. (2005). Two-step adsorption process for deep desulfurization of diesel oil. *Fuel*, *84*(7-8), 903–910. doi:10.1016/j.fuel.2004.11.019

Savage, D. W., Kaul, B. K., Dupre, G. D., O'Bara, J. T., Wales, W. E., & Ho, T. C. (1995). Deep desulfurization of distillate fuels. *US Patent*, 5454933.

Schlapbach, L., & Züttel, A. (2001). Hydrogen-storage materials for mobile applications. Hydrogen-storage materials for mobile applications. *Nature*, *414*(6861), 353–358. doi:10.1038/35104634 PMID:11713542

Seah, C. M., Chai, S. P., & Mohamed, A. R. (2014). Mechanisms of graphene growth by chemical vapour deposition on transition metals. *Carbon*, *70*, 1–21. doi:10.1016/j.carbon.2013.12.073

Seredych, M., Lison, J., Jans, U., & Bandosz, T. J. (2009). Textural and chemical factors affecting adsorption capacity of activated carbon in highly efficient desulfurization of diesel fuel. *Carbon*, *47*(10), 2491–2500. doi:10.1016/j.carbon.2009.05.001

Shafi, R., & Hutchings, G. J. (2000). Hydrodesulfurization of hindered dibenzothiophenes:an overview. *Catalysis Today*, *59*(3-4), 423–442. doi:10.1016/S0920-5861(00)00308-4

Shin, W. H., Jeong, H. M., Kim, B. G., Kang, J. K., & Choi, J. W. (2012). Nitrogen-doped multi-walled carbon nanotubes for lithium storage with extremely high capacity. *Nano Letters*, *12*(5), 2283–2288. doi:10.1021/nl3000908 PMID:22452675

Sinnott, S. B., & Andrews, R. (2001). Carbon nanotubes: Synthesis, properties and applications. *Critical Reviews in Solid State and Material Sciences*, *26*(3), 145–249. doi:10.1080/20014091104189

Song, C. (2003). An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel. *Catalysis Today*, *86*(1-4), 211–263. doi:10.1016/S0920-5861(03)00412-7

Stephanie, N. S., Goubert, R., Xiuling, Z., & Andrzej, W. (2010). Synthesis and characterization of carbon-supported transition metal oxide nanoparticles-Cobalt porphyrin as catalysts for electroreduction of oxygen in acids. *Electrochemistry Communications*, *12*(11), 1457–1461. doi:10.1016/j.elecom.2010.06.004

Sundaraman, R., Peduzzi, E., & Song, C. (2009). Catalytic cracking of oxidized sulfur compounds in gas oil stream. *Prepr Pap Am Chem Soc Div Fuel Chem*, *54*(2), 954–955.

Svoboda, K., Lin, W., Hannes, J., Korbee, R., & van den Beek, C. M. (1994). Low temperature flue gas desulfurization by alumina-CaO regenerable sorbents. *Fuel*, *73*(7), 1144–1150. doi:10.1016/0016-2361(94)90251-8

Terrones, M. (2003). Science and technology of twenty-five century: Synthesis, properties and applications. *Annual Review of Materials Research*, *33*, 419. doi:10.1146/annurev.matsci.33.012802.100255

Thess, A., Smalley, R. E., Roland, L., Nikolaev, P., Dai, H., & Petit, P. et al. (1996). Crystalline ropes of metallic carbon nanotubes. *Science*, *273*(5274), 483–487. doi:10.1126/science.273.5274.483 PMID:8662534

Velu, s., Ma, X., Song, C. (2003). Selective adsorption for removing sulfur from jet fuel over zeolite based adsorbents. *Industrial Engineering and Chemical Research*, 42(21), 5293–5304.

Viculis, L. M., Mack, J. J., & Kaner, R. B. (2003, February 28). A chemical route to carbon nanoscrolls. *Science*, *299*(5611), 1361. doi:10.1126/science.1078842 PMID:12610297

Wang, Y. H., Yang, F. H., Yang, R. T., Heinzel, J. M., & Nickens, A. D. (2006). Desulfurization of high sulfur jet fuel by π-Complexation with copper and palladium halide sorbents. *Industrial & Engineering Chemistry Research*, *45*(22), 7649–7655. doi:10.1021/ie060922w

Wang, Y. H., Yang, R. T., & Heinzel, J. M. (2008). Desulfurization of jet fuel by π-complexation with metal halides supported on MCM-41 and SBA-15 mesoporous materials. *Chemical Engineering Science*, *63*(2), 356–365. doi:10.1016/j.ces.2007.09.002

Williams, G., Seger, B., & Kamat, P. V. (2008). TiO_2-graphene nanocomposites. UV-assisted photocatalytic reduction of graphene oxide. *ACS Nano*, *2*(7), 1487–1491. doi:10.1021/nn800251f PMID:19206319

Xie, X., Ju, L., Feng, X., Sun, Y., Zhou, R., & Liu, K. et al. (2009). Controlled fabrication of high-quality carbon nanoscrolls from monolayer graphene. *Nano Letters*, *9*(7), 2565–2570. doi:10.1021/nl900677y PMID:19499895

Xue, Y. Z., Wu, B., Guo, Y. L., Huang, L. P., Jiang, L., & Chen, J. Y. et al. (2011). Synthesis of large-area,few-layer graphene on iron foil by chemical vapor deposition. *Nano Research*, *4*(12), 1208–1214. doi:10.1007/s12274-011-0171-4

Yang, F. H., Hernandez-Maldonado, A. J., & Yang, R. T. (2004). Selective adsorptipion of organosulfur compounds from transportation fuels by π-complexation. *Separation Science and Technology*, *39*(8), 1717–1731. doi:10.1081/SS-120035937

Yang, R. T. (2003). *Adsorbents: Fundamentals and Applications*. New York: Wiley. doi:10.1002/047144409X

Yang, R. T., Hernandez-Maldonado, A. J., & Yang, F. H. (2003). Desulfurization of transportation fuels with zeolites under ambient conditions. *Science*, *301*(5629), 79–81. doi:10.1126/science.1085088 PMID:12843388

Yang, R. T., Takahashi, A., & Yang, F. H. (2001). New sorbents for desulfurization of liquid fuels by pi-complexation. *Industrial & Engineering Chemistry Research*, *40*(26), 6236–6239. doi:10.1021/ie010729w

Yang, W., Ratinac, K. R., Ringer, S. P., Thordarson, P., Gooding, J. J., & Braet, F. (2010). Carbon nanomaterials in biosensors: Should you use nanotubes or graphene? *Angewandte Chemie International Edition*, *49*(12), 2114–2138. doi:10.1002/anie.200903463 PMID:20187048

Yang, X., Cao, C., Klabunde, K. J., Hohn, K. L., & Erickson, L. E. (2007). Adsorptive desulfurization with xerogel-derived zinc-based nanocrystalline aluminum oxide. *Industrial & Engineering Chemistry Research*, *46*(14), 4819–4823. doi:10.1021/ie0701928

Yoshida, H., Shimizu, T., Uchiyama, T., Kohno, H., Homma, Y., & Takeda, S. (2009). Atomic-scaleanalysis on the role of molybdenum in iron-catalyzed carbon nanotube growth. *Nano Letters*, *9*(11), 3810–3815. doi:10.1021/nl9019903 PMID:19731921

Yuan, L., Saito, K., Hu, W., & Chen, Z. (2001). Ethylene flame synthesis of well-aligned multi-walled carbon nanotubes. *Chemical Physics Letters*, *346*(1-2), 23–28. doi:10.1016/S0009-2614(01)00959-9

Yudasaka, M., Komatsu, T., Ichihashi, T., & Iijima, S. (1997). Single wall carbon nanotube formation by laser ablation using double-targets of carbon and metal. *Chemical Physics Letters*, *278*(1-3), 102–106. doi:10.1016/S0009-2614(97)00952-4

Zhang, Q., Huang, J. Q., Qian, W. Z., Zhang, Y. Y., & Wei, F. (2013). The Road for Nanomaterials Industry: A Review of Carbon Nanotube Production, Post-Treatment, and Bulk Applications for Composites and Energy Storage. *Small*, *9*(8), 1237–1265. doi:10.1002/smll.201203252 PMID:23580370

Zhang, Q., Yu, Z., Du, P., & Su, C. (2010). Carbon nanomaterials used as conductive additives in lithium ion batteries. *Recent Patents on Nanotechnology*, *4*(2), 100–110. doi:10.2174/187221010791208803 PMID:20415660

Zhou, H., Li, G., Wang, X., Jin, C., & Chen, Y. (2009). Preparation of a kind of mesoporous carbon and its performance in adsorptive desulfurization. *Journal of Natural Gas Chemistry*, *18*(3), 365–368. doi:10.1016/S1003-9953(08)60117-6

Zhou, W. W., Han, Z. Y., Wang, J. Y., Zhang, Y., Jin, Z., & Sun, X. et al. (2006). Copper catalyzing growth of single-walled carbon nanotubes on substrates. *Nano Letters*, *6*(12), 2987–2990. doi:10.1021/nl061871v PMID:17163745

Chapter 6

Advances in Nanotechnology Transition Metal Catalysts in Oxidative Desulfurization (ODS) Processes:

Nanotechnology Applied to ODS Processing

Raffaele Saladino
University of Tuscia, Italy

Giorgia Botta
University of Tuscia, Italy

Marcello Crucianelli
University of L'Aquila, Italy

ABSTRACT

Organosulfur compounds show a negative environmental impact because of SOx emissions by combustion of fuel oils. As a consequence, removal of sulfur is becoming a worldwide challenge. The hydrodesulfurization (HDS) process achieves limited performances in the case of refractory S-containing aromatic compounds, such as thiophene and substituted benzothiophenes (BTs), which require highly energy-demanding conditions (high temperature and pressure conditions). Oxidative desulfurization (ODS) is considered the most promising alternative to HDS. During ODS treatment, the organosulfur compounds are oxidized to corresponding sulfoxides and sulfones, which can be successively removed by extraction with polar solvents. Different stoichiometric oxidants have been used in the ODS processes with a different degree of efficacy and environmental impact. The design and development of catalytic procedures can increase the ODS energy efficiency as well as make it more economical and environmentally acceptable. Here we describe the advances in nanostructured organometallic catalysis and biotechology applied to ODS treatment.

DOI: 10.4018/978-1-4666-9545-0.ch006

INTRODUCTION

The removal of sulfur compounds in petroleum and fuels represents an important topic for the protection of the health of our planet, (Oliveira et al., 2013; Teixeira, Oliveira, Cristofani, & Moura, 2013). As a consequence of the combustion process, sulfur compounds are oxidized to corresponding sulfur oxides and acids that significantly influence the composition and stability of the atmospheric ozone layer, as well as the formation of acid rain, (De Souza, Guimaraes, Guerreiro, & Oliveira, 2009). These environmental risks prompted the U.S. Environmental Protection Agency (EPA) to issue a maximum sulfur content (15 ppm) in diesel fuel, a limit that was further reduced in the Euro V standard protocol (10 ppm). Thus the development of new technologies for deep sulfur removal has become an enormous challenge for production of clean fuels, (Song, 2003). The conventional procedure for the removal of sulfur contaminants in fuel is hydrodesulfurization (HDS), (Satterfeld, 1991; Speight, 1998). The HDS process consists in the hydrogenolysis reaction at elevated temperatures (ranging from 300 to 400 °C) and elevated pressures (10-130 atm) in the presence of catalysts, which are typically based on alumina or silica supports impregnated with different metal species (such as cobalt, molybdenum and nickel), (Schuit & Gates, 1973). The more challenging problems of HDS stem from the recalcitrant nature of aromatic sulfur compounds, such as benzothiophene (BT), dibenzothiophene (DBT) and other methyl substituted derivatives, which can irreversibly plug the active sites of catalyst, influencing the kinetic and the flow distribution in the reactor, (Babich & Moulijin, 2003). The oxidative desulfurization (ODS) is a promising alternative to HDS for the production of ultra low sulfur fuels, (Zannikos, Lois, & Stournas, 1995). In the ODS process, the stable and difficult-to-reduce DBT derivatives are oxidized to corresponding sulfones and sulfoxide under low temperature and pressure conditions. These polar derivatives are successively separated from the fuel by either extraction or adsorption units, (Campos-Martin, Capel-Sanchez, Perez-Presas, & Fierro, 2010). The ODS process is complementary to HDS, since some sulfur compounds, such as disulfides, are easy to be reduced but oxidize slowly. For this reason, ODS process is mainly applied for the treatment of fuel with low content of sulfur contaminants (500 ppm), already depleted of oxidation stable species, (Gatan, Barger, Gembicki, Cavanna, & Molinari, 2004). The oxidation of organic sulfur compounds is usually accomplished by the use of stoichiometric oxidants, such as potassium permanganate ($KMnO_4$), (Gokel, Gerdes, & Dishong, 1980) sodium bromate ($NaBrO_3$), (Shaabani, Behnam, & Rezayan, 2009) different carboxylic peracids, (Kubota & Takeuchi, 2004) sulfonic peracids (Kluege, Schulz, & Liebsch, 1996) and many other oxidants, (Shefer & Rozen, 2010; Hudlicky, 1990). On the other hand, increasing environmental concerns raised the interest to develop benign, selective and economical procedures, based on catalytic methods. Exhibiting both homogeneous and heterogeneous catalytic properties, nanocatalysts allow for rapid and selective chemical transformations, taking advantages of excellent conversion of substrate, product yield and easiness of catalyst separation and recovery (Zhang, Xu, & Wang, 2014). The high performance of these systems is related to the possibility of design nanomaterials with specific and carefully tuned catalytic properties by specific nanosized methodologies, including metal-metal oxide, metal-metal, metal-non-oxide and metal alone supporting procedures (Polshettiwar & Varma 2010). Nanosized materials show additional unique properties compared to macroscale (Campelo et al., 2009) which are associated at the high surface to volume ratio (S/V) of the catalytically active material (Teunissen, Bol, & Geus, 1999). Nanocatalysts, with dimensions of less than 100 nanometers (100 nm), have been used in ODS processes in the last years to activate primary oxidants, such as hydrogen peroxide (H_2O_2), alkylperoxides and peracids. In the following sections, a large panel of well recognized nanocatalysts for ODS will be described, classifying them in terms of different families on the basis of their prevalent catalytic shape like, that is nanocomposites, nanoparticles, nanotubes and more. This choice focuses on the role played by the physical form of the catalyst in synergy with the chemical properties of the metal (or metals) species in the system. Since several nanosized catalysts perform in a way similar to enzyme, a biodesulfurization (BDS) paragraph was introduced at the end to the manuscript, to better describe the scenario of environmental friendly procedures.

NANOCOMPOSITES

Nanocomposite are multiphase porous inorganic media in which the matrix is reinforced by one or more nanomaterials in order to improve the performance and the catalytic properties (Ray & Okamoto, 2003). Usually, the matrix of nanocomposites is composed by colloids, gels, ceramics, polymers (and their possible combinations), and metals with ordered and repeated properties (e.g. diameter, grain size, cross section, layer thickness) between the different phases that make up the material (Manias et al. 2001). The physical and chemical properties of nanocomposites differ markedly from that of the single component material, as well as, from that of conventional composite materials, mainly due to the exceptionally high surface to volume ratio of the reinforcing phase which is typically an order of magnitude greater than conventional composite materials (Hussain, Hojjati, Okamoto, & Gorga, 2006). Jordana et al. (2005) showed that, depending on the type of the reinforcing phase, nanocomposites can be classified into:

1. Metal oxide/metal oxide based nanocomposites,
2. Polymer-based nanocomposites,
3. Ceramic (glass)-based nanocomposites,
4. Carbon-based nanocomposites, and
5. Noble-metal based nanocomposites.

An example of application of noble-metal based nanocomposites strategy in ODS is the use of gold nanoparticles supported on red mud. The red mud is a wastewater produced in large amount during the Bayer process for the extraction of alumina (Al_2O_3), which contains active metal species (e.g. ferric oxide, Fe_2O_3) (S. Kumar, R. Kumar, & Bandopadhyay, 2006; Rivas Mercury et al., 2011). In these nanocomposites, the gold nanoparticles [as gold complex, $Au(en)_2Cl_3$] play the role of coordination centers for sulfur compounds on the basis of the known high affinity between sulfur and gold (soft/soft interaction) (Pasquali et al., 2009; Noh et al., 2007; Rodriguez et al., 2009). The nanoparticles have been embedded on the surface of three different mud supports, namely dried raw red mud (Rm), hydrogenated red mud (RmH_2), and chemical vapor deposited ethanol red mud (RmEt). At difference of Rm, the RmH_2 and RmEt supports showed magnetic properties without leaching phenomena. X-ray diffraction (XRD) analysis and Mössbauer spectroscopy of Au/Rm, Au/RmH_2 and AuRmEt, showed different distributions and nature of the iron phases, the hematite α-Fe_2O_3 prevailing in Au/Rm (beside to maghemite and goethite), while magnetite Fe_3O_4, was the most abundant phase in the other catalysts. Noteworthy, multiwalled carbon nanotubes (MWCNTs) were observed in TEM images of Au/RmEt, probably as a consequence of the EtOH deposition and successive pyrolysis. When applied in the oxidation of DBT as a simplified ODS model (performed in a biphasic medium with H_2O_2), Au/RmEt was more active than Au/Rm and AuRmH_2, probably as a consequence of the highest content of Fe^{2+} necessary for the generation of OH• radicals *via* the Haber-Weiss reaction (Figure 1) (Moura et al., 2005; Nogueira, Trovò, da Silva, Villa, & de Oliveira, 2007; Costa, Moura, Ardisson, Fabris, & Lago, 2008; Aguiar, Ferraz, Contreras, & Rodriguez, 2007).

Au/RmEt was more efficient than RmEt, confirming the benign role of Au nanoparticles in the coordination (and concentration) of dibenzotiophene in the oxidant phase. Moreover, the presence of MWCNTs increased the interaction of Au/RmEt with the substrate by increasing its amphiphilic properties. Ceramic (glass)-based nanocomposites have been also used for the activation of titanium silicalite in ODS. Titanium silicalite of type-1 (TS-1) are efficient catalysts for the deep removal of sulfur from fuel, due to their high activity in the oxidation of low electron density organic sulfur compounds, such as tiophene (Napanang & Sooknoi, 2009). Studies have been performed by Sengupta et al. (2012) on the immobilization of TS-1 nanoparticles on the surface of porous glass prepared by subcritical water treatment, avoiding the formation of TS-1 aggregates and contributing to easy recovery of the catalyst from the reaction mixture (Seung-Tae, Kwang-Eun, Soon-Yong, & Wha-Seung, 2012). Porous glass beads were treated with tetrapropyl ammonium hydroxide (TPAOH), titanium ethoxide (TEOT) and thetraethyl-orthosilicate (TEOS) to yield a uniform distribution of TS-1 nanoparticles on the matrix. The novel catalyst were efficient catalysts in the oxidation of DBT and other methylated derivatives, like 4,6-dimethyl dibenzotiophene (DMDBT), using cumene hydroperoxide (CHP) as oxidant at 343 K (Figure 2). The conversion of substrate and yield of sulfone was tuned by the amount of Ti in the porous glass beads, reaching 92% conversion within 5 minutes in the presence of 0.41 wt% of Ti (Shen, Wang, Xu, & Luo, 2015). In accordance with studies previously reported by Wang et al. (2013), coordinated Ti species (anatase phase) were the active centers for the oxidation.

Note that the oxidation rate slowed down during the time as a consequence of the deposition of DBT molecules on the surface of the catalyst, (Kong, Li, Wang, & Wu, 2006). For this reason, the high temperature regeneration of the catalyst was required when the system turned to yellow. A significant improvement in the catalytic activity of TS-1 in ODS was achieved by reducing intra-crystalline diffusional phenomena in zeolites with small size micropores (Taguchi & Schuth, 2005). In particular in according to Kong & Wang (2004), titanium mesoporous materials in the range of nanosized dimensions, (Tanev, Chibwe, & Pinnavaia, 1994) in which the bulky organic sulfur compounds can easily reach the active sites, were prepared. Zhao et al. (1998) described the preparation of structurally ordered mesoporous TS-1 (meso/TS-1) by a template procedure based on nanoporous CMK-3. The treatment of CMK-3 with TPAOH and TEOS (as the silica source) was performed in the presence of TiO_2 and SiO_2. The resulting meso/TS-1 were characterized by the presence of hexagonal-shaped nanocrystals (20-30

Figure 1. Oxidation of DBT with Au/RmEt nanocomposite by the Haber-Weiss reaction

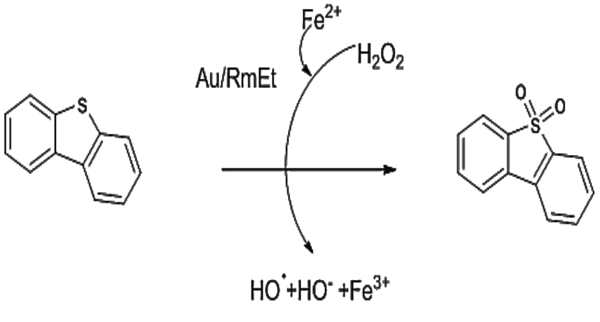
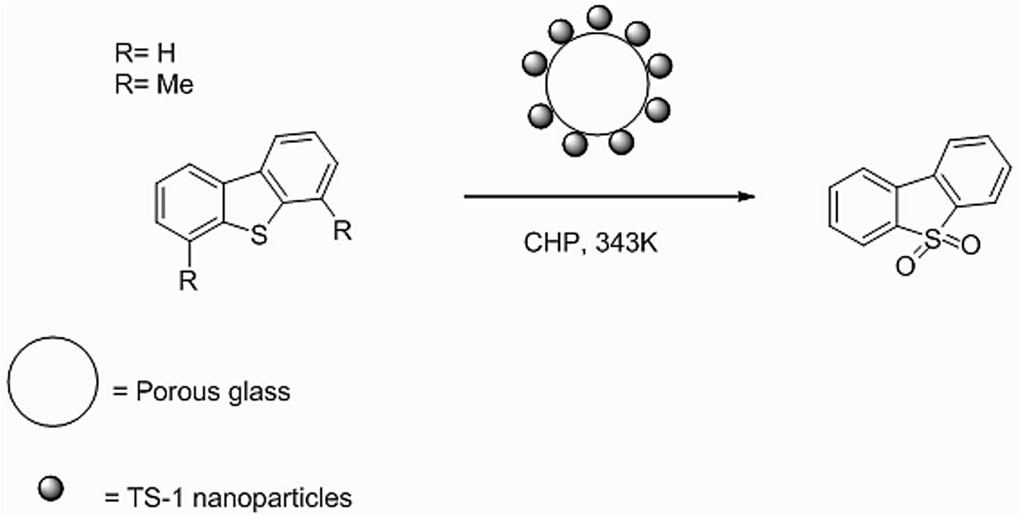


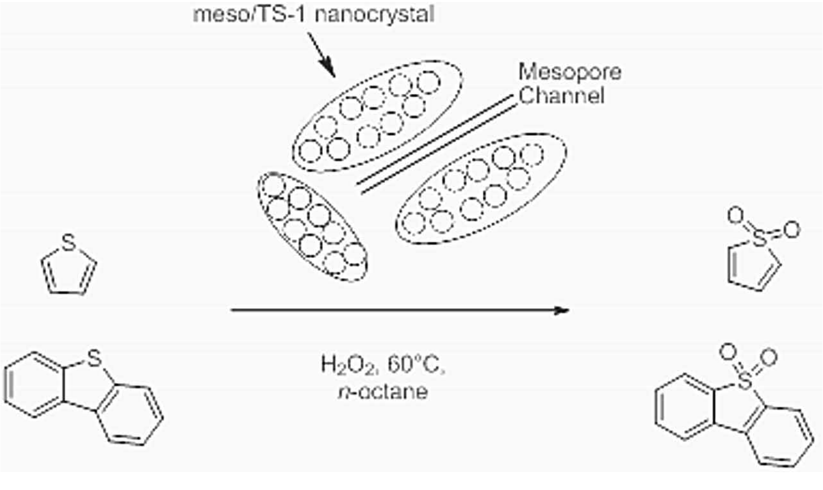
Figure 2. Oxidation of DBT and 4, 6-DMDBT with CPH in the presence of TS-1/porous glass nano-composite



nm) in accordance with the study of Jun et al. (2000), arranged in a random packed network with an average mesopore distribution centered at 3.65 nm, (Fang & Hu, 2007). Meso/TS-1 efficiently catalyzed the oxidation of thiophene and DBT to corresponding sulfones, using H_2O_2 as primary oxidant at 60°C in n-octane solution (Figure 3). Meso/TS-1 were catalysts more efficient than simple TS-1, reaching 100% conversion of DBT after only 30 min.

Mesoporous titanium dioxide (TiO_2)/ phosphotungstic acid (PWA) nanocomposites have also been prepared by Huang et al. (2006a) using a quaternary ammonium bromide salts as structure-directing agents. Tetrabutyl titanate and the appropriate quaternary ammonium bromide salt were added to PWA,

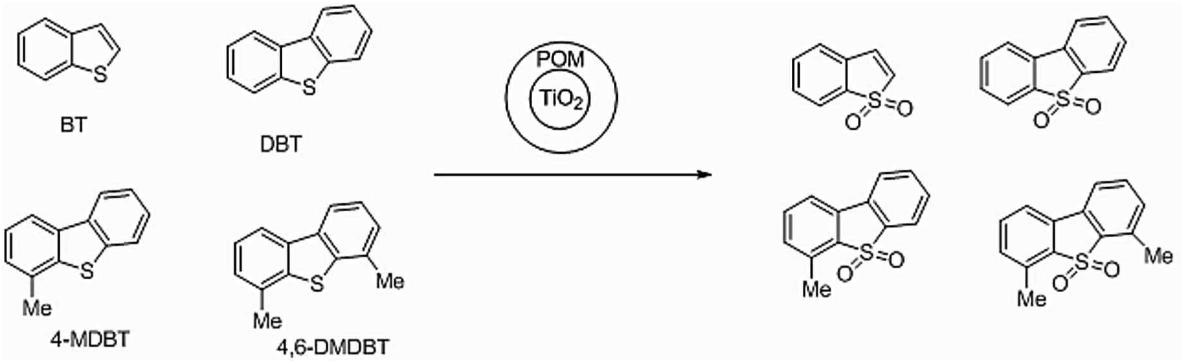
Figure 3. Oxidation of aromatic sulfur compounds with mesoporous zeolite/TS-1 nanocomposites; hexagonal-shaped nanocrystals (20-30 nm) are arranged in random packed networks with an average mesopore distribution centered at 3.65 nm.



and the resulting solid was treated at 500°C for 3h, (Huang, Wang, Cui, & Luo, 2008). The pore size-distribution of mesoporous TiO_2 nanoparticles (meso-TiO_2) was finely tuned by the chemical properties of the salt, that is the pore size increased by increasing the organic chain length, the highest value being obtained with octadecyl trimethyl ammonium bromide (STAB, 4.42 nm). The formation of hydrogen bond networks between PWA and hydroxylated tetrabutyl titanate, as well as, that between the salt and hydroxylated TEOS, contributed to yield larger volume and pore size. Meso-TiO_2 exhibited good performance in the oxidation of DBT in octane at 70°C using H_2O_2 as primary oxidant. In the optimal reaction temperature (that is the optimal amount of catalyst and oxidant, and optimal initial concentration of DBT), 98% removal was obtained from a 300 ppm total sulfur mixture in only 2 minutes. The amount of PWA was a crucial parameter for the formation of titania mesoporous structures. For example, 20-30% in weight of PWA were required in the synthesis of TiO_2 nanocomposites starting from tetrabutyltitanate [Ti $(C_4H_9O)_4$] and Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) as structure-directing agent, (Yan et al., 2009). Under these experimental conditions, the mesoporous HPW/TiO_2 nanocomposite (meso-HPW/TiO_2) was characterized by a network of TiO_2 nanoparticles of approximately 8 nm size as anchorage site for PWA. Further increase of PWA content to 40% accelerated the hydrolysis of $[Ti(C_4H_9O)_4]$ with concomitant formation of polymeric Ti-PWA entities that can't easily assemble with the template causing the degradation of the mesostructured, (Huang, Wang, Yang, & Luo, 2006b). In accordance with the degree of structural organization, the meso-HPW/TiO_2 containing 30% in weight of PWA was the best catalyst in the oxidation of DBT with H_2O_2 in petroleum ether at 33 K. Tungsten peroxo compounds of zirconium dioxide (WO_X-ZrO_2) have been used in both homogeneous, (Ciclosi et al., (2008) and heterogeneous ODS conditions, (Ramirez-Verduzco, De los Reyes, & Torres-Garcia, 2008). Experimental and theoretical data showed that the oxidative efficiency of WO_X-ZrO_2 species (expressed as number of W-atom in the system) increased by increasing the surface density of Bronsted acid sites, reaching the maximum value with the W-atom loading in the range of 4 and 7 W-atom/nm^2, (Rodriguez-Gattorno, Galano, & Torres-Garcia, 2009). Thus, n-meric domains of WO_3-x nanoparticles immobilized on the zirconium surface are more efficient than simple monomeric, dimeric and three-dimensional structures. The optimal reactive surface is characterized by aligned Bronsted sites on which the peroxyl radicals can add to generate active peroxotungsten intermediates, (Figueras et al., 2004). Solid heteropolyacids are efficient catalysts for the activation of H_2O_2 in the oxidation of several organic compounds, (Huang & Wang, 2006c). Tangestaninejad et al. (2008) showed that these systems increase their activity after immobilization on solids with high surface areas such as titanium dioxide (TiO_2), mainly due to benign interaction between the active species and the support. For example, nanocomposites formed by anatase sandwich type with polyoxometalates have been prepared by Sharifzadeh Baei and Rezvani (2011) supporting $(Bu_4N)_{7\ b}H_3[P_2W_{18}Cd_4(Br)_2O_{68}]$ on TiO_2. In particular, a thin film of $[P_2W_{18}Cd_4\ (Br)_2\ O_{68}]$ was coated on a bed of anatase nanoparticles with average size about 10 nm. The catalytic activity of $[P_2W_{18}Cd_4(Br)_2O_{68}]$-$TiO_2$ (POM-TiO_2) system was tested in the oxidation of BT, DBT, 4-methyldibenzothiazole (4-MDBT) and 4,6-DMDBT with H_2O_2 in n-heptane (Figure 4). The nanocomposite POM-TiO_2 was a catalyst more efficient than homogeneous POM. Sulfones were obtained as the only recovered products with the following order of reactivity: DBT>4,6-DMDBT>4-MDBT>BT. In the case of DBT, up to 98% removal of sulfur was obtained after 12 min. at 60°C. The POM-TiO_2 catalyst retained its activity for at least three runs.

The recoverability of nanocomposites from the reaction mixture was improved by immobilization of PWA on magnetic mesoporous silica rods, previously coated with the ionic liquid 1-methyl-3-[(triethoxysilyl)

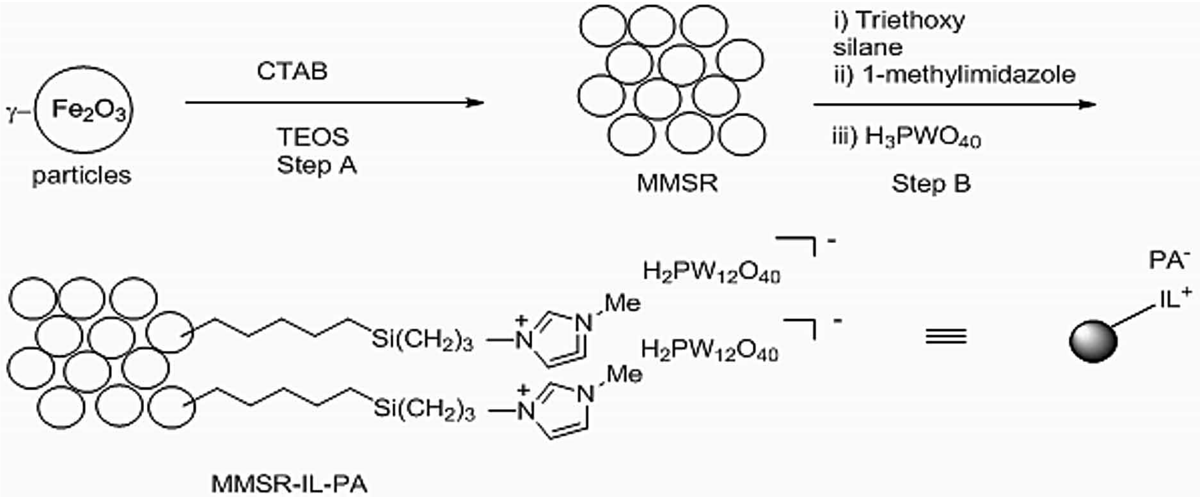
Figure 4. Oxidation of BT and other sulfur derivatives with nanocomposites based on polyoxometalate immobilized on TiO_2 anatase phase



propyl)]imidazolium chloride. Magnetite (γ-Fe_2O_3) nanoparticles (with an average diameter of 10 nm) were embedded on magnetic ordered mesoporous silica by treatment with cetyltrimethyl ammonium bromide (CTAB) and tetraethoxysilane (TEOS) (Figure 5, step A), (Kim et al., 2006).

The magnetic mesopourous silica road particles (MMSR) were successively functionalized with triethoxysilane and 1-methylimidazole, followed by immobilization of PWA to yield MMSR-IL-PA (Figure 5, step B). TEM analysis of MMSR-IL-PA showed a rod-like network structure characterized by an average diameter of 60 nm, length in the range of 100-200 nm, specific surface area 385.2 m^2/g and pore volume 0.35 cm^3/g. The reduced value of surface area and pore volume after loading of the PWA suggested that the acid was into the pores of the support, (Chen et al., 2013). MMSR-IL-PA was then used for the oxidation of DBT with H_2O_2 in CH_3CN. Optimal conversion of DBT to corresponding sulfone (99%) was obtained at 323 K after 4 h. The mechanism of oxidation of DBT by PWA and H_2O_2 was previously reported, (Zhang et al., 2011). Noteworthy, MMSR-IL-PA was easy recovered

Figure 5. Magnetic mesoporous silica road particles (MMSR) functionalized with triethoxysilane and 1-methylimidazole, followed by immobilization of phosphotungstic acid



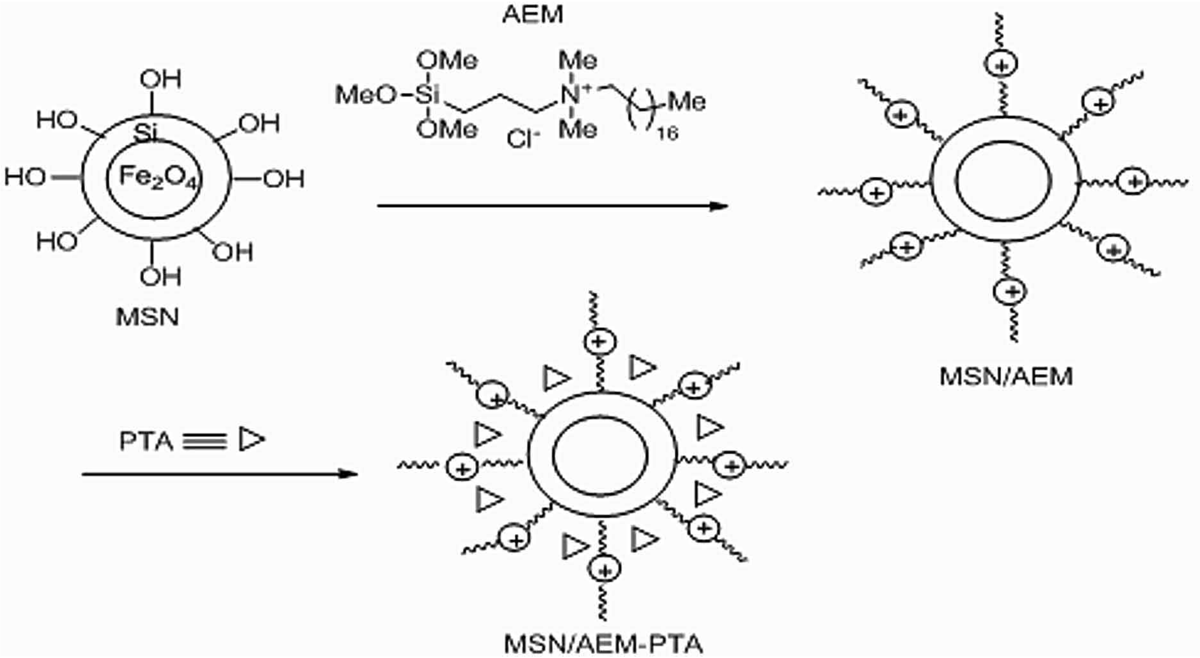
from the reaction medium applying an external magnetic field and used for further transformations. Besides to H_2O_2, dioxygen (O_2) can be used as primary oxidant in the ODS processes at relatively high reaction temperature. In this latter case, the presence of active metal species are required to catalyze the generation (and successive desorption) of reactive singlet oxygen species $^1O_2$ at the surface of the catalyst, (Vishnetskaya, Tomskii, & Khim, 2009). Different sulfur containing aromatic derivatives have been efficiently oxidized by O_2 in the presence of microsized vanadium and molybdenum mixed oxides (V_2O_5/MoO_3 systems) at temperature below 350°C, (Boikov, Vakhrushim, & Vishnetskaya, 2008) . The performance of the system was increased by moving from microsized to nanosized vanadium and molybdenum mixed oxides, (Sviridova, Stepanova, & Sviridov, 2012). The mixed oxides with elemental composition V: Mo = 1: 1 showed nano-crystallites with an average dimension of 50 nm and were mainly composed by hydrated vanadium oxide (with some vanadium ions replaced by molybdenum ions) and hexagonal molybdenum trioxide. The mixed oxides showed a significant catalytic activity in the oxidation of thiophene (in gas-phase), even if a conversion no higher than 40% was obtained.

NANOPARTICLES

The size of nanoparticles spans the range between 1 and 100 nm. Metallic nanoparticles show physical and chemical properties different from that of native metals, such as specific optical properties (different colour or different absorption coefficients), lower melting points, increased mechanical strengths, higher specific surface areas, and same times, magnetization capability, (Eustis & El-Sayed, 2006). In this latter context, paramagnetic nanoparticles have been used for the immobilization of catalysts in ODS. The procedure requires three main steps: a) preparation of magnetic silica nanospheres (MSN) with an internal Fe_3O_4 core; b) functionalization of MSN with a quaternary ammonium salt, e.g. 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride (AEM) and; c) the immobilization of $[(C_{18}H_{37})_2N^+(CH_3)_2]_3[PW_{12}O_{40}]$ (PTA) through ion-exchange procedure (Figure 6), (Cui, Yao, Li, Yang, & Hu, 2012).

The presence of the quaternary ammonium salt increased the amphiphilic nature of the catalyst allowing the easier access to active sites of PTA. Under the optimal conditions, 1% in weight of AEM furnished the highest catalytic activity. Under these experimental conditions the interaction of PTA with H_2O_2 was higher than in the presence of a large excess of the quaternary salt. MSN showed an average diameter of 20 nm with the Fe_3O_4 magnetic particles densely entrapped within the SiO_2 shell. AEM and PTA layers covered the surface of a particle as a gel. DBT was efficiently oxidized by MSN/AEM-PTA in decahydro naphthaline with H_2O_2 (30% water solution) at 60°C. High conversion of substrate and yield (90%) of sulfone were obtained. Moreover, the MSN/AEM-PTA magnetic nanoparticles were easily recovered from the reaction mixture by simple exposition to an external magnetic field. Photocatalytic oxidative desulfurization (PODS) is an alternative to conventional ODS, during which the recalcitrant sulfur compounds are first extracted by different polar phases and then oxidized to corresponding sulfones in the presence of O_2 and appropriate photocatalysts, (Lin et al., 2012; Li et al., 2012). TiO_2 is one of the most used photocatalyst in PODS, mainly due to its low toxicity, chemical stability and high reactivity, (Vargas & Nunez, 2008). The mechanism of action of TiO_2 is based on the electron transfer from the valence band (VB) to conduction band (CB) by photon absorption, which causes the formation of an electronic hole. The molecular oxygen or water molecules adsorbed on the mineral surface can be trapped by the hole to generate reactive superoxide anion radical ($O_2^-\bullet$) or hydroxyl radical ($OH\bullet$) spe-

Figure 6. Multisteps preparation of paramagnetic nanoparticles by functionalization of silica nanospheres with a Fe_3O_4 *core*

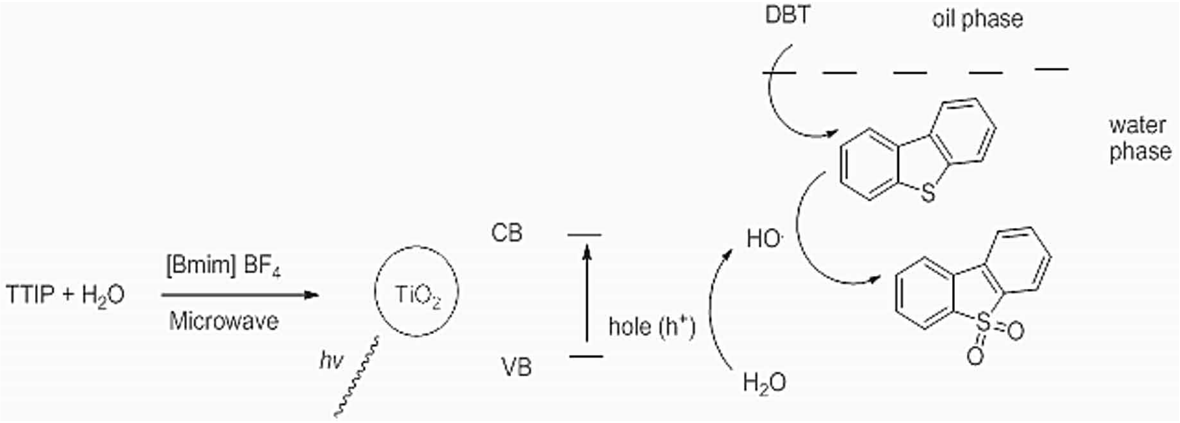


cies, respectively, (Nagaveni, Hegde, Ravishan-Kar, Subanna, & Madras, 2004). The balance between this phenomena and the simple recombination of electron-hole pairs determines the reactivity of TiO_2. The composition and dimension of TiO_2 nanoparticles affect the rate of electron-hole pairs recombination. For example, TiO_2 nanoparticles (anatase phase) with different dimensions (average diameter in the range of 4.74 nm to 7.65 nm) have been produced by microwave assisted hydrolysis of titanium isopropoxide (TTIP) in ionic liquid 1-buthyl-3-methyl imidazolium tetrafluoroborate [Bmim] BF_4 and water mixture. These nanoparticles showed an increased activity in the oxidation of DBT, the activity being increased by decreasing the value of their diameter, (Wang et al., 2012). 98.2% sulfur removal was obtained after 10 h in a model oil mixture. Spectrophotometric measurements conducted by Li et al. (2010) confirmed that the activity was correlated to the rate of generation of (OH•) radical intermediates (Figure 7). The system TiO_2/ionic liquid was recycled by simple evaporation and retained its reactivity at least for five runs. Doped activated carbon is a selective adsorbent for aromatic sulfur compounds showing photocatalytic activity, (Balzani, Credi, & Venture, 2008).

For example, polymer-derived sulfur and phosphorus doped activated carbon nanoparticles (WVA) and commercial available phosphoric acid activated carbon nanoparticles (CP) showed a strong photocatalytic activity under UV and visible light range. In a way similar to TiO_2, these materials generate electrons and holes, which are the driving-force for the activation of O_2 (Petit, Peterson, Mahle, & Bandosz, 2010; Seredych, Khine, & Bandosz, 2011).

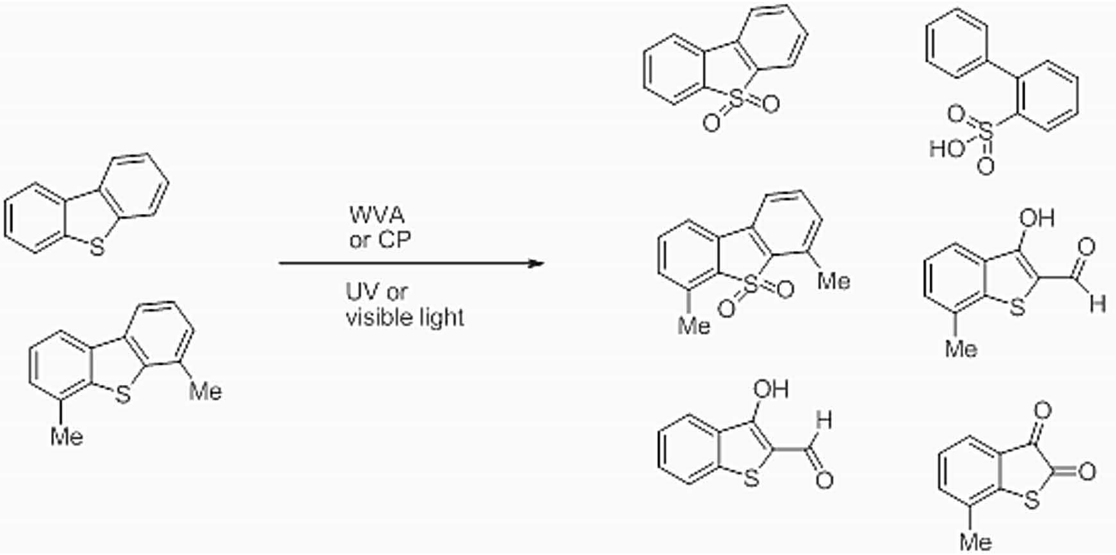
The presence of nitrogen and phosphorous groups increase the activity of doped carbon materials by decreasing the gap of energy between the valence and conduction bands, and by increasing the adsorption of DBT and DMDBT, (Strel Ko, Kutz, & Thrower, 2000; Seredych & Bandosz, 2011). EitherWVA and CP catalyzed the oxidation of DBT and DMDBT to corresponding sulfones. Moreover, some

Figure 7. Photocatalytic oxidative desulfurization (PODS) with TiO_2 (anatase phase) in the presence of ionic liquid [Bmim] BF_4



product of over oxidation, characterized by aromatic ring opening, (such as, among others, 3-hydroxy-2-formylbenzothiophene, 3-hydroxy-7-methylbenzothiophene-2-carbaldehyde and 7-methylbenzothiophene-2, 3-dione), were detected (Figure 8). WVA and CP were active also in dark conditions, (Seredych & Bandosz, 2013). Computational procedures have been used to model the oxidation of sulfur organic compounds in fuel. For example, the optimal experimental conditions and the most critical parameters concerning the oxidation of benzothiophene with Ti-beta nanoparticles and H_2O_2 were evaluated by the use of theoretical artificial neural network model (ANN), (Nikolas, Stergiade, Papadopoulou, & Karat-

Figure 8. PODS of aromatic sulfur compounds by functionalized activated carbon nanoparticles (WVA) and commercial phosphoric acid activated carbon nanoparticles (CP); products of oxidative ring opening were detected besides to expected sulfones derivatives.



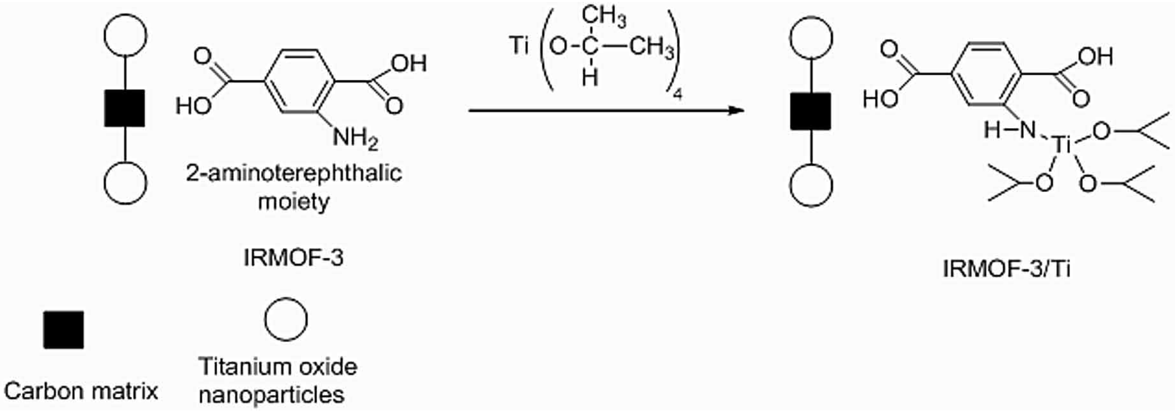
zas, 2008; Elmolla). The ANN is a computational method based on multi-layer of individual calculation units, namely neurons, which are connected together in a large network able to transform any input to a specific target output, (Giroto, Guardani, Teixeira, & Nascimento, 2006).

In particular, the oxidation of BT with Ti-beta was est imated using a three layered feed forward back propagation network comprising five reaction parameters (time, catalyst loading, BT initial concentration, temperature and H_2O_2 to substrate ratio) as the five main nodes in input layer, and the conversion of BT (as %) as the only output node. The input data were experimentally recovered by oxidation of BT in isooctane with Ti-beta zeolite, (Tatsumi & Jappar, 1998). Ti-beta zeolites were characterized by crystallites with an average size of 30-50 nm and BET surface area and micropore volume of 346.7 m^2/g and 0.143 cm^3/g, respectively. The computational study demonstrated that the reaction time, initial BT concentration and reaction temperature, were the most sensitive parameters for the optimization of the ODS process, (Maity, Basu, & Sengupta, 2013).

The extractive properties of ionic liquids are very useful in multi-phases ODS processes based on highly dispersed poly-oxometalates (POMs) nanoparticles. In particular, POM $Na_2H_2Law_{10}O_{36}\cdot 32\ H_2O$ was immobilized on mesoporous silica nanoparticles by electrostatic interaction with a positively charged (3-aminopropyl)triethoxysilane (APTES), (Chen, Zhao, & Song, 2013). The lanthanum content was 87 µmol/g, with a surface area of 135 m^2/g and a pore volume of 0.34 cm^3/g. The ODS efficacy of the novel catalyst was tested by oxidation of DBT with H_2O_2 in tri-phasic systems formed by n-octane (as fuel model), ionic liquid, and aqueous H_2O_2. Among the ionic liquid [bmim]BF_4 was the most active, affording 99% removal of sulfur after 80 min at 70°C. The catalyst was efficiently recycled and reused for at least ten runs without any appreciable decrease in the catalytic performance. Metal organic frameworks (MOFs) are a large family of organic/inorganic hybrid compounds with high catalytic activity associated to efficient dispersion of active sites, microporosity and tunable physicochemical properties, (Bae et al., 2007; Sun et al., 2013; Herm et al., 2013). In MOFs, the metal oxide is coordinated by organic ligands containing electron rich moieties, such as OH, NH_2 and heterocyclic groups, able to tune the reactivity and selectivity of the system, (Pintado-Sierra, Rosero-Almansa, Corma, Iglesias, & Sanchez, 2013). After extensive reduction at high temperature, MOFs perform as templates for the formation of reactive carbon-metal materials with increased chemical and thermal stability and reduced leaching of metals, (Su et al., 2013). In this context, Kim et al. (2013) reported a novel procedure for the preparation of titanium oxide nanoparticles supported on nanoporous carbon (Ti/NC) by carbothermal pyrolysis of Zn-based MOF. As schematically reported in Figure 9, IRMOF-3 was functionalized with titanium isopropoxide by formation of coordinative bond with the 2-amino-terephtholic moiety to yield IRMOF-3/Ti, followed by pyrolysis at 550°C under helium atmosphere. The novel material showed a high surface area (> 1000 m^2/g), high dispersion of metal oxide nanoparticles (zinc oxide and titanium oxide, respectively), average diameter of 4nm, mesopore volume of 1.19 cm^3/g, and micropore volume of 0.35 cm^3/g. Carbon supported nanoparticles were used for the oxidation of DBT in decane/dodecane mixture using tert-butyl hydroperoxide (TBHP) as primary oxidant. Ti/NC catalyst was more efficient than simple titanium oxide immobilized on activated carbon by simple wetness impregnation. Moreover, Ti/NC was enough stable to be recycled for more runs.

The efficacy of TS-1 in the oxidation of bulky substrates was increased by increasing the diameter of the pores, thus enhancing the diffusibility to active titanium sites in the framework, (Zhang, Koyama, Yamada, Imagaki, & Tatsumi, 1996) as in the case of ordered Ti-MCM-68 and so on, (Kubata, Koyama, Yamada, Imagaki, & Tatsumi, 2008). Stable and reactive mesoporous titanium silicates have been prepared by increasing their crystal properties, (Poladi & Landry, 2002) by direct assembly employing

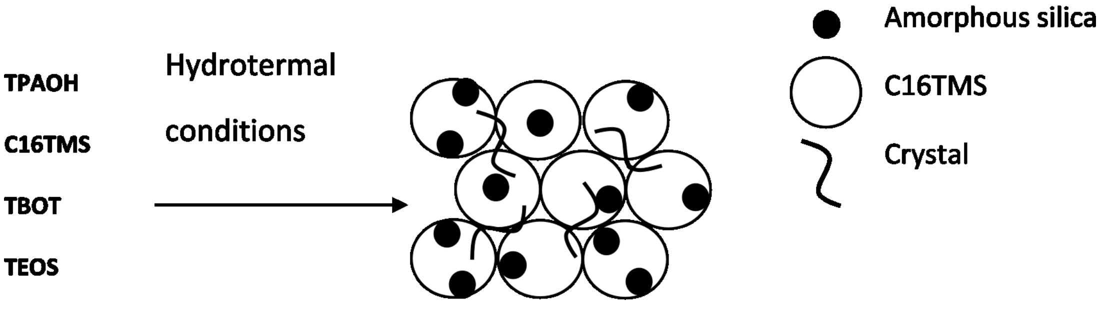
Figure 9. Preparation of titanium oxide nanoparticles supported on a matrix of nanoporous carbon (Ti/NC)



zeolite seeds, (Yang et al., 2012) by hard and soft templates techniques, (Wang, Li, Liu, & Liu, 2012a) or by supramolecular structure produced by interaction of zeolite nanosheets with bifunctional surfactants, (Wang et al.,2012b). Li et al. (2014) prepared nanosized hierarchical TS-1 (HTS-1) containing both micro- and mesopore structures (particles of 140-200 nm) using a hydrothermal procedure. The presence of the organo silane (with a lipophilic character) facilitated the separation and recovering of the catalyst from the solution (Figure 10). HTS-1 showed a catalytic activity higher than mesoporous Ti-MCM-41 in the oxidation of BT, DBT and 4,6-DMDBT, with H_2O_2. The final removal rate of sulfur compounds was nearly 100%.

Stable silica nanosized spheres of POMs have been developed for ODS. Usually, POMs are immobilized on silica supports by electrostatic interaction with positively charged groups, such as NH_2-modified mesoporous silica or silica supported ionic liquids, (Balula et al., 2013). Alternatives are represented by encapsulation procedures, during which the active species is entrapped in reverse micelle with or without the use of surfactants. Neves et al. (2013) described the possibility of incorporation of POMs on cross-linked organic/inorganic structures to afford well dispersed nanosized silica spheres. In these materials, the core is formed by $[PW_{11}Zn(H_2O)O_{39}]_5$ linked to support by an appropriate amine organosilane (APTES) and coated by a silica shell, (Noguera et al., 2014). These materials were efficient catalyst for the oxidation of DBT and 2, 4-DMBT in the biphasic system octane/MeCN using H_2O_2 as primary oxidant.

Figure 10. Preparation of nanosized hierarchical TS-1 (HTS-1) containing both micro- and mesopore structures, with particles of 140-200 nm



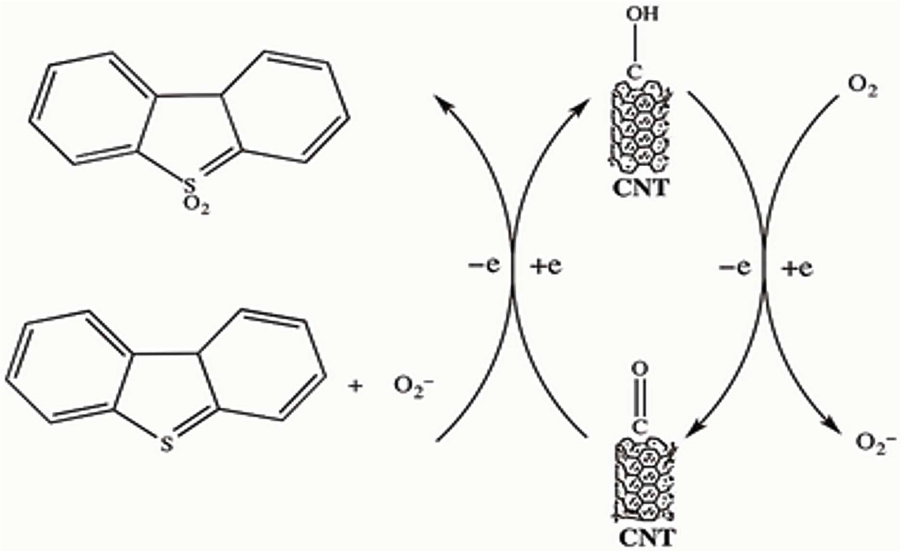
MeCN plays the role of extractive for sulfur compounds and optimal reaction medium for the oxidation. The reaction required an induction period (3h for DBT, and 4h for 2, 4-DMDBT) for the formation of the active W=O catalytic species, producing 100% of sulphur removal. It is interesting to note that silica nanosized spheres of POMs were more reactive than corresponding homogeneous POMs, confirming the benign role of the immobilization procedure. Organometallic compounds are also used in ODS processes, as in the case of methyltrioxorhenium (CH_3ReO_3, MTO). MTO is able to activate H_2O_2, (Saladino, Crucianelli, & De Angelis, 2010). In these reactions, the active catalytic forms are monoperoxorhenium $[MeRe(O)_2(O_2)]$ and bisperoxorhenium $[MeRe(O)(O_2)_2]$ complexes, which efficiently oxidize sulfides, disulfides, and sulfoxides to corresponding sulfones, (Hwang, Bryan, Goldsmith, Peters, & Scott, 2013). Heterogeneous rhenium catalysts based on the immobilization of MTO on commercially available organic resins, such as poly (4-vinylpyridine) (PVP) and poly(4-vinylpyridine)-N-oxide (PVPN), or by physical microencapsulation of MTO on polystyrene, have been prepared and used for the selective oxidation of BTs and DBTs derivatives in CH_2Cl_2, *n*-octane and in a model of fuel oil (MF), with H_2O_2 at 50°C. Irrespective to experimental conditions, the quantitative conversion of substrates was obtained in several of the studied cases, to afford selectively the corresponding sulfones after only 1 h of reaction time. The general reactivity trend was BT's < DBT's. In the case of MF, the sulphur derivatives were oxidized at a faster rate than as isolated substrates, suggesting the presence of synergic or autocatalysis effects, (Di Giuseppe, Crucianelli, De Angelis, Crestini, & Saladino, 2009)

CARBON NANOTUBES AND NANORODS

Carbon nanotubes (CNTs) are supramolecular allotropes of carbon with a cylindrical nanostructure and unusual properties, which are very useful for nanotechnology, electronic, catalysis and optic applications, (Vairavapandian, Vichchulada, & Lay, 2008). They are members of the fullerene family with a hollow structure characterized by one-atom-thick sheets of graphene walls. Depending on the number of walls, carbon nanotubes are classified as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs), in which the layers are held together by van der Waals (pi-stacking) interactions. Diameters of SWNTs and MWNTs are typically 0.8 to 2 nm and 5 to 20 nm, respectively. The CNT lengths range from less than 100 nm to several centimetres, (Xiea, Maia, & Zhoub, 2005). CNTs, either as SWCNTs or MWCNTs, show several benign properties, such as high surface area, biocompatibility, mechanical resistance and favourable electrochemical properties, (Volder, Tawfick, & Baughman, 2013). The dimension of nanorods (NRs) range from 1 to 100 nm, of 3 to 5 length to width ratio. During the preparation of NRs, specific ligands are used to bond the facets of the growing structure with different strengths. This allows the growing of the faces at different rates producing an elongated object, (Wang & Shi, 2014). The low-temperature hydrothermal procedure has been proposed to prepare different phases of MnO_2 NRs, based on a template-free synthetic method (i.e. without any surfactant or polymer matrix). Single-crystalline MnOOH (γ-MnOOH) and MnO_2 NRs (β-MnO_2 and α-MnO_2) have been synthesized by Sampanthar et al. (2007) applying redox reactions at various pH values (temperature range of 120–180 °C), obtaining a distribution of the surface area in the range of 20–80 nm. The catalytic performances of α-MnO_2 NRs were studied for the selective oxidation of 4, 6-DMDBT to the corresponding sulfone, in n-tetradecane at 150 °C, using air as primary oxidant. In some cases, the α-MnO_2 NR samples showed higher activity than commercial MnO_2, affording a quantitative oxidation of starting material in only 2 hours. The ability of titanium incorporated into microporous materials such as zeolites (Ti-ZSM-12, Ti-Beta, TS-1) and MCM-type mesoporous titano-silicates (Ti-MCM-41, Ti-HMS), in the oxidation of olefins, phenols, alcohols, thioethers, and sulfoxides, using H_2O_2 or TBHP as oxidants, has been described, (Moreau, Hulea, Gomez, Brunel, & Di Renzo, 1997; Hulea & Dimitriu, 2004; Hulea, Fajula, & Bousquet, 2011). Nevertheless, the microporosity of these systems can limit their application in the oxidation of large molecules. Chica et al. (2006) demonstrated that Ti-MCM-41, with a larger pore size than zeolites (i.e. about 4.0 nm), is able to desulfurize diesel in a continuous fixed bed reactor with high catalytic activity and long lifetime. Within this context, titanium oxide nanotubes (TiNTs), prepared by hydrothermal synthesis, have attracted special attention because these materials can be potentially used in several catalytic applications due to three main advantages: high specific area, low cost, and practicability to be produced in large quantities, (Bavykin, Friedrich, & Walsh, 2006; Kasuga. Hiramatsu, Hoson, Sekino, & Niihara, 1998). Most of the catalytic studies so far performed using TiNTs, have been limited to the use of nanotubes as support for highly dispersed metal nanoparticles, (Bavykin et al., 2006). Only a few publications have explored the properties of pristine titanate nanotubes in the field of catalysis, which includes photo-oxidation of organic contaminants and its use as solid-acid catalysts, (Kiatkittipong, Scott, & Amal, 2011; Kitano, Nakajima, Kondo, Hayashi, & Hara, 2010). Due to the ability of Ti (IV) sites to interact with H_2O_2 producing active radical species, (Antcliff, Murphy, Griffiths, & Giamello, 2003) these heterogeneous materials have shown interesting performances in oxidative transformations, (Kim et al. 2012). The use of large surface area Ti-containing materials, such as mesoporous Ti-modified SBA-15 (Ti-SBA15) and TiNTs, could be interesting alternatives in ODS processes. The activity of these catalysts in the oxidation of DBT, 4-MDBT, and 4, 6-DMDBT, with H_2O_2 under two (liquid-solid, L-S) or three (liquid-liquid-solid, L-L-S) phases systems, was studied by Cedeno-Caero et al. (2011). While Ti-SBA15 (19 wt. % of TiO_2) showed a low activity, calcined and un-calcined Ti nanotubes (containing more TiO_2-anatase active phase) behaved like highly active catalysts, ensuring almost quantitative DBT oxidation in 1 hour at 60 °C. In the L-L-S three phase system, the mass transfer between liquid phases limited the sulfur removal. In a different case, nanotubular titania have been used to support WOx species to obtain active WOx-TiO_2 catalysts, (Cortes-Jacom et al., 2007). These catalysts were synthesized by impregnating aqueous $(NH_4)_2WO_4$ on hydrous titania nanotubes, followed by annealing in air at 500 °C. After this treatment, the structure of the support was transformed from orthorhombic to tetragonal, yielding anatase nanoparticles decorated by tungsten nanoparticles on their surface. Interestingly, the nanotubes released residual Na^+ ions from the interlayer space, which reacted with tungstate species to change the W coordination from octahedral to tetrahedral (that is exclusively W^{6+} oxidation state). The reaction rate of DBT oxidation by H_2O_2 at 60 °C increased linearly with the W content, reaching the maximum value at W surface density of 6.9 W/nm^2. The turnover rate suggested that isolated W atoms (in tetrahedral coordination) were at least twice as active as octahedral ones. No results on recycling experiments have been reported. TiNTs with either, high sodium content (Na–TiNTs) or in the protonated version (H–TiNTs), have been recently synthesized by alkaline hydrothermal treatment of anatase TiO_2, in order to test the catalytic activity in the oxidation of DBT with H_2O_2, (Lorecon et al., 2014). Interestingly, the catalytic properties appeared to be strongly dependent on the counter-ion present in TiNTs structure: indeed, while Na–TiNTs were found to be inactive, probably due both to low DBT adsorption capacity and low radical production, H–TiNTs showed excellent catalytic performance under the same experimental conditions. Optimization studies showed that high concentrations of H_2O_2, and elevated temperatures, reduced the catalytic activity. Instead, room temperature and a 4:1 ratio H_2O_2/substrate were the most useful operating conditions. H–TiNTs was also recycled for four times without significant decrease in activity, while maintaining very high turnover numbers (about 30.000). Lorecon et al. 2014 observed that *N*-containing compounds (quinolines) may be simultaneously removed within the same reaction. Recent advances in carbon materials have focused on the use of one, two, and three dimensional carbon materials, (Lam & Luong, 2014). Multiwalled carbon nanotubes (MWCNTs) doped with titanium species have been extensively studied, (Chen, Zhang, & Oh, 2009; Woan, Pyrgiotakis, & Sigmund, 2009; Gui et al. 2010). MWCNTs have a large electricity-storage capacity, and therefore, they may accept photon-excited electrons. For these reasons, the combination of MWCNTs with TiO_2 can reduce charge recombination, enhance reactivity and enhance photocatalytic ability of the photoactive species. Such composite materials have been fabricated by various methods like the sol–gel method, (Jitianu, Berger, Benoit, Beguin, & Bonnamy, 2004; Wang, Serp, Kalck, & Faria, 2005) electro-spinning, (Aryal et al., 2008; Cho, Schaab, Roether, Boccaccini, 2008) and electrophoretic deposition, (Corrias et al., 2003). Recently, composites of MWCNTs and TiO_2, with uniform microstructure, were prepared through the heterogeneous gelation method, with the aim of studying their activities in PODS of DBT and 4, 6-DMDBT, in n-tetradecane, and commercial diesel (total sulfur content of 714 ppm). The irradiation was performed with high-pressure Hg lamp at room temperature, (Vu et al., 2012). After treating with the MWCNTs/TiO_2 composite for 120 min, followed by absorption of the sulfone and sulfoxide mixture with silica-gel, the sulfur content in the diesel was completely removed, in comparison to a residual sulfur content of 400 ppm after commercial TiO_2 treatment. This result confirmed the presence of synergic effect between TiO_2 and MWCNTs. Having in mind the issue of increase the recyclability of these types of heterogeneous catalysts for ODS applications, a composite system based on MWCNT supported Cs2.5H0.5$PW_{12}O_{40}$ (Cs2.5H0.5$PW_{12}O_{40}$/MWCNT) by impregnation technique, has been described, (Kozhevnikov, 2002; Wang, Yu, Zhang, & Zhao, 2010).The latter catalyst was very effective for the removal of DBT, with a desulfurization efficiency of up to 100%, using H_2O_2 at 60 °C for less than 3 hours. Noteworthy, after recycling tests, the recovered catalyst showed quite close catalytic activity to that of the fresh one, thus confirming the potential reliability of its use for industrial diesel desulfurization processes. Due to the hydrophobic surface of CNTs, it is difficult to achieve dispersion stability in polar solvents so, their functionalization (with concentrated solution of HNO_3 and H_2SO_4) by introducing oxygenated groups such as OH and COOH, has been reported to increase the wetting characteristics, and consequently, to increase the dispersion of metal particles on their surface (so called functionalized MWCNT, FMWCNT) (Mazov et al., 2012; Kundu, Wang, Xia, & Muhler, 2008). As an example, these oxygenated groups may serve as anchors for metal particles or metal oxides to the CNT surface. The preparation of FMWCNT supported MnOx nanocatalysts (MnOx/FMWCNT) has been reported to investigate their performance in deep desulfurization of sour naphtha with H_2O_2, Meman, Pourkhalil, Rashidi, & Zarenezhad, 2014a). The nanocatalyst was prepared by a wetness impregnation technique, using an appropriate amount of Mn $(NO_3)_{24}H_2O$ as the precursor for MnOx. MnOx/FMWCNT (about 10 wt% of MnOx) showed good performances in ODS, with a sulfur removal efficiency of 99.85% after 30 min at room temperature and atmospheric pressure. The results of recycling experiments confirmed that there was no significant decrease in the catalyst activity even after four runs. The same researchers applied this methodology for the preparation of FMWCNT supported palladium nanocatalyst (Pd/FMWCNT), (Meman, Zarenezhad, Rashidi, Hjjar, & Esmaeili, 2014b). FMWCNTs were impregnated using appropriate amount of aqueous solution of $PdCl_{22}H_2O$, then dried at 110 °C for 2 hours. Under optimized conditions, almost 90% of sulfur components were removed at 25 °C, in 30 min. The heterogeneous nanocatalysts were reusable several times for deep desulfurization of fuel as well. Interestingly, the latter authors compared their quite satisfactory results with those already reported by other groups in previous papers, by impregnating palladium catalysts on different heterogeneous phases such as Al_2O_3, Al_2O_3-MgO and ZrO_2. The results they have obtained proved to be better, in terms of conversions in the oxidation of sulfur compounds, in comparison with those previously reported, (Zapata, Pedraza, & Valenzuela, 2005; Salmones, Galicia, Wang, Valenzuela, & Aguilar-Rios, 2000; Wang et al., 2004).Very recently, CNTs have been proposed as catalysts itself for the ODS in a model fuel containing BT, DBT and 4, 6-DMDBT, (Zhang et al., 2014). CNT alone showed to be selective catalysts, affording the corresponding sulfones for each type of sulfur compounds in following order of reactivity: BT < DBT < 4, 6-DMDBT. By means of X-ray Photoelectron Spectroscopy (XPS), the content of various oxygen-containing functional groups on the surfaces of CNT catalysts, including C=O, –OH and adsorbed water, were quantitatively analyzed. Their molar fractions changed before and after the ODS reaction, thus strongly suggesting their active role in the catalytic process, (Liu, Su, & Schlogl, 2011; Su et al., 2005; Mestl, Maksimova, Keller, Roddatis, & Schlogl, 2001). A reaction mechanism proposed by authors suggested the following steps: i) molecular oxygen gains electrons from surface hydroxyl groups giving rise, simultaneously, to active oxygen species and, carbonyl groups; (ii) DBT is oxidized to $DBTO_2$ by the active oxygen while the carbonyl groups gain electrons to be reduced to hydroxyl groups (Figure 11). In this model, the electron-transport rate is mainly governed by the graphitization degree (that is the ratio between ordered sp2-hybridised and amorphous or disordered carbon atoms) of the CNT, (Begin et al., 2009). This could be due to the fact that higher degrees of graphitization would allow CNTs to have higher electric conductivity. In these conditions, the transfer of electrons involved in the oxidation–reduction reaction should increase, also improving the catalytic activity of the CNTs. CNT sample having a higher degree of graphitization showed the highest catalytic activity in the oxidation of DBT.

Interestingly, authors stated that deactivated CNTs were effectively regenerated by heat treatment under an argon atmosphere, at 900°C, and then recycled with an almost completely recovered catalytic activity. In comparison to conventionally microporous and mesoporous inorganic materials, the MOFs

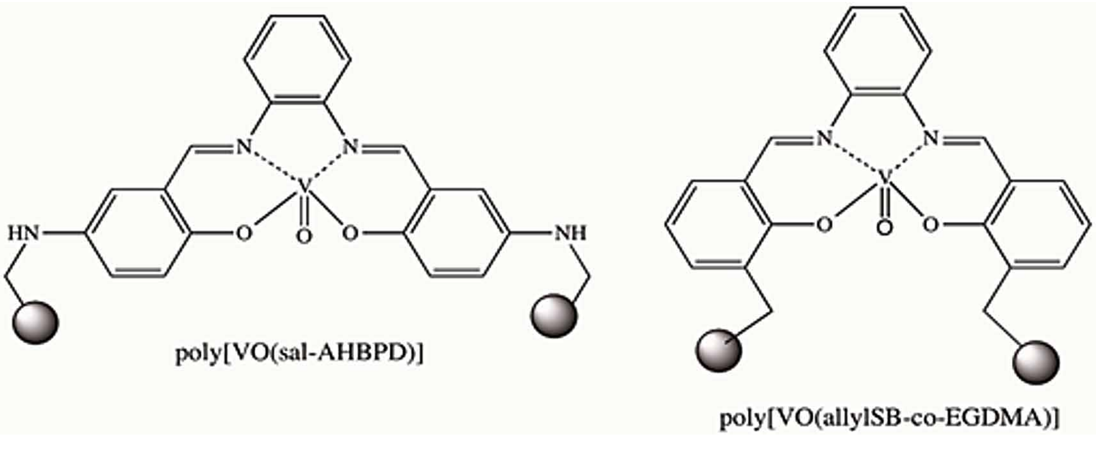
Figure 11. Proposed mechanism for the direct oxidation of DBT with functionalized MWCNTs (FMWCNTs) at 150°C in air



stuctures exhibit the potential for more flexible rational design, by controlling the size and the functionalization of the organic linkers, (Li, Eddaoudi, O'Keeffe, & Yaghi, 1999). In this context, porous materials based on chromium (III) terephthalate metal organic frameworks [Cr-MIL(101)] and their new composites with vanadium oxide has emerged as a potential catalyst because of their high specific surface area, tunable pore size, and unique structure. Recently, a series of mesoporous vanadium containing metal organic framework NR catalysts [V@ MIL (101), 4.2% of vanadium loading] were prepared by wet impregnation method, with the aim to study their activity toward functionalized aryl and alkyl sulfides, with H_2O_2. This catalyst was able to reduce the total sulfur level of commodity gasoline from 1423 g/g to 232 g/g, (Fazaeli, Aliyan, Moghadam, & Masoudinia, 2013). Heterogeneous vanadium containing catalysts, namely polymer-anchored oxovanadium(IV) catalysts like poly-[VO(sal-AHBPD)] and poly[VO(allylSB-co-EGDMA)] (Figure 12), have been also recently published for catalytic oxidation of organosulfur compounds, (Ogunlaja, 2013).

In this paper, the novel polymer-supported systems were employed as catalyst for the oxidation of thiophene (TH), BTH, DBT and 4, 6-DMDBT, with t-BuOOH, under a continuous flow system at 40 °C. These experimental conditions were selected with the aim to combine both the advantages of heterogeneous catalysis and of continuous flow process. Authors observed the maximum conversion values at a flow rate of 1 mL/h, with overall conversions ranging from 71% to 99%, being poly [VO (sal-AHBPD)] the better catalyst. Moreover, the stability of vanadium species within the polymer support (functionalized Merrifield beads) was confirmed for both catalysts by the very low level of vanadium leaching. The catalytic oxidation reactivity followed the order: BTH< 4, 6-DMDBT < DBT, according to the electron density and order of steric hindrance of the organosulfur compounds. After the oxidation, the sulfones were adsorbed using chitosan nanofibers through the hydrogen bonding interaction between sulfone groups and amine or hydroxyl residues of chitosan, as well as the sulfone imprinting properties. In these conditions, up to 84% of sulfones removal was obtained in diesel sample. As well known, sorbents materials such as molecularly imprinted polymers (MIPs) fabricated through imprinting of polymers with specific templates, act as potential adsorbents for the adsorption of these compounds, (Aburto & Le Borgne, 2004). Adsorbents for the selective extraction of sulfone compounds have been described in recent articles referring to cross-linked chitosan microspheres and electrospin produced chitosan

Figure 12. Heterogeneous vanadium containing catalysts, namely polymer-anchored oxovanadium (IV) catalysts like poly-[VO (sal-AHBPD)] and poly[VO(allylSB-co-EGDMA)]



nanofibers. These materials were produced by molecularly imprinted polymer techniques, through the formation of recognition sites which are complementary to benzothiophene sulfone (BTO_2), dibenzothiophene sulfone ($DBTO_2$) and 4,6-dimethyldibenzothiophene sulfone (4,6-$DMDBTO_2$), (Ogunlaja, du Sautoy, Torto, & Tshentu, 2014). The nature of molecular interactions occurring between imprinted chitosan adsorbent and sulfones was investigated by molecular modeling using the density functional theory (DFT). The results confirmed that interactions took place via hydrogen bonding. The molecularly imprinted polymer adsorbents gave better selectivity for the apsorbtion of sulfones with respect to non-imprinted polymers. The properties of molecularly imprinted polybenzimidazole (PBI) nanofibers (prepared by analogous procedure) toward the adsorption of BTO_2, $DBTO_2$ and 4, 6-$DMDBTO_2$ sulfone model compounds, were investigated, (Ogunlaja et al., 2014). Also in this case, DFT studies indicated that hydrogen bond interactions occurred between sulfone oxygen groups and NH moiety of the PBI, along with the positive role of the π–π stacking interactions between both, the benzimidazole and the aromatic sulfone compoundS. PBI nanofibers showed good sulfur removal abilities after continuous flow adsorption, below the limit of detection, corresponding to 2.4 mg/L.

DRAWBACKS DURING THE OXIDATION AND EXTRACTION STEPS

Even if the catalytic ODS efficiency is very high, as witnessed by the examples given in this review, some critical points still have to be solved. There are two major problems associated with ODS. First, the oxidants chosen do not always act selectively. Some oxidants cause unwanted side reactions on other components of the fuel, such as alkenes and aromatic hydrocarbons,that reduce the quantity and quality of the authentic oil, thus lowering the selectivity of the process. The second problem is the selection of a suitable solvent for the extraction of the oxidized sulfur compounds. Aromatic compounds in real fuels have structures that are analogous to sulfur containing substrates like DBT. If these compounds are easily extracted by the solvent, this could decrease the oil recovery. For example, contrasting opinions have been expressed toward acetonitrile that is frequently employed as solvent, due to its synergic action in the extraction−oxidation of DBT, along with a comparatively low dissolving capacity for aromatic compounds, (Tian, Yao, Zhi, Yan, & Lu, 2015). The employment of the wrong solvent may result in removing desirable aromatic/olefinic compounds from the fuel or, alternatively, extracting less than the desired amount of the sulfur compounds from the fuel. The use of ionic liquids to remove sulfur compounds from hydrocarbons by solvent extraction is the object of ongoing research. Most of the publications in this front, however, present two serious drawbacks: they are not based on rigorous thermodynamic data, and they do not consider the effect of the ionic liquid on the different fuel constituents, (Rodriguez-Cabo, Rodriguez, Rodil, Arce, & Soto, 2014). Moreover, adsorption solvents recyclability and recovery becomes challenging due to the similar properties (such as boiling point) that they share with the extracted compounds. Thus, a need to develop materials (adsorbents) that can selectively extract/remove sulfone compounds and be easily recycled is increasingly becoming important. About the catalyst leaching, in the design and application of processes based on the use of metal nanoparticles, the sintering or aggregation of metal nanoparticles is the main drawback leading to the reduction of catalytic activity or complete deactivation of the catalyst, (Chung, Erathodiyil, & Ying, 2013). In addition, irrespective to the nature of the employed catalytic systems, under ODS liquid phase processes, catalyst deactivation can occur due to metal leaching of soluble species, thus affording deactivated systems and vanishing the advantages of catalyst recycling, (Chica et al., 2006). In this review, many selected examples of ODS nanostructured catalysts to illustrate certain principles of catalytic activity enhancement via control of their dispersion, morphology, composition, oxidation state, and interaction with their supports, have been throughout analyzed. Developing various strategies to prevent the aggregation, sintering, or leaching of catalyst nanoparticles represents a stimulating but also a challenging issue for the effective synthesis and utilization of nanoparticles catalysts with desirable dimension and improved catalytic performance, irrespective to the type of catalytic technological process involved. The future of nanocatalyst based research on the ODS field lies in the judicious design and development of nanocomposite catalysts able to be stable and resistant to sintering and leaching, and yet highly active, even after multiple runs. It is highly desirable that, within the very important ODS technology, the research can continue especially for what it concerns the designing and finding of the most appropriate environment friendly and selective catalytic conditions, provided that the high fuel quality is maintained, (Scrivastava, 2012).

BIODESULFURIZATION (BDS)

So far, also biological methods have shown good potential for deep desulfurization of fuels. They can be classified as aerobic or anaerobic procedures depending on the nature of microorganism selected for the treatment. Irrespective to conditions applied, the reaction can proceed by aromatic degradation without sulfur removal or by removal of sulfur with production of H_2S or other sulfur low molecular weight derivatives, (Soleimani, Bassi, & Margaritis, 2007; Mohebali & Ball, 2008). The anaerobic desulfurization of aromatic sulfur derivatives such as BT and DBT with production of H_2S has been obtained using different anaerobic strains, including *Desulforibrio desulfurican*s, (H.Y. Kim, T. S. Kim, & B. H. Kim, 1990) *Desulfomicrobium scambium*, and *Desulforibrio long reachii*, (Yamada, Minoda, Kodama, Nakatani, & Aesaki, 1998; Yamada, Morimoto, & Tani, 2001) Usually the reaction proceeds through reduction of the thiophene ring and formation of biphenyl as the main product. Unfortunately, anaerobic processes are expensive and require difficult conditions to maintain active the microbial strains, (Armstrong, Samkey, & Voordan, 1995).

Aerobic Desulfurization

In principle, the aerobic desulfurization affords the degradation of aromatic moieties with retention of sulfur in the products (the so called destructive biodesulfurization) or by removal of high-oxidation sulfur derivatives from the starting molecule (specific oxidative desulfurization). Figure 13 reports the Kodama aerobic destructive pathway described for the treatment of DBT with *Pseudomonas* species, (Gupta & Raychondhury, 2005; Hartdegen, Cobrun, & Roberts, 1984). Briefly, the oxidation of the phenyl ring yield a catechol intermediate (A) which is further oxidized with concomitant ring-opening and side-chain scission to afford 3-hydroxy-2-formyl-benzothiophene (HFBT) and pyruvic acid (PA). Alkyl substituted DBT derivatives are recalcitrant to this degradation probably due to steric hindrance during the first hydroxylation step, (Kropp, Anderson, & Fedorak, 1997). Unfortunately the accumulation of water-soluble highly oxidized metabolites can determine the inhibition of microbial growth.

The general scheme for specific oxidative desulfuration, as proposed by Kilbane, is reported in Figure 14, (Kilbane, 1989). In this latter case DBT is oxidized to corresponding sulfoxide DBT(SO)

Figure 13. Schematic representation of the Kodama aerobic DBT destructive pathway

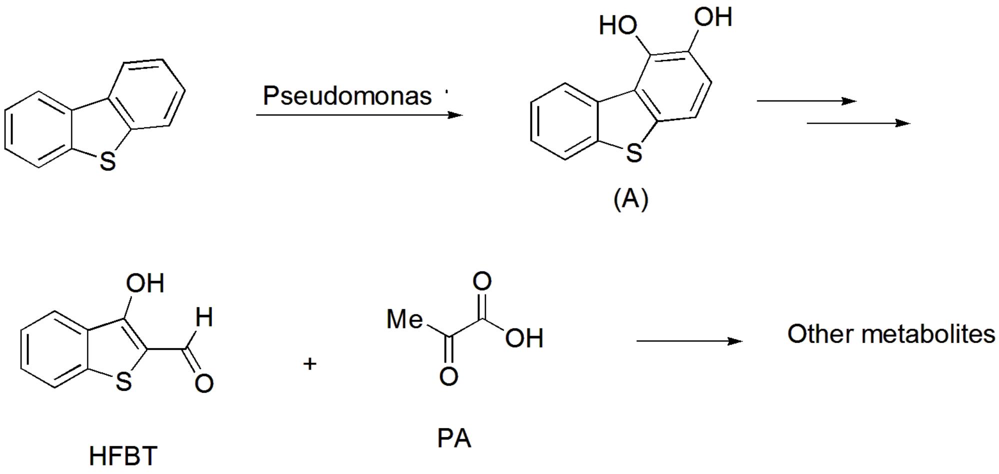
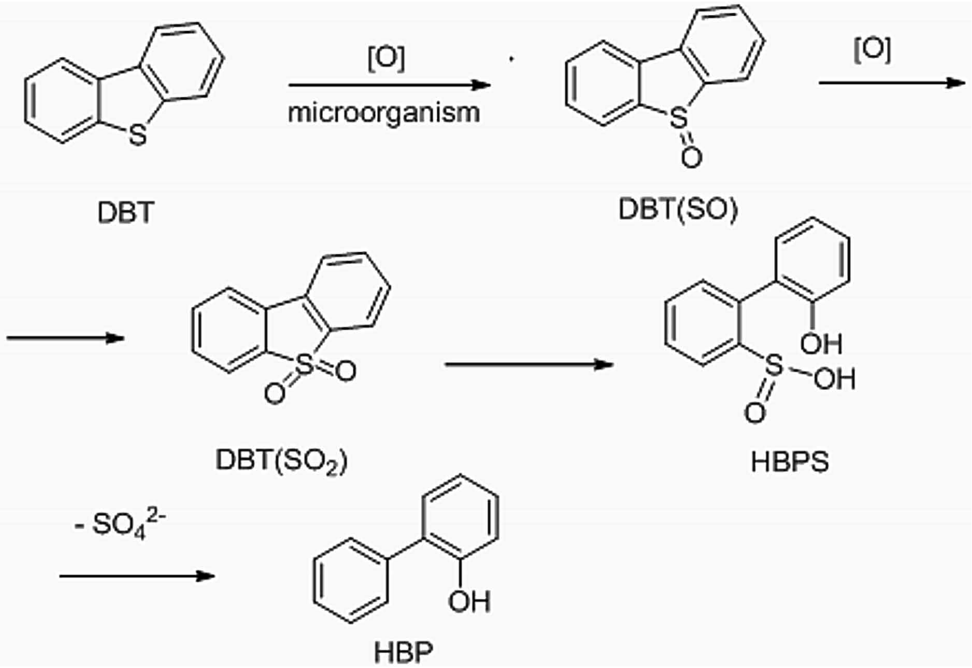


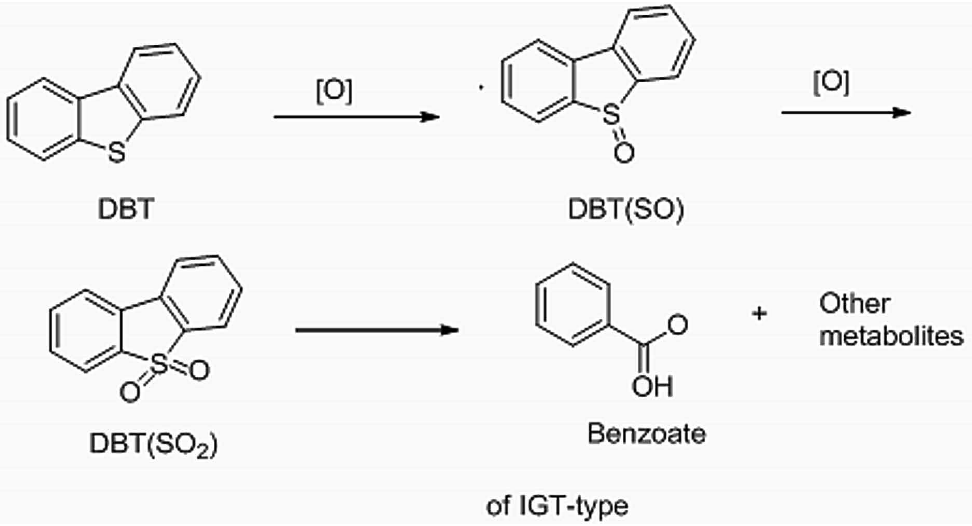
Figure 14. The oxidative biodesulfuration scheme as proposed by Kilbane



and sulfone DBT(SO_2) derivatives, followed by ring opening of the thiophene moiety with formation of a biphenyl sulphinic acid intermediate (HBPS) and final removal of inorganic sulfate (SO_4^{2-}) to yield hydroxybiphenyl derivative (HBP).

Alternatives for this reaction pathway have been reported by conversion of DBT (SO_2) to benzoate using *Brevibacterium sp*. (Afferden, Schacht, Klein, & Truper, 1990) and *Arthrobacter s*p. K_3b (DBTS_2), (Noijiri, Habe, & Omori, 2001). In other cases, as in the case of *Cunnighamella elegans*, the oxidation at the DBT (SO_2) step and sulfur could not be detached from the molecule (Figure 15), (Crawford & Gupta, 1990).

Figure 15. Oxidation scheme of DBT with Cunnighamella elegans



Highly efficient specific aerobic desulfurization were obtained with *Rhodococcus rhodochrou*s and *Bacillus sphaericus* strains by mutation procedures after treatment of native microorganism with 1-methyl-3-nitro-1-nitrosoguanidine, (Kilbane, 1996). These strains showed a selective oxidation of the C-S moiety removing up-to 90% of the total sulfur in the sample, (Kilbane & Jackowski, 1992). In these process, the accumulation of sulfate ion or HBP in the reaction medium could suppress desulfurization when the whole cells are used for the oxidation, (Oshiro, Hirata, & Izumi, 1996). On the other hand, isolated desulfurization enzymes usually show a low activity, (Oshiro, Kanbayashi, Hine, & Izumi, 1995). In particular, the conversion of DBT to DBT (SO), and that of DBT (SO) to DBT (SO_2) is catalyzed by two closely associated enzymes; NAD(P)H:FMN oxidoreductase and monooxygenase, (Xi, Squires Monticello, & Childs, 1997). Other strains such as *Rhodococcus erythropolis H-2* and *Microbacterium sp. ZD-M2* showed a relatively high efficiency in the oxidation of substituted DBT derivatives, including 3,4-benzoDBT, 2,8-DMDBT and 4,6-DMDBT, (Oshiro, Hirata, Hashimoto, & Izumi, 1996; Li, Zhang, Wang, & Shi, 2005). Even if *Rhodococcus erythropolis* IGTS8 is the bacteria mostly used for desulfurization processes, the overall reaction is energetically expansive due to the requirement of high reducing equivalents to support the oxidative steps. Genetically modified organisms can solve this problem. Thus, chimera have been produced starting from *Pseudomonas* introducing genes cloned from *Rhodococcus erytropolis IGTS8* and the flavinoxido reductase (hpaC) (to catalyze $FMNH_2$ production) from *Escherichia coly*, (Caro, Baltes, Leton, & Garcia-Calvo, 2007). This strain showed a significant enhancement of the DBT desulfurization efficacy in both aqueous and biphasic media, using hexadecane as model oil. While inhibition effects by products accumulation were observed in aqueous media, the activity was stable in the biphasic system. Noteworthy, *Rodococcus rhodochrous* strain was used in desulfurization of DBT also after immobilization on silica bed. In this latter experimental conditions the highest conversion of DBT was obtained with a long catalytic bed, larger dimension of silica particles and lower substrate flow in the reactor. As expected for heterogeneous conditions, the *Rhodococcu*s cells were recovered at the end of the oxidation and used for more transformations, (Dinamarca et al., 2014).

CONCLUSION

The ODS process is a valid alternative to HDS, especially in the case of fuels which are rich in aromatic sulphides, such as BT, DBT and derivatives thereof. Many of the nanosized catalysts reported in the literature are effective for the deep removal of sulfur, even in the presence of complex mixtures. The specific properties associated with their nanosize ensure high reactivity and efficiency compared to systems that are qualitatively similar but of larger size. The high number of catalysts described in the literature does not allow the easy comparison between their structure and the efficiency observed in ODS, although some general considerations can be made. First, the shape of the catalyst does not seem to be a crucial parameter for the efficiency in the oxidation. Nanocomposites, nanoparticles and nanotubes are all generally very active in the oxidation of sulfur derivatives. The main role of the shape of the catalyst might be envisaged in relation to the operating conditions of the catalytic bed and in the specific operative units of the plant, but only few data are available about this topic. As a general trend, the catalysts that are characterized by the presence of selective recognition sites for sulphur derivatives (e.g. Au sites), in addition to normal reactive sites, offer greater efficiency measured in terms of reaction times, conversion and reaction temperature. In a similar way, the systems that employ extracting solvents are generally more active than those lacking it. The processes of leaching is usually very limited, probably due to high stability of the catalysts. Despite the fact that the secondary reactions, which can significantly reduce the quality of the fuel, are rarely declared, it is reasonable to expect that alkenes, alkynes, and the same aromatic hydrocarbons, are significantly oxidized, especially in the case of catalysts able to produce radical species as reaction intermediates. This aspect certainly requires more attention. Next to chemical catalysis, the BDS represents a further alternative for the processes of ODS. Many advances have been achieved thanks to the application of selection techniques and genetic engineering,that significantly improve the yields of the processes. Indeed, problems remain to be solved, especially in the optimization of plant processes, so that the BDS becomes a highly efficient procedure.

REFERENCES

Aburto, J., & Le Borgne, S. (2004). Selective Adsorption of Dibenzothiophene Sulfone by an Imprinted and Stimuli-Responsive Chitosan Hydrogel. *Macromolecules*, *37*(8), 2938–2943. doi:10.1021/ma049961e

Afferden, van M., Schacht, S., Klein, J., & Truper, H. G. (1990). Degradation of dibenzothiophene by Brevibacterium s.p. DO. *Archives of Microbiology, 153*, 324-328.

Aguiar, A., Ferraz, A., Contreras, D., & Rodriguez, J. (2007). Mechanism and applications of the Fenton reaction assisted by iron-reducing phenolic compounds. *Quimica Nova*, *30*, 623–628. doi:10.1590/S0100-40422007000300023

Antcliff, K. L., Murphy, D. M., Griffiths, E., & Giamello, E. (2003). The interaction of H2O2 with exchanged titanium oxide systems (TS-1, TiO2, Ti–APO-5, Ti–ZSM-5). *Physical Chemistry Chemical Physics*, *5*(19), 4306–4316. doi:10.1039/b306398b

Armstrong, S. M., Samkey, B. M., & Voordan, G. (1995). Conversion of dibenzothiophene to biophenyl by sulfate reducing bacteria isolated from oil field production facilities. *Biotechnology Letters*, *17*(10), 1133–1136. doi:10.1007/BF00143117

Aryal, S., Kim, C. K., Kim, K. W., Khil, M. S., & Kim, H. Y. (2008). Multi-walled carbon nanotubes/TiO2 composite nanofiber by electrospinning. *Materials Science and Engineering C*, *28*(1), 75–79. doi:10.1016/j.msec.2007.10.002

Babich, I. V., & Moulijn, J. A. (2003). Science and technology of novel processes for deep desulfurization of oil refinery stream: A review. *Fuel*, *82*(6), 607–631. doi:10.1016/S0016-2361(02)00324-1

Bae, Y. S., Lee, C. Y., Kim, K. C., Farha, O. K., Nickias, P., & Hupp, J. T. … Goddard, W. A. (2007). Improved Designs of Metal–Organic Frameworks for Hydrogen Storag. Angewandte Chemie International Edition, 46, 6289-6292.

Balula, S. S., Cunha-Silva, L., Santos, I. C. M. S., Estrada, A. C., Fernandes, A. C., & Cavaleiro, A. M. V. et al. (2013). Mono-substituted silicotungstates as active catalysts for sustainable oxidations: Homo- and heterogeneous performance. *New Journal of Chemistry*, *37*(8), 2341–2350. doi:10.1039/c3nj00243h

Balzani, V., Credi, A., & Venture, M. (2008). Photochemical conversion of solar energy. *ChemSusChem*, *1*(1-2), 26–58. doi:10.1002/cssc.200700087 PMID:18605661

Bavykin, D. V., Friedrich, J. M., & Walsh, F. C. (2006). Protonated titanates and TiO2 nanostructured materials: Synthesis, properties, and applications. *Advanced Materials*, *18*(21), 2807–2824. doi:10.1002/adma.200502696

Bavykin, D. V., Lapkin, A. A., Plucinski, P. K., Torrente-Murciano, L., Friedrich, J. M., & Walsh, F. C. (2006). Deposition of Pt, Pd, Ru and Au on the surfaces of titanate nanotubes. *Topics in Catalysis*, *39*(3-4), 151–160. doi:10.1007/s11244-006-0051-4

Begin, D., Ulrich, G., Amadou, J., Su, D. S., Pham-Huu, C., & Ziessel, R. (2009). Oxidative dehydrogenation of 9, 10-dihydroanthracene using multi-walled carbon nanotubes. *Journal of Molecular Catalysis A Chemical*, *302*(1-2), 119–123. doi:10.1016/j.molcata.2008.12.006

Boikov, E. V., Vakhrushim, P. A., & Vishnetskaya, M. V. (2008). Oxidative desulfurization of hydrocarbon feedstock. *Chemistry and Technology of Fuels and Oils*, *44*(4), 271–274. doi:10.1007/s10553-008-0054-x

Campelo, J. M., Luna, D., Luque, R., Marinas, J. M., & Romero, A. A. (2009). Sustainable preparation of supported metal nanoparticles and their applications in catalysis. *ChemSusChem*, *2*(1), 18–45. doi:10.1002/cssc.200800227 PMID:19142903

Campos-Martin, J. M., Capel-Sanchez, M. C., Perez-Presas, P., & Fierro, J. L. G. (2010). Oxidative process of desulfurization of liquid fuels. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *85*(7), 879–890. doi:10.1002/jctb.2371

Capel-Sanchez, M. C., Campos-Martin, J. M., Fierro, J. L. G., de Frutos, M. P., & Padilla Polo, A. (2000). Effective alkene epoxidation with dilute hydrogen peroxide on amorphous silica-supported titanium catalysts. *Chemical Communications (Cambridge)*, *10*(10), 855–856. doi:10.1039/b000929f

Carati, A., Flego, C., Previde Massara, E., Millini, R., Carluccio, L., Parker, W. O. Jr, & Bellussi, G. (1999). Stability of Ti in MFI and Beta structures: A comparative study. *Microporous and Mesoporous Materials*, *30*(1), 137–144. doi:10.1016/S1387-1811(99)00018-9

Caro, A., Baltes, K., Leton, P., & Garcia-Calvo, E. (2007). Dibenzothiophene biodesulfurization in resting cell conditions by aerobic bacteria. *Biochemical Engineering Journal*, *35*(2), 191–197. doi:10.1016/j.bej.2007.01.013

Cedeño-Caero, L., Ramos-Luna, M., Méndez-Cruz, M., & Ramírez-Solís, J. (2011). Oxidative desulfurization of dibenzothiophene compounds with titania based catalysts. *Catalysis Today*, *172*(1), 189–194. doi:10.1016/j.cattod.2011.01.048

Chen, M. L., Zhang, F. J., & Oh, W. C. (2009). Synthesis, characterization, and photocatalytic analysis of CNT/TiO2 composites derived from MWCNTs and titanium sources. *New Carbon Materials*, *24*(2), 159–166. doi:10.1016/S1872-5805(08)60045-1

Chen, Y., Zhang, F., Fang, Y., Zhu, X., Zhen, W., Wang, R., & Ma, J. (2013). Phosphotungstic acid containing ionic liquid immobilized on magnetic mesoporous silica rod catalyst for the oxidation of dibenzothiophene with H2O2. *Catalysis Communications*, *38*, 54–58. doi:10.1016/j.catcom.2013.04.005

Chen, Y., Zhao, S., & Song, Y. F. (2013). An efficient heterogeneous catalyst based on highly dispersed Na2H2Law10O36· 32 H2O nanoparticles on mesoporous silica for deep desulfurization. *Applied Catalysis A, General*, *466*, 307–314. doi:10.1016/j.apcata.2013.06.030

Chica, A., Corma, A., & Dómine, M. E. (2006). Catalytic oxidative desulfurization (ODS) of diesel fuel on a continuous fixed-bed reactor. *Journal of Catalysis*, *242*(2), 299–308. doi:10.1016/j.jcat.2006.06.013

Cho, J., Schaab, S., Roether, J., & Boccaccini, A. R. (2008). Nanostructured carbon nanotube/TiO2 composite coatings using electrophoretic deposition (EPD). *Journal of Nanoparticle Research*, *10*(1), 99–105. doi:10.1007/s11051-007-9230-x

Chung, L. L., Erathodiyil, N., & Ying, J. Y. (2013). Nanostructured Catalysts for Organic Transformations. *Accounts of Chemical Research*, *46*(8), 1825–1837. doi:10.1021/ar300197s PMID:23350747

Ciclosi, M., Dinoi, C. C., Gonsalvi, L., Peruzzini, M., Monoury, E., & Poli, R. (2008). Oxidation of Thiophene Derivatives with H2O2 in Acetonitrile Catalyzed by [Cp*2M2O5] (M = Mo, W): A Kinetic Study. *Organometallics*, *27*(10), 2281–2286. doi:10.1021/om800035f

Corrias, M., Caussat, B., Ayral, A., Durand, J., Kihn, Y., Kalck, P., & Serp, P. (2003). Carbon nanotubes produced by fluidized bed catalytic CVD: First approach of the process. *Chemical Engineering Science*, *58*(19), 4475–4482. doi:10.1016/S0009-2509(03)00265-3

Cortes-Jácome, M. A., Morales, M., Angeles Chavez, C., Ramírez-Verduzco, L. F., López-Salinas, E., & Toledo-Antonio, J. A. (2007). WOx/TiO2 Catalysts via Titania Nanotubes for the Oxidation of Dibenzothiophene. *Chemistry of Materials*, *19*(26), 6605–6614. doi:10.1021/cm702010k

Costa, R. C. C., Moura, F. C. C., Ardisson, J. D., Fabris, J. D., & Lago, R. M. (2008). Highly active heterogeneous Fenton-like systems based on Fe0/Fe3O4 composites prepared by controlled reduction of iron oxides. *Applied Catalysis B: Environmental*, *83*(1-2), 131–139. doi:10.1016/j.apcatb.2008.01.039

Crawford, D. L., & Gupta, R. K. (1990). Oxidation of dibenzothiophene by Cunnighamella elegans. *Current Microbiology*, *21*(4), 229–231. doi:10.1007/BF02092161

Cui, X., Yao, D., Li, H., Yang, J., & Hu, D. (2012). Nano-magnetic particles as multifunctional microreactor for deep desulfurization. *Journal of Hazardous Materials*, *205*, 17–23. doi:10.1016/j.jhazmat.2011.11.063 PMID:22244972

De Souza, W. F., Guimaraes, I., Guerreiro, M. C., & Oliveira, L. C. A. (2009). Catalytic oxidation of sulfur and nitrogen compounds from diesel fuel. *Applied Catalysis A, General*, *360*(2), 205–209. doi:10.1016/j.apcata.2009.03.023

De Volder, M. F. L., Tawfick, S. H., Baughman, R. H., & Hart, A. J. (2013). Carbon Nanotubes: Present and Future Commercial Applications. *Science*, *339*(6119), 535–539. doi:10.1126/science.1222453 PMID:23372006

Di Giuseppe, A., Crucianelli, M., De Angelis, F., Crestini, C., & Saladino, R. (2009). Efficient oxidation of thiophene derivatives with homogeneous and heterogeneous MTO/H2O2 systems: A novel approach for oxidative desulfurization (ODS) of diesel fuel. *Applied Catalysis B: Environmental*, *89*(1-2), 239–245. doi:10.1016/j.apcatb.2009.02.009

Dinamarca, A. M., Orellana, L., Aguirre, J., Baeza, P., Espinoza, G., Canales, C., & Ojeda, J. (2014). Biodesulfurization of dibenzothiophene and gas oil using a bioreactor containing a catalytic bed with Rhodococcus rhodochrous immobilized on silica. *Biotechnology Letters*, *36*(8), 1649–1652. doi:10.1007/s10529-014-1529-y PMID:24748430

Elmolla, E. S., Chaudhure, M., & Eltoukhy, M. M. (2010). The use of artificial neural network (ANN) for modeling of COD removal from antibiotic aqueous solution by fenton process. *Journal of Hazardous Materials*, *179*(1-3), 127–134. doi:10.1016/j.jhazmat.2010.02.068 PMID:20307930

Eustis, S., & El-Sayed, M. A. (2006). Why gold nanoparticles are more precious than pretty gold: Noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes. *Chemical Society Reviews*, *35*(3), 209–217. doi:10.1039/B514191E PMID:16505915

Fang, Y., & Hu, H. (2007). Mesoporous TS-1: Nano casting synthesis with CMK-3 as template and its performance in catalytic oxidation of aromatic thiophene. *Catalysis Communications*, *8*(5), 817–820. doi:10.1016/j.catcom.2006.09.018

Fazaeli, R., Aliyan, H., Moghadam, M., & Masoudinia, M. (2013). Nano-rod catalysts: Building MOF bottles (MIL-101 family as heterogeneous single-site catalysts) around vanadium oxide ships. *Journal of Molecular Catalysis A Chemical*, *374*, 46–52. doi:10.1016/j.molcata.2013.03.020

Figueras, F., Palomeque, J., Loridant, S., Feche, C., Essayem, N., & Gelbard, G. (2004). Influence of the coordination on the catalytic properties of supported W catalysts. *Journal of Catalysis*, *226*(1), 25–31. doi:10.1016/j.jcat.2004.05.006

Gatan, R., Barger, P., Gembicki, V., Cavanna, A., & Molinari, D. (2004). Oxidative desulfurization: A new technology for U LSD. *American Chemical Society Fuel Chemistry*, *49*, 577–579.

Giroto, G. A., Guardani, R., Teixeira, A. C. S. C., & Nascimento, C. A. O. (2006). Study on the photo-phenton degradation of polyvininyl alcohol in aqueous solution. *Chemical Engineering and Processing*, *45*(7), 523–532. doi:10.1016/j.cep.2005.12.001

Gokel, G. W., Gerdes, H. M., & Dishong, D. M. (1980). Sulfur Heterocycles. 3. Heterogeneous, Phase Transfer and Acid Catalyzed Potassium Permanganate Oxidation of Sulfides to Sulfones and a Survey of their C-13 NMR Spectra. *The Journal of Organic Chemistry*, *45*, 3634–3639. doi:10.1021/jo01306a019

Gui, X., Wei, J., Wang, K., Cao, A., Zhu, H., & Jia, Y. et al. (2010). Carbon Nanotube Sponges. *Advanced Materials*, *22*(5), 617–621. doi:10.1002/adma.200902986 PMID:20217760

Gupta, N., & Roychondhury, P. K. (2005). Biotechnology of desulfurization of diesel: Prospects and challenges. *Applied Microbiology and Biotechnology*, *66*(4), 356–366. doi:10.1007/s00253-004-1755-7 PMID:15538557

Hartdegen, F. J., Coburn, J. M., & Roberts, R. L. (1984). Microbial desulfurization of petroleum. *Chemical Engineering Progress*, *80*, 63–67.

Herm, Z. R., Wiers, B. M., Mason, J. A., van Baten, J. M., Hudson, M. R., & Zajdel, P. et al. (2013). Separation of hexane isomers in a metal-organic framework with triangular channels. *Science*, *24*(6135), 960–964. doi:10.1126/science.1234071 PMID:23704568

Hermandex-Maldonado, A. J., Yang, F. H., Qi, G. S., & Yang, R. T. (2005). Desulfurization of transportation fuels by pi-complexation sorbents: Cu (I), Ni (II), and Zn (II)-zeolites. *Applied Catalysis B: Environmental*, *56*(1-2), 111–126. doi:10.1016/j.apcatb.2004.06.023

Huang, D., Wang, Y. J., Cui, Y. C., & Luo, G. S. (2008). Direct synthesis of mesoporous TiO2 and its catalytic performance in DBT oxidative desulfurization. *Microporous and Mesoporous Materials*, *116*(1-3), 378–385. doi:10.1016/j.micromeso.2008.04.031

Huang, D., Wang, Y. J., Yang, L. M., & Luo, G. S. (2006). Chemical Oxidation of Dibenzothiophene with a Directly Combined Amphiphilic Catalyst for Deep Desulfurization. *Industrial & Engineering Chemistry Research*, *45*(6), 1880–1885. doi:10.1021/ie0513346

Huang, D., Wang, Y. J., Yang, L. M., & Luo, G. S. (2006). Direct synthesis of mesoporous TiO2 modified with phosphotungstic acid under template free condition. *Microporous and Mesoporous Materials*, *96*(1-3), 301–306. doi:10.1016/j.micromeso.2006.06.040

Hudlicky, M. (1990). *Oxidations in Organic Chemistry. ACS monograph 186* (pp. 252–259). Washington, DC: ACS.

Hulea, V., & Dimitriu, E. (2004). Styrene oxidation with H2O2 over Ti-containing molecular sieves with MFI, BEA and MCM-41 topologies. *Applied Catalysis A, General*, *277*(1-2), 99–106. doi:10.1016/j.apcata.2004.09.001

Hulea, V., Fajula, F., & Bousquet, J. (2001). Mild Oxidation with H2O2 over Ti-Containing Molecular Sieves - A very Efficient Method for Removing Aromatic Sulfur Compounds from Fuels. *Journal of Catalysis*, *198*(2), 179–186. doi:10.1006/jcat.2000.3149

Hussain, F., Hojjati, M., Okamoto, M., & Gorga, R. (2006). Polymer-matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview. *Journal of Composites Material*, *40*(17), 1511–1575. doi:10.1177/0021998306067321

Hwang, T., Bryan, R., Goldsmith, B. R., Peters, B., & Scott, S. L. (2013). Water-Catalyzed Activation of H2O2 by Methyltrioxorhenium: A Combined Computational–Experimental Study. *Inorganic Chemistry*, *52*(24), 13904–13917. doi:10.1021/ic401343m PMID:24261486

Ismagilov, Z., Yashnik, S., Kerzhentsev, M., Parman, V., Bourane, A., Al-Shahrani, A. A., & Koseoglu, O. R. (2011). Oxidative desulfurization of hydrocarbon fuels. *Catalysis Reviews. Science and Engineering*, *53*(3), 199–255. doi:10.1080/01614940.2011.596426

Jitianu, T. C. A., Berger, M., Benoit, R., Béguin, F., & Bonnamy, S. (2004). New carbon multiwall nanotubes–TiO2 nanocomposites obtained by the sol–gel method. *Journal of Non-Crystalline Solids*, *345*, 596–600. doi:10.1016/j.jnoncrysol.2004.08.104

Jordana, J., Jacobb, K. I., Tannenbaumc, R., Sharafb, M. A., & Jasiukd, I. (2005). Experimental trends in polymer nanocomposite: A review. *Materials Science and Engineering A*, *393*(1-2), 1–11. doi:10.1016/j.msea.2004.09.044

Jun, S., Joo, S. H., Ryoo, R., Kruk, M., Jaroniec, M., & Liu, Z. et al. (2000). Synthesis of New, Nanoporous Carbon with Hexagonally Ordered Mesostructure. *Journal of the American Chemical Society*, *122*(43), 10712–10713. doi:10.1021/ja002261e

Kasuga, T., Hiramatsu, M., Hoson, A., Sekino, T., & Niihara, K. (1998). Formation of Titanium Oxide Nanotube. *Langmuir*, *14*(12), 3160–3163. doi:10.1021/la9713816

Kiatkittipong, K., Scott, J., & Amal, R. (2011). Hydrothermally synthesized titanate nanostructures: Impact of heat treatment on particle characteristics and photocatalytic properties. *ACS Applied Materials & Interfaces*, *3*(10), 3988–3996. doi:10.1021/am2008568 PMID:21939232

Kilbane, J. J. (1989). Desulfuration of coal: The microbial solution. *Trends in Biotechnology*, *7*(4), 97–101. doi:10.1016/0167-7799(89)90007-3

Kilbane, J. J., II. (1996). Enzyme from Rhodococcus rhodochrous ATCC 53968, Bacillus sphaericus ATCC 53969 or a mutant thereof for cleavage of organic C-S bonds. US patent number 5, 516, 677.

Kilbane, J. J. II, & Jackowski, K. (1992). Biodesulfurization of water soluble coal-derived material by Rhodococcus rhodochrous IGTS8. *Biotechnology and Bioengineering*, *40*(9), 1107–1114. doi:10.1002/bit.260400915 PMID:18601220

Kim, H. Y., Kim, T. S., & Kim, B. H. (1990). Degradation of organic compounds and the reduction of dibenzothiophene to biphenyl and hydrogen sulfide by Desulforibrio desulfuricans M6. *Biotechnology Letters*, *12*(10), 761–764. doi:10.1007/BF01024736

Kim, J., Lee, J. E., Yu, J. H., Kim, B. C., An, K., & Hwang, Y. et al. (2006). Magnetic fluorescent delivery vehicle using uniform mesoporous silica spheres embedded with mono disperse magnetic and semiconductor nanocrystals. *Journal of the American Chemical Society*, *128*(3), 688–689. doi:10.1021/ja0565875 PMID:16417336

Kim, J., McNamara, N. D., Her, T. H., & Hicks, J. C. (2013). Carbothermal reduction of Ti-modified IRMOF-3: An adaptable synthetic method to support catalytic nanoparticles on carbon. *ACS Applied Materials & Interfaces*, *5*(21), 11479–11487. doi:10.1021/am404089v PMID:24111792

Kim, T. W., Kim, M. J., Kleitz, F., Nair, M. M., Guillet-Nicolas, R., & Jeong, K. E. et al. (2012). Tailormade mesoporous Ti-SBA-15 catalysts for oxidative desulfurization of refractory aromatic sulfur compounds in transport fuel. *ChemCatChem*, *4*(5), 687–697. doi:10.1002/cctc.201100417

Kitano, M., Nakajima, K., Kondo, J. N., Hayashi, S., & Hara, M. (2010). Protonated titanate nanotubes as solid acid catalyst. *Journal of the American Chemical Society*, *132*(19), 6622–6623. doi:10.1021/ja100435w PMID:20426412

Kluge, R., Schulz, M., & Liebsch, S. (1996). Sulfonic peracids – III. Heeteroatom oxidation and chemoselectivity. *Tetrahedron*, *52*(16), 5773–5782. doi:10.1016/0040-4020(96)00202-5

Kong, L. Y., Li, G., & Wang, X. S. (2004). Mild oxidation of thiophene over TS-1/H2O2. *Catalysis Today*, *93*, 341–345. doi:10.1016/j.cattod.2004.06.016

Kong, L. Y., Li, G., Wang, X. S., & Wu, B. (2006). Oxidative desulfurization of organic sulfur in gasoline over Ag/TS-1. *Energy & Fuels*, *20*(3), 896–902. doi:10.1021/ef050252r

Kozhevnikov, I. V. (Ed.). (2002). *Catalysts for Fine Chemical Synthesis, Catalysis by Polyoxometalates* (Vol. 2). Chichester: John Wiley & Sons.

Kropp, K. G., Anderson, J. K., & Fedorak, P. M. (1997). Biotrasformations of three dimethyl dibenzothiophenes by pure and mixed bacterial cultures. *Environmental Science & Technology*, *31*(5), 1547–1554. doi:10.1021/es960869a

Kubata, Y., Koyama, Y., Yamada, T., Imagaki, S., & Tatsumi, T. (2008). Synthesis and catalytic performance of Ti-MCM-68 for effective oxidation reactions. *Chemical Communications (Cambridge)*, *46*(46), 6224–6226. doi:10.1039/b814286f PMID:19082127

Kubota, A., & Takeuchi, H. (2004). An Unexpected Incident with m-CPBA. *Organic Process Research & Development*, *8*(6), 1076–1078. doi:10.1021/op049825+

Kumar, S., Kumar, R., & Bandopadhyay, A. (2006). Innovative methodologies for the utilisation of wastes from metallurgical and allied industries. *Resources, Conservation and Recycling*, *48*(4), 301–314. doi:10.1016/j.resconrec.2006.03.003

Kundu, S., Wang, Y., Xia, W., & Muhler, M. (2008). Thermal Stability and Reducibility of Oxygen-Containing Functional Groups on Multiwalled Carbon Nanotube Surfaces: A Quantitative High-Resolution XPS and TPD/TPR Study. *The Journal of Physical Chemistry C*, *112*(43), 16869–16878. doi:10.1021/jp804413a

Lam, E., & Luong, J. H. T. (2014). Carbon Materials as Catalyst Supports and Catalysts in the Transformation of Biomass to Fuels and Chemicals. *ACS Catalysis*, *4*(10), 3393–3410. doi:10.1021/cs5008393

Li, F. T., Liu, Y., Sun, Z. M., Chen, L. J., Zhao, D. S., Liu, R. H., & Kou, C. G. (2010). Deep Extractive Desulfurization of Gasoline with xEt3NHCl·FeCl3 Ionic Liquids. *Energy & Fuels*, *24*(8), 4285–4289. doi:10.1021/ef100408h

Li, F. T., Liu, Y., Sun, Z. M., Zhao, Y., Liu, R. H., Chen, L. J., & Zhao, D. S. (2012). Photocatalytic oxidative desulfurization of dibenzothiophene under simulated sunlight irradiation with mixed-phase Fe2O3 prepared by solution combustion. *Catalysis Science and Technology*, *2*(7), 1455–1462. doi:10.1039/c2cy00485b

Li, H., Eddaoudi, M., O'Keeffe, M., & Yaghi, O. M. (1999). Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature*, *402*(6759), 276–279. doi:10.1038/46248

Li, Q., Li, G., & Sun, H. (2014). Synthesis of hierarchical TS-1 with convenient separation and the application for the oxidative desulfurization of bulky and small reactants. *Fuel*, *130*, 70–75. doi:10.1016/j.fuel.2014.04.042

Li, Q., Li, G., & Sun, H. (2014). Synthesis of hierarchical TS-1 with convenient separation and the application for the oxidative desulfurization of bulky and small reactants. *Fuel*, *130*, 70–75. doi:10.1016/j.fuel.2014.04.042

Li, W., Zhang, Y., Wang, M. D., & Shi, Y. (2005). Biodesulfurization of dibenzothiophene and other organic sulfur compounds by a newly isolated microbacterium strain 2D-M2. *FEMS Microbiology Letters*, *247*(1), 45–50. doi:10.1016/j.femsle.2005.04.025 PMID:15927746

Lin, F., Wang, D. E., Jiang, Z. H., Ma, Y., Li, J., Li, R. G., & Li, C. (2012). Photocatalytic oxidation of thiophene on Bi VO4 with dual co-catalysts Pt and RuO2 under visible light irradiation using molecular oxygen as oxidant. *Energy Environmental Science*, *5*(4), 6400–6406. doi:10.1039/C1EE02880D

Liu, X., Su, D. S., & Schlögl, R. (2008). Oxidative dehydrogenation of 1-butene to butadiene over carbon nanotube catalysts. *Carbon*, *46*(3), 547–549. doi:10.1016/j.carbon.2007.12.014

Lorençon, E., Alves, D. C. B., Krambrock, K., Ávila, E. S., Resende, R. R., Ferlauto, A. S., & Lago, R. M. (2014). Oxidative desulfurization of dibenzothiophene over titanate nanotubes. *Fuel*, *132*, 53–61. doi:10.1016/j.fuel.2014.04.020

Maity, U., Basu, J. K., & Sengupta, S. (2013). A neural network prediction of conversion of benzothiopene oxidation catalyzed by nano-Ti-beta catalyst. *Fuel*, *113*, 180–186. doi:10.1016/j.fuel.2013.05.079

Manias, E., Touny, A., Wu, L., Strawhecker, K., Lu, B., & Chung, T. C. (2001). Polypropylene/Montmorillonite Nanocomposites. Review of the Synthetic Routes and Materials. *Properties Chemical Materials*, *13*(10), 3516–3523. doi:10.1021/cm0110627

Mazov, I., Kuznetsov, V. L., Simonova, I. A., Stadnichenko, A. I., Ishchenko, A. V., & Romanenko, A. I. et al. (2012). Oxidation behavior of multiwall carbon nanotubes with different diameters and morphology. *Applied Surface Science*, *258*(17), 6272–6280. doi:10.1016/j.apsusc.2012.03.021

Meman, N. M., Pourkhalil, M., Rashidi, A., & Zarenezhad, B. (2014). Synthesis, characterization and operation of a functionalized multi-walled CNT supported MnOx nanocatalyst for deep oxidative desulfurization of sour petroleum fractions. *Journal of Industrial and Engineering Chemistry*, *20*(6), 4054–4058. doi:10.1016/j.jiec.2014.01.004

Meman, N. M., Zarenezhad, B., Rashidi, A., Hajjar, Z., & Esmaeili, E. (in press). Application of palladium supported on functionalized MWNTs for oxidative desulfurization of naphtha. *Journal of Industrial and Engineering Chemistry*.

Mestl, G., Maksimova, N. I., Keller, N., Roddatis, V. V., & Schlögl, R. (2001). Carbon Nanofilaments in Heterogeneous Catalysis: An Industrial Application for New Carbon Materials? *Angewandte Chemie International Edition*, *40*(11), 2066–2068. doi:10.1002/1521-3773(20010601)40:11<2066::AID-ANIE2066>3.0.CO;2-I PMID:11433444

Mohebali, G., & Ball, S. A. (2008). Biocatalytic desulfurization (BDS) of petrodiesel fuels. *Microbiology*, *154*(8), 2169–2183. doi:10.1099/mic.0.2008/017608-0 PMID:18667551

Moreau, P., Hulea, V., Gomez, S., Brunel, D., & Di Renzo, F. (1997). Oxidation of sulfoxides to sulfones by hydrogen peroxide over Ti-containing zeolites. *Applied Catalysis A, General*, *155*(2), 253–263. doi:10.1016/S0926-860X(96)00400-0

Moura, F. C. C., Araujo, M. H., Costa, R. C. C., Fabrisa, J. D., Ardisson, J. D., Macedo, W. A. A., & Lago, R. M. (2005). Efficient use of Fe metal as an electron transfer agent in a heterogeneous Fenton system basedon Fe0/Fe3O4 composites. *Chemosphere*, *60*(8), 1118–1123. doi:10.1016/j.chemosphere.2004.12.076 PMID:15993160

Nagaveni, K., Hegde, M. S., Ravishan-Kar, N., Subbanna, G. N., & Madras, G. (2004). Synthesis and structure of nanocrystalline TiO2 with lower band gap showing high photocatalytic activity. *Langmuir*, *20*(7), 2900–2907. doi:10.1021/la035777v PMID:15835170

Napanang, T., & Sooknoi, T. (2009). Oxidative extraction of thiophene from n-dodecane over TS-1 in continuous process: A model for non-severe sulfur removal from liquid fuels. *Catalysis Communications*, *11*(1), 1–6. doi:10.1016/j.catcom.2009.07.022

Neves, C. S., Granadeiro, C. M., Cunha-Silva, L., Ananias, D., Gago, S., Feio, G., & Pereira, E. (2013). Europium polyoxometalates encapsulated in silica nanoparticles-characterization and photoluminescence studies. *European Journal of Inorganic Chemistry*, *16*(16), 2877–2886. doi:10.1002/ejic.201201482

Nikolas, I. K., Stergiade, M., Papadopoulou, M. P., & Karatzas, G. P. (2008). Artificial neural networks as an alternative approach to groundwater modeling and environmental design. *Hydrological Processes*, *22*(17), 3337–3348. doi:10.1002/hyp.6916

Nogueira, R. F. P., Trovò, A. G., da Silva, M. R. A., Villa, R. D., & de Oliveira, M. C. (2007). Fundaments and environmental application of fenton and photofenon processes. *Quimica Nova*, *30*, 400–408. doi:10.1590/S0100-40422007000200030

Noguera, L. S., Ribeiro, S., Granadeiro, C. M., Pereira, E., Feio, G., Cunha-Silva, L., & Balula, S. S. (2014). Novel polyoxometalate silica nano-sized sphere: Efficient catalysts for olefin oxidation and the deep desulfurization process. *Dalton Troins*, *43*(25), 9518–9528. doi:10.1039/c3dt53444h

Noh, J., Jang, S., Lee, D., Shin, S., Ko, Y. J., Ito, E., & Joo, S. W. (2007). Abnormal adsorption behavior of dimethyl disulfide on gold surfaces. *Current Applied Physics*, *7*(6), 605–610. doi:10.1016/j.cap.2006.12.007

Noijiri, H., Habe, H., & Omori, T. (2001). Bacterial degradation of aromatic compounds via angular dioxygenation. *The Journal of General and Applied Microbiology*, *47*(6), 279–305. doi:10.2323/jgam.47.279 PMID:12483604

Ogunlaja, A. S., Coombes, M. J., Torto, N., & Tshentu, Z. R. (2014). The adsorptive extraction of oxidized sulfur-containing compounds from fuels by using molecularly imprinted chitosan materials. *Reactive & Functional Polymers*, *81*, 61–76. doi:10.1016/j.reactfunctpolym.2014.04.006

Ogunlaja, A. S., du Sautoy, C., Torto, N., & Tshentu, Z. R. (2014). Design, fabrication and evaluation of intelligent sulfone-selective polybenzimidazole nanofibers. *Talanta*, *126*, 61–72. doi:10.1016/j.talanta.2014.03.035 PMID:24881535

Ogunlaja, A. S., Walmsley, R. S., du Sautoy, C., Torto, N., Zenixole, R., & Tshentu, Z. R. (2013). Development of a Continuous Flow System for the Oxidative Desulfurization of Refractory Organosulfur Compounds in Hydrotreated Diesel. *Energy & Fuels*, *27*(12), 7714–7723. doi:10.1021/ef401708f

Ohshiro, T., Hirata, T., Hashimoto, I., & Izumi, Y. (1996). Characterization of dibenzothiophene desulfurization reaction by whole cell of Rhodococcus erythropolis H-2 in the presence of hydrocarbons. *Journal of Fermentation and Bioengineering*, *82*(6), 610–612. doi:10.1016/S0922-338X(97)81264-0

Ohshiro, T., Hirata, T., & Izumi, Y. (1996). Desulfurization of dibenzothiophene derivatives by whole cells of Rhodococcus erythropolis H-2. *FEMS Microbiology Letters*, *142*(1), 65–70. doi:10.1111/j.1574-6968.1996.tb08409.x

Oliveira, A. A., Teixeira, I. F., Leandro, P., Ribeiro, E. L., Lorencon, E., Ardisson, J. D., & Moura, C. C. (2013). Magnetic amphiphilic nanocomposites produced via chemical vapor deposition of CH4 on Fe-Mo/nano-Al2O3. *Applied Catalysis A, General*, *456*, 126–134. doi:10.1016/j.apcata.2013.02.027

Oshiro, T., Kanbayashi, Y., Hine, Y., & Izumi, Y. (1995). Involvment of flavin coenzyme in dibenzothiophene degrading enzyme system from Rhodococcus erythropolis D-1. *Bioscience, Biotechnology, and Biochemistry*, *59*(7), 1349–1351. doi:10.1271/bbb.59.1349

Otsuki, S., Nonaka, T., Takashima, N., Qian, W. H., Ishihara, A., Imai, T., & Kabe, T. (2000). Oxidative desulfurization of light gas oil and vacuum gas oil by oxidation and solvent extraction. *Energy & Fuels*, *14*(6), 1232–1239. doi:10.1021/ef000096i

Pasquali, L., Terzi, F., Montecchi, M., Doyle, B. P., Lukkari, J., & Zanfrognini, B. et al. (2009). Adsorption of 3, 4-ethylenedioxytiophene (EDOT) on noble metal surfaces: A photoemission and X-ray absorption study. *Journal of Electron Spectroscopy and Related Phenomena*, *172*(1-3), 114–119. doi:10.1016/j.elspec.2009.03.014

Petit, C., Peterson, G. W., Mahle, J., & Bandosz, T. J. (2010). The effects of oxidation on the surface chemistry of sulfur-containing carbons and their arsine adsorption capacity. *Carbon*, *48*(6), 1779–1787. doi:10.1016/j.carbon.2010.01.024

Pintado-Sierra, M., Rosero-Almansa, A. M., Corma, A., Iglesias, M., & Sanchez, F. (2013). Bifunctional iridium-(2-aminoterephthalate)–Zr-MOF chemoselective catalyst for the synthesis of secondary amines by one-pot three-step cascade reaction. *Journal of Catalysis*, *299*, 147–145. doi:10.1016/j.jcat.2012.12.004

Poladi, R. H., & Landry, C. C. (2002). Oxidation of octane and ciclohexane using a new porous substrate, Ti-MMM1. *Microporous and Mesoporous Materials*, *52*(1), 11–18. doi:10.1016/S1387-1811(02)00272-X

Polshettiwar, V., & Varma, R. S. (2010). Green Chemistry by Nano-catalysis. *Green Chemistry*, *12*(5), 743–754. doi:10.1039/b921171c

Ramirez-Verduzco, L. F., De los Reyes, J. A., & Torres-Garcia, E. (2008). Solvent Effect in Homogeneous and Heterogeneous Reactions to Remove Dibenzothiophene by an Oxidation-Extraction Scheme. *Industrial & Engineering Chemistry Research*, *47*(15), 5353–5361. doi:10.1021/ie701692r

Ray, S. S., & Okamoto, M. (2003). Polymer/layered silicate nanocomposites: A review from preparation to processing. *Progress in Polymer Science*, *28*(11), 1539–1641. doi:10.1016/j.progpolymsci.2003.08.002

Rivas Mercury, J., Cabra, A. A., Paiva, A. E. M., Angelica, R. S., Neves, R. F., & Scheller, T. (2011). Thermal behavior and evolution of the mineral phases of Brazilian red mud. *Journal of Thermal Analysis and Calorimetry*, *104*(2), 635–643. doi:10.1007/s10973-010-1039-7

Rodriguez, J. A., Liu, P., Takahashi, Y., Nakamura, K., Vines, F., & Illas, F. (2009). Desulfurization of Thiophene on Au/TiC(001): Au-C Interactions and Charge Polarization. *Journal of the American Chemical Society*, *131*(24), 8595–8602. doi:10.1021/ja901522a PMID:19530731

Rodríguez-Cabo, B., Rodríguez, H., Rodil, E., Arce, A., & Soto, A. (2014). Extractive and oxidative-extractive desulfurization of fuels with ionic liquids. *Fuel*, *117*, 882–889. doi:10.1016/j.fuel.2013.10.012

Rodriguez-Gattorno, G., Galano, A., & Torres-Garcia, E. (2009). Surface acid-basic properties of WOX-ZrO2 and catalytic efficiency in oxidative desulfurization. *Applied Catalysis B: Environmental*, *92*(1-2), 1–8. doi:10.1016/j.apcatb.2009.07.031

Saladino, R., Crucianelli, M., & De Angelis, F. (2010). Methyltrioxorhenium catalysis in nonconventional solvents: A great catalyst in safe reaction medium. *Chemistry and Sustainability*, *3*, 524–540. PMID:20391453

Salmones, J., Galicia, J. A., Wang, J. A., Valenzuela, M. A., & Aguilar-Rios, G. (2000). Synthesis and characterization of nanocrystallite MgAl2O4 spinels as catalysts support. *Journal of Materials Science Letters*, *19*(12), 1033–1037. doi:10.1023/A:1006734902538

Sampanthar, J. T., Dou, J., Joo, G. G., Widjaja, E., & Eunice, L. Q. H. (2007). Template-free low temperature hydrothermal synthesis and characterization of rod-shaped manganese oxy-hydroxides and manganese oxides. *Nanotechnology*, *18*(2), 525–601. doi:10.1088/0957-4484/18/2/025601

Satterfeld, C. N. (1991). *Heterogeneous Catalysis in Industrial Practice.* New York, NY: McGraw-Hill Book Company.

Schuit, G. C. A., & Gates, B. C. (1973). Chemistry and Engineering of catalytic hydrodesulfurization. *AlChE Journal*, *1913*(3), 417–438. doi:10.1002/aic.690190303

Sengupta, A., Kamble, P. D., Basu, J. K., & Sengupta, S. (2012). Kinetic study and optimization of oxidative desulfurization of benzothiophene using mesoporous titanium silicate-1 catalyst. *Industrial & Engineering Chemistry Research*, *51*(1), 147–157. doi:10.1021/ie2024068

Seredych, M., & Bandosz, T. J. (2011). Removal of dibenzothiophene from model diesel fuel on sulfur rich activated carbons. *Applied Catalysis B: Environmental*, *106*, 133–141.

Seredych, M., & Bandosz, T. J. (2013). Visible light photoactivity of sulfur and phosphorus doped monoporous carbons in oxidation of dibenzothiophenes. *Fuel*, *108*, 846–849. doi:10.1016/j.fuel.2012.12.064

Seredych, M., Khine, M., & Bandosz, T. J. (2011). Enhancement in dibenzothiophene reactive adsorption from liquid fuel via incorporation of sulfur heteroatoms into nanoporous carbon matrix. *Chemistry and Sustainability*, *4*, 139–147. PMID:21226224

Seung-Tae, Y., Kwang-Eun, J., Soon-Yong, J., & Wha-Seung, A. (2012). Synthesis of mesoporous TS-1 using a hybrid SiO2-TiO2 xerogel for catalytic oxidative desulfurization. *Materials Research Bulletin*, *47*(12), 4398–4402. doi:10.1016/j.materresbull.2012.09.041

Shaabani, A., Behnam, M., & Rezayan, A. H. (2009). Tungstophosphoric Acid (H3PW12O40) Catalyzed Oxidation of Organic Compounds with NaBrO3. *Catalysis Communications*, *10*(7), 1074–1078. doi:10.1016/j.catcom.2008.12.059

Sharifzadeh Baei, M., & Rezvani, M. A. (2011). An Efficient, New, Simple and Rapid Method for Synthesis and Isomerization of Heteropolyanion B-[PW9O34]9. *Asian Journal of Chemistry*, *23*, 5381–5389.

Shefer, N., & Rozen, S. (2010). The Oxigenation of Thieno [2,3,-b]thiophenes. *The Journal of Organic Chemistry*, *75*(13), 4623–4625. doi:10.1021/jo100702f PMID:20521759

Shen, C., Wang, Y. J., Xu, J. H., & Luo, G. S. (2015). Synthesis of TS-1 on porous glass beads for catalytic oxidative desulfurization. *Chemical Engineering Journal*, *259*, 552–556. doi:10.1016/j.cej.2014.08.027

Soleimani, M., Bassi, A., & Margaritis, A. (2007). Biodesulfurization of refractory organic sulfur compounds in fossil fuels. *Biotechnology Advances*, *25*(6), 570–596. doi:10.1016/j.biotechadv.2007.07.003 PMID:17716849

Song, C. (2003). An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel. *Catalysis Today*, *86*(1-4), 211–263. doi:10.1016/S0920-5861(03)00412-7

Speight, J. C. (1998). In M. Henz, (Ed.), *The Chemistry and Technology of Petroleum* (3rd ed.). New York, NY: Marcel Dekker.

Srivastava, V. C. (2012). An evaluation of desulfurization technologies for sulfur removal from liquid fuels. *Royal Society of Chemistry Advances*, *2*, 759–783.

Strel Ko, V. V., Kutz, V. S., & Thrower, P. A. (2000). On the mechanism of possible influence of heteroatoms of nitrogen, boron and phosphorus in a carbon matrix on the catalytic activity of carbon in electron transfer reactions. *Carbon*, *38*(10), 1499–1524. doi:10.1016/S0008-6223(00)00121-4

Su, D. S., Maksimova, N., Delgado, J. J., Keller, N., Mestl, G., Ledoux, M. J., & Schlögl, R. (2005). Nanocarbons in selective oxidative dehydrogenation reaction. *Catalysis Today*, *102*, 110–114. doi:10.1016/j.cattod.2005.02.012

Su, P., Xiao, H., Zhao, J., Yao, Y., Shao, Z., Li, C., & Yang, Q. (2013). Nitrogen-doped carbon nanotubes derived from Zn–Fe-ZIF nanospheres and their application as efficient oxygen reduction electrocatalysts with in situ generated iron species. *Chemical Sciences*, *4*, 2941–2946.

Sun, F., Yin, Z., Wang, Q. Q., Sun, D., Zeng, M. H., & Kurmao, M. (2013). Tandem Postsynthetic Modification of a Metal–Organic Framework by Thermal Elimination and Subsequent Bromination: Effects on Absorption Properties and Photoluminescence. *Angewandte Chemie International Edition*, *52*(17), 4538–4543. doi:10.1002/anie.201300821 PMID:23564565

Sviridova, T. V., Stepanova, L. I., & Sviridov, D. V. (2012). Molybdenum: characteristics, production and applications. In M. Ortiz & T. Herrera (Eds.), *Nova Science* (pp. 147–179). New York, NY.

Taguchi, A., & Schuth, F. (2005). Ordered mesoporous materials in catalysis. *Microporous and Mesoporous Materials*, *77*(1), 1–45. doi:10.1016/j.micromeso.2004.06.030

Tanev, P. T., Chibwe, M., & Pinnavaia, T. J. (1994). Titanium-containing mesoporous molecular sieves for catalytic oxidation of aromatic compounds. *Nature*, *368*(6469), 321–323. doi:10.1038/368321a0 PMID:8127366

Tangestaninejad, S., Mirkhani, V., Moghadam, M., Mohammadpoor-Baltork, I., Shams, E., & Salavati, H. (2008). Hydrocarbon oxidation catalyzed by vanadium polyoxometalate supported on mesoporous MCM-41 under ultrasonic irradiation. *Ultrasonics Sonochemistry*, *15*(4), 438–447. doi:10.1016/j.ultsonch.2007.06.009 PMID:17692553

Tatsumi, T., & Jappar, N. (1998). Properties of Ti-beta zeolites synthesized by dry-gel conversion and hydrothermal methods. *Journal of Physical Chemistry*, *102*(37), 7126–7131. doi:10.1021/jp9816216

Teixeira, I. F., Oliveira, A. A., Christofani, T., & Moura, F. C. C. (2013). Biphasic oxidation promoted by magnetic amphiphilic nanocomposites undergoing a reversible emulsion process. *Journal of Material Chemistry A*, *1*(35), 10203–10208. doi:10.1039/c3ta11535f

Teunissen, W., Bol, A. A., & Geus, J. W. (1999). Magnetic catalyst bodies. *Catalysis Today*, *48*(1-4), 329–336. doi:10.1016/S0920-5861(98)00389-7

Tomskii, I. S., Vishnetskaya, M. V., & Rufov, Y. N. (2009). The oxidation of toluene on transition metal oxides. *Russian Journal of Physical Chemistry A*, *83*(11), 1868–1872. doi:10.1134/S0036024409110107

Tian, Y., Yao, Y., Zhi, Y., Yan, L., & Lu, S. (2015). Combined Extraction−Oxidation System for Oxidative Desulfurization (ODS) of a Model Fuel. *Energy & Fuels*, *29*, 618–625.

Vairavapandian, D., Vichchulada, P., & Lay, M. D. (2008). Preparation and modification of carbon nanotubes: Review of recent advances and applications in catalysis and sensing. *Analytica Chimica Acta*, *626*(2), 119–129. doi:10.1016/j.aca.2008.07.052 PMID:18790113

Vargas, R., & Nunez, O. J. (2008). The photocatalytic oxidation of dibenzothiophene (DBT). *Journal of Molecular Catalysis A Chemical*, *294*(1-2), 74–81. doi:10.1016/j.molcata.2008.08.001

Vu, T. H. T., Nguyen, T. T. T., Nguyen, P. H. T., Do, M. H., Au, H. T., & Nguyen, T. B. et al. (2012). Fabrication of photocatalytic composite of multi-walled carbon nanotubes/TiO2 and its application for desulfurization of diesel. *Materials Research Bulletin*, *47*(2), 308–314. doi:10.1016/j.materresbull.2011.11.016

Wang, J., Xu, L., Zhang, K., Peng, H., Wu, H., & Jiang, J. G. et al. (2012). Multilayer structured MFI-type titanosilicate: Synthesis and catalytic properties in selective epoxidation of bulky molecules. *Journal of Catalysis*, *288*, 16–23. doi:10.1016/j.jcat.2011.12.023

Wang, J. A., Chen, L. F., Valenzuela, M. A., Montoya, A., Salmones, J., & Del Angel, P. (2004). Rietveld refinement and activity of CO oxidation over Pd/Ce0.8Zr0.2O2 catalyst prepared via a surfactant-assisted route. *Applied Surface Science*, *230*(1-4), 34–43. doi:10.1016/j.apsusc.2003.08.111

Wang, R., Yu, F., Zhang, G., & Zhao, H. (2010). Performance evaluation of the carbon nanotubes supported Cs2.5H0.5PW12O40 as efficient and recoverable catalyst for the oxidative removal of dibenzothiophene. *Catalysis Today*, *150*(1-2), 37–41. doi:10.1016/j.cattod.2009.10.001

Wang, W., Li, G., Liu, L., & Chen, Y. (2013). Synthesis and catalytic performance of hierarchical TS-1 directly using agricultural products sucrose as meso/macropores template. *Microporous and Mesoporous Materials*, *179*, 165–171. doi:10.1016/j.micromeso.2013.06.012

Wang, W., Li, G., Liu, L., & Liu, H. (2012). Titanium silicalite synthesized by dry gel conversion metrhod and its catalytic performance. *Chinese Journal of Catalysis*, *33*, 1236–1241.

Wang, W. D., Serp, P., Kalck, P., & Faria, J. L. (2005). Photocatalytic degradation of phenol on MWNT and titania composite catalysts prepared by a modified sol–gel method. *Applied Catalysis B: Environmental*, *56*(4), 305–312. doi:10.1016/j.apcatb.2004.09.018

Wang, X., Li, F., Liu, J., Kou, C., Zhao, Y., Hao, Y., & Zhao, D. (2012). Preparation of TiO2 in Ionic Liquid via Microwave Radiation on in situ Photocatalytic Oxidative Desulfurization of Diesel Oil. *Energy & Fuels*, *26*, 6777–6782.

Wang, X., Li, Z., Shi, J., & Yu, Y. (2014). One-Dimensional Titanium Dioxide Nanomaterials: Nanowires, Nanorods, and Nanobelts. *Chemical Reviews*, *114*(19), 9346–9384. doi:10.1021/cr400633s PMID:24725155

Woan, K., Pyrgiotakis, G., & Sigmund, W. (2009). Photocatalytic Carbon-Nanotube–TiO2 Composites. *Advanced Materials*, *21*(21), 2233–2239. doi:10.1002/adma.200802738

Xi, L., Squires, C. H., Monticello, D. J., & Childs, J. D. (1997). A flavin reductase stimulates DszA and DszC proteins of Rhodococcus erytthropolis IGTS8 in vitro. *Biochemical and Biophysical Research Communications*, *230*(1), 73–75. doi:10.1006/bbrc.1996.5878 PMID:9020064

Xie, X. L., Mai, Y. W., & Zhou, X. P. (2005). Dispersion and alignment of carbon nanotubes in polymer matrix: A review. *Materials Science and Engineering R Reports*, *49*(4), 89–112. doi:10.1016/j.mser.2005.04.002

Xu, P., Feng, J., Yu, B., Li, F., & Ma, C. (2009). Recent developments in biodesulfurization of fossil fuels. *Advances in Biochemical Engineering/Biotechnology*, *113*, 255–274. PMID:19475378

Yamada, K., Minoda, Y., Kodama, K., Nakatani, S., & Aesaki, T. (1998). Microbial conversion of petrosulfur compounds. Part I Isolation and identification of dibenzothiophene utilizing bacteria. *Agricultural and Biological Chemistry*, *32*(7), 840–845. doi:10.1271/bbb1961.32.840

Yamada, K. O., Morimoto, M., & Tani, Y. (2001). Degradation of dibenzothiophene by sulfate-reducing bacteria cultured in the presence of only nitrogen gas. *Journal of Bioscience and Bioengineering*, *91*(1), 91–93. doi:10.1016/S1389-1723(01)80119-5 PMID:16232954

Yan, X. M., Mei, P., Lei, J., Mi, Y., Xiong, L., & Guo, L. (2009). Synthesis and characterization of mesoporous phosphotungstic acid/TiO2 nanocompositive as a novel oxidative desulfurization catalyst. *Journal of Molecular Chemical Catalysis A. Chemical*, *304*, 52–57.

Yang, X., Han, Y., Lin, K., Tian, G., Feng, Y., & Meng, X. (2012). Ordered mesoporous titanosilicates with catalytically stable and active four-coordinated titanium sites. *Chemical Communications (Cambridge)*, *60*, 1236–1241.

Zannikos, F., Lois, E., & Stournas, S. (1995). Desulfurization of petroleum fractions by oxidation and solvent extraction. *Fuel Processing Technology*, *42*(1), 35–45. doi:10.1016/0378-3820(94)00104-2

Zapata, B., Pedraza, F., & Valenzuela, M. A. (2005). Catalyst screening for oxidative desulfurization using hydrogen peroxide. *Catalysis Today*, *106*(1-4), 219–221. doi:10.1016/j.cattod.2005.07.134

Zhang, W., Froba, M., Wang, J., Tanev, P. T., Wang, J., & Pinnavaia, T. J. (1996). Mesoporous titanosilicate molecular sieve prepared at ambient temperature by electrostatic and neutral assembly pathways: A comparison of physical properties and catalytic activity for peroxide oxidations. *Journal of the American Chemical Society*, *118*(38), 9164–9171. doi:10.1021/ja960594z

Zhang, W., Zhang, H., Xiao, J., Zhao, Z., Yu, M., & Zhong Li, Z. (2014). Carbon nanotube catalysts for oxidative desulfurization of a model diesel fuel using molecular oxygen. *Green Chemistry*, *16*(1), 211–220. doi:10.1039/C3GC41106K

Zhang, Z. C., Xu, B., & Wang, X. (2014). Engineering nanointerfaces for nanocatalysis. *Chemical Society Reviews*, *43*(22), 7870–7886. doi:10.1039/C3CS60389J PMID:24745032

Zhang, Z. X., Zhang, F. W., Zhu, Q. Q., Zhao, W., Ma, B. C., & Ding, Y. (2011). Magnetically separable polyoxometalate catalysts for the oxidation of dibenzothiophene with H2O2. *Journal of Colloid and Interface Science*, *360*(1), 189–194. doi:10.1016/j.jcis.2011.04.045 PMID:21546033

Zhao, D., Feng, J., Huo, Q., Melosh, N., Fredrickson, H. G., Chmelka, F. B., & Stucky, D. G. (1998). Triblock copolymer synthesis of mesoporous silica with periodic 50 to 300 angstrom pores. *Science*, *279*(5350), 548–552. doi:10.1126/science.279.5350.548 PMID:9438845

Chapter 7

Ni/ZnO Nano Sorbent for Reactive Adsorption Desulfurization of Refinery Oil Streams

Hui Ge
Institute of Coal Chemistry, Chinese Academy of Sciences, China

Mingxing Tang
Institute of Coal Chemistry, Chinese Academy of Sciences, China

Xiao-Dong Wen
Chinese Academy of Sciences, China & Synfuels, China

ABSTRACT

The aim of this chapter is to present the Ni/ZnO nano-sorbent for reactive adsorption desulfurization (RADS) of refinery oil steams. The preparation and modification of nano-sorbent are reviewed. Various characterizations involving in the relation of properties with components, structures and dynamic phase change during RADS, are extensively provided. The mechanisms of desulfurization, sulfur transfer and sulfur adsorption are proposed. The contradictories in literature about active structures and reaction mechanism are discussed and the solutions are suggested. This chapter unfolds the impressive application of RADS of Ni/ZnO nano-sorbent to produce a cleaner gasoline. It also delves into the inadequately engineer areas which require further attention so as to make the RADS process more economic and more efficient. The perspective applications other than gasoline desulfurization are also presented.

INTRODUCTION

Desulfurization is one of the most important processes in the petroleum refining industry. The conventional measure is by hydrodesulfurization (HDS) where molybdenum or tungsten supported on an alumina carrier with addition of cobalt or nickel is used as catalyst (Babich and Moulijn 2003). For eliminating

DOI: 10.4018/978-1-4666-9545-0.ch007

the detrimental impact of acid rain, many governments have made more stringent regulations controlling the sulfur content in fuels. For example, in the new Europe V standard, the sulfur content in gasoline and diesel is limited below 10 ppm. But the HDS process faces challenge to achieve this objective. Thus other desulfurization technologies are heavily investigated. Among them, reactive adsorption desulfurization (RADS) emerges as a perspective direction, which uses a sorbent to remove the sulfur impurity from oil stream and keeps the sulfur in the sorbent. The great challenge for RADS technology is to develop a sorbent with high desulfurization activity and high sulfur capacity. Nano Ni/ZnO sorbent is found an ideal candidate for this objective, where metallic Ni catalyzes the HDS of sulfur-containing compounds, meanwhile ZnO component as a sulfur acceptor regenerates Ni species from the sulfided to the metallic (Tawara et al. 2000, 2001a).

Ryzhikov et al. (2008) observed that NiO/ZnO can be reduced in situ and shows better RADS of thiophene than pre-reduced counterpart. It was suggested that the H_2 pretreatment results in the formation of Ni-Zn alloy and agglomeration of nano particles, leading the decrease of activity. However, the pre-reduction for NiO/ZnO-SiO_2-Al_2O_3 sorbent improves the desulfurization capability (Fan et al. 2010), which is attributed to the additives of alumina and silica stabilizing the particles (Wen et al. 2012, Meng et al. 2013). Decreasing the size of ZnO nano particles increases the efficient contact between Ni and ZnO particles and enhances the desulfurization ability and sulfur adsorption capacity (Zhang et al. 2012a). But ZnO particles are not stable under the calcination or reaction conditions, the sinter of particles lead a noticeable drop of activity (Bezverkhyy et al. 2008). Thus structure additives, such as diatomite, perlite, attapulgite, silicasol, pseudoboehmite or their mixtures are often added to reinforce the texture of nano sorbent (Shangguan et al. 2013, Zhou et al. 2013).

Babich and Moulijn (2003) proposed a RADS mechanism of Ni/ZnO sorbent. H_2S as a sulfur carrier transfers the sulfur from Ni surface to ZnO bulk. It has been accepted by a lot of authors, but the recent DFT calculation showed that the direct sulfur transfer from Ni site to Zn site has lower energy barrier. This suggests a new mechanism that sulfur may be transferred through the interface between Ni and ZnO phases (Zhang et al. 2012b). The sulfur accumulation in the sorbent leads a gradual deactivation. Regeneration at above 500 ^{o}C can partly recover the RADS activity. However, the formation of new species, such as Ni_2SO_4, $ZnSO_4$, NiAl or AlZn spinel, influences the performance of regenerated sorbent (Wen et al. 2012, Meng et al. 2012).

The RADS of Ni/ZnO nano sorbent has been successfully applied in the desulfurization of gasoline. The S-Zorb technology is the representative one. It was first developed by Conoco Philips Petroleum Co. and then was bought out by China Petroleum & Chemical Corp. (Sinopec). This RADS process was demonstrated to possess some valuable features like low hydrogen consumption and low loss in octane number (Khare 1999, Gyanesh 2001). The first commercial S-Zorb unit was run at Borger refinery in April of 2001. And over thirty units have been built and operated by the end of 2014 (Jia et al. 2014).

This chapter discusses the new emerged and fast developing RADS technology. It begins with the preparation of nano Ni/ZnO sorbent as well as its modification. Various characterization methods are used to reveal the structures and properties of the sorbent. Based on these data the relation of structure with reaction activity and adsorption capacity is built. The RADS paths are simulated by DFT method. And the reaction mechanism is postulated. The controversies regarding active structures and reactive mechanism are raised hoping to be solved in future. The commercial application of Ni/ZnO nano sorbent for RADS is presented. S-Zorb RADS technique is introduced historically and compared with HDS technologies. The perspective of RADS is provided. And further engineering research is proposed.

BACKGROUND

The conventional HDS technology was originated from the coal hydrogenation and liquefaction in 1930s and was introduced for the sulfur removal in petroleum refining prior to World War II. But recently, it faces with challenges. On the one hand, the sulfur content in petroleum continually rises. On the other hand, the environmental regulation places increasing severe restrictions on the sulfur content in the product fuels. This poses a major driving force for introducing novel desulfurization technology or improving the HDS ones.

It notes that the quality of fuel product can be impacted by desulfurization. For gasoline, deep HDS leads the loss of octane number owing to the saturation to olefins. Thus a process of octane number recovery is usually followed, such as isomerization or addition of high octane-number compounds MTBE. This is especially true for the fluidized catalytic cracker (FCC) gasoline, which contains large olefins and refractory sulfur compounds thiophene and its derivatives. In modern refining, there is a trend to make more light fractions from the heavy fractions. This lead the FCC gasoline increase apparently. For the deep desulfurization of FCC gasoline, avoiding hydrogenation to olefins is preferred. But as for diesel, the hydrogenation for aromatics can increase the cetane number; the objective of diesel deep desulfurization is to enhance HDS activity of catalysts.

To meet the strict regulations of sulfur content, alternative desulfurization techniques are extensively explored, including physical adsorption (Pawelec et al. 2010; Samokhvalov and Tatarchuk 2010), oxidation extraction (Chica et al. 2006; Rodriguez-Gattorno et al. 2009), bio-desulfurization (Monticello 2000; Davoodi-Dehaghani et al. 2010) and RADS (Ania and Bandosz 2006a; Huang et al. 2010a). Among these, RADS is deemed the most promising one and is viewed as a better option to conventional HDS for gasoline desulfurization (Sharma et al. 2013).

Ni/ZnO was found an excellent sorbent for the RADS. The metallic Ni captures sulfur from the sulfur containing compound in feed forming NiS_x, then the sulfur is transferred to the ZnO component in the presence of hydrogen, and the Ni active center is regenerated, while the hydrocarbon portion of the sulfur containing compound is released back into the process stream. Due to the dual identities of Ni/ZnO, as both catalyst and sorbent, it has been called different names in references, such as "catalyst", "sorbent", or "adsorbent" etc.. In this chapter, for the consistence, we adopt the term "sorbent". For RADS sorbent, there are three key specifications, one is the activity of desulfurization, another is the sulfur capacity, namely possible adsorbed sulfur quantity when sulfur content is kept below some limit, and the third is the selectivity to olefin hydrogenation. Many methods have been used to improve the properties of RADS sorbents. The activity and sulfur capacity can be remarkably improved by controlling the nano morphology and structures of Ni/ZnO sorbent (Zhang et al. 2012a). Addition of Mn forms the new phase of $ZnMnO_3$, which enhances activity and regenerability (Zhang et al. 2013). Substitution ZnO component with MnO increases the sulfur capacity (Tang et al. 2015). Introduction of second metal, such as Co, Fe, Cu, Silver, can inhibit the hydrogenation to olefins (Khare 1999, Gyanesh 2001).

Other reactive sorbents investigated for desulfurization include chemical modified carbon (Jiang et al. 2003; Ania and Bandosz 2006b; Seredych et al. 2011); Polymer-derived activated carbons (Seredych et al. 2010), organic waste derived carbon (Ania et al. 2007); Metal supported activated carbons (Ania and Bandosz 2006a); Ni nanoparticles supported mesoporous silica (Park et al. 2008); Zeolites (Yang et al. 2003; Chica et al. 2005), and organic sulfur sorbent (Shalaby et al. 2009) etc.. But these sorbents are studied only in laboratory, which are beyond the scope of this chapter.

Conoco Philips Petroleum Co. was the first one using the nano-Ni/ZnO sorbent for the RADS of gasoline in refinery. They termed this technology "S-Zorb" (Johnson et al. 2001). Using the latest sorbent and circulated fluidized bed technology, the clean gasoline can be produced with sulfur content below 10 ppm and little octane number loss (Qiu et al. 2013). Recently the fix bed technique of RADS has also been developed.

In Ni/ZnO RADS, there are two important cycles, one is the micro-cycle; the Ni active sites are continually auto-regenerated by the process of sulfur transfer from the Ni surface to the ZnO component. Another macro-cycle, the deactivated Ni/ZnO sorbent is regenerated periodically by oxidation and then H_2 reduction. Understanding the two cycles and making them run effectively warrant the excellent performance of Ni/ZnO nano sorbent for RADS. We will unfold this chapter revolving around these two cycles.

REACTIVE ADSORPTION DESULFURIZATION OVER NANO SORBENT

Until now, Ni/ZnO is the most effective sorbent for RADS. In this section, we bring readers insight into the intrinsic structures and properties of Ni/ZnO and its reaction mechanism. We start with the preparation and modification of nano sorbent, which is then characterized by BET, XRD, TGA, TEM and XANES. The possible reaction processes are investigated by density functional theory (DFT), and the reaction mechanisms are proposed. At end, the relation of structures with RADS activities and sulfur capacity is provided.

Preparation and Modification of Ni/ZnO Sorbent

1. **Co-Precipitation Method:** NiO/ZnO composite can be prepared by co-precipitation technique. It is fit for the preparation of sorbent with high Ni content. In a typical example (Ryzhikov et al. 2008), $Zn(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in water to make 0.2 M solution. Equimolar quantity of 0.5 M solution of Na_2CO_3 was dropped under vigorous stirring. The suspension was stirred for another 12 h, and then filtered, washed with water thoroughly and dried in oven overnight at 100 ºC. The sample was then calcined in air at 400 ºC for 4 h. Co-precipitation by Na_2CO_3 alkaline allows a highly dispersed solid. But the Na^+ ions must be washed out totally avoiding the negative influence (Huang et al. 2010a). Replacing of Na_2CO_3 precipitant with $(NH_4)_2CO_3$ can decrease the washing times.
2. **Impregnation Method:** By impregnation method, NiO can be sufficiently dispersed on the ZnO nano particles. Versatile manufacture methods of ZnO particles have been reviewed by Moezzi et al. (2012). One example is given here. Zinc acetate was dissolved in i-propanol under vigorous stirring at 50 °C and quenched in ice bath. After addition of PVP, the reaction mixture was kept stirring for 12 h. The hydrolyzation was performed by the addition of NaOH solution in i-PrOH under ultrasonic agitation for 2 h. The solvents were removed by rotavaporization. The resulting mixture was washed with water, then was centrifuged and dried in vacuum. The samples show different particle sizes when calcined at different temperature. Ni was supported on ZnO by incipient wetness impregnation and then calcined at 300 °C (Zhang et al. 2012a).
3. **Kneading Method:** Zinc oxide and nickel sesquioxide is sufficiently mixed, then pseudoboehmite or/and diatomite is added to the mixture to achieve the desirable strength and attrition resistance.

Next, dilute nitric acid is added to the mixture to make slurry. After intrusion and drying, the resulting materials were calcined at 600 °C. Sorbent prepared with this method showed improvement of regeneration (Meng et al. 2013).

4. **Modification:** The pure ZnO particle is not stable. Calcination usually results in sinter and agglomeration of nano particles. Addition of structure auxiliaries, such as diatomite, perlite, attapulgite, silicasol or pseudoboehmite, increases the strength and resistance to abrasion (Meng et al. 2013; Babich & Moulijn 2003), and the texture properties can be kept during reaction and regeneration. But the desulfurization activity and sulfur capacity may be impacted by the additives, thus a compromise among various components is necessary for the best performance of RADS sorbent. Addition of Mn forms the new phase of $ZnMnO_3$, the sorbent 5%NiO/8%MnO-ZnO was found improving the desulfurization and regenerability (Zhang et al. 2013). With MnO replacing the ZnO as the adsorption component, the Ni/MnO sorbent showed higher sulfur capacity than its counterpart Ni/ZnO (Tang et al. 2015).

Preparation parameter and procedure determine the structure and morphology of sorbents, as well as the properties. Nano ZnO can present versatile morphologies, like needle, bar, disk etc., with different crystal surfaces exposed. Thus Ni/ZnO sorbents may be prepared with different morphologies and structures. This can bring new chances to improve the sorbent.

It is noteworthy that the nano sorbent is always under change during RADS process. The metallic Ni and ZnO are transformed to NiS_x and ZnS, respectivley. This brings the expansion of volume of nano particles, even the collapse of pores. Thus the sorbent must has some tolerance to the structure expansion. Except for addition of low density materials, other measures may be considered, such as using the low expansion MnO adsorption component.

The inhibition to olefins hydrogenation is scarcely investigated in references, but it is very important for the application of deep desulfurization of gasoline. Patents of Khare 1999 and Gyanesh 2001 provided the clues by addition of second metal, such as Co, Mo, Cu and Ag. More study is requisite to illustrate the mutual interaction of metals and find the better combination of them.

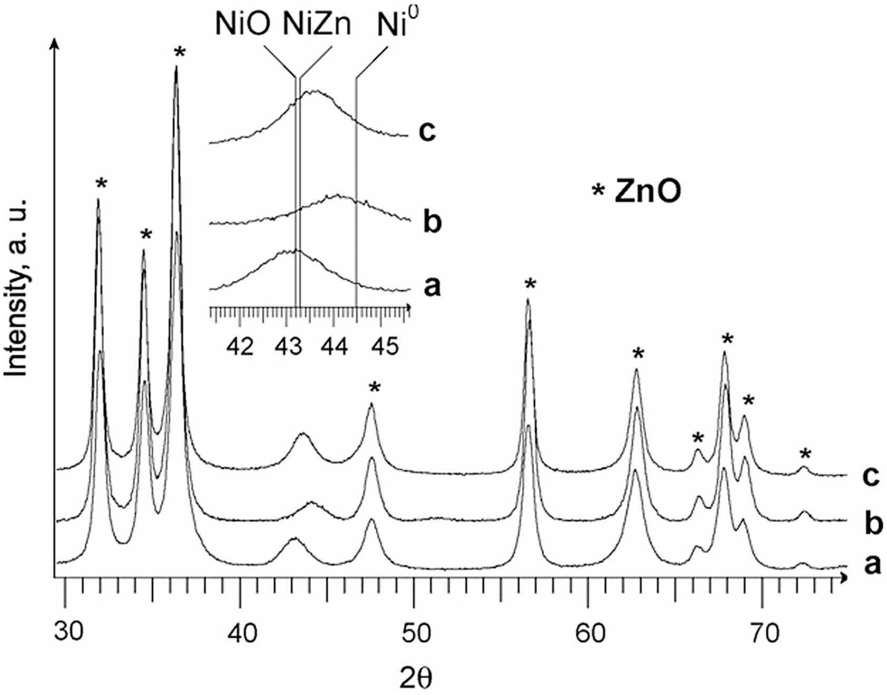
Characterizations of Ni/ZnO Nano Sorbents

1. **XRD:** Comparison of XRD patterns between calcined and reduced NiO/ZnO, it is found that the calcined sample (Figure 1a) contains the peaks characteristic of the hexagonal ZnO. The additional peak (at $2\theta = 43.2^{\circ}$) corresponds to NiO. For the sample reduced in H_2 at 360 °C for 6 h, a similar additional peak which is slightly displaced to $2\theta = 43.7^{\circ}$ is observed (Figure 1c), this may belong to the pattern of a Ni-Zn alloy (Homs et al. 2006). To verify this, a reduction treatment for a shorter time in order to reduce Ni but avoid the alloy formation was done. The peak in this case is situated at $2\theta = 44.1^{\circ}$ which is close to metallic Ni (Figure 1b). This nicely illustrates that the species obtained after a longer treatment is metallic Ni-Zn alloy.

The change of crystal phases during diesel RADS was detected by XRD (Figure 2). The NiO was completely reduced to metallic Ni after 2h on stream. The ratio of $I_{28.6(ZnS)}/I_{36.3(ZnO)}$ grows from 26 to 122 h, indicating that the ZnS content in the sorbent increases monotonously with the time on stream. The peak of Ni_3S_2 appears after 98 h on stream, which correspond the apparent deactivation of sorbent. It was

Figure 1. XRD patterns for NiO/ZnO samples after calcination (a) and after reduction in H_2 at 360 °C for 30 min (b) and for 6 h (c)

(Ryzhikov et al. 2008; Copyright 2008 Elsevier).



found that the reduction resulted in the increase of crystallite sizes of ZnO and Ni species. During the RADS process, however, the crystallite sizes of ZnO and Ni phases were basically stable.

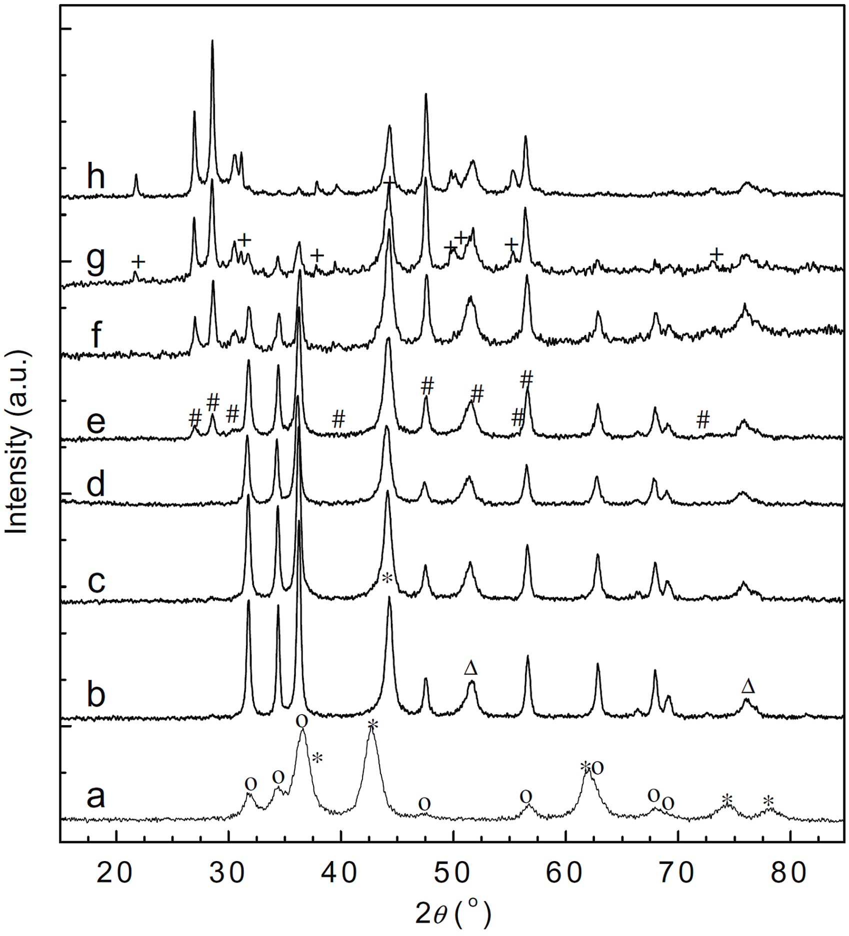
After RADS reaction of thiophene, a complex XRD pattern was observed. It contains the peaks characteristic of sphalerite, wurtzite-2H, metallic Ni and Ni_3S_2 (heazlewoodite). ZnO was completely sulfided, while nickel was only partial sulfided. And after reaction Ni^0 adopts the hexagonal structure rather than the cubic one in the initial sample (Ryzhikov et al. 2008).

The synchrotron radiation XRD was carried out to follow the reaction between reduced Ni/ZnO (containing NiZn alloy) and thiophene (Figure 3). In the beginning, the alloy was decomposed, producing metallic Ni particles. Their cell parameter (a =3.68 Å) indicates that the structure of Ni phase is dilated (a = 3.55 Å of pure cubic Ni). After decomposition of the NiZn alloy, the dilated Ni particles remained unchanged throughout the ZnO sulfidation, but yielded the hexagonal Ni_3C phase after ZnO transformation completed. It was tentatively proposed by authors that the expansion of lattice is due to the permeation of carbon.

2. **TGA:** The thermal gravimetric analysis (TGA) was conducted to study kinetics of reduced Ni/ZnO sorbent reacted with thiophene/H_2 (Bezverkhyy et al. 2008). It was observed that reaction between Ni/ZnO and thiophene goes through three different stages. The first one is that the metallic Ni surface is fast sulfided by the thiophene HDS. Second one is kinetically dominated by a nucleation-controlled sulfidation of ZnO surface. The sulfur on Ni surface is continually transferred to ZnO, leading the regeneration of Ni surface. At the third stage, the surface of ZnO has totally be

Figure 2. XRD patterns of the calcined adsorbent (a) and used adsorbents after the RADS of diesel oil for different reaction times on stream (b, c, d, e, f, g, and h represent 2, 6, 12, 26, 75, 98, and 122 h on stream, respectively; *, NiO; Δ, Ni; +, Ni_3S_2; o, ZnO; #, ZnS);RADS conditions:350 ^oC, 6 MPa, H_2/ diesel = 500, LHSV = 3.20 h^{-1}

(Huang et al. 2010b; Copyright 2010 Elsevier).

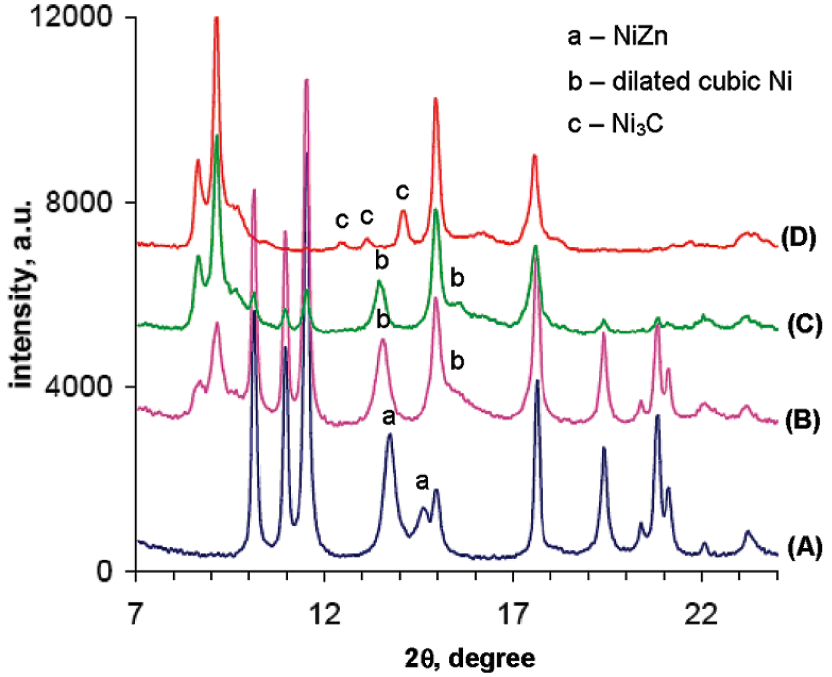


sufided and the reaction rate decreases. The thiophene HDS on NiS_x surface and sulfur diffusion from surface to ZnO bulk have comparable rates and their contributions vary with temperature due to the difference in activation energies.

3. **TEM:** The instability of Ni/ZnO sorbent was observed by comparing unreduced sample before and after RADS reaction. TEM shows that initial sample consists of strongly agglomerated shapeless particles of about 10-30 nm (Figure 4a). Sulfidation significantly changed textural properties of the solid (Figure 4b): particle size is visibly increased and the smaller particles, observed in the initial sample, disappear. This observation is in line with a decrease of BET surface area from 60 to 26.3 m^2/g after sulfidation. The shape of the particles was changed after reaction. An irregular corrugated structure of the facets and a strong variation of contrast throughout a particle point out to a polycrystalline nature and a complex morphology of the particles in sulfide solids.

Figure 3. XRD patterns of the NiO/ZnO sample after reduction in H_2 flow at 360 °C for 3 h (A) and its further reaction with thiophene at 360 °C for 30 min (B), 150 min (C), and 260 min (D). All unmarked peaks are those of ZnO and/or ZnS.

(Bezverkhyy et al. 2009; Copyright 2009 American Chemical Society).



4. **In Situ XANEX:** The in-situ XANES technique was performed to study the phase transformation during RADS reaction of diesel oil. Figure 5 shows the sulfur K-edge XANES spectra of the standard samples NiS, Ni_3S_2 and ZnS and the Ni/ZnO sorbent at different times on stream in RADS of diesel. The relative concentrations of each sulfur species can be evaluated by least-squares fitting (LSF) of the spectra with those of standard samples; combined with the total sulfur content in the sorbents, the contents of each sulfur species can be estimated (Figure 6). At the beginning, the sulfur content in Ni_3S_2 is higher than that of ZnS. The content of ZnS increases steadily with the reaction time on stream, while the content of Ni_3S_2 keeps relatively stable. The content of Ni_3S_2 in the sorbent is in the level of 0.08 g-S/g-NiO/ZnO and changes little with reaction time; and the steady-state activity of RADS is attained. After 75 h, the content of Ni_3S_2 increases gradually, accompanied with the slow decrease of the desulfurization efficiency of Ni/ZnO. But using XRD, the Ni_3S_2 phase cannot be detected until the apparent deactivation of sorbent (Huang 2010b). This illustrates that the early formed Ni_3S_2 is amorphous. Different from the thiophene RADS, the Ni_3C was not observed. It was proposed that the metallic Ni should be responsible for keeping the high HDS activity of the diesel. Ni_3S_2 corresponds to the final state of Ni species and has low HDS activity for desulfurization.

Figure 4. TEM micrographs of the unreduced Ni/ZnO sample before (a) and after reaction at 360 ^{o}C and 20 mbar of thiophene (b)
(Ryzhikov et al. 2008; Copyright 2008 Elsevier).

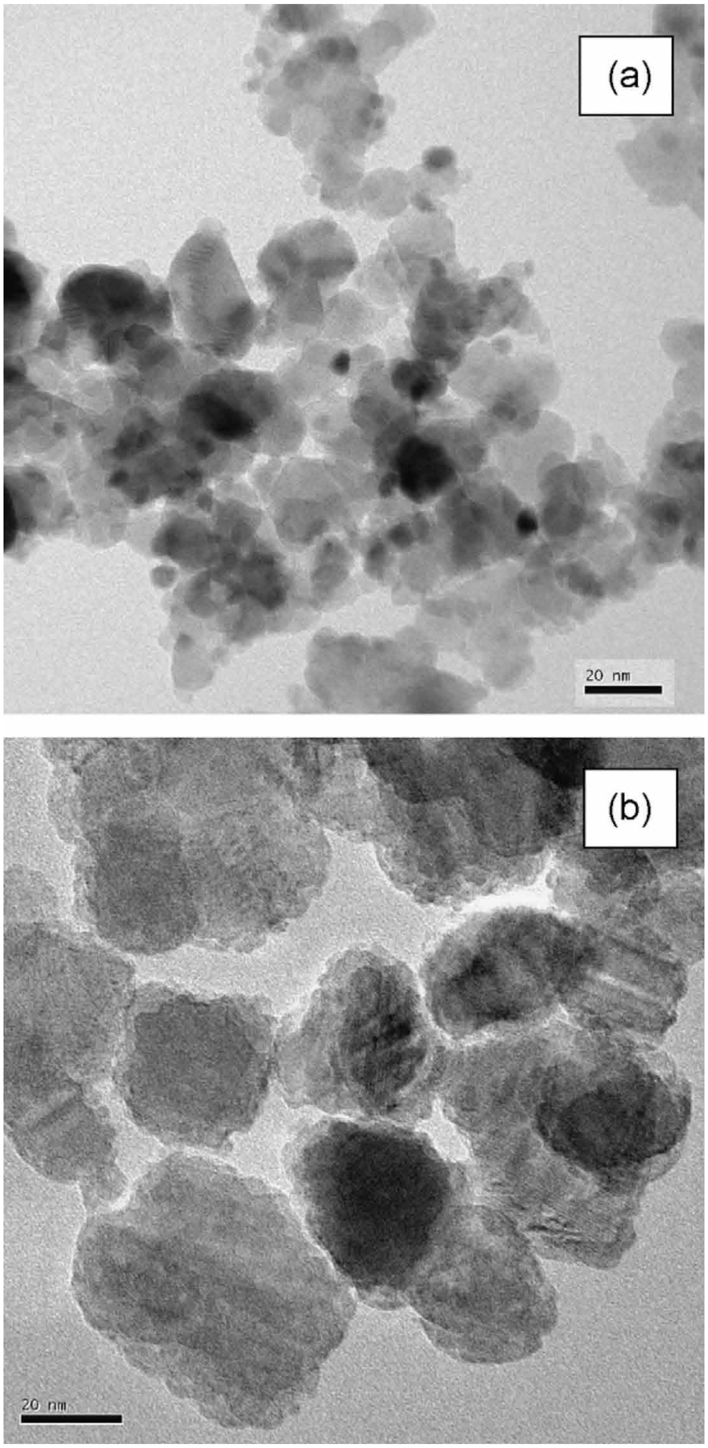
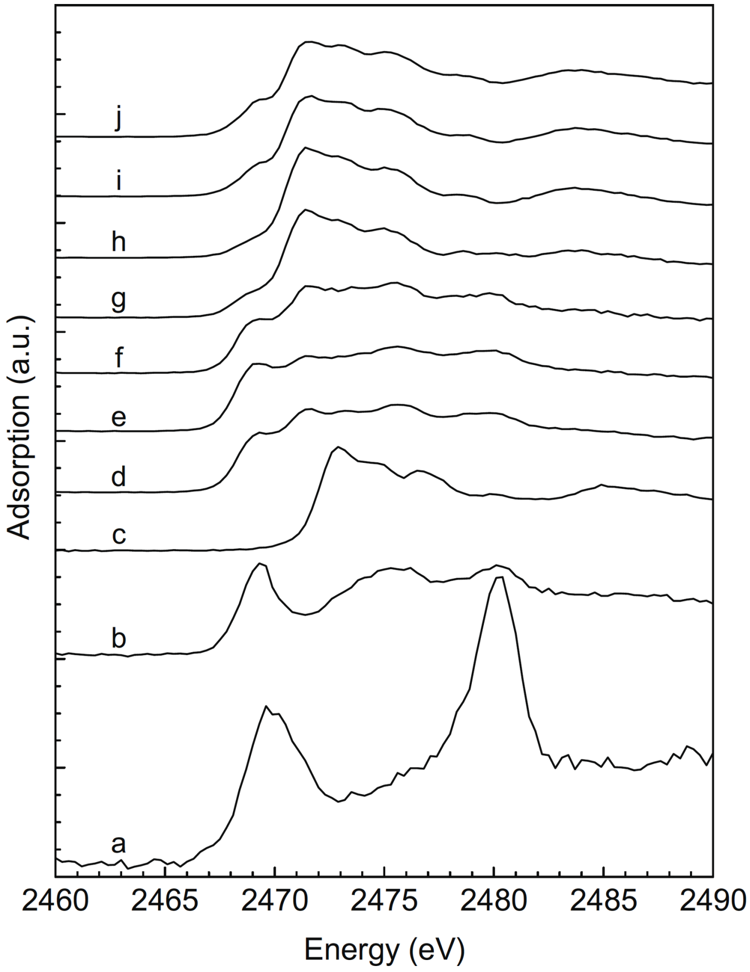


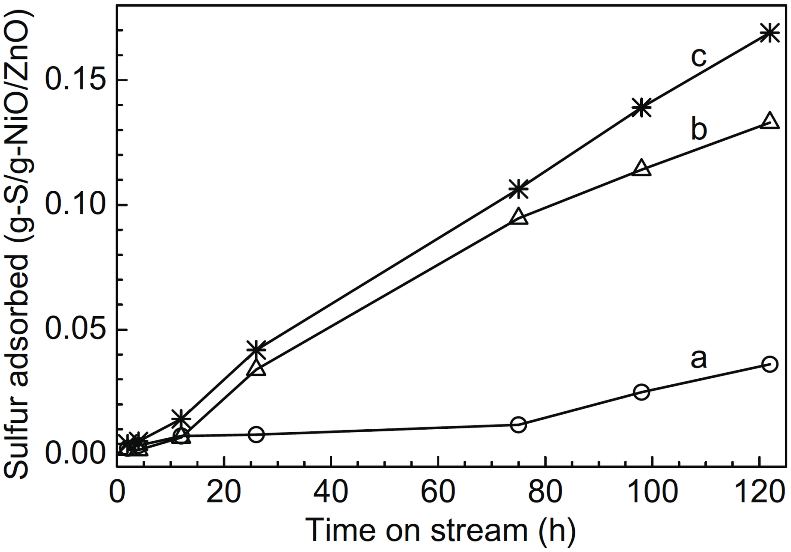
Figure 5. Sulfur K-edge XANES of the standard samples (a, NiS; b, Ni_3S_2; c, ZnS) and the used Ni/ZnO catalysts after the RADS of diesel oil for different times on stream (d, e, f, g, h, i, and j represent 2, 4, 12, 26, 75 98, and 122 h on stream, respectively)
(Huang et al. 2010b; Copyright 2010 Elsevier).



Density Functional Theory Revealing the Reaction Path on Ni/ZnO Nano-Sorbent

1. **The Process of Reactive Adsorption Desulfurization:** DFT calculation has become an important tool for investigation of the reaction path; in this regard experiment is usually difficult to conduct. Using the DMol3 software Zhang et al. (2012b) investigated the adsorption and desulfurization of thiophene over a Zn_3NiO_4 cluster. They observed that thiophene is favored to adsorb on Ni site. It then decomposed on the Ni site to form nickel sulfide. The reduction of the nickel sulfide is through two reaction pathways. One is to form H_2S by the attack of H_2 with an energy barrier of 0.859 eV. The other is that sulfur is directly transferred from Ni site to Zn site in the cluster passing a barrier of only 0.634 eV. This result provides a clue that direct sulfur transfer from Ni to ZnO may be a favored path.

Figure 6. Amounts of different sulfur species adsorbed in NiO/ZnO samples collected after RADS of diesel oil with the reaction time on stream: (a) Ni_3S_2; (b) ZnS; (c) total sulfur
(Huang et al. 2010b; Copyright 2010 Elsevier).

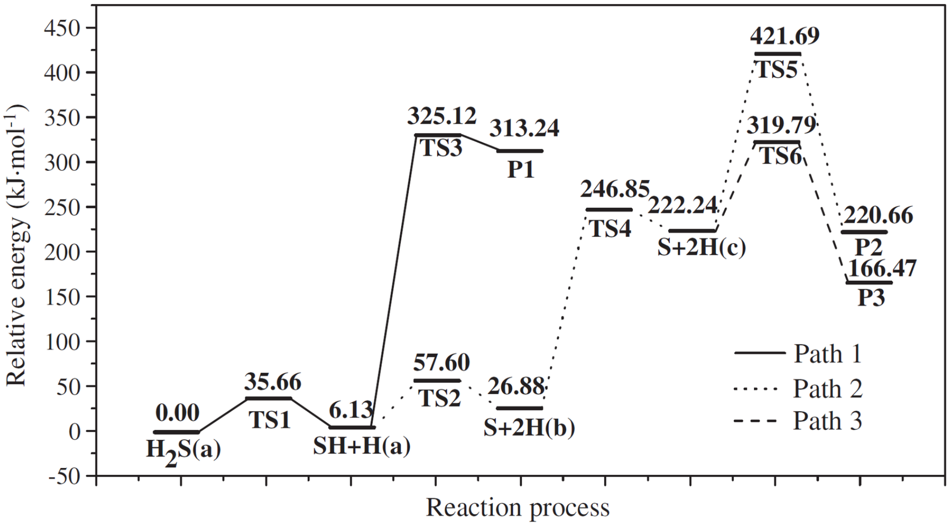


2. **The Sulfurization on the ZnO Sorbent by H_2S:** For Ni/ZnO sorbent, thiophene adsorbs and decomposes on Ni active sites by hydrogenation and hydrogenolysis. The sulfur atoms adsorbed on the Ni surface then are transferred to ZnO to form ZnS where H_2S is proposed as the sulfur carrier (Babich and Moulijn 2003). Ling et al (2013) investigated the sulfurization on ZnO ($10\bar{1}0$) by H_2S. The paths of H_2S decomposition and H_2O formation is showed in Figure 7, the stable and transient structures are presented in Figure 8. It is observed that the dissociative adsorption of H_2S molecule on the ZnO ($10\bar{1}0$) surface is preferred. The most stable configuration for SH adsorption on the ZnO ($10\bar{1}0$) surface is that the S atom is bonded to two adjacent Zn atoms via the bridge bond mode. The S atom bridging a Zn-O bond is the most stable configuration for single S atom adsorption. The H atom is preferentially adsorbed on the O-top site. In the coadsorption structure of SH and H, the adsorption sites are the same as the sites of SH and H adsorption separately. But in the coadsorption of S and 2H, the most stable structure is that the S atom is adsorbed on two adjacent Zn atoms via the bridge bond mode, and two H atoms are located on the O-top sites. The surface adsorbed hydrogen atoms can further combine to form H_2 by the dehydrogenation processes, or react with oxygen to form H_2O. The H_2O-forming via H_2S-ZnO interaction is the most probable reaction route. An oxygen vacancy is generated on the surface after the formation of H_2O, and the H_2S can adsorb on the vacancy.

The RADS Reaction Mechanism of Ni/ZnO Nano-Sorbent

1. **Mechanism of Thiophene RADS:** Based on the data of Tawara et al. (2000, 2001a), Babich and Moulijn (2003) proposed the mechanism of reactive adsorption desulfurization of thiophene over Ni/ZnO sorbent. The NiO is firstly reduced to metallic Ni, which serves as the active site for adsorption and hydrogenolysis of thiophene. The sulfur species on Ni surface is transferred to ZnO forming ZnS by H_2S under hydrogen atmosphere, and the Ni active surface is regenerated.

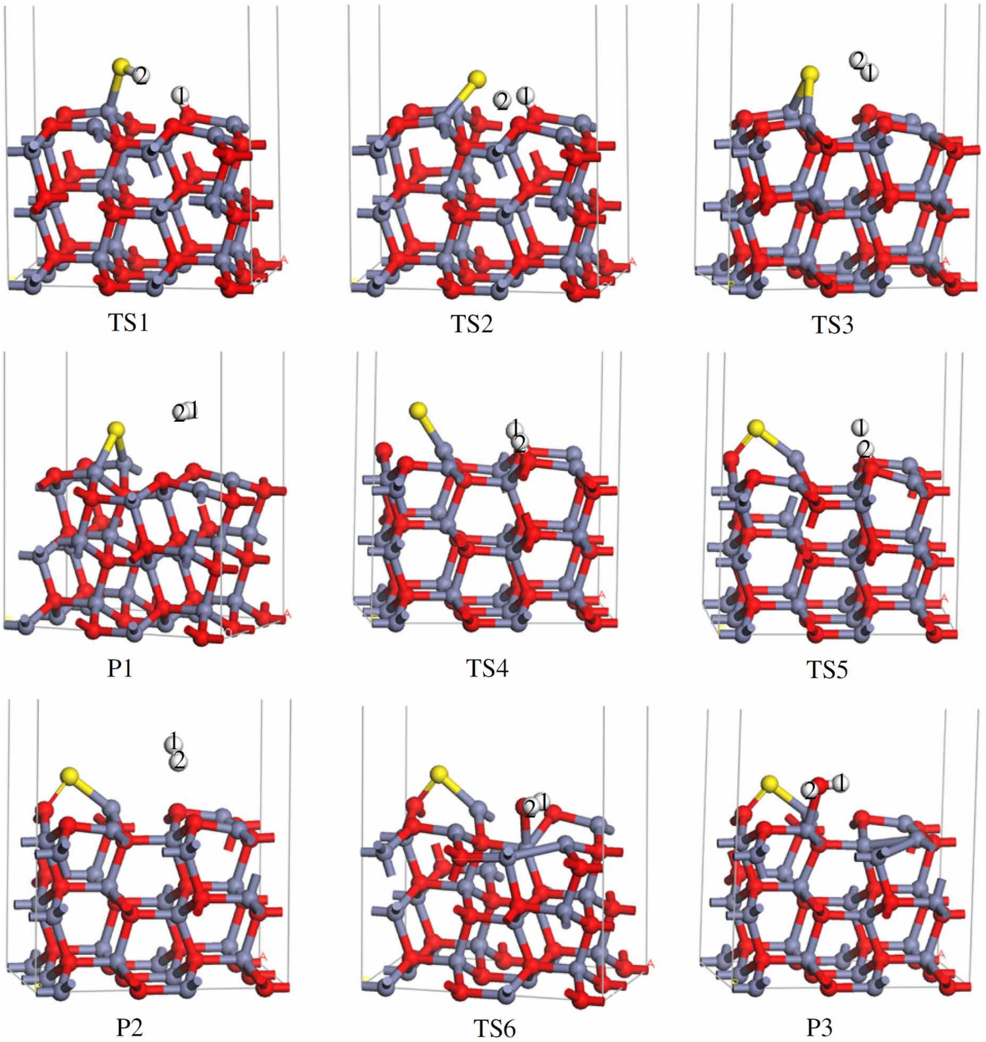
Figure 7. Potential energy profiles for the interaction of H_2S *and ZnO(10*$\bar{1}$*0) surface. The energies are relative to that of the adsorption structure of* H_2S*.*
(Ling et al 2013; Copyright 2013 Elsevier).



This mechanism has been accepted by most of authors to explain their results of RADS. But DFT study shows that the sulfur direct transfer from Ni to Zn site goes through lower energy barrier than the transfer by H_2S (Zhang et al. 2012c). It has been observed that the Ni (111) surface has the highest adsorption energy to sulfur among the different surfaces of Ag (111), Au (111), Cu (111), Ir (111), Ni (111), Pd (111) and Pt (111) (Alfonso 2008). This illustrates that the sulfur on Ni surface is the most difficult to be desorbed. Marécot found that Ni catalyst poisoned by sulfur lost the hydrogenation activity and cannot be reversed by hydrogen treatment. Thus this RADS mechanism may need further investigation.

2. **Mechanism of Dibenzothiophene RADS:** Huang et al (2011) proposed a three-stage mechanism of Ni/ZnO sorbent of diesel RADS. At the beginning, the surface Ni regenerating rate is basically equal to its poisoning rate and the reaction activity is kept at a stable state. In the second stage, the Ni regeneration rate is lower than the Ni poisoning rate; the sulfur transfer from Ni_3S_2 to ZnO is slowed down owing to the decrease of the active surface of ZnO. As a result, the content of Ni_3S_2 is increased gradually at the expense of metallic Ni phase. Thus a gradual deactivation occurs. In the last stage, most of ZnO is converted to ZnS and the sulfur transfer rate is access zero; the DBT conversion is mainly ascribed to the HDS catalyzed by Ni_3S_2. At this stage sulfur removed from the fuel product is mainly released to the effluent as H_2S.
3. **Relation between Structures and RADS Reaction of Ni/ZnO Sorbent:** Some important features can be drawn from the discussion above. The pre-reduction of NiO/ZnO sorbent may be unnecessary. The reduction of NiO can be achieved under reaction condition, meanwhile avoiding the formation of Ni-Zn alloy and the agglomeration of nano particles. The metallic Ni phase is partly sulfurized to form Ni_3S_2 when contacting with sulfur containing compounds. Carbon species originated from the decomposition of organic compound may dissolve into Ni phase and slows down the sulfur poison to Ni bulk. The sulfur atoms on Ni surface is continually transferred to ZnO phase to form

Figure 8. The structures of transition states and products
(Ling et al 2013; Copyright 2013 Elsevier).



ZnS, thus the Ni active sites can be auto-regenerated. After an induced time, a balance between sulfur deposition and sulfur transfer is built, the ratio of Ni^0 (or carburized Ni) is kept constant, and RADS reaction is in stable state. With the accumulation of ZnS, the sulfur transfer and sulfur diffusion in ZnO bulk are inhibited, and the content of Ni_3S_2 increases with the expanse of Ni^0. The sorbent begin deactivated until a quick drop of activity. At last the Ni surface has been totally covered by Ni_3S_2, and ZnO have been transformed into ZnS completely. The H_2S formed by HDS on Ni_3S_2 surface is released directly into effluent gas. Regeneration of the deactivated sorbent is required for the next cycle usage. The growth of nano particles and the collapse of pores seriously influence the regeneration effectiveness. Thus additives of structure are often used to stabilize the active components.

The fundamental research helps us understand the micro-cycle process of Ni/ZnO sorbent. It was found that the Ni surface is auto-regenerated by the sulfur transfer from Ni phase to the ZnO particles. But some important issues have to be solved. For example, why is the adsorbed sulfur transferred to the ZnO component rather than diffuse into the Ni bulk? Does the carbon permeation during RADS reaction inhibit the sulfidation of Ni bulk? Whether is the sulfur transferred by H_2S or directly through the interface? Thus deeper fundamental investigation is prerequisite for the better application of nano RADS sorbent.

APPLICATION OF RADS TECHNOLOGY

The S-Zorb Technique for RADS of Gasoline

The History of S-Zorb Technique

S-Zorb technique was firstly developed by Conoco Philips Petroleum Co. for desulfurization of gasoline and diesel. The first industrial unit of S-Zorb was built at Borger refinery in September of 1999 and started operation in April of 2001. During the test period, it was found that the attrition resistance of sorbent can be noticeable enhanced with expanded perlite replacing diatomite as structural additive.

After the 1st generation sorbent, the 2nd generation sorbent was developed by Süd-Chemie AG, which could produce clean gasoline with sulfur content less than 30 ppm. The 3rd generation S-Zorb sorbent was researched by Engelhard Co. A new expanded perlite was used and the preparation process was optimized. But this sorbent is inferior to the followed sorbent of Süd-Chemie AG (4th generation) in desulfurization activity and attrition resistance. It was given up before application. A new mineral was used in the 4th generation S-Zorb sorbent. The strength of attrition resistance was largely increased. Owing to the excellent desulfurization activity and attrition resistance, this S-Zorb sorbent has been commercially used to produce clean gasoline since 2002 (Table 1). The 5th generation sorbent was prepared with simpler method, there was only one key step-spray drying. The cost was decreased and the preparation efficiency was improved remarkably. Test showed that the 5th generation sorbent had very high activity of desulfurization and high ability of keeping octane number. However, it produced much more fine powders than the 4th generation sorbent, influencing the stable run of unit. Thus it has not been commercially applied.

In 2007, the S-Zorb technique was bought out by Sinopec, which began developing new generation sorbent. Based on the concept formulation provided by Conoco Phillips Co., the Research Institute of Petroleum Processing of Sinopec developed the FCAS sorbents and applied them successfully. Twenty four S-Zorb units have been built in the refineries of Sinopec by September 2014; the total processing capacity has reached over 30 Mt/y. And another 10 units are under design. The RADS technique of Sinopec has also been transferred to two other refineries in China. There are another six refineries producing deep desulfurized gasoline with S-Zorb units; they are Borger refinery, 0.25 Mt/y; Ferndale refinery, 0.85 Mt/y; Lake Charles refinery, 1.57 Mt/y; Wood River refinery, 1.30 Mt/y; Pasadena Refining Systems refinery, 1.60 Mt/y; Western Yorktown (Giant) refinery, 1.20 Mt/y.

Table 1. 4th generation of S-Zorb process for RADS of gasoline

	Unit 1 (Ferndale)	Unit 2 (Western)
Pressure /MPa	1.64	2.5
Temperature /°C	429	440
LHSV /h^{-1}	3.5	2.8
H_2/oil mol/mol)	0.5	0.42
S content in feed /ppm	1000	840
S content in product /ppm	13	8
desulfurization degreee /%	98.7	99
RON loss	1	1.6

(Adapted from Hou and Zhuang 2013).

The Circulating Fluidized Bed Process of S-Zorb

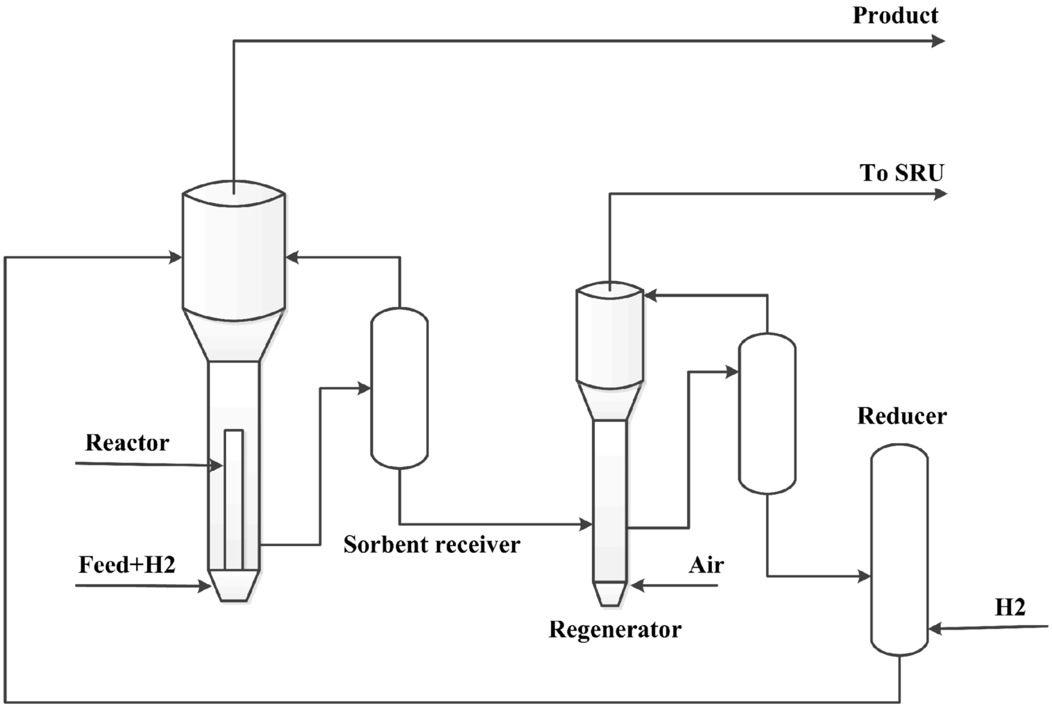
The S-Zorb technique uses the circulating fluidized bed process to produce clean gasoline with low sulfur content and high content olefins (Figure 9) where the partly deactivated sorbent is continually regenerated by oxidation and reduction. For the reactor, the temperature and pressure at inlet is controlled at about 420 ^{o}C and 2-3 MPa with a temperature rising about 22 ^{o}C and a pressure drop about 0.17 MPa, the LHSV and the mole ratio of H_2/oil is about 4 $h^{-1}$and <0.3, respectively. At this condition, the sulfur capacity of sorbent is about 8 wt%. The H_2 consumption compared with feed is about 0.2 wt%, and the loss of (RON+MON)/2 are about 0.3. The regenerator is run at about 525 ^{o}C and 0.1 MPa with 0.2 v/v% O_2 as a regeneration gas. The cycle time of sorbent is 20 min/per cycle (Hou and Zhuang, 2013). The supplement of sorbent are needed due to the abrasion loss. The sorbent are made with at least two additives to increase the strength and the resistance to the volume expansion from ZnO to ZnS. It is especially fitful to dispose the FCC gasoline fraction, which usually contain high contents of refractory thiophene analogs and olefins. The industrial application shows that this process can decrease the sulfur content in FCC gasoline from 1000 to 10 ppm with little loss of octane number.

Engineering parameters are very important for the smooth run of circulating fluidized bed. The sorbent must be tolerated the fast move and the friction among particles. The ratio of H_2/oil impacts the depth of desulfurization, hydrogen consumption and octane number of product. For different oil stream, the reaction temperature and pressure need adjustment to achieve the best desulfurization. The temperature and gas components in regenerator directly influence the structure and components of regenerated sorbent. Usually the sulfur in sorbent is not burnt out totally for the cause of energy efficiency and the protection to the sorbent. Improvements of the engineering technique parameters will accelerate the application of RADS nanotechnology.

The Regeneration of Sorbent

During the RADS reaction, the sorbent is transformed into a mixture of sulfides and gradually deactivated. To extend the lifetime of sorbent, it is necessary to regenerate deactivated sorbent in a two-step

Figure 9. The scheme of circulating fluidized progress of S-Zorb

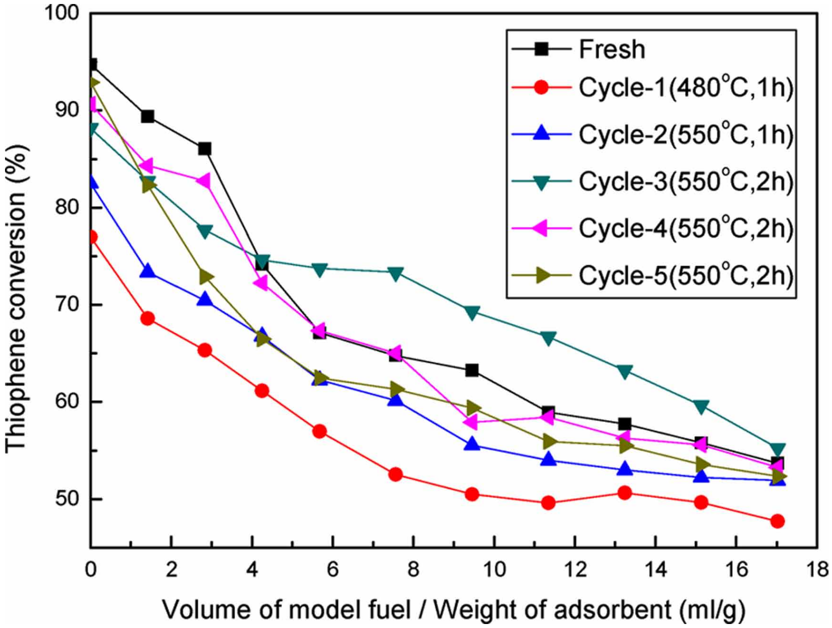


process: sulfides are firstly calcined to obtain oxides which are than treated in H_2. As for S-Zorb process, the $ZnAl_2O_4$ and Zn_2SiO_4 spinel analog are formed in regenerated sorbent, which decrease remarkably the content of the active component ZnO. Furthermore, the sorbent is easily crushed with the $ZnAl_2O_4$ and Zn_2SiO_4 in sorbent. The $ZnSO_4$ and $NiSO_4$ were found in regenerated sorbent also by XRD and XPS (Meng et al. 2013, Qiu et al. 2013). The formation of $ZnSO_4$ should be avoided. But the $NiSO_4$ seems to have some positive effect due to its Lewis acidity. The formation of $Zn_3O(SO_4)_2$ was observed in Wang et al.'s (2010) study.

Meng et al. (2013) investigated the regeneration over NiZnO/Al_2O_3-diatomite adsorbent. The regeneration was achieved in two-step: 1) nickel sulfide and zinc sulfide species are oxidized to nickel oxide and zinc oxide species using air at 480-550 °C for 1-2 h; 2) nickel oxide species is reduced to Ni^0 using hydrogen at 370 °C for 1 h. Figure 10 compares the RADS results of the fresh one with the regenerated ones after different regeneration cycles. 480 °C was found too low to regenerate the deactivated sorbent. The adsorptive capacity is recovered to 90% that of the fresh sorbent after regeneration at 550 °C for 1 h. As the regeneration time extends to 2 h (cycle-3 in Figure 10), the regeneration performance has recovered further. In fact, the desulfurization activity in cycle-3 is slightly higher than that in the fresh process. This was postulated as $NiSO_4$ gradually formed, increasing the Lewis acidity in the regenerated sorbent. However, in the following cycles, the loss of the NiO activity component in the regenerated sorbent inevitably causes the decrease of the RADS activities.

Figure 10. Adsorptive desulfurization curves in successive RADS cycles of NiZnO/Al$_2$O$_3$-diatomite adsorbent using model fuel

(Meng et al. 2013; Copyright 2013 American Chemical Society).



Fix Bed Techniques for RADS of Gasoline

The fix bed technique affords the advantages of low cost and easy maintenance. Several RADS processes have adopted this technique. A fix bed unit of RADS with ability of 0.5 Mt/y had started up successfully at Huizhou refinery of China National Offshore Oil Corporation (CNOOC) at the end of 2013. This technique was collaboratively developed by Beijing Haishunde Titanium Catalyst Co. Ltd. and CNOOC. The produced gasoline can meet the V national standard of China, which is corresponding to the Europe V standard. The YDCADS technique developed by Dalian Institute of Chemical Physics and Shaanxi Yanchang Petroleum (Group) Corp. Ltd. was tested in a pilot plant in July, 2013. It decreases the sulfur content in gasoline from 100 ppm to below 10 ppm. The loss of octane number is lower than 0.8 units and the hydrogen consumption is less than 0.2 wt%. Institute of Coal Chemistry, CAS applied the RADS fix-bed technique for ultra-deep desulfurization of arene raffinate oil in three petro-chemical enterprises. The sulfur content can be reduced below 0.1ppm.

Other Potential Application of RADS Technology

Tawara et al. (2001a and 2001b) investigated the RADS sorbent for the ultra-deep desulfurization of kerosene of the fuel cell (FC). A 13% Ni/ZnO sorbent was certified to decrease the average sulfur content of kerosene to less than 0.03 ppm for 1 year. They predicted that 1-year operation of petroleum feed FC cogenerations and 1110 thousand-km running of FC vehicles are possible by applying this sorbent.

Ni/ZnO sorbent can be effective for producing low-sulfur diesel. Huang et al. (2010) observed that the sulfur content in the diesel oil is reduced from the original 560.0 ppm to below 10 ppm after an induced period over a NiO/ZnO sorbent with 36.6 wt% Ni content. However, the sulfur content increased slowly after 12 h on stream, until to 120.0 ppm at 122 h on stream. This primary results illustrates that for diesel RADS the sulfur capacity and desulfurization ability are necessary to be largely improved before application.

RADS can be applicable for deep desulfurization in the production of chemicals. The sulfur level can be dropped to very low (<0.03 ppm); and the process disposing the pollutant H_2S gas can be omitted due to the adsorption of ZnO to sulfur. This is favored for the small chemical plants.

The Comparison of RADS Technology with HDS Technology

RADS technology has good activity for the deep desulfurization of gasoline. Because the hydrogenation of olefins is inhibited, the hydrogen consumption can be decreased largely. And the octane number has little drop. This brings the merits of cost. But the circulating fluidized bed process is complicated; the operation parameters are more difficult to be controlled. Meanwhile there is high demand for the strength and resistance to abrasion of sorbent. Although fix-bed technology has been developed, the sorbent still need frequently regeneration.

HDS technology can be used for deep desulfurization of versatile feeds. But the hydrogenation to olefin results in the loss of octane number of gasoline. This can be solved with a followed process recovering octane number. But the cost is usually higher. On the other hand, the fix bed process is simpler, and the catalysts usually have longer life.

Both technologies will play important roles in the deep desulfurization of petroleum refining. The RADS shows its merit to deep desulfurization of FCC gasoline, while HDS is more fitful for deep desulfurization of diesel.

FUTURE RESEARCH DIRECTIONS

With the more stringent regulations regarding the sulfur content in gasoline, the extensive application of RADS for deep desulfurization of gasoline can be expected. But not limit to this, the RADS may also be used in the deep desulfurization of kerosene, diesel and petro-chemicals in future. The successful application relies on the further improvement of sorbent and related technique. But some key problems need to be resolved. For example, the active structure for desulfurization is carbided Ni, metallic Ni or partly sufided Ni is not clear yet. It has not be answered that if the auto-regeneration of Ni active sites can be fulfilled by direct sulfur transfer through the interface. From the perspective of engineering, the structure additives need to be investigated deeply. If the formation of $ZnSO_4$, $ZnAl_2O_4$ and Zn_2SiO_4 can be inhibited, the regeneration of sorbent can be improved further. The relation of double metals with the olefin hydrogenation should be researched in future. The RADS represent one of fastest developing field in petroleum refining industry. Its effective and extensive application needs the good cooperation between researchers and engineers.

CONCLUSION

The fundamental research reveals the micro-cycle of Ni/ZnO sorbent. During the RADS reaction the Ni active center are auto-regenerated continually by the sulfur transfer from Ni surface to the ZnO particles. Thus the metallic Ni catalytic centers does not be poisoned by sulfur, the desulfurization activity can be kept stable although the ZnO phase is always sulfided. The deactivation does develop after longer reaction time due to the inhibition of sulfur transfer by the accumulation of ZnS on the surface of ZnO; this can be partly recovered by the regeneration. But the deactivation by the sinter of sorbent is difficult to be recovered, thus the structure reagent, such as alumina, silica or perlite, are usually added into the sorbent to increase the strength and resistance to the abrasion. The formation of spinel during regeneration has negative influence on the performance of sorbent. The macro cycle, namely the periodic deactivation-regeneration of Ni/ZnO sorbent, guarantees the long time usage of sorbent in commercial application.

ACKNOWLEDGMENT

The authors are acknowledged of the sponsorship from the National Natural Science Foundation of China (21473231) for the fundamental research of RADS of Ni/ZnO sorbent.

REFERENCES

Alfonso, D. R. (2008). First-principles studies of H_2S adsorption and dissociation on metal surfaces. *Surface Science*, *602*(16), 2758–2768. doi:10.1016/j.susc.2008.07.001

Ania, C. O., & Bandosz, T. J. (2006a). Metal-loaded polystyrene-based activated carbons as dibenzothiophene removal media via reactive adsorption. *Carbon*, *44*(12), 2404–2412. doi:10.1016/j.carbon.2006.05.016

Ania, C. O., & Bandosz, T. J. (2006b). Sodium on the surface of activated carbons as a factor enhancing reactive adsorption of dibenzothiophene. *Energy & Fuels*, *20*(3), 1076–1080. doi:10.1021/ef050425c

Ania, C. O., Parra, J. B., Arenillas, A., Rubiera, F., Bandosz, T. J., & Pis, J. J. (2007). On the mechanism of reactive adsorption of dibenzothiophene on organic waste derived carbons. *Applied Surface Science*, *253*(13), 5899–5903. doi:10.1016/j.apsusc.2006.12.065

Babich, I. V., & Moulijn, J. A. (2003). Science and technology of novel processes for deep desulfurization of oil refinery streams: A review. *Fuel*, *82*(6), 607–631. doi:10.1016/S0016-2361(02)00324-1

Bezverkhyy, I., Ryzhikov, A., Gadacz, G., & Bellat, J. P. (2008). Kinetics of thiophene reactive adsorption on Ni/SiO_2 and Ni/ZnO. *Catalysis Today*, *130*(1), 199–205. doi:10.1016/j.cattod.2007.06.038

Bezverkhyy, I., Safonova, O. V., Afanasiev, P., & Bellat, J. P. (2009). Reaction between thiophene and Ni nanoparticles supported on SiO_2 or ZnO: In situ synchrotron X-ray diffraction study. *The Journal of Physical Chemistry C*, *113*(39), 17064–17069. doi:10.1021/jp903488p

Chica, A., Corma, A., & Dómine, M. E. (2006). Catalytic oxidative desulfurization (ODS) of diesel fuel on a continuous fixed-bed reactor. *Journal of Catalysis*, *242*(2), 299–308. doi:10.1016/j.jcat.2006.06.013

Chica, A., Strohmaier, K. G., & Iglesia, E. (2005). Effects of zeolite structure and aluminum content on thiophene adsorption, desorption, and surface reactions. *Applied Catalysis B: Environmental*, *60*(3-4), 223–232. doi:10.1016/j.apcatb.2005.02.031

Davoodi-Dehaghani, F., Vosoughi, M., & Ziaee, A. A. (2010). Biodesulfurization of dibenzothiophene by a newly isolated Rhodococcus erythropolis strain. *Bioresource Technology*, *101*(3), 1102–1105. doi:10.1016/j.biortech.2009.08.058 PMID:19819129

Fan, J., Wang, G., Sun, Y., Xu, C., Zhou, H., Zhou, G., & Gao, J. (2010). Research on reactive adsorption desulfurization over Ni/ZnO-SiO_2-Al_2O_3 adsorbent in a fixed-fluidized bed reactor. *Industrial & Engineering Chemistry Research*, *49*(18), 8450–8460. doi:10.1021/ie100923v

Gyanesh, K. (2001). Sorbent composition, process for producing and use in desulfurization. *PCT Int. Appl.* WO 0114051.

Homs, N., Llorca, J., & de la Piscina, P. R. (2006). Low-temperature steam-reforming of ethanol over ZnO-supported Ni and Cu catalysts: The effect of nickel and copper addition to ZnO-supported cobalt-based catalysts. *Catalysis Today*, *116*(3), 361–366. doi:10.1016/j.cattod.2006.05.081

Hou, X., & Zhuang, J. (Eds.). (2013). *Technology handbook of S-Zorb unit for desorption desulfurization of FCC gasoline*. Beijing, China: China Petrochemical Press.

Huang, L., Qin, Z., Wang, G., Du, M., Ge, H., & Li, X. et al. (2010a). A detailed study on the negative effect of residual sodium on the performance of Ni/ZnO adsorbent for diesel fuel desulfurization. *Industrial & Engineering Chemistry Research*, *49*(10), 4670–4675. doi:10.1021/ie100293h

Huang, L., Wang, G., Qin, Z., Dong, M., Du, M., & Ge, H. et al. (2011). In situ XAS study on the mechanism of reactive adsorption desulfurization of oil product over Ni/ZnO. *Applied Catalysis B: Environmental*, *106*(1-2), 26–38.

Huang, L., Wang, G., Qin, Z., Du, M., Dong, M., & Ge, H. et al. (2010b). A sulfur K-edge XANES study on the transfer of sulfur species in the reactive adsorption desulfurization of diesel oil over Ni/ZnO. *Catalysis Communications*, *11*(7), 592–596. doi:10.1016/j.catcom.2010.01.001

Ito, E., & van Veen, J. A. R. (2006). On novel processes for removing sulphur from refinery streams. *Catalysis Today*, *116*(4), 446–460. doi:10.1016/j.cattod.2006.06.040

Jia, G. (2014). Domestic FCAS of catalyst used to achieve long period (in Chinese). Retrieved from http://www.sinopecnews.com.cn/news/content/2014-02/17/content_1377530.shtml

Jiang, Z., Liu, Y., Sun, X., Tian, F., Sun, F., & Liang, C. et al. (2003). Activated carbons chemically modified by concentrated H_2SO_4 for the adsorption of the pollutants from wastewater and the dibenzothiophene from fuel oils. *Langmuir*, *19*(3), 731–736. doi:10.1021/la020670d

Johnson, B. G., Slater, P., & Kidd, D. (2001). Application of Phillips's Zorb process to distillates-meeting the challenge. Proceedings of AM-01-14. New Orleans.

Khare, G. P. (1999). *Sorbent compositions* (p. 5958830). US: US Pat Appl.

Ling, L., Zhang, R., Han, P., & Wang, B. (2013). DFT study on the sulfurization mechanism during the desulfurization of H_2S on the ZnO desulfurizer. *Fuel Processing Technology*, *106*, 222–230. doi:10.1016/j.fuproc.2012.08.001

Marécot, P., Paraiso, E., Dumas, J. M., & Barbier, J. (1992). Deactivation of nickel catalysts by sulphur compounds: I. Benzene hydrogenation. *Applied Catalysis A*, *80*(1-2), 79–88. doi:10.1016/0926-860X(92)85109-O

Meng, X., Huang, H., & Shi, L. (2013). Reactive mechanism and regeneration performance of NiZnO/Al_2O_3-diatomite adsorbent by reactive adsorption desulfurization. *Industrial & Engineering Chemistry Research*, *52*(18), 6092–6100. doi:10.1021/ie303514y

Moezzi, A., McDonagh, A. M., & Cortie, M. B. (2012). Zinc oxide particles: Synthesis, properties and applications. *Chemical Engineering Journal*, *185-186*, 1–22. doi:10.1016/j.cej.2012.01.076

Monticello, D. J. (2000). Biodesulfurization and the upgrading of petroleum distillates. *Current Opinion in Biotechnology*, *11*(6), 540–546. doi:10.1016/S0958-1669(00)00154-3 PMID:11102787

Park, J. G., Ko, C. H., Yi, K. B., Park, J. H., Han, S. S., Cho, S. H., & Kim, J. N. (2008). Reactive adsorption of sulfur compounds in diesel on nickel supported on mesoporous silica. *Applied Catalysis B: Environmental*, *81*(3-4), 244–250. doi:10.1016/j.apcatb.2007.12.014

Pawelec, B., Navarro, R. M., Campos-Martin, J. M., & Fierro, J. L. G. (2010). Towards near zero-sulfur liquid fuels: A perspective review. *Catalysis Science & Technology*, *1*(1), 23–42. doi:10.1039/c0cy00049c

Qiu, L., Zou, K., & Xu, G. (2013). Investigation on the sulfur state and phase transformation of spent and regenerated S zorb sorbents using XPS and XRD. *Applied Surface Science*, *266*, 230–234. doi:10.1016/j.apsusc.2012.11.156

Rodriguez-Gattorno, G., Galano, A., & Torres-García, E. (2009). Surface acidbasic properties of WO_x-ZrO_2 and catalytic efficiency in oxidative desulfurization. *Applied Catalysis B: Environmental*, *92*(1-2), 1–8. doi:10.1016/j.apcatb.2009.07.031

Ryzhikov, A., Bezverkhyy, I., & Bellat, J. (2008). Reactive adsorption of thiophene on Ni/ZnO: Role of hydrogen pretreatment. *Applied Catalysis B: Environmental*, *84*(3-4), 766–772. doi:10.1016/j.apcatb.2008.06.009

Samokhvalov, A., & Tatarchuk, B. J. (2010). Review of experimental characterization of active sites and determination of molecular mechanisms of adsorption, desorption and regeneration of the deep and ultradeep desulfurization sorbents for liquid fuels. *Catalysis Reviews*, *52*(3), 381–410. doi:10.1080/01614940.2010.498749

Seredych, M., Deliyanni, E., & Bandosz, T. J. (2010). Role of microporosity and surface chemistry in adsorption of 4, 6-dimethyldibenzothiophene on polymer-derived activated carbons. *Fuel*, *89*(7), 1499–1507. doi:10.1016/j.fuel.2009.09.032

Seredych, M., Khine, M., & Bandosz, T. J. (2011). Enhancement in dibenzothiophene reactive adsorption from liquid fuel via incorporation of sulfur heteroatoms into the nanoporous carbon matrix. *ChemSusChem*, *4*(1), 139–147. doi:10.1002/cssc.201000366 PMID:21226224

Shalaby, C., Ma, X., Zhou, A., & Song, C. (2009). Preparation of organic sulfur adsorbent from coal for adsorption of dibenzothiophene-type compounds in diesel fuel. *Energy & Fuels*, *23*(5), 2620–2627. doi:10.1021/ef801135t

Shangguan, J., Zhao, Y., Fan, H., Liang, L., Shen, F., & Miao, M. (2013). Desulfurization behavior of zinc oxide based sorbent modified by the combination of Al_2O_3 and K_2CO_3. *Fuel, 108*, 80-84.

Sharma, M., Vyas, R. K., & Singh, K. (2013). A review on reactive adsorption for potential environmental applications. *Adsorption*, *19*(1), 161–188. doi:10.1007/s10450-012-9436-9

Tang, M., Zhou, L., Du, M., Lyu, Z., Wen, X.-D., Li, X., & Ge, H. (2015). A novel reactive adsorption desulfurization Ni/MnO adsorbent and its hydrodesulfurization ability compared with Ni/ZnO. *Catalysis Communications*, *61*, 37–40. doi:10.1016/j.catcom.2014.11.005

Tawara, K., Nishimura, T., & Iwanami, H. (2000). Ultra-deep hydrodesulfurization of kerosene for fuel cell system (Part 2) Regeneration of sulfur-poisoned nickel catalyst in hydrogen and finding of auto-regenerative nickel catalyst. *Sekiyu Gakkaishi*, *43*(2), 114–120. doi:10.1627/jpi1958.43.114

Tawara, K., Nishimura, T., Iwanami, H., Nishimoto, T., & Hasuike, T. (2001a). New hydrodesulfurization catalyst for petroleum-feed fuel cell vehicles and cogenerations. *Industrial & Engineering Chemistry Research*, *40*(10), 2367–2370. doi:10.1021/ie000453c

Tawara, K., Nishimura, T., Iwanami, H., Nishimoto, T., & Hasuike, T. (2001b). Ultra-deep hydrodesulfurization of kerosene for fuel cell system (Part 3) Development and evaluation of Ni/ZnO catalyst. *Sekiyu Gakkaishi*, *44*(1), 43–51. doi:10.1627/jpi1958.44.43

Wang, M. Z., & Ruan, Y. J. (2010). Study on process conditions of adsorption desulfurization reaction of FCC gasoline. *Petroleum Refinery Engineering*, *40*(9), 5–10.

Wen, Y., Wang, G., Wang, Q., Xu, C., & Gao, J. (2012). Regeneration characteristics and kinetics of Ni/ZnO-SiO_2-Al_2O_3 adsorbent for reactive adsorption desulfurization. *Industrial & Engineering Chemistry Research*, *51*(10), 3939–3950. doi:10.1021/ie202730w

Yang, R. T., Hernandez-Maldonado, A. J., & Yang, F. H. (2003). Desulfurization of transportation fuels with zeolites under ambient conditions. *Science*, *301*(5629), 79–81. doi:10.1126/science.1085088 PMID:12843388

Zhang, J., Liu, Y., Tian, S., Chai, Y., & Liu, C. (2010). Reactive adsorption of thiophene on Ni/ZnO adsorbent: Effect of ZnO textural structure on the desulfurization activity. *Journal of Natural Gas Chemistry*, *19*(3), 327–332. doi:10.1016/S1003-9953(09)60076-1

Zhang, S., Zhang, Y., Huang, S., Wang, P., & Tian, H. (2012b). Mechanistic investigations on the adsorption of thiophene over Zn_3NiO_4 bimetallic oxide cluster. *Applied Surface Science*, *258*(24), 10148–10153. doi:10.1016/j.apsusc.2012.06.096

Zhang, Y., Yang, Y., Hana, H., Yang, M., Wang, L., & Zhang, Y. et al. (2012a). Ultra-deep desulfurization via reactive adsorption on Ni/ZnO: The effect of ZnO particle size on the adsorption performance. *Applied Catalysis B: Environmental*, *119-120*, 13–19. doi:10.1016/j.apcatb.2012.02.004

Zhang, Y., Yang, Y., Lin, F., Yang, M., Liu, T., Jiang, Z., & Li, C. (2013). Improvement of adsorptive desulfurization performance of Ni/ZnO adsorbent by doping with Mn additive. *Chinese Journal of Catalysis*, *34*(1), 140–145. doi:10.1016/S1872-2067(11)60513-5

Zhou, G., Sun, W., Jiang, W., & Zhou, H. (2013). Deep desulfurization of hydro-gasoline by adsorption in H_2 atmosphere over Ni/ZnO-SiO_2-Al_2O_3. *Petroleum Processing and Petrochemicals*, *44*(7), 17–21.

KEY TERMS AND DEFINITIONS

Circulating Fluidized Bed (CFB): A process in which the deactivated or partly deactivated catalyst in reactor are continually moved out, and then into regenerator to be regenerated, and then are transferred back into reactor, achieving the continually cycle of reaction, deactivation and regeneration of catalyst.

Density Functional Theory (DFT): A computational quantum mechanical modelling method used in physics, chemistry and materials science to investigate the electronic structure (principally the ground state) many-body systems, as well as adsorption, desorption and reaction in particular atoms, molecules, and the condensed phases. With this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density. Hence the name density functional theory comes from the use of functionals of the electron density.

Fluid Catalytic Cracking (FCC): One of the most important conversion processes used in petroleum refineries. It is widely used to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils to more valuable gasoline, olefinic gases, and other products with an acid catalyst.

Hydrodesulfurization (HDS): A catalytic chemical process widely used to remove sulfur (S) under hydrogen atmosphere from natural gas and from refined petroleum products such as gasoline or petrol, jet fuel, kerosene, diesel fuel, and fuel oils. The purpose of removing the sulfur is to reduce the sulfur dioxide (SO_2) emissions that result from using those fuels in automotive vehicles, aircraft, railroad locomotives, ships, gas or oil burning power plants, residential and industrial furnaces, and other forms of fuel combustion.

Hydrogenolysis: A chemical reaction whereby a carbon-carbon or carbon-heteroatom single bond is cleaved or undergoes "lysis" by hydrogen. The heteroatom may vary, but it usually is oxygen, nitrogen, or sulfur.

Reactive Adsorption Desulfurization (RADS): A process using a sorbent with the metal-based catalytic component for sulfur capture to form metal sulfide in the presence of hydrogen, then the sulfur is transferred and retained on the sorbent component, while the hydrocarbon portion of the sulfur containing molecule is released back into the process stream.

Thermogravimetric Analysis (TGA): A method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature, or as a function of time. It can provide information about physical phenomena, such as second-order phase transitions, including vaporization, sublimation, absorption, adsorption, and desorption. Likewise, it can provide information about chemical phenomena including chemisorptions, desolvation (especially dehydration), decomposition, and solid-gas reactions (e.g., oxidation or reduction).

Chapter 8

Trimetallic Sulfide Catalysts for Hydrodesulfurization

Rafael Huirache-Acuña
Universidad Michoacana de San Nicolás de Hidalgo, Mexico

Eric M. Rivera-Muñoz
National Autonomous University of Mexico, Mexico

Gabriel Alonso-Nuñez
National Autonomous University of Mexico, Mexico

Omar Gutierrez
Instituto Tecnológico Superior de Ciudad Hidalgo, Mexico

Barbara Pawelec
Instituto de Catálisis y Petroleoquímica, C.S.I.C., Spain

ABSTRACT

The more stringent environmental regulations enacted throughout the world have increased the need of more active hydrotreating (HDT) catalysts, in the petroleum refining industry. Usually, the catalysts used for diesel oil hydrotreatment are γ*-*Al_2O_3 *supported molybdenum or tungsten sulfides promoted with cobalt or nickel. Current strategies for the design of novel HDS catalysts often include variations in the support formulation, catalyst preparation method and active phase formulation. In this sense, the new generations of catalysts, such as NEBULA®, are based on a totally different concept of bulk-like. In this chapter, we present recent research related to the synthesis, characterization and performance of trimetallic sulfide nanocatalysts for hydrodesulfurization. The present chapter analyses the state of art of the ternary sulfide hydrotreating catalysts.*

1. INTRODUCTION

Traditionally, in the early 1990s, sulfur used to be removed from petroleum-derived feedstocks by a hydrodesulphurization (HDS) process using γ-Al_2O_3-supported Mo or W sulfide catalysts promoted by Co or Ni (Topsøe *et al.,* 1996*;* Ho, 2004 and 2008). However, because the thermodynamic limitations of bimetallic Co(Ni)Mo(W)/Al_2O_3 catalyst formulation to perform deep HDS reactions at high temperature, it was impossible to satisfy stringent legislative requirements for ultra-low sulfur transport fuels using

DOI: 10.4018/978-1-4666-9545-0.ch008

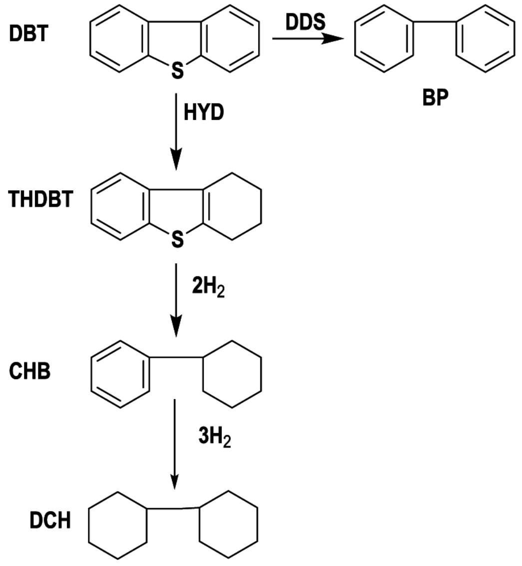
those catalysts. After many efforts in the design novel catalyst formulations, supports and new preparation procedures, the recent catalyst developments and technologies allow production of ultra-low sulfur diesel (ULSD) (Soled *et al.,* 2000; Topsøe *et al.,* 1996). However, the determination that catalyst could be used depends on the specific refinery configuration, feedstock blends employed, and it might be a simple matter of economics (Topsøe *et al.,* 2005).

The S-containing refractory compounds, which should be removed from the feedstock's, are dibenzothiophene (DBT) and alkyl-substituted DBT. For those molecules, the HDS reaction occurs mainly *via* hydrogenation (HYD) and direct desulfurization (DDS) pathways. For the HDS of DBT reaction (see Box 1), direct desulfurization pathway (DDS) leads to formation of biphenyl (BP), whereas hydrogenation pathway (HYD) leads to formation of tetrahydrodibenzothiophene (THDBT), cyclohexylbenzene (CHB) and dicyclohexyl (DCH) (Ho, 2004 and 2008). It is well established that DDS route of this reaction is favored for the Co-promoted catalysts whereas Ni-promoted ones exhibit enhanced HYD route of DBT transformation, as it was confirmed for the all catalysts studied in this chapter. The presence of alkyl groups in the highly refractory 4,6-dimethyldibenzothiophene (4,6-DMDBT) hardly affects the hydrogenation (HYD) pathway whereas the DDS pathway is severely inhibited. The hindrance of the C-S bond cleavage in the THDBT was claimed to be the most probably reason for the low reactivity of 4,6-DMDBT (Ho, 2004 and 2008). To overcome this problem, novel HDS catalysts exhibit enhanced hydrogenation function.

Actually, many refineries used a BRIM™ hydroprocessing technology developed by Haldor Topsøe (Topsøe *et al.,* 2005) whereas others successfully employed unsupported catalysts called NEBULA (Soled *et al.,* 2000; Plantenga *et al*., 2003). The Ni-Mo/Al_2O_3 catalysts based on the BRIM™ hydroprocessing technology possess Mo(W)S_2 phases having a large amount of "*brim sites*". Owing their metallic character, those catalysts exhibit enhanced hydrogenation function, and in consequence, display superior hydrodesulphurization activity and excellent stability (Lauritsen *et al.* 2004a, b).

Box 1. General reaction scheme for the hydrodesulfurization of dibenzothiophene over unsupported and supported trimetallic catalysts

HYD: hydrogenation reaction route
DDS: direct desulfurization reaction route
DBT: dibenzothiophene
THDBT: tetrahydrodibenzothiophene (nd.: non detected)
BP: biphenyl
CHB: cyclohexylbenzene
DCH: dicyclohexyl



A totally different concept of bulk-like materials was developed in 2001 by ExxonMobil, Akzo Nobel and Nippon Ketjen (Soled *et al.,* 2000; Plantenga *et al.,* 2003). Those unsupported catalysts, so-called NEBULA, possess Ni-Mo-W trimetallic formulation especially suitable for production of fuels with ultra-low sulfur content and for nitrogen elimination and saturation of aromatic compounds in diesel (Soled *et al.,* 2000; Plantenga *et al.,* 2003). In the catalyst formulation, molybdenum is partially substituted by tungsten. As a consequence, the unsupported Ni-Mo-W exhibit enhanced activity relative to unsubstituted (Ni-Mo) phase.

Because the surface properties of bulk catalysts can be easily tuned by supporting them on different substrates, the research into novel and improved ternary Co(Ni)MoW sulfide catalysts for hydrotreatment has renewed interest. However, as compared with unsupported bimetallic Co(Ni)-Mo(W)S_2 systems, the number of reports about supported trimetallic Co(Ni)-Mo-W catalyst formulations is limited being alumina- and silica-supported catalysts mainly studied. Moreover, the number of active sites is still not precisely known although common understanding is emerging about the structure of the sulfided trimetallic Co(Ni)-Mo-W catalysts. (Olivas *et al*., 2009; Huirache-Acuña *et al*., 2009; 2010 and 2012; Guzmán *et al*., 2013).

In general, for the supported ternary Ni(Co)-Mo-W sulfide catalysts, the use of Ni as promoter demonstrated to be more effective than Co (Huirache-Acuña *et al.,* 2012). On the contrary, for unsupported ones prepared *ex* thiosalts, the activity results obtained for Co-promoted samples were considerably better than those for Ni-promoted counterparts, as demonstrated by Olivas *et al.* (2009). However, the effect of type of promoter depends not only on the support, but also on the reaction conditions employed. Indeed, at low H_2 pressure and high space velocities, Co-promoted catalysts exhibited often better activity than Ni-promoted ones (Topsøe *et al*., 2005).

A disadvantage of mixed oxides is their low surface area, as it was confirmed for Ni-Mo-W mixed oxide nanostructures by Paraguay-Delgado *et al.* (2008). Moreover, different phases such as WO_3, $W_{0.4}Mo_{0.6}O_3$, MoO_3 and $NiWO_4$ can be obtained after hydrothermal annealing (Paraguay-Delgado *et al*., 2008). To overcome this, anisotropic layered precursors, such as alkylthiometallates, could be used to obtain mixed oxides with high surface areas if *in situ* decomposition of thiometallates was employed (Nava *et al*, 2005). This type of precursors generally produces volatile compounds during calcination, which may generate porosity and therefore high surface areas. Furthermore, since a bimetallic precursor compound is obtained by mixing of the metals at a molecular level, a good mixing of the active metals is expected after calcination and subsequent sulfidation (Quintana-Melgoza *et al*., 2001; Amaya *et al*., 2014) (see Table 1). However, the textural properties and the catalyst response in the HDS of DBT reaction are strongly affected by the nature of alkyl groups of thiometallates (Huirache-Acuña *et al*., 2006 (a)), the precursor decomposition conditions (*ex situ* and *in situ* modes) (Bocarando *et al*, 2009(a)), the type of precursor employed (Ni, Co) (Huirache-Acuña *et al*., 2006(a),(b)), and the effect of the amount of Ni promoter (Bocarando *et al*., 2009(b)). With respect unsupported ternary Ni-Mo-W sulfide systems, Olivas *et al*. (2009) demonstrated that the synergistic effect of Ni is higher in bimetallic (Mo,W)S_2 than in monometallic MoS_2 and WS_2 phases studied separately. Such a behavior was attributed to the formation of metallic states in the Ni-Mo-W-S catalyst due to the electronic interaction of Mo with W and Ni, as shown by Extended Hückel calculations (Olivas *et al*., 2009). According to these calculations, the combination of Mo and W atoms forming binary (Mo,W)S_2 compounds change the semiconductor character of MoS_2 or WS_2 to the metallic one. Incorporation of Ni to form trimetallic Ni(Mo-W)S_2 compounds increases additionally availability of electrons over the Fermi level. It was hypothesized that the favorable position of Ni in the Mo(W)S_2 structure might enhance this effect (Olivas *et al*., 2009).

Table 1. Summary of synthesis reports using oxide precursors

Catalysts	Synthesis Method Conditions	Reference
NEB_{H2S} NEB_{DMDS} NEB_{DMS}	Two aqueous solutions were prepared (A and B). Solution A consisted of ammonium heptamolybdate and ammonium metatungstate dissolved in water at 363 K under stirring. The pH of this solution was maintained at about 9.8 by adding NH_4OH. Solution B consisted of nickel nitrate dissolved in water at 363 K, while stirring, solution B was slowly added to solution A at 363 K, a precipitate was formed, then the solid was filtered, washed with hot water and dried at 393 K. The molar ratio Mo:W:Ni of precipitate was 1:1:2 and was represented as NH_4-Ni-$Mo_{0.5}$ $W_{0.5}$-O. Sulfidation was carried out in a tubular furnace at 673K for 2 h using H_2S, DMDS or DMS (10 vol.% in hydrogen).	Gochi *et al.* 2005
Mo-Ni-W	Ammonium heptamolibdate, ammonium metatungstate and nickel nitrate were used as reagents with an atomic ratio of 1:1:1. The mixture was stirred at 333 K for 48 h. Then 20 mL of the resulting solution was diluted with 20 mL of deionized water and acidified with 2.2 N of nitric acid (2 mL) in order to adjust the pH to 1.5. The solution was transferred to Teflon-lined stainless steel autoclave and heated up to 473 K for 48 h. Resulting materials were washed, filtered and dried for 5 h. Finally, Mo-Ni-W compound was annealed at 823 K and 1173 K, respectively.	Paraguay-Delgado *et al.* (2008)
Ni-SR673 Ni-SR798 Co-SR673 Co-SR798	The precursors were synthesized by co-precipitation (CoMoW) and hydrothermal (NiMoW) methods. Solutions containing the metal salts were separately prepared and then mixed, always adding the nickel (or cobalt) solution to the other ones; ammonia was used as a precipitating agent. In the co-precipitation method, the slurry produced was maintained at 298 K under stirring during 4 h. In the hydrothermal method, additionally, the mixture was heated at 473 K for 96 h in Teflon-lined autoclaves. After the heating, the solids were filtered, washed with water, and dried at 373 K. Ni-O and Co-O were sulfided by heating ex-situ under a H_2S/H_2 (15%, v/v) mixture from 298 K to 673 or 798 K for 4 h with a heating rate of 5 K/min.	Amaya *et al*., 2014

Within this scenario, in this chapter we present some of the recent research related to the synthesis, characterization, and catalytic performance of unsupported and supported trimetallic sulfide catalysts. A new metals promoter and dopants support are identified. Examples are given to show the superiority of the use of trimetallic catalyst formulation with respect to the bimetallic one.

2. UNSUPPORTED TRIMETALLIC CATALYSTS FOR HDS

Unsupported trimetallic catalysts could be prepared by sulfidation of the metal oxide precursors or by thiosalt decomposition. The former method has the disadvantage of imperfect catalyst sulfidation leading to a lower catalyst activity whereas the latter method is a simple and reproducible method for obtaining Co(Ni)-Mo-W catalysts. The main advantage of the thiosalt decomposition method resides in the fact that the catalyst activation by sulfidation should be avoided (Lumbreras *et al.,* 2010). Moreover, the preparation of unsupported sulfide systems by sulfidation of their oxide precursors present a disadvantage due to the low surface of mixed oxides (Quintana-Melgoza *et al.,* 2001). To overcome this, layered precursors could be used to obtain the mixed oxides with high surface areas and porosity generated during calcination by production of volatile compounds (Amaya *et al*. 2014). Furthermore, since the mixing of the metal promoters occurs at a molecular level, one might to expect a good mixing of the active phases during solid's calcination and its subsequent sulfidation. On the contrary, the thiosalts already have sulfur bound to the metal atoms in a tetrahedral coordination, thus, its position did not change during thiosalt decomposition.

2.1. Catalysts Prepared by Sulfidation of Oxide Precursors

One way to prepare unsupported trimetallic catalysts for HDS is through metal oxide precursors, which are subsequently activated by sulfidation with H_2S/H_2 gas mixture or by using a feed containing sulfur compounds and H_2. In this sense, it was found that the use of different sulfiding agents does not only influence on the degree of sulfidation, but also leads to catalysts with different crystalline phases and surface areas. In particular, it was found that the sulfiding agent plays a very important role in the catalyst morphology, as revealed by XRD, scanning electron microscopy (SEM), TEM and BET results (Gochi *et al.,* 2005).

The influence of the type of sulfiding agent employed for the catalyst activation on the final catalyst response in the HDS of dibenzothiophene (DBT) reaction was investigated by Gochi *et al.* (2005). The Ni-Mo-W catalytic system was prepared according to the patent reported by Soled *et al*. (2000) using a trimetallic precursor (NH_4-Ni-$Mo_{0.5}W_{0.5}$-O) (Table 1). The catalyst was sulfided using H_2S, dimethyl disulfide (DMDS) and dimethyl sulfide (DMS). Results suggested that dimethyl sulfide (DMDS) can be used as sulfiding agent instead of H_2S to generate catalyst with high activity. This is because the sulfidation with DMDS yielded a catalyst with greater specific surface area and elemental mapping showed that all elements (Mo-W-Ni) are homogeneously distributed. On the contrary the study by Gochi *et al.* (2005), Huirache-Acuña *et al.* (2006) observed that the precursor decomposition at reductive atmosphere (H_2S/H_2) had a beneficial effect on the HDS activity.

Thermal decomposition of Ni and Co layered precursors is effective method to obtain unsupported Ni(Co)-Mo-W catalysts with high surface area. Using this preparation method, the purpose of the works by Rodemerck and Linke (2009) and Amaya *et al.* (2014) was to establish the relationship between the activation temperature and the catalytic properties of the Ni(Co)–Mo–W oxides. NiMoW layered precursor, which was synthetized by Rodemerck and Linke (2009), was prepared using solutions containing the metal salts separately prepared and then mixed, always adding the nickel solution to the others; ammonia was used as a precipitating agent. After *ex-situ* sulfidation, all catalysts showed structural, textural, and morphological changes that were reflected by the formation of several nickel phases such as Ni_3S_2, NiS and NiS_2, decrease in the values of surface area, and defects of mixed stack and curvature of layers observed in the TEM micrographs which were attributed to the activation temperature. A linear tendency was observed between the activation temperatures (from 673 to 823 K) and DBT conversion. The unsupported NiMoW catalysts demonstrated to be structurally stable and active during HDS of DBT reaction. Thus, it was concluded that the NiMoW layered material and NiMoW mixed oxide were good precursors of the sulfide catalysts (Rodemerck and Linke, 2009).

Recently, the catalytic response of the unsupported Ni-Mo-W and Co-Mo-W catalysts was investigated also by Amaya *et al.* (2014). The catalysts were prepared by calcination at 673 K of the layered precursors $(NH_4)H_{1.4}Ni_{2.3}O(OH)(MoO_4)_{1.4}(WO_4)_{0.6}$ and $(NH_4)H_2Co_2O(OH)(MoO_4)_{1.6}(WO_4)_{0.4}$, respectively (Amaya *et al.*, 2015). After *ex-situ* sulfidation at 673 K or 798 K, the catalyst activity was evaluated in the HDS of DBT reaction carried out in a batch reactor at 593 K and 5.5 MPa. The catalyst characterization by different techniques demonstrated that type of metal precursor (Ni vs. Co) together with sulfidation temperature (673 K or 798 K) strongly influenced on the textural properties and morphology of the sulfided catalysts. The best catalytic behavior was obtained with unsupported Ni-Mo-W catalysts sulfide at 798 K.

2.2. Catalysts Derived from Thiosalts Decomposition

The use of S-containing precursors like thiometallates is another interesting alternative of catalyst preparation procedure of trimetallic Ni-Mo-W sulfide catalysts because several important features, e.g. high purity and high dispersion properties, can be achieved by hydrothermal syntheses. Their catalyst behavior depended strongly on the way in which the promoter atoms are introduced on the Mo(W)S_2 phases, the reacting atmosphere and heating conditions (Huirache-Acuña *et al.*, 2006(a), (b)). Mo(W)S_2 phases synthesized by hydrothermal method has a needle-like morphology. The length of slabs is generally larger than those obtained by sulfidation of oxide precursors (generally over 10 nm), while the layer number is not very high (Zhang, 2015).

The use of ammonium thiometallates was extensively studied as potential active phase precursors for HDS catalysts with the objective to better understand the correlation between the electronic structure of transition metal sulfides and the hydrodesulphurization catalytic activity (Bocarando *et al.*, 2009(b)). In this sense, interesting results on the synthesis of trimetallic Ni-Mo-W sulfide catalysts were reported by Olivas *et al.* (2009). The optimal composition and distribution of atoms in the precursor was obtained by controlling the reactions occurring during the preparation steps yielded a very active catalyst. It was found that the trimetallic NiMoW sulfide catalyst with Ni/(Mo+W) ratio of 0.85, prepared by the impregnation of bimetallic ATMW thiosalts, showed good Ni dispersion, adequate mesoporosity, significant synergistic effect and twofold larger activity (in a weight basis) than an industrial NiMo/alumina catalyst. For this trimetallic catalyst, the synergistic effect of Ni was found to be higher than for Ni(MoS_2) and Ni(WS_2) studied separately.

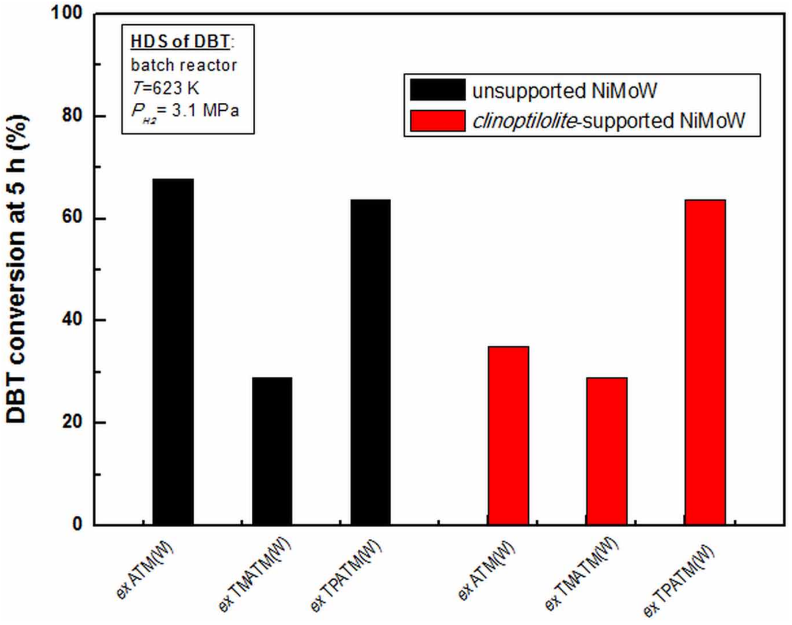
Recently, improved textural and catalytic properties were obtained by substituting the sulfur-containing precursors by tetraalkylammonium thiometallates (Alvarez *et al.*, 2004; Poisot *et al.*, 2007; Trakarnpruk *et al.*, 2007; Alvarez *et al.*, 2009). These effects could be related to the generation of carbon-containing metal-sulfide sites, as previously patented (Naumann and Behan, 1981; Chianelli and Pecoraro, 1985). Thus, active species of the type Mo(W)S_xC_y have been considered (Alonso *et al.*, 1998; Sundaramurthy *et al.*, 2008). The use of carbon-containing precursors with different C/Mo ratios offers the possibility to evaluate the influence of carbon on the genesis of the metal sulfide catalysts. In this sense, the study by Nava *et al.* (2006) demonstrated that the type of alkyl group of the precursors has a strong influence on the HDS activity. The Ni–Mo–W catalysts activated by *in situ* decomposition of alkylthiomolybdotungstates (where alkyl is methyl, propyl, butyl or cetyltrimethyl groups) exhibited appropriate morphological properties and enhanced HDS activity compared to NiMo/Al_2O_3 reference systems.

In the study by Alvarez *et al.* (2004) particular attention was devoted to the use of carbon-containing precursors, such as tetramethylammonium thiomolybdate (TMATM) and tetrapropylammonium thiomolybdate (TPATM), and to the mode of their decomposition (*ex situ* or *in situ*) to synthesize unsupported MoS_2 and $CoMoS_2$ catalysts. The catalysts were activated *ex situ* by precursor's decomposition under a H_2S/H_2 flow before the hydrodesulphurization of dibenzothiophene or by direct decomposition under HDS conditions (*in situ* decomposition). It was found that in situ decomposition of precursors led to catalysts with larger superficial areas than those obtained with the ex situ method. It was found that the cobalt synergetic effect depends both on the method of activation and the use of carbon-containing precursor. For *in situ* activated catalysts, the use of carbon containing precursor enhanced the promotional effect of cobalt while an opposite effect was observed for *ex situ* activated catalysts. Their results suggested that a certain amount of carbon could replace surface sulfur atoms at the edges of the Mo(W)S_2 layers taking part of the active phase (Chianelli and Berhault, 1999). However, the catalysts prepared by Huirache-Acuña *et al.* (2006(a)) using tetramethylammonium thiomolybdates and thiotungstates showed the highest C/(Mo+W) atomic ratio and the lowest catalytic activity. Thus, contrary to the work by Chianelli and Berhault (1999), the excess of carbon formed during HDS reaction played negative role by reducing the number of active sites accessible for adsorption of DBT molecules.

The strong influence of the type of alkyl groups of the precursors on the HDS activity was also confirmed recently by Espinoza-Armenta *et al*. (2014) for unsupported CoMoW sulfide catalysts. The catalysts were prepared by *in situ* decomposition of ammonium and alkyltrimethylammonium-thiomolybdate-thiotungstate-cobaltate (II) precursors having lauryl (dodecyl, C_{12}), myristil (tetradecyl, C_{14}), cetyl (hexadecyl, C_{16}), and stearyl (octadecyl, C_{18}) as alkyl groups. It was found that the catalyst derived from the precursor containing the tetradecyl group exhibited the highest catalytic activity ($k = 421 \times 10^{-7}$ mol/g s). However, it was concluded that the surface area and high catalytic activity do not show direct correlation with the length of the hydrocarbon chains of the precursors.

The nature of alkyl groups, the precursors pretreatment, and the type of promoter (Co vs. Ni) on the HDS activity of unsupported Ni(Co)-Mo-W sulfide catalysts was investigated by Huirache-Acuña *et al.,* 2006 (a,b)). The catalysts were prepared by *ex situ* hydrothermal decomposition of ammonium and tetraalkylammonium thiomolybdates and thiotungstates, and $Ni(Co)Cl_2 \cdot 6H_2O$. The unsupported catalytic systems prepared by this method exhibited a low specific surface area and a large amount of carbon was formed, but they displayed good catalytic performance in the HDS of dibenzothiophene reaction carried out in a batch reactor (T= 623 K, H_2 pressure of 3.1 MPa). The highest activity was observed for the Ni-Mo-W catalyst prepared *ex* ATM/ATW (Figure 1). The catalysts prepared *ex* ammonium and

Figure 1. Comparison of the HDS activities of unsupported and zeolite-supported NiMoW sulfide catalysts prepared using different metal precursors: ATM(W): ammonium tetrathiomolybdate/tetrathiotungstate (ATM(W); tetramethylammonium thiomolybdate/thiotungstate (TMATM(W)); tetrapropylammonium thiomolybdate/thiotungstate (TPATM(W))



propylammonium thiomolybdates and thiotungstates) showed a slightly higher activity in HDS of DBT than a commercial NiMo/ Al_2O_3 catalyst (Huirache-Acuña *et al.,* 2006(a)). Moreover, it was found that an increase in the size of the alkyl groups led to a decrease in the HYD/DDS selectivities ratio. Contrary to the Ni-promoted catalysts, the Co-promoted ones showed a marked tendency for the DDS reaction pathway (see Box 1). Ni-Mo-W catalysts exhibited a marked decrease in the stacking of Mo/W)S_2 layers along the *c* direction when alkyl groups were incorporated to the precursor, as confirmed by XRD and HRTEM.

Similar promising results were reported recently by Yi *et al*. (2011), which claimed that unsupported NiMoW catalysts could be promising candidates for wide application in hydrotreating of fuel oil. The catalysts were prepared by thermal decomposition of mechanically ground tetramethylammonium thiomolybdotungstate and $Ni(NO_3)_2$ $6H_2O$. After *ex situ* precursor's decomposition, the sulfide catalyst was passivated by exposure to air at room temperature. To remove the passivation layer, the catalyst was activated upon H_2 flow at 613 K for 0.5 h, and then tested in the HDS of DBT reaction. From the catalyst structure-activity correlation the authors concluded that catalyst structure and its catalytic properties strongly depend on the nickel content and thiosalt decomposition conditions. It was found that the use of low Ni content is more beneficious for the HDS activity than use of its large content. As expected, it was found that the addition of nickel to MoW catalyst promoted the hydrogenation route of DBT transformation (see Box 1).

Concerning the double promotion, results reported by Ho *et al*. (2012(a,b,c)) demonstrated that doubly promoted unsupported molybdenum sulfides prepared by thermal decomposition of metal amine

Table 2. Metal sulfide precursors employed for the synthesis of unsupported Co(Ni)MoW catalysts

Catalysts	Metallic Precursors/Synthesis Method	Reference
NiMoW	• Ammonium thiomolybdate (ATM) • Ammonium thiotungstate (ATT) • $Ni(NO_3)_2.6H_2O$	Nava *et al*., 2005 Huirache-Acuña *et al*., 2006(a)
NiMoW–methyl NiMoW–propyl NiMoW–butyl NiMoW– cetyltrimethyl	• Ammonium thiomolybdate (ATM) • Ammonium thiotungstate (ATT) • Tetraalkylammonium bromide (TAAB): *Alkyl*: methyl; propyl; butyl; cetyltrimethyl	Nava *et al*., 2005
NiMoW-methyl NiMoW-propyl	• $(R_4N)_2MoS_4$ and $(R_4N)_2WS_4$ (R = methyl or propyl), • $Ni(NO_3)_2.6H_2O$	Huirache-Acuña *et al*., 2006
Ni(Co)MoW	• Ammonium thiomolybdate (ATM) • Ammonium thiotungstate (ATT) • $Ni(Co)Cl_2.6H_2O$	Huirache-Acuña *et al.* 2006(b)
Ni(Co)MoW-Methyl Ni(Co)MoW-Propyl	• Tetramethyl(propyl)ammonium chloride • Ammonium thiomolybdate (ATM) • Ammonium thiotungstate (ATT) • $Ni(Co)Cl_2.6H_2O$	Huirache-Acuña *et al.* 2006(b)
CoMoWP-C12 CoMoWP-C14 CoMoWP-C16 CoMoWP-C18	• Alkyltrimethylammonium thiomolybdate • Alkylltrimethylammoniumthiotungstate • $Co(NO_3)_2•6H_2O$ where alkyl= dodecyl, tetradecyl, cetyl and octadecyl	Espinoza-Armenta Y., *et al*., 2014
$Fe_{0.5}$ $Cr_{0.5}$ Mo_y	• Ammonium thiomolybdate (ATM) • Ethylenediamine • $Cr(en)_3Cl_3$ • $FeCl_2·4H_2O$	Ho *et al*., 2012

thiomolybdates were highly active in HDN and HDS reactions. Using iron as promoter, it was observed that the $Ni_{0.5}Fe_{0.5}Mo$ and $Co_{0.5}Fe_{0.5}Mo$ trimetallic sulfides were more active than the FeMo, NiMo and CoMo bimetallic sulfides (Ho *et al*. (2012(b,c)). A subsequent study showed that chromium was a more effective promoter than iron (Ho *et al.* 2012(b)). The predominant phases in the chromium-containing catalysts were nanocrystalline MoS_2 and amorphous Cr_2S_3. The $Fe_{0.5}Cr_{0.5}Mo_y$ ($1 \leq y \leq 1.5$) trimetallic sulfide was more active and selective for HDN than FeMo and $CrMo_y$ bimetallic sulfides. Thus, it was concluded that chromium and iron were synergistic co-promoters for enhancing the HDN activity of MoS_2 (Ho *et al*. (2012(b)).

Table 3. Reaction rate constants and HYD/DDS selectivities ratio (at 5 h) of different unsupported Ni(Co)-Mo-W sulfide catalysts tested in the HDS of DBT (batch reactor, 623 K, total H_2 pressure of 3.1 MPa); Data of a commercial $NiMo/Al_2O_3$ catalyst are included (reference sample).

Catalyst	**Phases Detected (XRD)**	***k* (x 10^{-7} mol/g s)**	**HYD/DDS**	**Ref.**
$NiMo/Al_2O_3$ (commercial)	NiMoS MoS_2	12		Alonso *et al.* 2005
Unsupported NiMoW-H	NiS MoS_2 WS_2	25.4	1.26	Huirache-Acuña *et al.* 2006(b)
Unsupported NiMoW *ex* methyl	NiS MoS_2 WS_2	10.3	1.25	Huirache-Acuña *et al.* 2006(b)
Unsupported NiMoW *ex* propyl	NiS MoS_2 WS_2	4.7	0.88	Huirache-Acuña *et al.* 2006(b)
$NEB_{H2S}(2)$	NiS MoS_2 WS_2	17.11	1.15	Gochi *et al*, 2005
Unsupported NiMoW-H	NiS MoS_2 WS_2	17.2	0.51	Nava *et al*. 2005
Unsupported CoMoW-H	$CoS_{1.097}$ Co_9S_8 $CoMoS_{3.13}$ MoO_3 WS_2	20.0	0.39	Huirache-Acuña *et al*. 2006(b)
Unsupported CoMoW *ex* methyl	$CoS_{1.097}$ Co_9S_8 $CoMoS_{3.13}$ WS_2	16.2	0.39	Huirache-Acuña *et al*. 2006(b)
Unsupported CoMoW *ex* propyl	Co_9S_8 WS_2	15.6	0.36	Huirache-Acuña *et al*. 2006(b)
Unsupported $Ni(Mo\text{-}W)S_2$	NiS MoS_2 WS_2	23	1.24	Olivas *et al*., 2009
Unsupported CoMoW-H in situ	MoS_2 WS_2 $CoS_{1.097}$ Co_9S_8	16	0.49	Huirache-Acuña *et al*. 2015

The detrimental effect of phosphorous addition during synthesis of unsupported Ni-Mo-W catalysts was observed by Nava *et al*. (2006). The unsupported trimetallic Ni–Mo–W catalysts were prepared by *in situ* activation of nickel-containing tetramethylammonium thiomolybdotungstate and tested in the HDS of dibenzothiophene (DBT) reaction (Nava *et al*., 2006). X-ray diffraction showed that the structure of unsupported Ni-Mo-W sulfide catalysts corresponds to a low-stacked and poorly crystalline 2H–MoS_2 or 2H–WS_2 structure. It was found that phosphorus induced the formation of less-folded slabs without modifying the dispersion along the basal plane or the stacking degree. However, the main effect of phosphorus was favored segregation of nickel sulfide and the loss of the promotional effect. This phenomenon would probably result from the stronger interaction of Mo and/or W with P than with Ni during the *in situ* preparation of these trimetallic NiMoW catalysts (Nava *et al*., 2006). Moreover, phosphorus led to a strong decrease in BET specific surface area (from 46.9 m^2/g to 14.3 m^2/g) due to pore plugging.

3. SUPPORTED TRIMETALLIC CATALYSTS

Bulk HDS catalysts possess high HDS activity, but they have the disadvantage of low utilization of active phases and high cost. Thus, many efforts have been developed to enhance the active sites dispersion by using different supports. Alumina is doubtless the most used support for this purpose (see Section 3.1). The origin of the almost exclusive use of alumina as support has been ascribed to its outstanding textural and mechanical properties and its relatively low cost (Satterfield, 1996). However, the presence of undesirable strong metal-support interactions in the alumina-supported catalysts has triggered research devoted to the development of new supports for HDS applications. In this sense, the use of ordered mesoporous siliceous molecular sieves as supports has been intensively investigated (see Section 3.2). In particular, the use of SBA-15 as support was investigated because of its a hexagonal array of uniform mesopores, a narrow pore size distribution, high surface area, high sorption capacity and thermal stability (Zhang *et al*., 2005). As compared with alumina and siliceous molecular sieves, the number of reports on the use of other materials for supporting trimetallic catalysts is very limited (see Section 3.3). The materials used as supports were only three: carbon (Severino *et al.,* 2000), Al-Ti mixed oxides modified with MgO (Cervantes-Gaxiola *et al.,* 2012) and natural Mexican zeolite clinoptilolite (Huirache-Acuña *et al*., 2014).

3.1. Alumina-Supported Catalysts

For technical and economic reasons, the impregnation method is the one most frequently used for preparing supported Co(Ni)-Mo-W catalysts with a high surface area in order to improve the accessibility of active sites. This impregnation method was employed by Thomazeau (2007) for preparation of Co- and Ni-promoted MoW/γ-Al_2O_3 catalysts tested in thiophene HDS and gas oil conversion. Using DFT calculations, an approach based on a linear interpolation model of surface ΔE_{MS} between the binary XMoS and XWS phases (X = Co and Ni) it was proposed. According to the interpolated ΔE_{MS} values, the distinct catalytic effects of the two Ni and Co promoters on the $Mo_xW_{1-x}S_2$ solid solution were anticipated. The ΔE_{MS} value of NiMoWS phase was improved, becoming closer to the volcano curve's optimum and a new synergy effect with respect to NiMoS and NiWS phases was subsequently expected. In contrast, Co was expected to reveal no new synergy effect in $CoMoWS_2$ phase with respect to CoMoS and CoWS phases due to the too high ΔE_{MS} value. The prediction by DFT calculations and the linear interpolation model were supported by the catalytic activity measurements. In model reaction or gas oil feed conversion, the catalytic activity's enhancement in the range of 30% was obtained for $NiMo_{0.5}W_{0.5}S_2$ catalyst. On the other hand, the $CoMo_{0.5}W_{0.5}S$ catalyst does not reveal any new synergy effect. These ternary sulfide catalysts designed with the use of DFT calculations show that the best HDS catalysts must exhibit sulfur metal bond energies close to $NiMo_{0.5}\ W_{0.5}\ S_2$ system, meaning between NiMoS and NiWS ones.

The impregnation solution-based combustion method using urea as fuel was employed by González-Cortés *et al.* (2014) for the preparation of γ-alumina-supported Ni-Mo-W catalysts. The catalyst activity was evaluated for deep hydrotreating using various feedstock's and the results have been compared with a commercial alumina-supported NiMo catalyst. It was concluded that the addition of Ni and Mo to WO_x-loaded alumina facilities a strong interaction between NiO and MeO_x species, which promotes the reducibility of the metal oxides deposited on alumina. The impregnation solution based combustion method in the controlled combustion mode avoids the formation of crystalline mixed-metal oxides such as $Al_2(MoO_4)_3$, $NiMoO_4$ and/or $NiWO_4$, instead it facilitates a strong interaction of NiO with MeO_x species that could enhance the promoter effect of Ni on the edges of Mo (and/or W) sulfide.

The number of reports about alumina-supported Co-Ni-Mo is limited (Severino, *et al.*, 2000; Homma, *et al.*, 2005). Moreover, contradictory activity results have been reported in the literature because an increase in activity or a decrease were observed in different laboratories (Cáceres *et al.* 1986; Benyamna *et al.* 1998; Severino *et al.* 2000; Homma *et al.*, 2005). For example, it was reported that trimetallic $CoNiMo/Al_2O_3$ catalysts were less active than their analogous CoMo or NiMo for thiophene HDS performed at atmospheric pressure (Benyamna *et al.* (1998). On the other hand, at the same raction conditions, an increase of HDS activity was observed by others (Cáceres *et al.* 1986). Considering the study by Cáceres *et al.* 1986, the differences in the catalyst behavior could be linked with different Co/(Co+Ni) atomic ratio and different catalyst preparation methods employed. The loss in activity was explained as due to the formation of a separate mixed Co–Ni sulfide phase, which results by lowering the amount of promoted catalytic sites (Benyamna *et al.*, 1998).

Klimova *et al.* (2010) reported the possibility of increasing the HYD ability of the conventional $NiMo/\gamma\text{-}Al_2O_3$ catalyst by the incorporation of small amounts of different noble metals (Pt, Pd, Ru) in order to make it more appropriate for deep HDS. The catalysts were characterized and tested in 4,6-dimethyldibenzothiophene HDS reaction. Pt and Pd-containing ternary catalysts showed activity 10–20% higher than the reference conventional $NiMo/\gamma\text{-}Al_2O_3$ sample, while Ru addition had a negative effect on the catalytic activity.

Recently, another interesting approach for the novel catalyst formation was presented by Díaz de León *et al.* (2012). The $NiW/Ga\text{-}Al_2O_3$ catalysts with vary Ga loading (0.6-3.0 wt.%) were prepared by classical wetness impregnation method of the Ga-modified alumina. The catalyst activity was evaluated in the HDS of dibenzothiophene and 4,6-dimethyldibenzothiophene reactions. It was found that gallium addition leads to a significant increase of conversion in both reactions, with a maximum of promotion observed for the catalyst modified with optimized gallium content (2.4 wt.%).

Contrary to the unsupported Ni-Mo-W catalysts (Nava *et al*, 2006), the phosphorous addition has positive effect for the HDS and HDN activities of $NiMoW/\gamma\text{-}Al_2O_3$ sulfide catalysts (Sigurdson *et al.,* 2008). Both HDN and HDS activities steadily increased with the P content up to an optimum concentration of 1.6 wt.% At this concentration, the P-doped trimetallic catalyst showed better hydrotreating activity than the bimetallic and commercial catalysts. It was apparent from DRIFT spectroscopy that the P doping creates new acidic sites in $NiMoW/\gamma\text{-}Al_2O_3$ catalysts. The acidic sites brought about by phosphorus incorporation accelerates the C–N bond breaking, a rate determining step, and promotes the

HDN activity to a higher degree than the HDS activity with coker gas oil. In addition, the hydrotreating performance of Ni_2P-NiMoW/γ-Al_2O_3 catalysts has been carried out and compared with NiMoW/γ-Al_2O_3 and the commercial catalysts (Lan *et al.*, 2011). These results demonstrated that the Ni_2P promoted NiMoW/γ-Al_2O_3 catalysts were highly active in HDS and HDN of diesel fuels. The Ni_2P was introduced into the γ-Al_2O_3 supported NiMoW catalyst by thermal decomposition of nickel hypophosphite at low temperature. The moderate decomposition did not change the surface area, pore size and volume, acidic site, strength and B/L ratios of the support, but provided highly dispersed Ni_2P species over the catalyst. Owing to the high hydrogenation capability of Ni_2P species, the as-prepared supported Ni_2P-NiMoW catalyst exhibited high HDS and HDN activities in the HDS of DBT and diesel hydrotreating reactions.

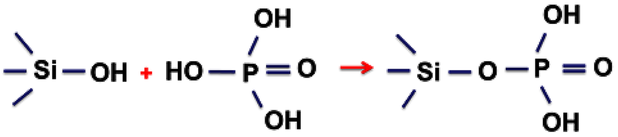
Recently, the effect of Ni_2P promotion of γ-alumina-supported NiMoW catalysts was reported by Lan *et al.* (2011). The catalyst response was evaluated in the HDS of DBT reaction and in FCC diesel oil hydrotreating experiments carried out in a fixed bed reactor under typical industrial conditions. It was found that the presence of Ni_2P in the catalyst formulation brought a strong promotional effect on the HDS activity using both model compound and the real feedstock containing both S and N compounds. The as-prepared Ni_2P-Ni-MoW/Al_2O_3 catalyst exhibited better hydrotreating performance than its Ni_2P-free counterpart and commercial sample. This was ascribed more to the effect of new active sites of Ni_2P than that of acidity modification.

3.2. Silica Supports

Among different ordered mesoporous silica materials, SBA-type substrates (SBA = Santa Barbara Amorphous) were the most frequently employed as supports (Zhang *et al.,* 2005). This is because their interesting textural properties, such as large specific surface areas (above 1000 $m^2 \cdot g^{-1}$), uniform-sized pores (in range 4–30 nm), thick framework walls, small crystallite size of primary particles and complementary textural porosity. The advantage of the use of SBA-15 material as support includes also its high surface-to-volume ratio, variable framework compositions and high thermal stability (Rahmat *et al.*, 2010). The superiority of the trimetallic NiMoW/SBA-15 sulfide catalysts with respect to binary NiMo(W)/SBA-15 ones was confirmed for both HDS of DBT and 4,6-DMDBT reactions by Mendoza-Nieto *et al.* (2013). Their results point out that it is possible to prepare highly active trimetallic catalysts using co-impregnation method and SBA-15 as support. The importance of the high dispersion of the active phases on the HDS activity was confirmed also by Liu *et al.* (2010), which observed the superior HDS activity of the silica-supported NiMoW catalysts with respect to unsupported NiMoW ones synthetized using ammonium molybdate and ammonium metatungstate as Mo and W precursors, respectively. Concerning the influence of the support morphology on the catalyst activity, one might to expect that larger pore size might to favor diffusion of large molecules such as DBT into the inner pore network of the catalyst. This was confirmed by Huirache-Acuña *et al.* (2012) by the comparison of the catalytic response of HMS- and SBA-16-suported catalysts. Under the reaction conditions used, the catalyst supported on hexagonal mesoporous silica (HMS) demonstrated to be more active than its counterpart supported on SBA-16 mesoporous silica having cage-like structure.

Since purely siliceous materials have no Brønsted acidity, the attempt was made to generate acidity by support modification with phosphorous (Huirache-Acuña *et al.*, 2009; (Guzmán *et al.*, 2013). Box 2 shows the possible mechanism of acid sites generation by impregnation of mesoporous silica material with phosphoric acid.

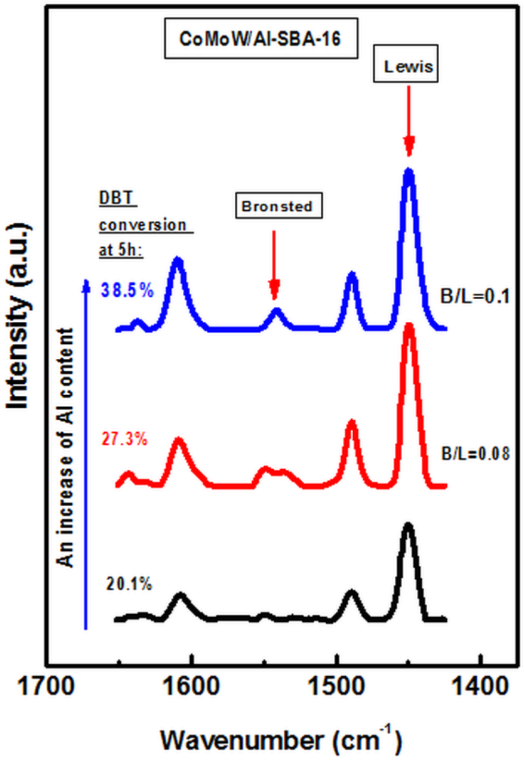
Box 2. The possible mechanism of acid sites generation by impregnation of mesopoous silica material with phosphoric acid.



To create acid sites in the silica-based materials, the isomorphous substitution of Si^{4+} ions by trivalent Al^{3+} cations Al^{3+} ion was employed also (Huirache-Acuña *et al.,* 2012, 2014). However, the study by Huirache-Acuña *et al.* (2012) demonstrated that the presence of extraframework $AlNO_3$ phases on the support surface compromised the catalyst behavior because of the forced formation of less active "onion-type" $Mo(W)S_2$ structures. The effect of promoter (Ni vs. Co) and support morphology (Al-HMS vs. Al-SBA-16) on the HDS activity of ternary Ni(Co)-Mo-W catalysts was investigated. The activity results revealed that use of Ni as promoter was much more effective than the use of Co. The HDS activity was markedly influenced by the textural properties of support and the dispersion of the active phases on the catalyst surface. The use of Al-HMS as support was found to be more effective than the use of Al-SBA-16 with cage-like structure. To explain this, the effect of Al modification of the SBA-16 substrate was deeply evaluated for Co-Mo-W/Al-SBA-16 systems (Huirache-Acuña *et al.,* 2014). The catalyst activity was studied in the HDS of DBT carried out in a batch reactor at 623 K and total H_2 pressure of 2.3 MPa. As expected, it was found that Al incorporation into a SBA-16 substrate produces both Brønsted and Lewis acid sites, which was beneficial for the catalyst activity. For all catalysts, the DBT transformation proceeded mainly *via* direct desulfurization reaction pathway (see Box 1). However, it was concluded that the direct synthesis method of Al-SBA-16 supports did not result in appropriate supports for HDS catalysts because a low amount of Brønsted acid sites were formed (Huirache-Acuña *et al.,* 2014).

The effect of the SBA-15 and SBA-16 modification with phosphorous was reported by Huirache-Acuña *et al.* (2009). Regardless of the support morphology (SBA-15 against SBA-16), the addition of phosphate was found to be detrimental for catalytic HDS activity of both CoMoW/SBA-15 and CoMoW/SBA-16 sulfide catalysts (Figure 3). However, the catalysts tested in a reaction of hydrodesulfurization (HDS) of dibenzothiophene (DBT) at 623 K and 3.1 MPa of total H_2 pressure demonstrated to be more active than a $CoMo/Al_2O_3$ commercial catalyst containing a small amount of phosphorous in its formulation. In general, the SBA-16 material proved to be a better substrate to developing a large density of $Mo(W)S_2$ clusters on the surface (see Figure 4) than its SBA-15 counterpart (Figure 5). The irregular oxide Mo^{6+} and W^{6+} particles were proposed to be the precursors of the active phases formed upon sulfidation. Moreover, it was found that the density of the active phases on the support surface, together with the inhibitor effect of the phosphate on the coke formation, are two important factors which govern the HDS activity of CoMoW catalysts supported on mesoporous silica substrates (Huirache-Acuña *et al.*, 2009). The inhibition effect of phosphorus was reported also for unsupported NiMoW catalysts tested in the HDS of DBT at the same reaction conditions (Nava *et al.* 2006). For both SBA-15 and SBA-16 catalyst series, the inhibition of the HDS activity of catalysts by phosphorus was mainly due to a decrease in the metal–support interaction leading to formation of a large metal sulphide clusters, and a pore plugging phenomenon (Huirache-Acuña *et al.*, 2009).

Figure 2. FT-IR spectra of adsorbed pyridine for the calcined CoMoW/SBA-16 modified with Al; an increase of Al loading led to an increase of Bronsted-to-Lewis acidities ratio influencing positively on the HDS activity.



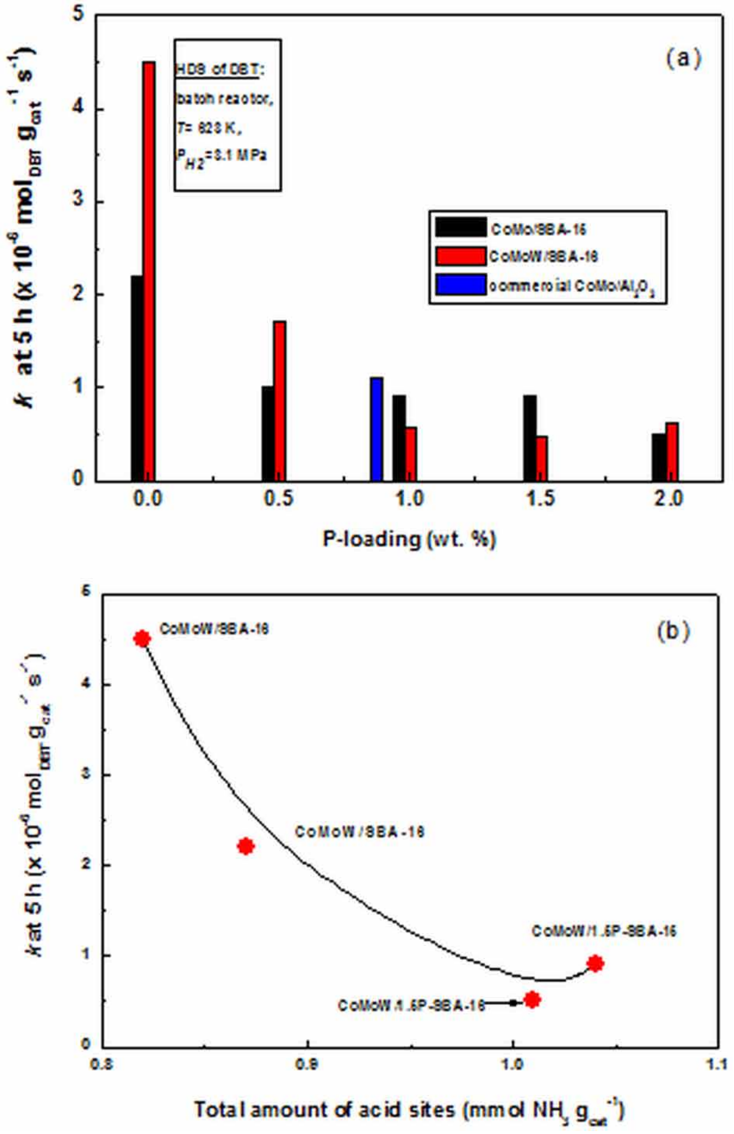
The effect of SBA-16 support modification with phosphorous was investigated also for ternary NiMoW/SBA-16 catalyst formulation (Guzmán *et al.,* 2013). X-ray diffractograms of oxide precursors of those catalysts evidenced the formation of crystalline Mo_1-xWxO_3 and $NiMoO_4$ phases on the surface of oxide catalyst precursors with high P-loadings (1.0 and 1.6 wt.%). After sulfidation by H_2S/H_2 gas mixture, the sulfided catalysts were tested in separate HDS of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) reactions performed in a batch reactor at 320°C and H_2 pressure of 5.0 MPa. For both HDS reactions, the initial catalyst activity displayed a volcano-type curve indicating that catalyst behavior depends strongly on the phosphorous loading being all catalysts more active in the HDS of DBT then in the HDS of 4,6-DMDBT. The NiMoW/SBA-16 catalyst loaded with optimized amount of phosphorous (1.0 wt. %) showed superior initial activity than the P-free counterpart (see Figure 3). This effect was attributed to the enhancement of active phase dispersion on the support surface, as revealed by High Resolution Transmision Microscopy (HRTEM) measurements (Guzmán *et al.*, 2013).

3.3. Other Supports

The use of carbon as support has many advantages:

1. A low metal-support interaction, which facilities complete sulfidation of oxides,
2. Large specific surface area with controlled pore volume,

Figure 3. Inhibition of the HDS activities of sulfided CoMoW/SBA-15(16) catalysts by support modification with phosphorous



3. Variable amount of surface functional groups,
4. Reduced coked propensity due to lower polarity, and finally
5. Easy metal recovering by burning of the carbon support (Pawelec *et al*. 2001).

The effect of double promotion of MoS_2 phase by Co and Ni was investigated for carbon-supported CoNiMo catalysts by Severino *et al.* (2000). The CoNiMo/C catalysts were prepared by a two-step impregnation method. All samples exhibited MoO_3 loading of 10 wt.% and CoO+NiO concentration of 5 wt.%. The Co/(Co + Ni) atomic ratios of the catalysts was in range 0.0- 1.0. Minimum HDS activity was observed for the catalyst having the intermediate value of Co/(Co+Ni) atomic ratio, contrasting with previous findings reporting a maximum for alumina-supported CoNiMo catalysts.

Figure 4. HRTEM images for CoMoW/SBA-15 catalyst

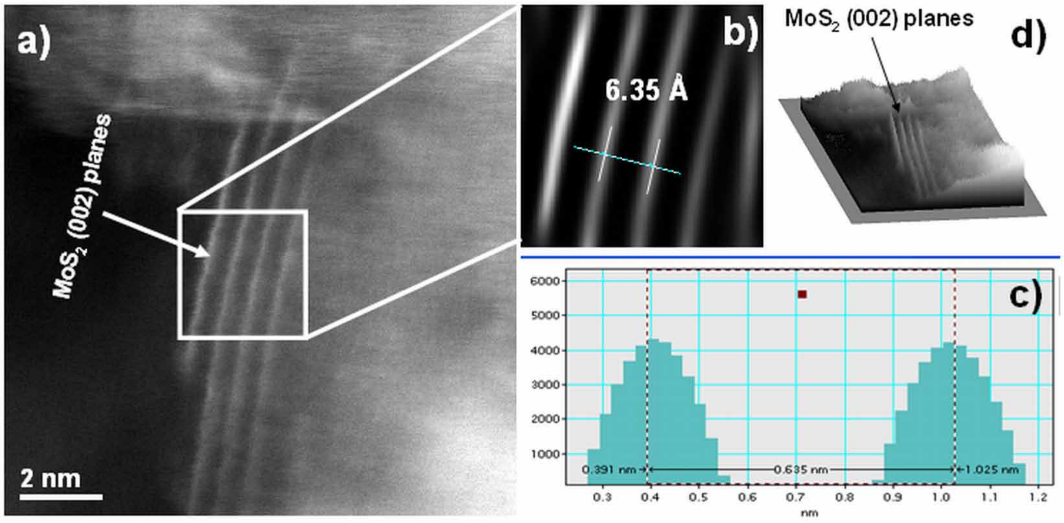
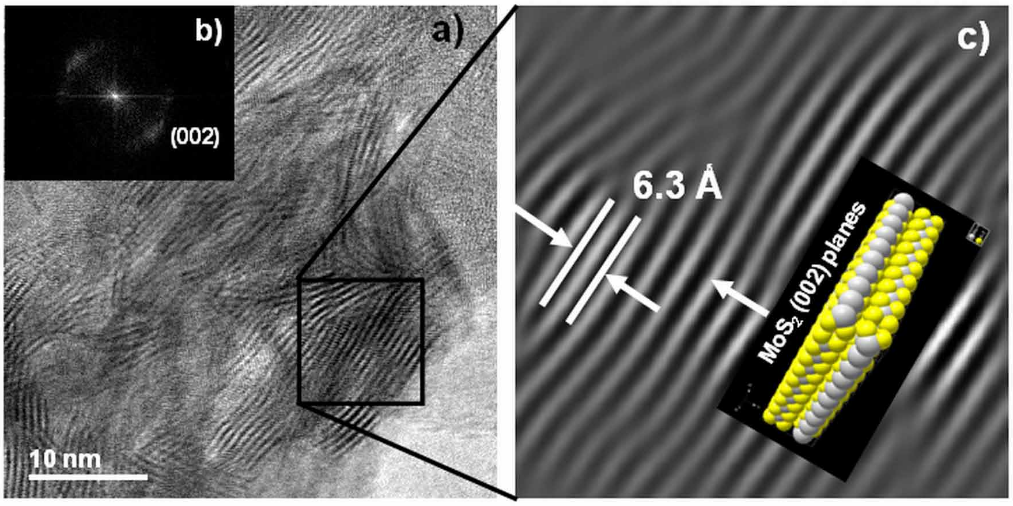


Figure 5. HRTEM images for CoMoW/SBA-16 catalyst



The use of Al_2O_3-TiO_2-MgO mixed oxides for supporting trimetallic Ni-Mo-W sulfide catalysts was investigated by Cervantes-Gaxiola *et al.* (2012). MgO was added to the Al-Ti mixed oxides in order to obtain more favorable interaction between the support and acidic molybdenum species leading to the formation of highly dispersed sulfide species (Klicpera and Zdražil, 1999). In the support formulation, the role of binary Al_2O_3-TiO_2 was to facility redox processes for the active phases of Mo and W, and therefore, to facility the formation of active octahedral-type sites of Mo oxide species. NiMoW trimetallic catalysts were synthesized using the co-impregnation method with constant atomic ratio Ni/[Ni + (W + Mo)] = 0.5 and a molar ratio of W:Mo 1:1 (18 wt.%). As precursors were used: ammonium thiomolybdate, ammonium thiotungstate and $Ni(NO_3)_2.6H_2O$. The activity and selectivity of NiMoW/

Al-Ti-Mg sulfide catalysts was evaluated in the HDS of DBT reaction carried out in a continuous flow tricked-bed microreactor at 563 K and total H_2 pressure of 3 MPa. The activity results obtained were discussed in terms of the effect of MgO loading to the Al-Ti support. Although for all catalysts the direct desulfurization pathway was favored, it was found that the modification of the NiMoW/Al-Ti catalyst by the addition of 5 wt.% MgO improved slightly the catalyst hydrogenation function. Thus, it was claimed that NiMoW/Al-Ti-Mg modified with optimized amount of MgO could be a promising catalyst for deep hydrodesulphurization of petroleum fractions (Cervantes-Gaxiola *et al.,* 2012).

On the other hand, Huirache-Acuña *et al.* (2014) investigated the properties of ternary Ni–Mo–W catalysts supported on natural Mexican zeolite clinoptilolite to explore the potential use of this zeolite as support for HDS catalysts. Considering that the role of nickel in the ternary Ni–Mo–W formulation is to act as the promoter of $W(Mo)S_2$ phases, all catalysts were prepared by sequential support impregnation using metal precursor concentrations appropriately selected to obtain Ni/(Mo + W) atomic ratio of 0.5 and a total metal content of 26 wt.%. The ammonium thiotungstate, ammonium thiomolybdate and nickel nitrate were employed as precursors of W, Mo and Ni, respectively. The HDS of DBT reaction over NiMoW sulphide catalysts supported on natural Mexican zeolite (clinoptilolite) was performed in a batch reactor at 623 K and under 3.1 MPa of H_2 pressure (Figure 1). All catalysts exhibited a low activity and a lower hydrogenation function with respect to their unsupported counterparts (Huirache-Acuña *et al*, 2006). DBT was mainly transformed *via* direct desulfurization reaction pathway (see Box 1). It was found that catalyst activity and hydrogenation function increased with decreasing $Mo(W)S_2$ crystallite size. The ammonium thiometallates were found to be more efficient precursors of $Mo(W)S_2$ species than the tetraalkylammonium ones. The most active catalyst in the HDS of DBT reaction showed the largest density of active phases on the support surface determined from HRTEM measurements.

4. FINAL REMARKS

On the basis of the present revision of the recent progress in the synthesis of unsupported and supported Co(Ni)-Mo-W, one might to conclude that considerable progress has been made in understanding their functionality in the hydrotreating reactions. Despite this progress, a number of fundamental questions persist. In general, the revised literature information strongly suggested that the use of trimetallic catalyst formulation could be more effective than those of binary ones.

In general, the catalysts prepared through hydrothermal technique were more active than their counterparts prepared by sulfidation of the oxide precursors. The main advantage of the catalyst synthesis through hydrothermal technique was a variety of controllable parameters. However, more investigation can be carried out on the improvement of the synthesis procedure and/or on the type of metal precursor employed. In addition, besides the exceptional wok by Sigurdson *et al.* (2008), no study has been performed for hydrotreating a real feedstock with either unsupported or supported trimetallic catalysts. Moreover, contrary to $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ systems (Topsøe *et al.* 2005), the active phases of the Ni(Co)-Mo-W systems were not cleared yet. In general, the literature results strongly suggest that the formation of ‘‘onion-type’’ $Mo(W)S_2$ phases on the catalyst surface could be detrimental for the HDS activity of ternary systems (Huirache-Acuña *et al.* (2012); Guzmán *et al*., 2013; Rivera-Muñoz *et al*., 2015). This is probably because a low edge-to-basal sites ratio was obtained (Rivera-Muñoz *et al*., 2015). Moreover, concerning the carbon-containing precursors, the question is what is the role of carbon in trimetallic sulfide catalytic materials? Evidence presented by Lumbreras *et al*. (2010) indicated that the use of the carbon-containing precursor (hexamethylenediammonium) for the preparation of Ni-Mo(W) sufide catalysts was more beneficial for the final HDS catalytic activity than using the classical ammonium tetrathiomolybdate (ATM) without carbon. This was explained as due to a correct nickel accommodation on the WS_2 edges (Lumbreras *et al*., 2010). However, the results obtained by Huirache-Acuña *et al.* (2009(b)) point to the inhibitory effect of the presence of carbon on the catalyst surface for the HDS activity. Finally, concerning the novel supports, the use of zeolites for supporting trimetallic systems can be more in deep investigated. This is because their unique crystal and pore structure which allows the preparation of highly dispersed supported metal sulfide catalysts. They also combine a large number of acid sites distributed through the network of channels and cavities, which provide bifunctional HDS catalysts. In particular, the use of natural Mexican zeolite clinoptilolite for supporting HDS catalysts should be explored because it is the most common zeolite occurring in nature. However, this material requires previous modification of its textural properties in order to make it suitable as support, as one might to deduce from the comparison of the HDS activities of unsupported and zeolite-supported catalysts (Figure 1). The studies in this direction are in progress.

ACKNOWLEDGMENT

R. Huirache-Acuña acknowledge the financial support of CONACYT 182191 and CIC-UMSNH 2014-2015 Projects. G. Alonso-Núñez thanks to CONACyT (sabbatical 259931) at IRCELYON, Lyon, France.

REFERENCES

Alonso, G., Del Valle, M., Cruz-Reyes, J., Licea-Claverie, A., Petranovskii, V., & Fuentes, S. (1998). Preparation of MoS_2 catalysts by in situ decomposition of tetraalkylammonium thiomolybdates. *Catalysis Today*, *43*(1-2), 117–122. doi:10.1016/S0920-5861(98)00140-0

Alvarez, L., Berhault, G., & Alonso, G. (2008). Unsupported NiMo sulfide catalysts obtained from nickel/ammonium and nickel/tetraalkylammonium thiomolybdates: Synthesis and application in the hydrodesulfurization of dibenzothiophene. *Catalysis Letters*, *125*(1-2), 35–45. doi:10.1007/s10562-008-9541-2

Alvarez, L., Espino, J., Ornelas, C., Rico, J. L., Cortez, M. T., Berhault, G., & Alonso, G. (2004). Comparative study of MoS_2 and Co/MoS_2 catalysts prepared by ex situ/in situ activation of ammonium and tetraalkylammonium thiomolybdates. *Journal of Molecular Catalysis A Chemical*, *210*(1-2), 105–117. doi:10.1016/j.molcata.2003.09.002

Amaya, S. L., Alonso-Núñez, G., Cruz-Reyes, J., Fuentes, S., & Echavarría, A. (2015). Influence of the sulfidation temperature in a NiMoW catalyst derived from layered structure $(NH_4)Ni_2OH(H_2O)(MoO_4)_2$. *Fuel*, *139*, 575–583. doi:10.1016/j.fuel.2014.09.046

Amaya, S. L., Alonso-Núñez, G., Zepeda, T. A., Fuentes, S., & Echavarría, A. (2014). Effect of the divalent metal and the activation temperature of NiMoW and CoMoW on the dibenzothiophene hydrodesulfurization reaction. *Applied Catalysis B: Environmental*, *149*, 221–230. doi:10.1016/j.apcatb.2013.10.057

Benyamna, A., Bennouna, C., Leglise, J., van Gestel, J., Duyme, M., & Duchet, J.-C. et al. (1998). Effect of the association of Co and Ni on the Catalytic Properties of Sulfided CoNiMo/Al_2O_3. *Am. Chem. Soc. Div. Petrol. Prep.*, *43*, 39–42.

Bocarando, J., Alonso-Núñez, G., Bensch, W., Huirache-Acuña, R., Del Valle, M., & Cruz-Reyes, J. (2009). (a)). Comparative study of *in situ/ex situ* activated trimetallic NiMoW sulfide catalysts prepared from ammonium thiomolybdotungstates. *Catalysis Letters*, *130*(3-4), 301–307. doi:10.1007/s10562-009-9913-2

Bocarando, J., Huirache-Acuña, R., Bensch, W., Huang, Z.-D., Petranovskii, V., Fuentes, S., & Alonso-Núñez, G. (2009). (b)). Unsupported Ni-Mo-W sulphide HDS catalysts with the varying nickel concentration. *Applied Catalysis A, General*, *363*(1-2), 45–51. doi:10.1016/j.apcata.2009.04.031

Cáceres, C., Fierro, J. L. G., López Agudo, A., Severino, F., & Laine, L. (1986). Relationship between hydrodesulfurization activity and the state of promoters in precursor calcined Ni-Co-Mo/Al_2O_3 catalysts. *Journal of Catalysis*, *97*(1), 219–227. doi:10.1016/0021-9517(86)90052-7

Cervantes-Gaxiola, M. E., Arroyo-Albiter, M., Maya-Yescas, R., Rico-Cerda, J. L., Guevara-Lara, A., & Espino-Valencia, J. (2012). Synthesis, characterization and catalytic activity during hydrodesulphurization of dibenzothiophene of NiMoW catalysts supported on Al-Ti mixed oxides modified with MgO. *Fuel*, *100*, 57–65. doi:10.1016/j.fuel.2011.12.040

Chianelli, R. R., & Berhault, G. (1999). Symmetrical synergism and the role of carbon in transition metal sulfide catalytic materials. *Catalysis Today*, *53*(3), 357–366. doi:10.1016/S0920-5861(99)00130-3

Chianelli, R. R., & Pecoraro, T. A. (1985). Carbon-containing molybdenum and tungsten sulphide catalysts. *U.S. Patent* 4,508,847.

Díaz de León, J. N., Picquart, M., Massin, L., Vrinat, M., & de los Reyes, J. A. (2012). Hydrodesulfurization of sulfur refractory compounds: Effect of gallium as an additive in NiWS/-Al_2O_3 catalysts. *Journal of Molecular Catalysis A Chemical*, *363–364*, 311–321. doi:10.1016/j.molcata.2012.07.006

Espinoza-Armenta, Y., Cruz-Reyes, J., Paraguay-Delgado, F., Del Valle, M., Alonso, G., Fuentes, S., & Romero-Rivera, R. (2014). CoMoW sulfide nanocatalysts for the HDS of DBT from novel ammonium and alkyltrimethylammonium-thiomolybdate-thiotungstate-cobaltate (II) precursors. *Applied Catalysis A, General*, *486*, 62–68. doi:10.1016/j.apcata.2014.08.017

Gochi, Y., Ornelas, C., Paraguay, F., Fuentes, S., Alvarez, L., Rico, J. L., & Alonso-Núñez, G. (2005). Effect of sulfidation on Mo-W-Ni trimetallic catalysts in the HDS of DBT. *Catalysis Today*, *107-108*, 531–536. doi:10.1016/j.cattod.2005.07.068

González-Cortés, S. L., Rugmini, S., Xiao, T., Green, M. L. H., Rodulfo-Baechler, S. M., & Imbert, F. E. (2014). Deep hydrotreating of different feedstocks over a highly active Al_2O_3-supported NiMoW sulfide catalyst. *Applied Catalysis A, General*, *475*, 270–281. doi:10.1016/j.apcata.2014.01.045

Guzmán, M. A., Huirache-Acuña, R., Loricera, C. V., Hernández, J. R., Díaz de León, J. N., de los Reyes, J. A., & Pawelec, B. (2013). Removal of refractory S-containing compounds from liquid fuels over P-loaded NiMoW/SBA-16 sulfide catalysts. *Fuel*, *103*, 321–333. doi:10.1016/j.fuel.2012.07.005

Ho, T. C. (2004). Deep HDS of diesel fuel: Chemistry and catalysis. *Catalysis Today*, *98*(1-2), 3–18. doi:10.1016/j.cattod.2004.07.048

Ho, T. C. (2008). Hydroprocessing catalysis on metal sulfides prepared from molecular complexes. *Catalysis Today*, *130*(1), 206–220. doi:10.1016/j.cattod.2007.06.076

Ho, T. C., Pan, W. H., Jacobson, A. J., & Chianelli, R. R. (2012). Hydroprocessing on chromium-containing metal sulfide catalysts. *Applied Catalysis A, General*, *421–422*, 38–47. doi:10.1016/j.apcata.2012.01.031

Homma, T., Echard, M., & Leglise, J. (2005). Investigation of CoNiMo/Al_2O_3 catalysts: Relationship between H_2S adsorption and HDS activity. *Catalysis Today*, *106*(1-4), 238–242. doi:10.1016/j.cattod.2005.07.187

Huirache-Acuña, R., Albiter, M. A., Espino, J., Ornelas, C., Alonso-Núñez, G., & Paraguay-Delgado, F. et al. (2006). (a)). Synthesis of Ni–Mo–W sulphide catalysts by ex situ decomposition of trimetallic precursors. *Applied Catalysis A, General*, *304*, 124–130. doi:10.1016/j.apcata.2006.02.032

Huirache-Acuña, R., Albiter, M. A., Ornelas, C., Paraguay-Delgado, F., Martínez-Sánchez, R., & Alonso-Núñez, G. (2006). (b)). Ni(Co)-Mo-W sulphide unsupported HDS catalysts by ex situ decomposition of alkylthiomolybdotungstates. *Applied Catalysis A, General*, *308*, 134–142. doi:10.1016/j.apcata.2006.04.015

Huirache-Acuña, R., Alonso-Núñez, G., Paraguay-Delgado, F., Lara-Romero, J., Berhault, G., & Rivera-Muñoz, E. M. (2015). Unsupported trimetallic CoMoW sulfide HDS catalysts prepared by *in situ* decomposition of sulfur-containing precursors. *Catalysis Today*, *250*, 28–37. doi:10.1016/j.cattod.2014.06.044

Huirache-Acuña, R., Pawelec, B., Loricera, C. V., Rivera-Muñoz, E. M., Nava, R., Torres, B., & Fierro, J. L. G. (2012). Comparison of the morphology and HDS activity of ternary Ni(Co)-Mo-W catalysts supported on Al-HMS and Al-SBA-16 substrates. *Applied Catalysis B: Environmental*, *125*, 473–485. doi:10.1016/j.apcatb.2012.05.034

Huirache-Acuña, R., Pawelec, B., Rivera-Muñoz, E., Nava, R., Espino, J., & Fierro, J. L. G. (2009). Comparison of the morphology and HDS activity of ternary Co-Mo-W catalysts supported on P-modified SBA-15 and SBA-16 substrates. *Applied Catalysis B: Environmental*, *92*(1-2), 168–184. doi:10.1016/j.apcatb.2009.07.012

Huirache-Acuña, R., Rivera-Muñoz, E. M., Pawelec, B., Ostrooumov, M., Maya-Yescas, R., & Rico, J. L. (2014). The use of a natural Mexican zeolite as support of NiMoW sulphide hydrotreating catalysts. *Catalysis Today*, *220-222*, 301–309. doi:10.1016/j.cattod.2013.07.019

Huirache-Acuña, R., Sánchez-Bautista, M. G., Lemus-Ruiz, J., Ornelas, C., Paraguay-Delgado, F., & Rivera-Muñoz, E. M. (2010). Synthesis and characterization of partially sulfided CoMoW oxides nanostructures and their application in the HDS of DBT DBT. *Revista Mexicana de Ingeniería Química*, *9*(2), 209–218.

Klicpera, T., & Zdrazil, M. (1999). High surface area MoO_3 /MgO: Preparation by the new slurry impregnation method and activity in sulphided state in hydrodesulphurization of benzothiophene. *Catalysis Letters*, *58*(1), 47–51. doi:10.1023/A:1019036724583

Klimova, T., Mendoza Vara, P., & Puente Lee, I. (2010). Development of new NiMo/g-alumina catalysts doped with noble metals for deep HDS. *Catalysis Today*, *150*(3-4), 171–178. doi:10.1016/j.cattod.2009.08.003

Lan, L., Ge, S., Liu, K., Hou, Y., & Bao, X. (2011). Synthesis of Ni_2P promoted trimetallic NiMoW/γ-Al_2O_3 catalysts for diesel oil hydrotreatment. *Journal of Natural Gas Chemistry*, *20*(2), 117–122. doi:10.1016/S1003-9953(10)60173-9

Lauritsen, J. V., Bollinger, M. V., Lægsgaard, E., Jacobsen, K. W., Nørskov, J. K., & Clausen, B. S. et al. (2004 a). Atomic-scale insight into structure and morphology changes of MoS_2 nanoclusters in hydrotreating catalysts. *Journal of Catalysis*, *221*(2), 510–522. doi:10.1016/j.jcat.2003.09.015

Lauritsen, J. V., Nyberg, M., Nørskov, J. K., Clausen, B. S., Topsøe, H., Lægsgaard, E., & Besenbacher, F. (2004 b). Hydrodesulfurization reaction pathways on MoS_2 nanoclusters revealed by scanning tunneling microscopy. *Journal of Catalysis*, *224*(1), 94–106. doi:10.1016/j.jcat.2004.02.009

Liu, D., Liu, L., Li, G., & Liu, C. (2010). Synthesis, characterization and hydrodesulfurization activity of silica-dispersed NiMoW trimetallic catalysts. *Journal of Natural Gas Chemistry*, *19*(5), 530–533. doi:10.1016/S1003-9953(09)60108-0

Lumbreras, J. A., Huirache-Acuña, R., Rivera-Muñoz, E. M., Berhault, G., & Alonso-Núñez, G. (2010). Unsupported Ni/Mo(W)S2 catalysts from hexamethylenediammonium thiometallates precursors: In situ activation during the HDS of DBT. *Catalysis Letters*, *134*(1-2), 138–146. doi:10.1007/s10562-009-0209-3

Mendoza-Nieto, J. A., Vera-Vallejo, O., Escobar-Alarcón, L., Solís-Casados, D., & Klimova, T. (2013). Development of new trimetallic NiMoW catalysts supported on SBA-15 for deep hydrodesulfurization. *Fuel*, *110*, 268–277. doi:10.1016/j.fuel.2012.07.057

Naumann, A. W., & Behan, A. S. (1981). Molybdenum disulfide catalyst and the preparation thereof. U.S. Patent 4,243,554.

Nava, H., Espino, J., Berhault, G., & Alonso-Nuñez, G. (2006). Effect of phosphorus addition on unsupported Ni–Mo–W sulfide catalysts prepared by the in situ activation of nickel/tetramethylammonium thiomolybdotungstate. *Applied Catalysis A, General*, *302*(2), 177–184. doi:10.1016/j.apcata.2005.12.025

Nava, H., Pedraza, F., & Alonso, G. (2005). Nickel-Molybdenum-Tungsten sulfide catalysts prepared by *in situ* activation of tri-metallic (Ni-Mo-W) alkylthiomolybdotungstates. *Catalysis Letters*, *99*(1-2), 65–71. doi:10.1007/s10562-004-0777-1

Olivas, A., Galván, D. H., Alonso, G., & Fuentes, S. (2009). Trimetallic NiMoW unsupported catalysts for HDS. *Applied Catalysis A, General*, *352*(1-2), 10–16. doi:10.1016/j.apcata.2008.09.022

Paraguay-Delgado, F., Huirache-Acuña, R., Jose-Yacaman, M., & Alonso-Nuñez, G. (2008). Synthesis and structural characterization of Mo-Ni-W oxide nanostructures. *Journal of Nanoscience and Nanotechnology*, *8*(6), 2983–2989. doi:10.1166/jnn.2008.117 PMID:18681035

Pawelec, B., Mariscal, R., Fierro, J. L. G., Greenwood, A., & Vasudevan, P. T. (2001). Carbon-supported tungsten and nickel catalysts for hydrodesulfurization and hydrogenation reactions. *Applied Catalysis A, General*, *206*(2), 295–307. doi:10.1016/S0926-860X(00)00605-0

Plantenga, F. L., & Leliveld, R. G. (2003). Sulfur in fuels: More stringent sulfur specifications for fuels are driving innovation. *Applied Catalysis A, General*, *248*(1-2), 1–7. doi:10.1016/S0926-860X(03)00133-9

Poisot, M., Bensch, W., Fuentes, S., Ornelas, C., & Alonso, G. (2007). High activity Ni/MoS_2 catalysts obtained from alkylthiometalate mixtures for the hydrodesulfurization of dibenzothiophene. *Catalysis Letters*, *117*(1-2), 43–52. doi:10.1007/s10562-007-9143-4

Quintana-Melgoza, J. M., Cruz-Reyes, J., & Avalos-Borja, M. (2001). Synthesis and characterization of $NiWO_4$ crystals. *Materials Letters*, *47*(4-5), 314–318. doi:10.1016/S0167-577X(00)00272-X

Rahmat, N., Zuhairi Abdullah, A., & Rahman Mohamed, A. (2010). A Review: Mesoporous Santa Barbara Amorphous-15, Types, Synthesis and Its Applications towards Biorefinery Production. *American Journal of Applied Sciences*, *7*(12), 1579–1586. doi:10.3844/ajassp.2010.1579.1586

Rivera-Muñoz, E. M., Pawelec, B., Nava, R., Cortés, J. A., & Huirache-Acuña, R. (2015). SBA-16 Mesoporous Silica as Catalytic Support for Hydrodesulfurization Catalysts. In *Comprehensive Guide for Mesoporous Materials: Application and Commercialization* (Vol. 4, pp. 343–361). Hauppauge, New York, USA: Nova Science Publishers, Inc.

Rodemerck, U., & Linke, D. (2009). High-throughput experimentation. In K. P. De Jong (Ed.), *Synthesis of solid catalysts* (pp. 217–240). Weinheim, Germany: Wiley-VCH. doi:10.1002/9783527626854.ch11

Satterfield, C. N. (1996). *Heterogeneous Catalysis in Industrial Practice: Catalyst Preparation and Manufacture* (2nd ed., pp. 87–129). Malabar, FL, USA: Krieger Publishing Co.

Severino, F., Laine, J., & López-Agudo, A. (2000). Compensation effect and dual promotion effect in activated carbon-supported CoNiMo hydrodesulfurization catalysts. *Journal of Catalysis*, *189*(1), 244–246. doi:10.1006/jcat.1999.2683

Sigurdson, S., Sundaramurthy, V., Dalai, A. K., & Adjaye, J. (2008). Phosphorous promoted trimetallic NiMoW/γ-Al_2O_3 sulfide catalysts in gas oil hydrotreating. *Journal of Molecular Catalysis A Chemical*, *291*(1-2), 30–37. doi:10.1016/j.molcata.2008.05.011

Soled, S. L., Miseo, S., Krycak, R., Vroman, H., Ho, T. C., & Riley, K. L. (2000). Nickel Molybdotungstate Hydrotreating Catalysts. US Patent 6,156,695.

Sundaramurthy, V., Dalai, A. K., & Adjaye, J. (2008). Thetraalkylthiomolybdates-derived Co(Ni)Mo/γ-Al_2O_3 sulfide catalysts for gas oil hydrotreating. *Journal of Molecular Catalysis A Chemical*, *294*(1-2), 20–26. doi:10.1016/j.molcata.2008.07.004

Thomazeau, C., Geantet, C., Lacroix, M., Danot, M., Harlé, V., & Raybaud, P. (2007). Predictive approach for the design of improved HDT catalysts: γ-Alumina supported (ni, Co) promoted $Mo_{1-x}W_xS_2$ active phases. *Applied Catalysis A, General*, *322*, 92–97. doi:10.1016/j.apcata.2007.01.016

Topsøe, H., Clausen, B. S., & Massoth, F. E. (1996). *Hydrotreating Catalysis. Science and Technology* (J. R. Anderson & M. Boudart, Eds.). Vol. 11). Berlin Heidelberg Germany: Springer-Verlang.

Topsøe, H., Hinnemann, B., Nørskov, J. K., Lauritsen, J. V., Besenbacher, F., & Hansen, P. L. et al. (2005). The role of reaction pathways and support interactions in the development of high activity hydrotreating catalysts. *Catalysis Today*, *107-108*, 12–22. doi:10.1016/j.cattod.2005.07.165

Trakarnpruk, W., & Seentrakoon, B. (2007). Hydrodesulfurization Activity of MoS_2 and Bimetallic Catalysts Prepared by in Situ Decomposition of Thiosalt. *Industrial & Engineering Chemistry Research*, *46*(7), 1874–1882. doi:10.1021/ie061176y

Yi, Y., Zhang, B., Jin, X., Wang, L., Williams, C. T., & Xiong, G. et al. (2011). Unsupported NiMoW sulfide catalysts for hydrodesulfurization of dibenzothiophene by thermal decomposition of thiosalts. *Journal of Molecular Catalysis A Chemical*, *351*, 120–127. doi:10.1016/j.molcata.2011.09.024

Zhang, F., Yan, Y., Yang, H., Meng, Y., Yu, C., Tu, B., & Zhao, D. (2005). Understanding Effect of Wall Structure on the Hydrothermal Stability of Mesostructured Silica SBA-15. *The Journal of Physical Chemistry B*, *109*(18), 8723–8732. doi:10.1021/jp044632+ PMID:16852033

Chapter 9

Polymolybdate Supported Nano Catalyst for Desulfurization of Diesel

Wan Azelee Wan Abu Bakar
Universiti Teknologi Malaysia, Malaysia

Rusmidah Ali
Universiti Teknologi Malaysia, Malaysia

Wan Nazwanie Wan Abdullah
Universiti Teknologi Malaysia, Malaysia

Wan Nur Aini Wan Mokhtar
Universiti Teknologi Malaysia, Malaysia

ABSTRACT

The Catalytic oxidative desulfurization (Cat-ODS) comprises of molybdenum based catalyst, tert-butyl hydroperoxide (TBHP) as oxidant and dimethylformamide (DMF) as solvent for extraction. A series of polymolybdates supported alumina were prepared using the wet impregnation method. This potential catalyst was characterized by FTIR, FESEM-EDX and XPS for its physical properties. From catalytic testing, Fe/MoO3-Al2O3 calcined at 500°C was revealed as the most potential catalyst which gave the highest sulfur removal under mild condition .The sulfur content in commercial diesel was successfully reduced from 440 ppmw to 88 ppmw under mild condition followed by solvent extraction. Response surface methodology involving Box-Behnken was employed to evaluate and optimize Fe/MoO3/Al2O3 preparation parameters (calcination temperature, catalyst loading, and Fe loading) and their optimum values were found to be 550 ºC, 10 g/L, and 10%. of calcination temperature, catalyst loading, and Fe loading. Based on these results, the reaction mechanisms of peroxy oxygen were proposed.

INTRODUCTION

Diesel can be considered the most potential fuel for transportation following gasoline. However, sulfur containing compounds in diesel are the main sources of acid rain and air pollution. In many countries around the world, environmental regulations have been introduced to reduce the sulfur content of diesel fuel and other transportation fuels to ultra-low levels (10–15 ppm)(Zongxuan et al. 2011).

Hydrodesulfurization (HDS) is the conventional method for lowering sulfur levels in diesel oil, but this technology requires severe conditions and is expensive. Hence, oxidative desulfurization (ODS) has

DOI: 10.4018/978-1-4666-9545-0.ch009

been considered as an alternative technology for deep desulfurization of light oil (Wang et al., 2012). The aim of the present work was to develop alumina-supported polymolybdate oxide-based catalysts - *tert*-butyl hydroperoxide system - in oxidative desulfurization activity. Secondly, the potential catalyst was applied to be used in investigating oxidative reaction mechanism. This work also aimed to produce ultra-low sulfur diesel (< 15 ppm-S).

BACKGROUND

Various studies on catalytic oxidation systems have been reported such as, $H_2O_2/Mo/Al_2O_3$ (García Gutiérrez et al 2006) and Fe^{2+}-CH_3COOH-H_2O_2 (Bhasarkar et al. 2013, Bolla et al. 2012). *Tert*-butyl hydroperoxide (TBHP) has been considered a powerful oxidant amongst sulfur compounds, and the best result is achieved when utilizing TBHP with heterogeneous catalysts (Wan Abu Bakar et al. 2012). Among heterogeneous catalysts, transition metal oxides such as Cu, Ti, Cr, Fe, Co, W and V are intensely studied in oxidation reactions (Al-Shahrani et al. 2007); (Bagiyan et al. 2004) ; (Murata et al. 2004). However, this kind of process was limited to monometallic oxides catalysts and most studies focused on model diesel.The use of alumina supported polymolybdate based catalyst for the activation of TBHP is an interesting alternative as it is the most desirable improvement of the ODS process (Abdullah et al. 2015). To date, the polymolybdate oxide catalyst doped with Fe has never been reported and explored for ODS reaction. Thus, the performance of new supported bimetallic oxide catalysts in commercial diesel will be reported. Secondly, the potential catalyst was also used to investigate the activity and oxidative reaction mechanism. This work was focused on developing a cost effective catalyst for ODS of commercial diesel under mild reaction conditions. Response surface methodology (RSM) is a set of techniques used to develop models from experimental or simulation data and can be used to obtain an optimal response (Dube et al. 2013). Compared to other RSM designs, Box-Behnken design (BBD) is the most frequently employed and offers some advantages; requiring few experimental points and high efficiency (Box et al. 1960). A Box-Behnken design was applied to determine the optimum sulfur removal, and also to explain the relationships between sulfur removal and three parameters, calcination temperature, catalyst loading and Fe loading.

METHOD

Materials

All solvents and chemicals were used without further purification. Phosphomolybdic acid hydrate and *tert*-butyl hydroperoxide (aqueous, 70wt%) were obtained from Across Organic. Iron(III) nitrate nonahydrate (99%), copper(II) nitrate trihydrate (99.5%) and cobalt(II) nitrate hexahydrate (99%) were obtained from QRëc. λ-Al_2O_3 beads (3-5 mm diameter) was obtained from Sigma-Aldrich, and di-methylformamide (DMF) was purchased from MERCK. Commercial diesel fuel (440 ppm sulfur) was obtained from Petronas, Malaysia.

Preparation and Characterization of Catalyst

Fe -doped Mo/Al_2O_3 solution was prepared by dissolving 1 g phosphomolybdic acid with 0.05 g iron(III) nitrate nonahydrate in 4 mL of water. The procedure was repeated using copper(II) nitrate trihydrate and cobalt(II) nitrate hexahydrate. The solution was used for the impregnation of Al_2O_3 (surface area: 292 m^2/g) at room temperature. The sample was dried overnight at room temperature, and was finally calcined from 400ºC to 900ºC for 5 h in air atmosphere. FESEM-EDX analysis was accomplished by using a Philips XL 40 microscope with energy of 15.9 kV coupled with EDX analyzer and bombarded using electron gun with tungsten filament under 25 kV resolutions to get the required magnification image. XPS surface study was conducted using X-ray photoelectron spectrometer (Omnicon Technology Instrument) with Al Kα X-ray source 20 Ev. The FTIR were recorded using Perkin Elmer Spectrum One Spectrometer with a resolution of 4 cm^{-1} and 15 scans in the mid IR region (500-4000 cm^{-1}).

Catalytic Oxidative Desulfurization

Each ODS reaction was conducted in a 100 mL round-bottom flask, equipped with a magnetic stirrer and fitted with condenser. In a typical run, the oil bath was first heated and stabilized at a constant temperature (45°C). Then, 10 mL of commercial diesel (440 ppm) was poured to the flask, followed by the addition of sulfur/TBHP in a ratio of 3 and 0.12 g catalyst. Each mixture was refluxed for 30 minutes under vigorous stirring at atmospheric pressure. The oxidized diesel was extracted with DMF at a ratio of diesel/solvent = 1. Extraction was performed by stirring the solvent for 30 minutes followed by phase separation. The treated diesel was then analyzed using a gas chromatograph (GC, Agilent 6890N) equipped with a FPD detector. Dibenzothiophene (DBT) was used as the model compound to study the ODS mechanism of commercial diesel using TBHP. The oxidation steps were performed as previously described for the ODS procedure. Samples were drawn from the flask at regular intervals for analysis. The GC-FPD was used to identify the oxidation products.

Experimental Design

The sulfur removal in ODS was optimized by response surface methodology using Box-Behnken design (BBD) with three independent variables: calcinations temperature, X_1 (400-600ºC), catalyst loading, $X_{2(}$3-15 g/L), Fe loading, X_3 (5-15%). The statistical software Design Expert 7.0 was used for the analysis. Three independent variables with their levels are presented in Table 1. The following quadratic equa-

Table 1. The amount and levels (coded and uncoded) of the independent variables in experimental design

Independent Variables	Range and Level		
	-1	0	1
Calcination temperature ºC, X_1	400	500	600
Catalyst loading, g/L, X_2	3	9	15
Fe loading, %, X_3	5	10	15

tion was used for the optimization process. The response variable (sulfur removal,%) was fitted with a full quadratic model (given in Equation (1) in order to correlate it to the experimental parameters or independent variables.

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (1)$$

where *Y* is the response variable, *i.e*. sulfur removal,% . β_0, β_i, β_{ii} and β_{ij} are coeffecients of the intercept, linear, square and interaction effects. x_i *and* x_j are coded independent variables.

MAIN FOCUS OF THE CHAPTER[1]

Hydrogen peroxide (H_2O_2) and TBHP are the most popular oxidants in the Cat-ODS process due to their appreciable oxidation power, thus they were chosen as oxidants in this study(Abdullah et al 2015). Their efficiency for the desulfurization of diesel fuel was compared in the presence of a metallic catalyst. Results clearly showed that reactivity of the MoO_3/Al_2O_3 catalyst was significantly increased when TBHP was used compared to H_2O_2 (Table. 2). A total removal of about 76% sulfur was achieved in the first extraction with the TBHP polymolybdate based catalyst system. In addition, MoO_3/Al_2O_3 has been reported to be an active oxidation catalyst, suitable for oxidation of thiophenic compounds with TBHP using a flow-type reactor (Otsuki et al 2001) . It can be expected that tert-butyl hydroperoxide is better oxidant than hydrogen peroxide in the oxidation of dibenzothiophene in commercial diesel, because of more hydrophobic property of tert-butyl hydroperoxide.

According to a previous study Sampanthar et al(2006), transition metal oxide catalysts supported on Al_2O_3 have been effective in catalyzing the oxidation of sulfur impurities in diesel to the corresponding sulfoxide or sulfone. In this study, MoO_3/Al_2O_3 was doped with Fe, Co and Cu. The catalysts were tested in order to find the best catalyst for the oxidation process. Table 3 shows the effect of dopants on MoO_3/Al_2O_3 catalyst on the ODS reaction for calcination temperature of 500°C.The results showed that the catalytic activity of the alumina supported Mo catalyst decreased in the order: Fe/Mo > Mo> Co/Mo >Cu/Mo. Thus, Fe was regarded as the best dopant for the molybdenum-based catalyst. Fe-MoO_3 (10:90)/Al_2O_3 calcined at the optimum temperature of 500°C showed 80% sulfur removal. In terms of catalytic activity, it was revealed that Fe/MoO_3 (10:90)/Al_2O_3 calcined at 500°C gave the optimum calcination temperature, with 82% of sulfur removal.

Table 2. Effect of oxidants on the ODS reaction in commercial diesel in presence of MoO_3/Al_2O_3

Type of Oxidant	Sulfur Removal, %
TBHP	76
H_2O_2	70

Catalytic oxidation = O: S molar ratio = 3:1, solvent DMF, commercial diesel/solvent ratio 1, oxidation T: 45 ºC, oxidation time: 30 min.

Table 3. Effect of different dopants

Dopants	Sulfur Removal, %
Fe/ MoO_3/Al_2O_3	82
Co/ MoO_3/Al_2O_3	74
Cu/MoO_3/Al_2O_3	69
Without dopant	76

Effect of the dopants on MoO_3/Al_2O_3 catalyst on the ODS reaction in commercial diesel. Catalytic oxidation = O:S molar ratio = 3:1, solvent DMF, commercial diesel/solvent ratio:1, oxidation T: 45 ºC, oxidation time: 30 min.

Table 4 shows the effect of calcination temperatures of bimetallic catalyst, calcined at 400, 500,600, 700 and 900ºC on the ODS reaction of commercial diesel.In terms of catalytic activity, it was revealed that Fe/MoO_3 (10:90)/Al_2O_3 calcined at 500°C gave the optimum calcination temperature, with 82% of sulfur removal. The catalytic activity increased up to 500°C and slowly decreased at calcination temperature of 900°C. These results are in good agreement with Vaudagna et al (1998), who observed that the higher the calcination temperature, the smaller the surface area, and thus decrease in catalytic conversion of sulfur compounds. Besides, it was suggested that mild calcination temperatures assured that the surface of metal oxides were fully oxidized and dispersed and that the formation of solid solutions or compounds were avoided (Wachs 1996).

Effect of Fe/MoO_3/Al_2O_3 catalyst loading calcined at 500 ºC in ODS of commercial diesel is shown in Table 5.It is clear that the oxidative removal of sulfur increased gradually with increased of catalyst dosage because higher m(catalyst)/m(oil) could provide more opportunity for the sulfide and the catalyst to be in contact, making the sulfide be more easily oxidized and removed as also discussed by Qiu et al(2012). When the ratio of catalyst to oil was increased from 6 to 9, the catalyst provided more active sites for sulfur compounds to react. Therefore, the removal of sulfur was increased. However, when the catalyst loading exceeded 12 g/L, the catalytic activity decreased with increasing catalyst dosage. As reported by Li et al (2012), this was due to the decrease of contact area between fuel and catalyst as a result of the reunion of catalyst.

Table 6 shows the oxidation activity of commercial diesel in the presence of Fe/MoO_3/Al_2O_3 catalyst at various Fe loading. The highest sulfur removal was observed at 10% Fe loading .At a higher Fe/Mo ratio such as 20%, the catalytic activity was decreased slightly. These results suggested that Fe which acted as a promoter was only required in a small quantities. An excess of Fe in the catalyst caused the agglomeration of molybdenum oxide on the catalyst surface which lowered the degree of dispersion of molybdenum, hence weakening the catalytic activity. As reported by Sampanthar et al(2006), the surface area and total pore volume of the catalyst decreased with increased iron oxide loading possibly due to the blockage of the inner pores, especially smaller ones, by iron. This is in agreement with our results which showed that the surface area decreased around 24% upon the increase of Fe loading to 20wt%. The activity of a catalyst only occurs on the surface of a metal oxide. Hence, it can be concluded that the presence of Fe at 10wt% was sufficient, as a structural promoter, to significantly enhance the catalytic activity and selectivity of the catalyst.

Table 4. Effect of calcination temperature

Calcination Temperature (ºC)	Sulfur Removal, %
400	76
500	82
600	73
700	69
900	60

Effect of calcination temperature of bimetallic catalyst on the ODS reaction in commercial diesel. Catalytic oxidation = O:S molar ratio = 3:1, solvent DMF, commercial diesel/solvent ratio: 1, oxidation T:45ºC, oxidation time: 30 min.

Table 5. Effect of the catalyst/oil ratio on the desulfurization rate

Catalyst Loading g/L	Sulfur Removal, %
3	59
6	62
9	76
12	73

Effect of on the catalyst/oil ratio on the ODS reaction in commercial diesel. Catalytic oxidation = O:S molar ratio = 3:1, solvent DMF, commercial diesel/solvent ratio: 1, oxidation T:45ºC, oxidation time: 30 min.

The presented results in Table 7 show that there is no significant decrease in catalyst activity even after four recycled runs indicating the superior performance of the fabricated catalyst in this work. Indeed, it explains that Fe/MoO_3/Al_2O_3 catalyst exhibits high catalytic activity for the ODS of commercial diesel and high resistance to sulfur poisoning.

The effect of the number of extractions of sulfur from oxidized diesel was further studied (Table 8). The extraction process was conducted via two methods; a single extraction and double extractions. The result showed that the single extraction process gave sulfur removal of 82%, while the double extraction method successfully removed 96% of sulfur from oxidized diesel. It was suggested that the single extraction was insufficient to remove sulfones or sulfoxides, and that two successive extractions would be better.

Characterization of Catalyst

Figure 1 shows the infrared spectra for Fe/MoO_3/Al_2O_3 and MoO_3/Al_2O_3 calcined at 500ºC. The existence of bending vibration of H-O-H at 1638 cm^{-1} .revealed that the crystalline water was coordinated as H_2O molecules, the broad band around 3448 cm^{-1} and 3433 cm^{-1} was assigned to OH stretching of the hydroxyl groups or adsorbed H_2O.(Harb et al 1989). According to Imamura et al 1998, the peak at around 897 cm^{-1} can be ascribed to isolated M=O species while the band at 650 cm^{-1} was due to bridged M-O-M or O-M-O octahedral polymolybdate species (see Figure 1).

Table 9 shows the textural properties and elemental analysis of the bimetallic oxide catalysts, obtained by N2 physisorption and EDX analysis. The elemental analysis by EDX confirmed the presence of Mo, P and Fe in the catalyst. The surface area of Fe/MoO_3/Al_2O_3 catalyst increased after calcination process at 400°C. This result was attributed to the elimination of organic precursors which covered the

Table 6. Effect of Fe loading in alumina-supported Fe/MoO_3/Al_2O_3 catalysts calcined at 500ºC on ODS of commercial diesel

Dopants Loading	Sulfur Removal, %
5	78
10	82
15	76
20	74

The Effect of Fe loading on the ODS reaction in commercial diesel. Catalytic oxidation = O:S molar ratio = 3:1, solvent DMF, commercial diesel/solvent ratio: 1, oxidation T:45ºC, oxidation time: 30 min.

Table 7. Reproduciblity test

Cycles	Sulfur Removal, %
1	82
2	81
3	80
4	77

Effect of reproducibility on the ODS reaction in commercial diesel. Catalytic oxidation = O:S molar ratio = 3:1, solvent DMF, commercial diesel/solvent ratio: 1, oxidation T:45ºC, oxidation time: 30 min.

Table 8. Effect of number of extraction on ODS reaction in commercial diesel

Number of Extractions	Sulfur Removal, %
1	82
2	96

Catalytic oxidation = O:S molar ratio = 3:1, solvent DMF, commercial diesel/solvent ratio 1, oxidation T:45 ºC, oxidation time 30 min.

Figure 1. IR spectra of a) Fresh Fe/MoO$_3$/Al$_2$O$_3$ and b) MoO$_3$/Al$_2$O$_3$ calcined at 500ºC

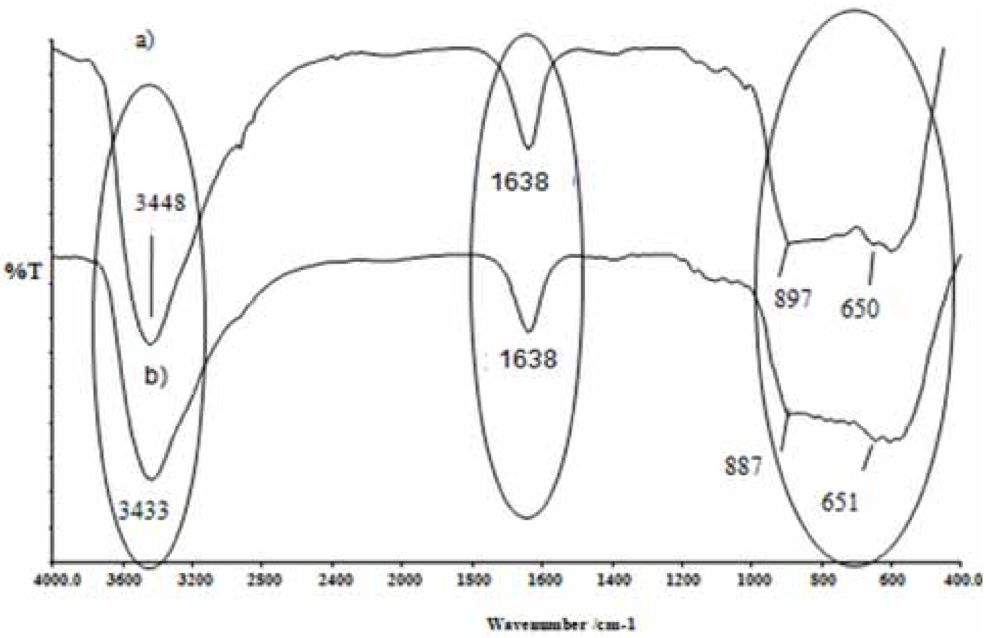


Table 9. Textural properties and elemental analysis of the bimetallic oxide catalysts

Catalysts	Calcination T (°C)	*S$_{BET}$ (m^2/g)	Loading[a] (wt.%)		
			Mo	P	Fe
Al$_2$O$_3$	-	253	-	-	-
Fe/MoO$_3$ (10:90)/Al$_2$O$_3$	400	299	14	0.5	1
Fe/MoO$_3$ (10:90)/Al$_2$O$_3$	500	239	14	0.40	2.1
Fe/MoO$_3$ (10:90)/Al$_2$O$_3$	600	202	18	0.45	-

[a] Measured by energy dispersive x-ray spectroscopy (EDX).

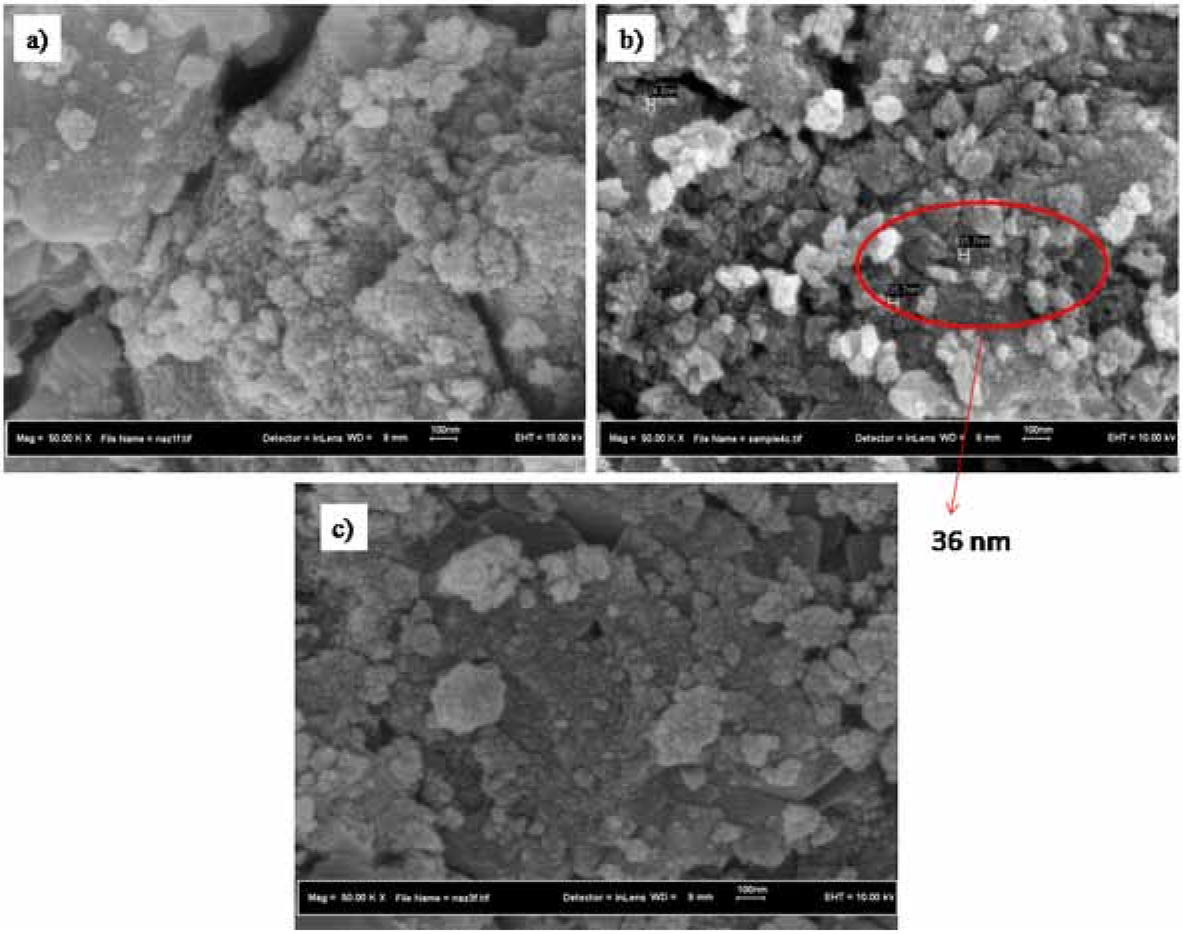
*S$_{BET}$: Surface Brunauer-Emmett-Teller (BET).

catalyst surface and pore into metal oxide as stated by Vicente et al (2004). Further increment calcination temperature of Fe/MoO$_3$/Al$_2$O$_3$ catalyst from 500°C to 600°C led to catalyst denatured, and hence diminished the surface area.

Fe/MoO$_3$/Al$_2$O$_3$ calcined at 500ºC gave a more homogeneous structure and smaller particle size as shown in the FESEM micrographs (Figure 2b). However, calcination of Fe/MoO$_3$/Al$_2$O$_3$ at 400ºC and 600ºC led to the formation of aggregates and agglomerates with undefined shapes and mixture of larger and smaller sized particles (Figure 2a and 2c).The particle sizes of the catalyst is less than 100nm which categorized as nanoparticle size.

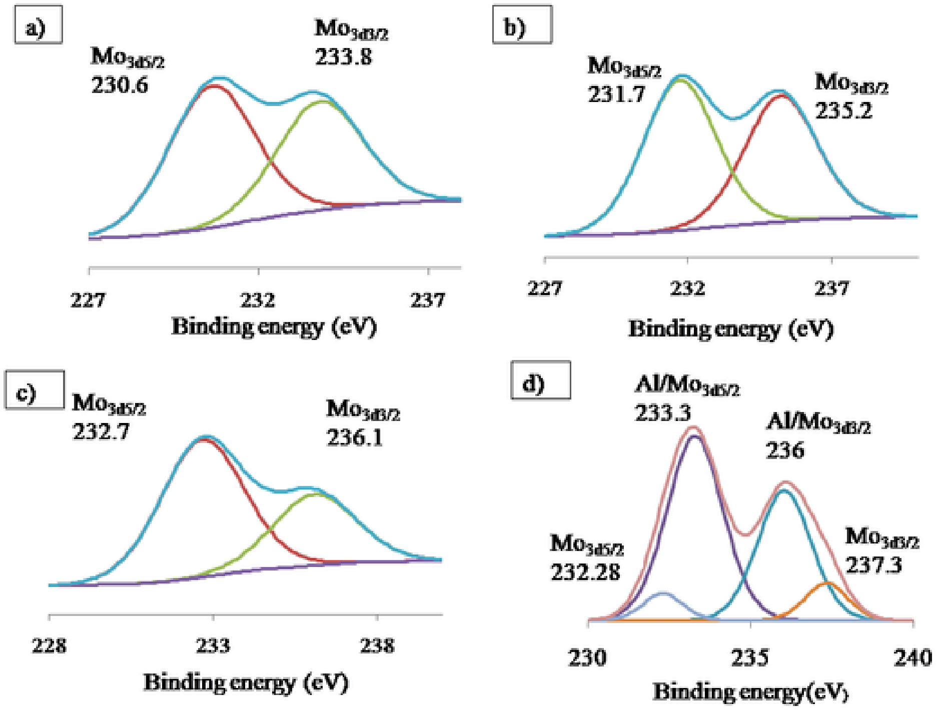
Figure 3 shows the Mo 3d XPS spectra of Fe/MoO$_3$/Al$_2$O$_3$ catalyst calcined at 400ºC, 500ºC, 600ºC versu MoO$_3$/Al$_2$O$_3$ calcined at 500°C. XPS analysis for the surface of Fe-MoO$_3$/Al$_2$O$_3$ calcined at 400ºC showed the binding energy Mo 3d$_{5/2}$ 230.6 eV and Mo 3d$_{3/2}$ 233.8 eV corresponding to Mo^{5+}, as also

Figure 2. FESEM micrographs of $Fe/MoO_3/Al_2O_3/Al_2O_3$ *calcined at (a) 400°C (b) 500°C (c) 600°C, magnification: 50k, scale bar: 1μm*



observed by Li *et al* (2014). At higher calcination temperatures of 500ºC and 600ºC, Mo^{5+} had transformed to Mo^{6+}. Spectral deconvulation indicated the presence of two signals at Mo $3d_{5/2}$ 231.7 eVand Mo $3d_{3/2}$ 235.2 eV for $Fe/MoO_3/Al_2O_3$ catalyst calcined at 500ºC while at 600ºC, showed equipvalent peak at the binding energy of Mo $3d_{5/2}$ 232.7 eV and Mo $3d_{3/2}$ 236.1 eV. As reported by Garcia-Gutierrez et al(2006), these binding energies corresponded to the Mo^{6+}. For MoO_3/Al_2O_3 catalyst, the binding energy around Mo $3d_{5/2}$232.28 eV and Mo $3d_{3/2}$ 237.3 corresponds to Mo^{6+}.Besides that, the binding energy due to spinel compound of $Al_2(MoO_4)_3$ can be seen at Al-Mo $3d_{5/2}$ 233.3 eV and Al-Mo $3d_{3/2}$ 236 eV. As reported by Wan Abu Bakar et al. (2012), this attested that the presence of MoO_3 was probably due to the solid state reaction with Al_2O_3 to produce well crystallized $Al_2(MoO_4)_3$. From this results, the existence of iron, as dopant in $Fe/MoO_3/Al_2O_3$ inhibit the formation of spinel compound and thus enhance the catalytic activity (refer Figure 2).The presence of iron and phosphate in the Mo catalyst cannot be detected because of very low concentration as shown in EDX analysis in Table 3. As reported Spojakina and Kraleva (2005), when the concentration of Fe and P is too low, deconvulation of the XPS peak is very difficult (see Figure 3).

Figure 3. X-ray photoelectron spectra of the Fe/MoO_3/Al_2O_3 catalyst calcined at a) 400ºC, b) 500ºC c) 600ºC and d) MoO_3/Al_2O_3 catalyst calcined at 500°C



Optimization of the Fe/MoO_3 /Al_2O_3 Catalyst

In the Box-Behnken design, 15-experimental observations were taken at random orders for the optimization of sulfur removal in the ODS process. Table 10 presents the data resulting from the experiments which involved their actual values and the corresponding responses (predicted values). Three variables were selected; calcinations temperature (X1), catalyst dosage (X2) and Fe loading (X3) and the experimental results were analyzed through RSM to obtain an empirical model for the best response. The final quadratic equation was obtained to explain the mathematical relationship between the independent parameters and the dependent responses (Y) and is presented below:

$$Y = 81.02 + 0.54X_1 + 0.52X_2 - 0.44X_3 + 0.83X_1X_2$$
$$+X_1X_3 - 2.13X_2X_3 - 0.36X_1^2 - 5.49X_2^2 - 3.66X_3^2$$

The results of analysis of variance presented in Table 11 shows the successful fitting of the experimental data to the quadratic model. The degree of freedom values (F-test) for the model was found to be 752.92, which implied that the model was significant; and only a 0.01% chance that F-value this large could occur due to noise. A low p-value ($p < 0.05$) indicate that the model is statistically significant for sulfur removal. Therefore, obtained model ensures an accurate representation of the experimental data.

Table 10. Box-Behnken design matrix

Observation	**Actual Values**			**Sulfur Removal**		
	X_1	X_2	X_3	Y_{exp}	Y_{pred}	**Residual**
1	400	15	10	74.20	74.34	-0.14
2	600	15	10	77	77.06	-0.06
3	500	9	10	81	81.02	-0.02
4	600	9	15	78	78.01	-0.10
5	600	9	5	77	76.98	0.02
6	500	15	5	75	74.96	0.03
7	500	9	10	80.97	81.02	-0.05
8	400	9	15	75	75.03	-0.02
9	600	3	10	74.50	74.36	0.14
10	500	3	15	73	73.04	-0.03
11	500	15	15	70	69.84	0.16
12	500	3	5	69.50	69.66	-0.16
13	500	9	10	81.10	81.02	0.077
14	400	9	5	78.01	77.91	0.10
15	400	3	10	75	74.94	0.06

Table 11. Analysis of variance (ANOVA) for conversion

Source	**DF**[b]	**SS**[b]	**MS**[b]	**F**[b]	**P**[b]	**CE**
Model[a]	9	181.32	20.15	752.92	<0.0001	
Calcination temperature, X_1	1	2.30	2.30	85.97	0.0002	0.54Z
Catalyst loading, X_2	1	2.20	2.20	82.40	0.0003	0.52
Fe loading, X_3	1	1.54	1.54	57.55	0.0006	-0.44
X_1X_2	1	2.72	2.72	101.74	0.0002	0.83
X_1X_3	1	4.02	4.02	150.23	<0.0001	1.00
X_2X_3	1	18.06	18.06	675.02	<0.0001	-2.13
X_1^2	1	0.48	0.48	17.92	0.0082	-0.36
X_2^2	1	111.20	111.20	4155.79	<0.0001	-5.49
X_3^2	1	49.47	49.47	1848.84	<0.0001	-3.66
Residual	5	0.13	0.027			
Lack of fit	3	0.12	0.042	8.96	0.1021	
Pure error	2	0.009	0.004			
Total	14	181.46				

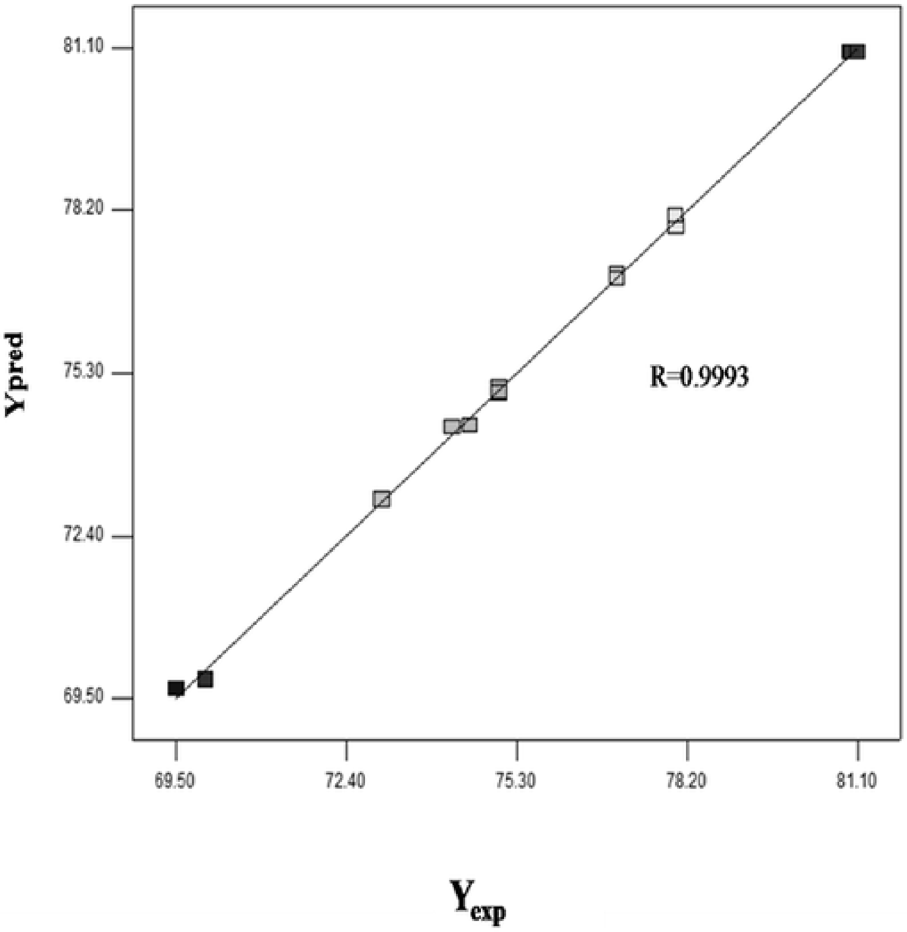
[a] R-Sq = 99.93%, R-Sq (adj) = 99.79%, R-Sq (pred) = 98.89%.

[b] DF: degree of freedom of different source, SS: sum of square, MS: mean of square, F: degree of freedom, P: probability, CE: coefficient estimate.

A very high R^2 (R-Sq) value of 0.9993 indicated that the predicted quadratic model was reasonably well fitted with the data. The predicted R2 (Pred R-Sq) value of 0.9889 is in line with the adjusted R^2 (Adj R-Sq) value of 0.9979 The comparison between experimental and predicted values of Y is shown graphically with a 45 -line in Figure 4.

The importance of each of three independent factors (calcination temperature, catalyst loading and Fe loading) on sulfur removal was determined by illustrating the response surfaces as three dimensional (3D) plots. In Figure 4 (a), the Fe loading was kept constant at 10%, while the catalyst loading and calcination temperature were kept constant at 9g/L and 500ºC in Figure 5 (b) and (c) . As can been seen from Figure 5 (a), the sulfur removal increase as increase the catalyst loading. It was obvious from Figure 5(a) that the variation of catalyst loading is more important than calcinations temperature on sulfur removal. Meanwhile, as can be understood from Figure 5 (b), the variation of Fe loading remarkably affects the sulfur removal, while the variation of calcination temperature was less important. Moreover, the elliptical of the contour plot of Fe loading and calcination temperature indicated that the interaction between these variables is effective on sulfur removal, as the calcinations temperature has a larger effect on the

Figure 4. Comparison between experiment and predicted Y

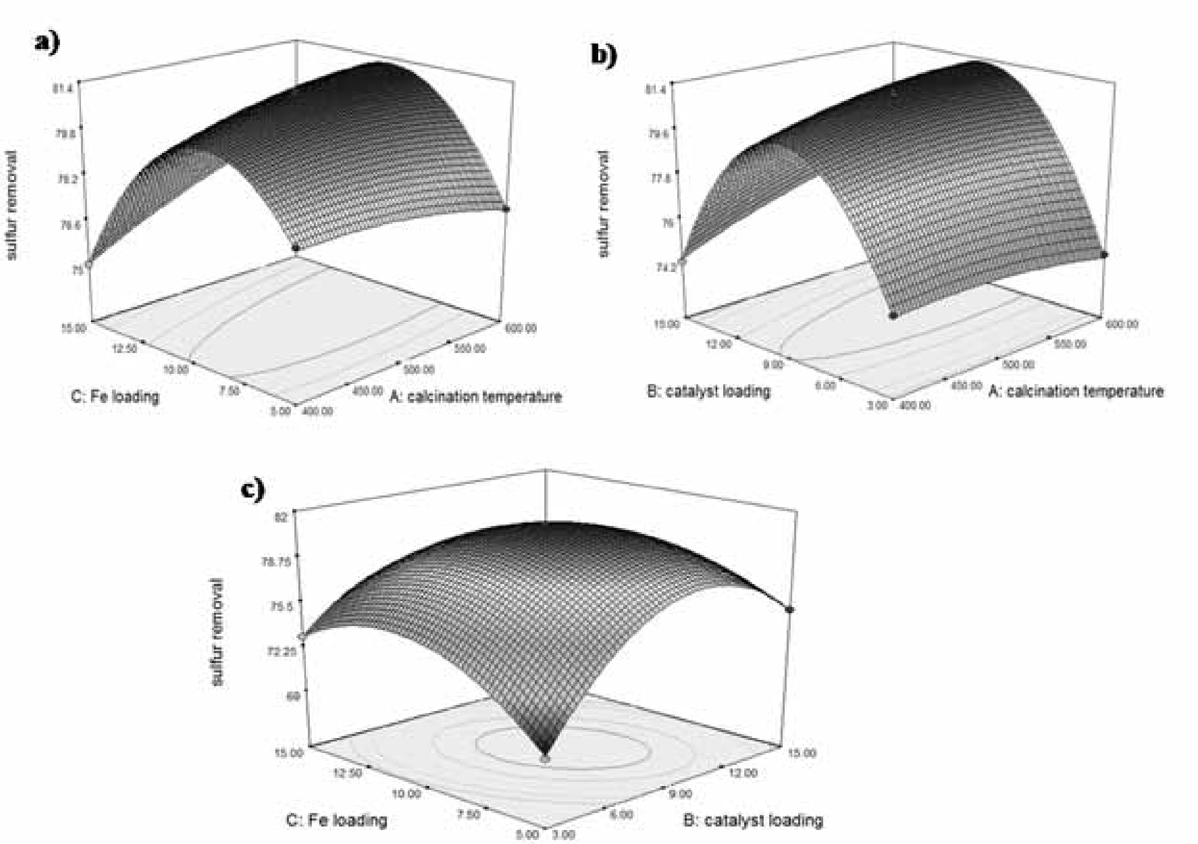


sulfur removal when the Fe loading was high. Figure 5 (c) represents the effect of catalyst loading and Fe loading on sulfur removal while keeping the calcination temperature at 500ºC. Figure 5 (c) clearly stated that as the catalyst amount and Fe loading increases, the sulfur removal improved. Desulfurization reactions were intensified because more sulfur molecules were adsorbed in the more active center of the catalyst surface (Wang et al 2013). Overall, the important degree ofthese parameters on sulfur removal was: calcinations temperature > catalyst loading > Fe loading.

Optimization Response and Verification Test

The main objective of the optimization was to determine the optimum conditions of Fe/MoO_3 /Al_2O_3 catalyst preparation for optimizing sulfur removal in commercial diesel. The factor setting can be adjusted to get the initial solution. The values of the independent variables are obtained by considering the starting values of calcination temperature, catalyst loading and Fe loading of 400ºC, 3g/l, and 5%, respectively.

Figure 5. 3-D surface plots of sulfur removal as a function of (a) calcination temperature and Catalyst loading), (b) calcinations temperature and Fe loading and (c) catalyst loading and Fe loading



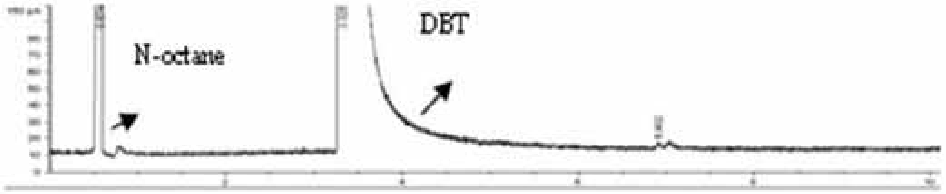
The sulfur removal was estimated as 81.1% within these optimum conditions (calcinations temperature 550ºC, catalyst loading 10 g/L and Fe loading 10%). An additional experiment was conducted under the optimum conditions to confirm the agreement of the model and experimental results. The experimental value 82% is in great agreement with the predicted result and hence validated the findings of response surface optimization.

Mechanism Proposal for Fe/MoO_3/Al_2O_3 Catalyst in ODS Reaction

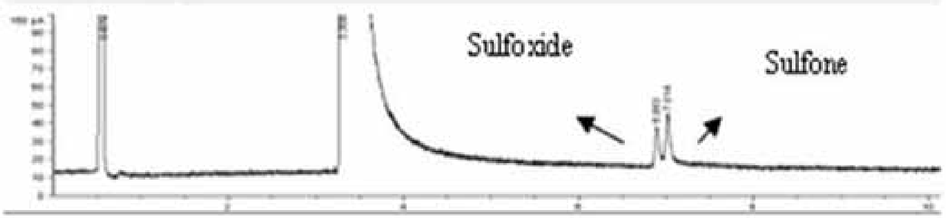
DBT was used as a model compound to study the oxidative desulfurization process over TBHP-Fe/MoO_3/Al_2O_3 system at a time of interval 5 min, 30 min and 45 min. The GC-FPD chromatogram of model compound of DBT extracted by DMF in presence of catalyst are shown in Figure 6. The results of GC-FPD analysis in the model compound of DBT extracted by DMF of Fe/MoO_3 /Al_2O_3 catalyst showed that the desulfurization products were DBT sulfoxide and DBT sulfone. It was observed that the DBT sulfone was increased with increased oxidation time because longer time could provide more opportunity for the DBT and the catalyst to be in contact, making the DBT be more easily oxidized into sulfone. From this result, it is important to highlight that catalyst is vital in the desulfurization for oxidation of DBT into DBT sulfone (see Figure 6).

Figure 6. Chromatogram of GC-FPD analysis for DBT oxidation desulfurization by TBHP after 5 min, 30 min and 45 min using Fe/MoO_3 /Al_2O_3 catalyst

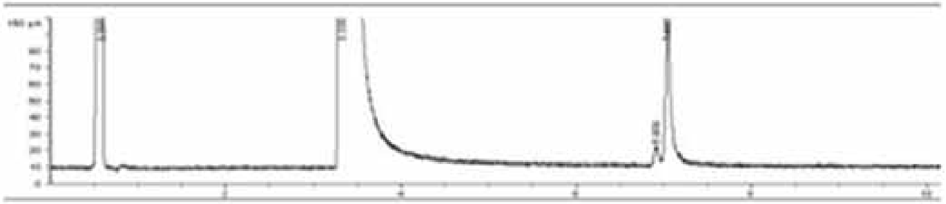
Catalytic oxidation= O: S molar ratio=3:1, solvent= DMF, commercial diesel/solvent ratio=1, oxidation T= 45ºC, oxidation time= 30 min.



After 5 min



After 30 min

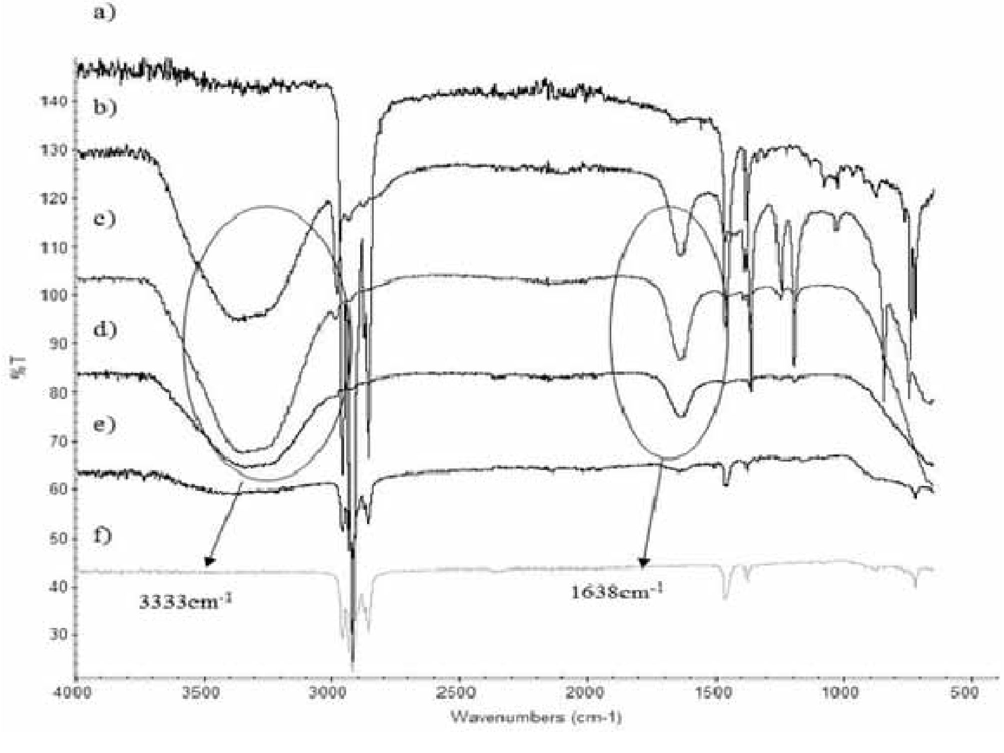


After 45 min

To understand the reaction mechanism of oxidative desulfurization with TBHP- Fe/MoO_3 /Al_2O_3 system, the surface of the catalysts were analyzed by FTIR. The FTIR spectra of TBHP, model DBT and surface of Fe/MoO_3 /Al_2O_3 catalyst after 0 min, 5 min, 30 min and 45 min oxidation are shown in Figure 7. From IR spectrums of TBHP and surface Fe/MoO_3/Al_2O_3 catalyst after 0 min and 5 min oxidation, the broad band at 3333 cm^{-1} and 1638 cm^{-1} were observed, which were assigned to –OH stretching and bending vibration band of H–O–H respectively (Harb et al 1989). The presence of water molecule and OH group due to presence of water in TBHP. After 30 min and above, the peaks that assigned to TBHP disappeared on the catalyst surface. From this result, it showed that the TBHP was completely reacted with the active sites on catalyst surface after 30 min (see Figure 7).

On the basis of above-mentioned results, our proposed peroxidic oxidation mechanism of DBT on Fe/MoO_3/Al_2O_3 catalyst with TBHP is shown in Figure 8. The reaction pathway proceeded initially through the nucleophilic attack of TBHP on Fe/MoO_3/Al_2O_3 to form species (1). The oxidation process must proceed by nucleophilic attack of the sulfur in the DBT (2) on the positively charged peroxometallic complex (1) to form DBT sulfoxide (3) and regenerated polymolybdate species, respectively. Subsequently, the sulfoxide (3) undergoes further oxidation to form DBT sulfone (4) (Tang et al 2013). Phosphate would help withdraw electron density from the polymolybdate species, thereby conferring a higher electrophilic character to the Mo (VI) atoms .At the same time, Fe dopant will provide a relatively more positive net charge on the polymolybdate catalyst surface. This property will enhance the reaction of TBHP with the catalyst to form active species. In overall, the activation mechanism of peroxy oxygen is according

Figure 7. IR spectra of a) model DBT, b) TBHP, Fe/MoO_3 /Al_2O_3 catalyst after c) 0 min, d) 5 min e) 30 min and f) 45 min oxidation

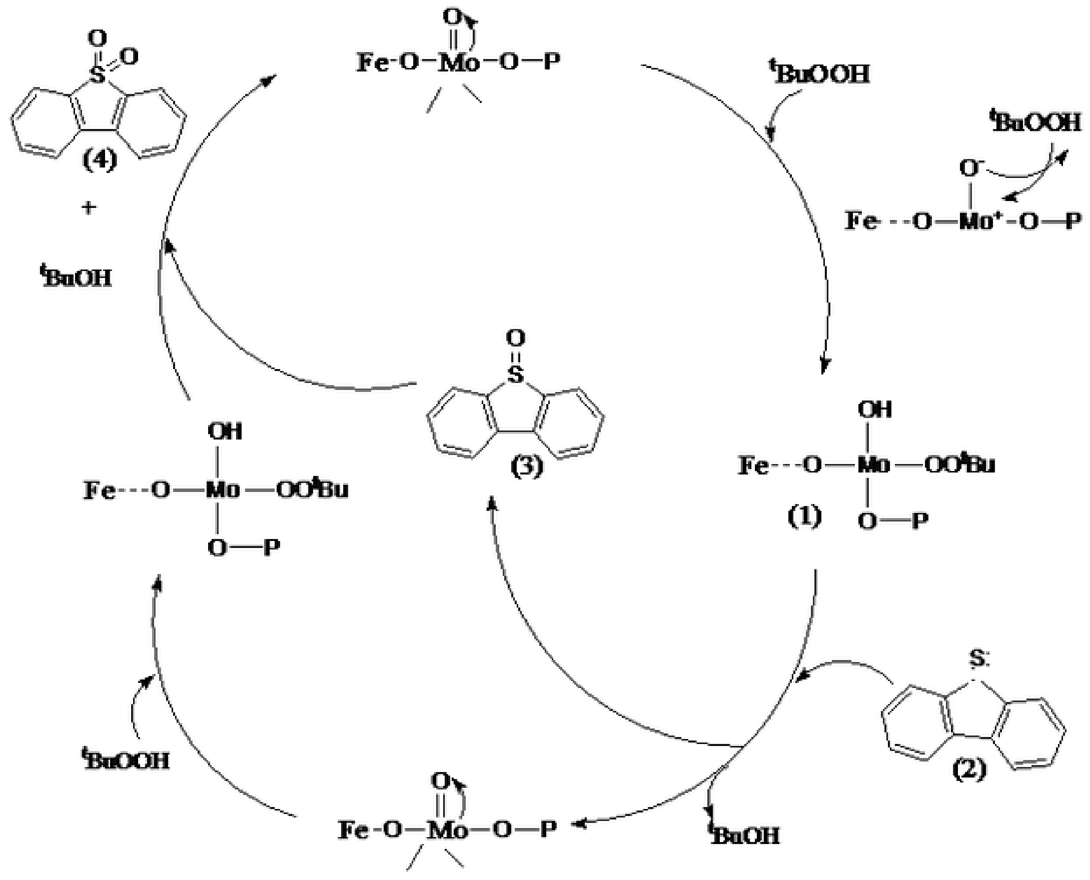


to Garcia Gutierrez et al (2006) in which the peroxide reacts with DBT to produce DBT sulfoxide, and further oxidation produces the corresponding sulfone in presence of Fe/MoO_3/Al_2O_3 catalyst (see Figure 8).

CONCLUSION

It is possible to reduce the level of sulfur in Malaysian commercial diesel from 440 ppm to 18 ppm under mild conditions using a Fe/MoO_3/Al_2O_3 catalyst calcined at 500ºC. A screening of catalytic testing showed that the Mo catalyst provided a higher conversion of sulfur for removal in the presence of a transition metal as promoter. These results were also verified using Box-Behnken experimental design. The obtained model equation using BBD showed the high coefficient of determination ($R^2 = 0.9993$) indicating that the predicted data well fitted with the actual data. According to the statistical design method, the optimal operation conditions were determined at calcinations temperature = 550°C, catalyst loading = 10g/L and Fe loading = 10%. Verification experiment was performed at the optimum

Figure 8. A proposed cyclic mechanism for the oxidation of dibenzothiophene by TBHP in the presence of Fe/MoO_3/Al_2O_3 catalyst



conditions and the experimental value (82%) closely agreed with predicted value (81.1%). The results indicate that alumina supported polymolybdate based catalyst has the potential to be used as a catalyst in Cat-ODS to meet the regulation of sulfur in diesel fuel.

REFERENCES

Abdullah, W. N. W., Bakar, W. A. W. A., & Rusmidah, A. (2015). Catalytic oxidative desulfurization of diesel fuel utilizing a polymolybdate alumina supported catalyst: Characterization, catalytic activity and mechanistic study. *Reaction Kinetics, Mechanisms and Catalysis*, *114*(2), 547–560. doi:10.1007/s11144-014-0801-4

Al-Shahrani, F., Xiao, T., Llewellyn, S. A., Barri, S., Jiang, Z., & Shi, H. et al. (2007). Desulfurization of diesel via the H_2O_2 oxidation of aromatic sulfides to sulfones using a tungstate catalyst. *Applied Catalysis B: Environmental*, *73*(3-4), 311–316. doi:10.1016/j.apcatb.2006.12.016

Bagiyan, G. A., Koroleva, I. K., Soroka, N. V., & Ufimtsev, A. V. (2004). Kinetics of the catalytic oxidation reactions of thiol compounds in aqueous solutions in the presence of copper ions. *Kinetics and Catalysis*, *45*(3), 372–380. doi:10.1023/B:KICA.0000032171.81652.91

Bhasarkar, J. B., Chakma, S., & Moholkar, V. S. (2013). Mechanistic features of oxidative desulfurization using sono-fenton-peracetic acid (ultrasound/Fe^{2+}-CH_3COOH-H_2O_2) system. *Industrial & Engineering Chemistry Research*, *52*(26), 9038–9047. doi:10.1021/ie400879j

Bolla, M. K., Choudhury, H. A., & Moholkar, V. S. (2012). Mechanistic features of ultrasound-assisted oxidative desulfurization of liquids fuels. *Industrial & Engineering Chemistry Research*, *51*(29), 9705–9712. doi:10.1021/ie300807a

Box, G. E. P., & Behnken, D. W. (1960). Some new three level designs for the study of quantitative variables. *Technometrics*, *2*(4), 455–475. doi:10.1080/00401706.1960.10489912

Dube, G., Osifo, P., & Rutto, H. (2013). *Preparation of bagasse ash/CaO/ammonium acetate sorbent and modelling their desulphurization reaction*. Clean Techn Environ Policy; doi:10.1007/s10098-013-0681-8

García-Gutiérrez, J. L., Fuentes, G. A., Hernández-Terán, M. E., Murrieta, F., Navarrete, J., & Jiménez-Cruz, F. (2006). Ultra-deep oxidative desulfurization of diesel fuel with H_2O_2 catalyzed under mild conditions by polymolybdates supported on Al_2O_3. *Applied Catalysis A*, *305*(1), 15–20. doi:10.1016/j.apcata.2006.01.027

Harb, F., Gérand, B., Nowogrocki, G., & Figlarz, M. (1989). Structural filiation between a new hydrate $MoO_{3.}$ ⅓H_2O and a new monoclinic form of MoO_3 obtained by dehydration. *Solid State Ionics*, *32-33*(Part 1), 84–90.

Imamura, S., Sasaki, H., Shono, M., & Kanai, H. (1998). Structure of molybdenum supported on α-, γ-, and x-aluminas in Relation to Its Epoxidation Activity. *Journal of Catalysis*, *177*(1), 72–81. doi:10.1006/jcat.1998.2088

Li, H., Li, M., Chu, Y., Liu, F., & Nie, H. (2014). Effect of different preparation methods of MoO_3/Al_2O_3 catalysts on the existing states of Mo species and hydrodesulfurization activity. *Fuel*, *116*, 168–174. doi:10.1016/j.fuel.2013.07.127

Li, Q., Wang, G., Qiu, J., Wang, N., Zhang, Q., & Lei, Q. et al. (2012). Catalytic Oxidative Desulfurization of Model Fuel using $[HPMo][HTAC]_2/SiO_2$ as a Amphiphilic Catalyst. *Adv. Mater. Res.*, *82*, 396–398.

Ma, X., Zhou, A., & Song, C. (2007). A novel method for oxidative desulfurization of liquid hydrocarbon fuels based on catalytic oxidation using molecular oxygen coupled with selective adsorption. *Catalysis Today*, *123*(1-4), 276–284. doi:10.1016/j.cattod.2007.02.036

Murata, S., Murata, K., Kidena, K., & Nomura, M. A. (2004). Novel oxidative desulfurization system for diesel fuels with molecular oxygen in the presence of cobalt catalysts and aldehydes. *Energy & Fuels*, *18*(1), 116–121. doi:10.1021/ef034001z

Otsuki, S., Nonaka, T., Qian, W., Ishihara, A., & Kabe, T. (2001). Oxidative desulfurization of middle distillate-oxidation of dibenzothiophene using t-butyl hypochlorite. *Journal of the Japan Petroleum Institute*, *44*(1), 18–24. doi:10.1627/jpi1958.44.18

Qiu, J., Wang, G., Bao, Y., Zhang, Y., & Zeng, D. (2012). Catalytic Oxidative desulfurization of model fuel oil with phosphomolybdic acid loaded on $SiO_{2.}$ *Advanced Materials*, *512-515*, 2110–2114. doi:10.4028/www.scientific.net/AMR.512-515.2110

Sampanthar, J. T., Xiao, H., Dou, J., Nah, T. Y., Rong, X., & Kwan, W. P. (2006). A novel oxidative desulfurization process to remove refractory sulfur compounds from diesel fuel. *Applied Catalysis B: Environmental*, *63*(1-2), 85–93. doi:10.1016/j.apcatb.2005.09.007

Spojakina, A., Kraleva, E., Jiratova, K., & Petrov, L. (2005). TiO2-supported iron–molybdenum hydrodesulfurization Catalystd. *Applied Catalysis A, General*, *288*(1–2), 10–17. doi:10.1016/j.apcata.2005.02.034

Tang, Q., Lin, S., Cheng, Y., Liu, S., & Xiong, J.-R. (2013). Ultrasound-assisted oxidative desulfurization of bunker-C oil using tert-butyl hydroperoxide. *Ultrasonics Sonochemistry*, *20*(5), 1168–1175. doi:10.1016/j.ultsonch.2013.02.002 PMID:23538118

Vaudagna, S. R., Canavese, S. A., Comelli, R. A., & Figoli, N. S. (1998). Platinum supported WOx–ZrO2: Effect of calcination temperature and tungsten loading. *Applied Catalysis A, General*, *168*(1), 93–111. doi:10.1016/S0926-860X(97)00343-8

Vicente, M. A., Belver, C., Trujillano, R., Rives, V., Alvarez, A. C., & Lambert, J. F. et al. (2004). Preparation and characterization of Mn- and Co-supported catalysts derived from Al-pillared clays and Mn- and Co-complexes. *Appl. Catal. A*, *267*(1-2), 47–58. doi:10.1016/j.apcata.2004.02.023

Wachs, I. E. (1996). Raman and IR studies of surface metal oxide species on oxide supports: Supported metal oxide catalysts. *Catalysis Today*, *27*(3-4), 437–455. doi:10.1016/0920-5861(95)00203-0

Wan Abu Bakar, W. A., Ali, R., Abdul Kadir, A. A., & Wan Mokhtar, W. A. (2012). Effect of transition metal oxides catalyst on oxidative desulfurization of model diesel. *Fuel Processing Technology*, *101*, 78–84. doi:10.1016/j.fuproc.2012.04.004

Wang, L., Cai, H., Li, S., & Mominou, N. (2013). Ultra-deep removal of thiophene compounds in diesel oil over catalyst TiO_2/Ni-ZSM-5 assisted by ultraviolet irradiating. *Fuel*, *105*, 752–756. doi:10.1016/j.fuel.2012.09.069

Wang, L., Sun, B., Yang, F. H., & Yang, R. T. (2012). Effects of aromatics on desulfurization of liquid fuel by p-complexation and carbon adsorbents. *Chem Engineering Science*, *7*, 208–217. doi:10.1016/j.ces.2012.01.056

Zongxuan, J., Hongying, L., Yogna, L., & Can, L. (2011). Oxidative Desulfurization of Fuel Oils. *Chinese Journal of Catalysis*, *32*(5), 707–715. doi:10.1016/S1872-2067(10)60246-X

Chapter 10

Molecularly Imprinted Polymer Nanofibers for Adsorptive Desulfurization

Adeniyi S. Ogunlaja
Nelson Mandela Metropolitan University, South Africa

Zenixole R. Tshentu
Nelson Mandela Metropolitan University, South Africa

ABSTRACT

Desulfurization of fuel oils is an essential process employed in petroleum refineries to reduce the sulfur concentration in fossil fuels in order to meet the mandated environmental protection limit of 10 ppm sulfur. The hydrodesulfurization (HDS) process, which is currently being employed for desulfurization, is limited in treating refractory organosulfur compounds as it only reduces sulfur content in fuels to a range of 200-500 ppm sulfur. Oxidative desulfurization (ODS) is considered a new technology for desulfurization of fuel oils as the process is capable of desulfurizing fuels to reach the ultra-low sulfur levels and can serve as a complementary step to HDS. The chapter discusses, briefly, the oxidation of refractory sulfur compounds found in fuels using vanadium as a catalyst to form organosulfones, a first step in ODS process. The chapter also discusses, in detail, the chemistry involved in molecular imprinting of organosulfones on functional polymers, and the electrospinning of the polymeric matrix to produce molecularly imprinted nanofibers employed for selective adsorption of organosulfones from the oxidized mildly hydrotreated fuels, a second step in the ODS process. Chemical interactions, apart from the imprinting effect, that can be exploited in molecularly imprinted polymers for selective extraction of organosulfones, such as hydrogen bonding, π-π interactions, van der Waals forces and electrostatic interactions, were discussed by employing density functional theory calculations. The possibilities of electrospinning on a large scale as well as prospects for future industrial applications of functional molecularly imprinted nanofibers in desulfurization are also discussed.

DOI: 10.4018/978-1-4666-9545-0.ch010

INTRODUCTION

Crude oil is a complex blend containing thousands of hydrocarbons, non-hydrocarbon compounds and heavy metals (Sami *et al*. 1994). The hydrocarbons are mixed with variable quantities of sulfur-, nitrogen-, and oxygen-containing compounds. Crude oil is expected to be the source of energy in the world for several decades to a century, and the crude oil reserves are distributed around all the continents (Figure 1). The Middle East has the highest reserves of over 750 thousand million barrels and the Asia pacific region having the least reverses of just over 40 thousand million barrels of oil. Generally, crude oils are refined to separate the complex mixture into simpler fractions that can be used as fuels, lubricants, and as intermediate feedstock for petrochemical industries.

However, it is known that over 70% of the world's oil reserves tend to be of heavier and sourer composition, i.e. have a high sulfur content. The sulfur content distribution in some crude oil reservoirs around the world is depicted in Figure 2. It can be seen that the sulfur content of crude oils varies appreciably from one reservoir to another. The low sulfur containing crude oils are referred to as sweet oils, while the high sulfur containing crude oils are referred to as sour crudes and are less desirable due to the high cost involved in refining the oils (Source: EPA, 2013; Crude oil reserve, 2013). Sulfur oxides are produced from fuel containing sulfur compounds during combustion and these emissions constitute a serious environmental hazard such as acid rain and the generation of airborne particulate (such as smog and sulfates). Sulfur oxides also poison and deactivate catalytic converters in vehicles,

Figure 1. Crude oil reserves distribution around the continents of the world
(Source: EPA, 2013; Crude oil reserve, 2013).

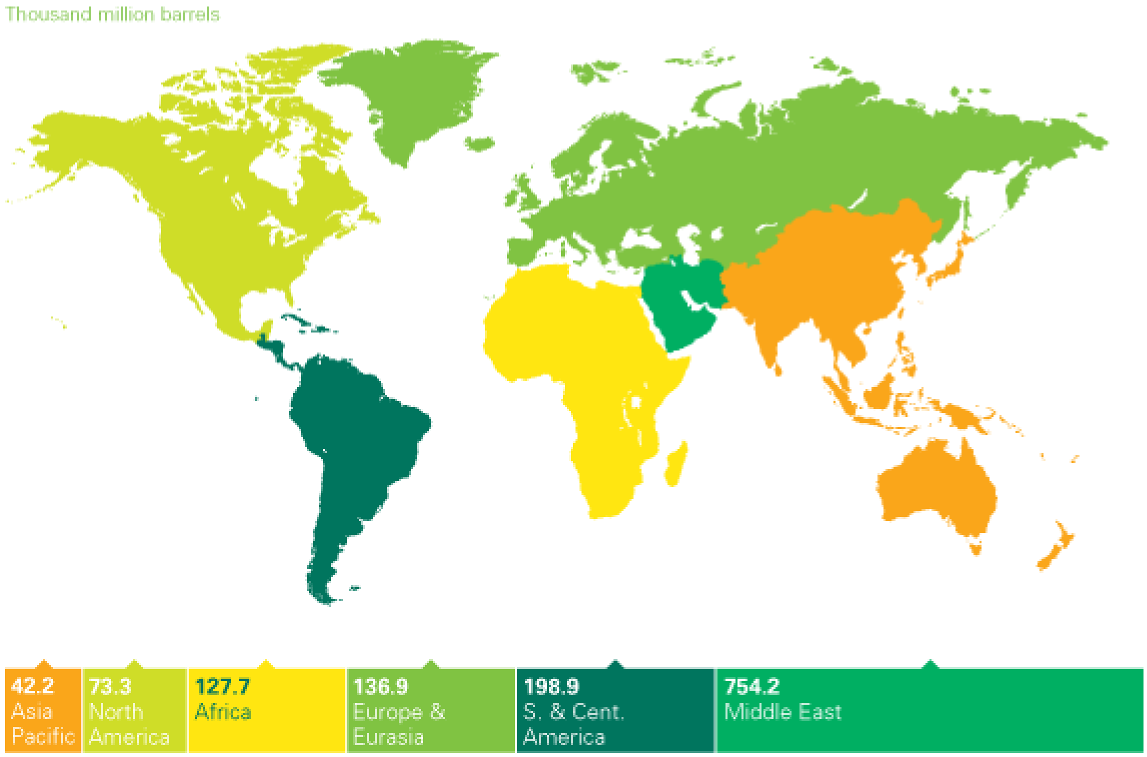
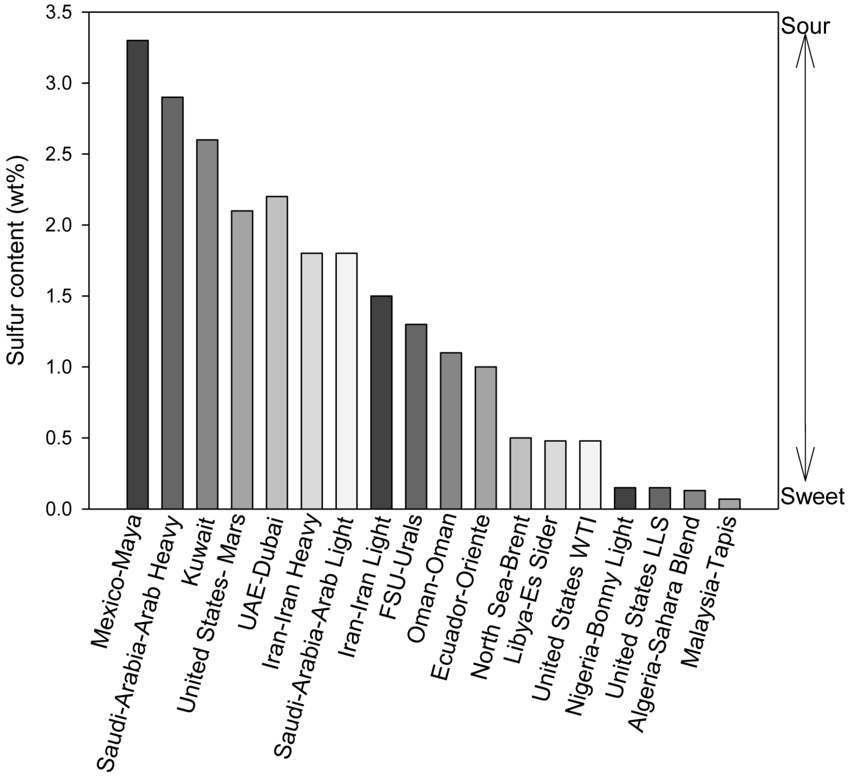


Figure 2. Sulfur distribution in crude oils in the world (1 wt.% Sulfur = 10000 ppm)
(Source: EPA, 2013; Crude oil reserve, 2013).

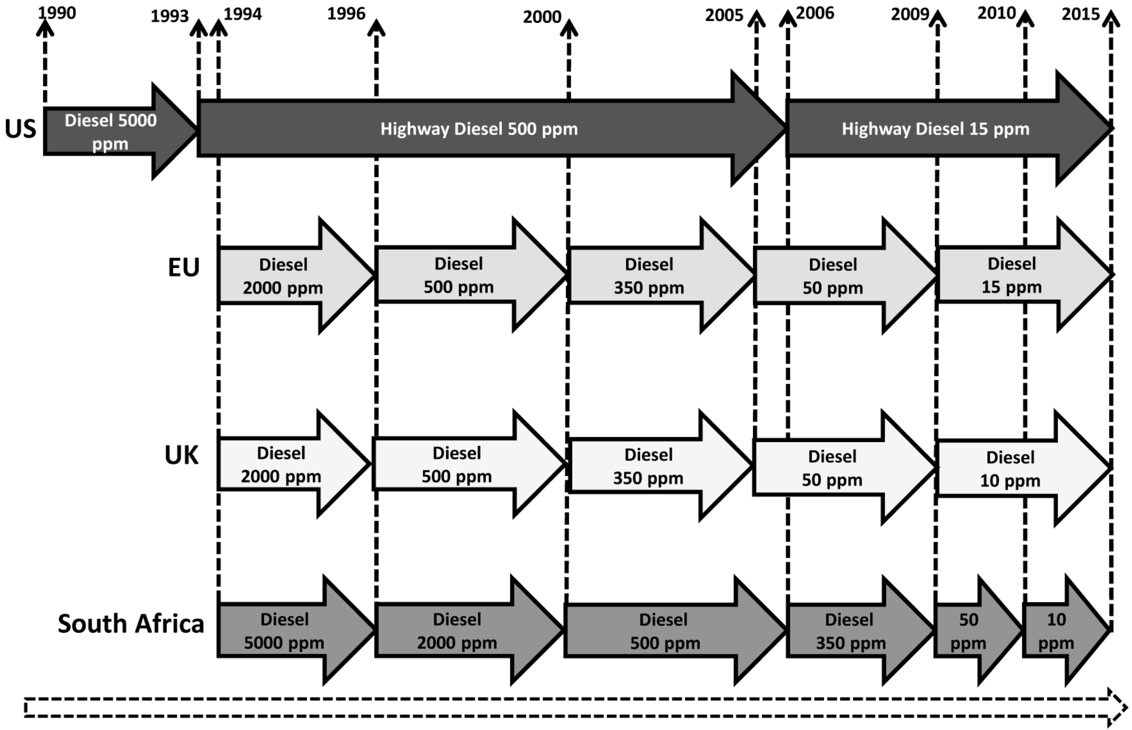


while smog and particulates on the other hand can cause serious respiratory illness such as asthma when inhaled. The lowering and/or elimination of the emission of sulfur in fuels is currently being addressed through regulation of sulfur in diesel and gasoline by the environmental protection agencies (EPA) and other regulatory bodies.

The current process employed for the removal of sulfur compounds from crude oils is hydro-desulfurization; in this process hydrogen gas passes through a stream of crude oil under high temperature and pressure in the presence of a catalyst (such as Co–Mo/ɣ-Al_2O_3). Hydrogen sulfide gas is produced, and it is scrubbed off and converted to elemental sulfur in the Claus process. The environmental regulating agencies have mandated stringent legislation with the aim of reducing sulfur levels in fuels to an ultra-low level of between 10-15 ppm by 2015 (Figure 3) (Barbara *et al.* 2011; Song *et al.* 2003; Ogunlaja A.S. *et al.* 2013).

Investigations by researchers demonstrated that sulfur compounds remaining in diesel fuels at sulfur level lower than 500 ppm are dominantly the dibenzothiophenes and dibenzothiophenes with alkyl substituents at the 4- and/or 6-position (Song *et al.* 2006; Whitehurst *et al.* 1998; Badich *et al.* 2003, Ma *et al.* 1996; Andersson *et al.* 2006, 2007). These species are lower in hydro-desulfurization (HDS) reactivity, and are termed refractory sulfur compounds. Steric hindrance and electronic factor were reported as factors responsible for the observed low HDS reactivity of DBTs and 4- and 6-substituted DBTs (Ma *et al.*1995). The HDS reactivity of sulfur species in fuel have been reported in detail (Ma *et al.* 1994,

Figure 3. Trends in diesel sulfur fuel specifications from the United States (US), United Kingdom (UK), European Union (EU) and South Africa (SA) over the years; the SA target is not yet legislated.



Trends in diesel sulfur specifications over the years.

1996); the authors employed a high-resolution gas chromatograph (GC) with a sulfur-selective flame photometry detector (FPD) to quantify the sulfur species in diesel and gas fuel oils. It was observed that dibenzothiophenes and dibenzothiophenes having alkyl substituents at the 4 and/or 6 positions are the most resistive to hydrodesulfurization. Hydrogen sulfide (H_2S) formed during the HDS process also inhibits HDS catalyst activity by modifying the catalyst surface (Topsoe *et al.* 1996; Song *et al.* 2006). Topsoe and co-workers reported that high concentrations of H_2S are known to increase the density of Brönsted acid sites on a commercial catalyst and it is also responsible for the poisoning of mainly hydrogenolysis sites on a sulfided $Co\text{-}Mo/\gamma\text{-}Al_2O_3$ catalyst. This leaves the sulfur content relatively high. However, if the HDS processing conditions are further pushed to produce ultra-low sulfur fuels, the aromatic and polynuclear aromatic content would fall outside the requisite specification. Some other fuel specifications that could be altered are cetane index, polyaromatic hydrocarbons (PAH), and T_{95} distillation temperature (Barbara *et al.* 2011). Several techniques have been developed for the elimination of sulfur in fuel to the ultra-low levels, v.i.z. bio-desulfurization (BDS) and oxidative-desulfurization (ODS).

ODS process is carried out under mild conditions in the presence of a catalyst (metal ions mostly transition metals in high oxidation states) and an oxidant agent, and the oxidized sulfur compounds (sulfones) are subsequently removed by extraction, adsorption, or distillation (Abdullah *et al.* 2015; Wang *et al.* 2003; Ishilara *et al.* 2005; Chica *et al.* 2006; Zhou *et al.* 2007; Kuznetsova *et al.* 2008; Prasad *et al.* 2008; Torres *et al.* 2011). The main advantage of ODS is that refractory sulfur compounds can be removed without using hydrogen, at relatively low temperatures and at atmospheric pressure. A suitable extraction solvents is always important for effective ODS process. Extraction solvents have been reported to extract large quantity of aromatics along with sulfones hence altering fuel specification (Campos-Martin *et al*. 2010). Lyondell chemicals (Karas *et al*. 2008; Karas *et al*. 2004) and EniChem/UOP (Kocal *et al*. 2001; Kocal *et al*. 2002) independently patented the ODS process. In the Lyondell process, solvent extraction was used for separation of sulfones while EniChem/UOP process removed the sulfone species by adsorption. In both processes, *tert*-butylhydroperoxide was employed as the oxidant due to its solubility in fuel. Lyondell chemicals and EniChem/UOP ODS processes produced *tert*-butyl alcohol after the oxidation step, and this compound was employed as potential octane-booster compound for gasoline. Heterogeneous catalysts have been prepared using a variety of support materials, such as: alumina, zirconia, titania, zeolites, silica, polymer microspheres and Metal-Organic Frameworks (MOFs) (Campos-Martin *et al*. 2010; Barbara *et al*. 2011; Karas *et al*. 2008). Molybdenum oxide was investigated in the catalysed oxidation of hydro-treated fuels (Prasad *et al.* 2008) and it showed good ODS activity. The catalyst was employed as a heterogeneous catalyst, by incorporating molybdenum (Mo) unto alumina ($Mo/\gamma-Al_2O_3$) (Prasad *et al.* 2008; Abdullah *et al.* 2015). Other heterogeneous catalysts which are more stable during use have been investigated; some examples of such catalysts include Ti, Mo, V, W (Campestrini *et al.* 1988), gold (Au) (Si *et al.* 2008) and rhenium (Re) (Di-Giuseppe *et al.* 2009). Titanium catalysts gave the best results in catalysed oxidation step during oxidative-desulfurization (Chica *et al*. 2006). However, titanium (Ti) is known to be expensive and the use of titanium in catalysed reactions in industry, generally, would result to an increase in cost of production. Hence, the search for a cheaper and more robust potential catalyst that can be applied industrially in the ODS process as well as a robust material with a high surface area that can selectively remove sulfones without changing the fuel specification. Vanadium lends itself useful in this regard.

The chapter, therefore, discusses briefly the oxidation of refractory sulfur compounds found in fuels using oxidovanadium(IV) as a catalyst to form organosulfones, a first step in ODS process. The chapter also discusses, in detail, the chemistry involved in molecular imprinting of organosulfones on functional polymers, and the electrospinning of the polymeric matrix to produce molecularly imprinted nanofibers employed for selective adsorption of organosulfones from the oxidized mildly hydrotreated fuels, a second step in the ODS process. Chemical interactions, apart from the imprinting effect, that can be exploited in molecularly imprinted polymers for selective extraction of organosulfones include hydrogen bonding, π-π interactions, van der Waals forces and electrostatic interactions, and these have been discussed by employing density functional theory calculations. The theoretical calculations are instrumental in predicting suitable polymers for adsorption of organosulfones. In this chapter, the use of molecularly imprinted chitosan, polyvinyl alcohol, polyvinyl phenol, polyvinyl benzyl alcohol and polybenzimidazole, respectively, as sorption materials for the removal of organosulfones is discussed in detail. The chemical possibilities for adsorptive removal of organosulfones from fuels are presented while the potential industrial application of the functional nanofibers is recommended.

METHODS OF DESULFURIZATION

The refining process employed for the elimination of sulfur in the production of cleaner fuels is known as desulfurization. Amongst others, the following three methods of desulfurization will be described briefly:

1. Bio-desulfurization,
2. Hydro-desulfurization,
3. Oxidative-desulfurization, and
4. Adsorptive desulfurization.

Bio-Desulfurization (BDS)

Bio-desulfurization involves the use of micro-organisms (e.g. bacteria) to desulfurize fuels under biological processes.[4] Microorganisms require sulfur for their growth and biological activities. The dried weight of bacterial cells comprises 0.5-1% sulfur atoms. Sulfur generally occurs in the structure of some enzyme cofactors (such as co-enzyme A, thiamine and biotin), amino acids and proteins (cysteine, methionine, and disulfide bonds). Depending on their metabolic pathways, micro-organisms may have the ability to obtain the sulfur from different sources. Some micro-organisms consume the sulfur in thiophenic compounds such as dibenzothiophene (DBT), thus reducing the sulfur content in fuel. Energy BioSystems Corporation (EBC) was initially the only commercial venture dedicated to the development of bio-desulfurization technology. EBC's concept of a bio-desulfurization process was to treat diesel, but also to produce a value-added surfactant by-product to achieve a more economical process (Monticello *et al.* 2000; Chang *et al.* 2000; Soleimani *et al.* 2007; Chang *et al.* 1998). Bacteria that convert dibenzothiophene and alkyl sulfides are relatively well known while fewer bacteria are found for benzothiophene, and only a few bacteria detected for thiophene (Campos-Martin *et al.* 2010 and Kodame *et al.* 1973).

The two main pathways known for the utilization of dibenzothiophene by bacteria are: destructive (degradation) pathway and sulfur-specific (desulfurization) pathway.

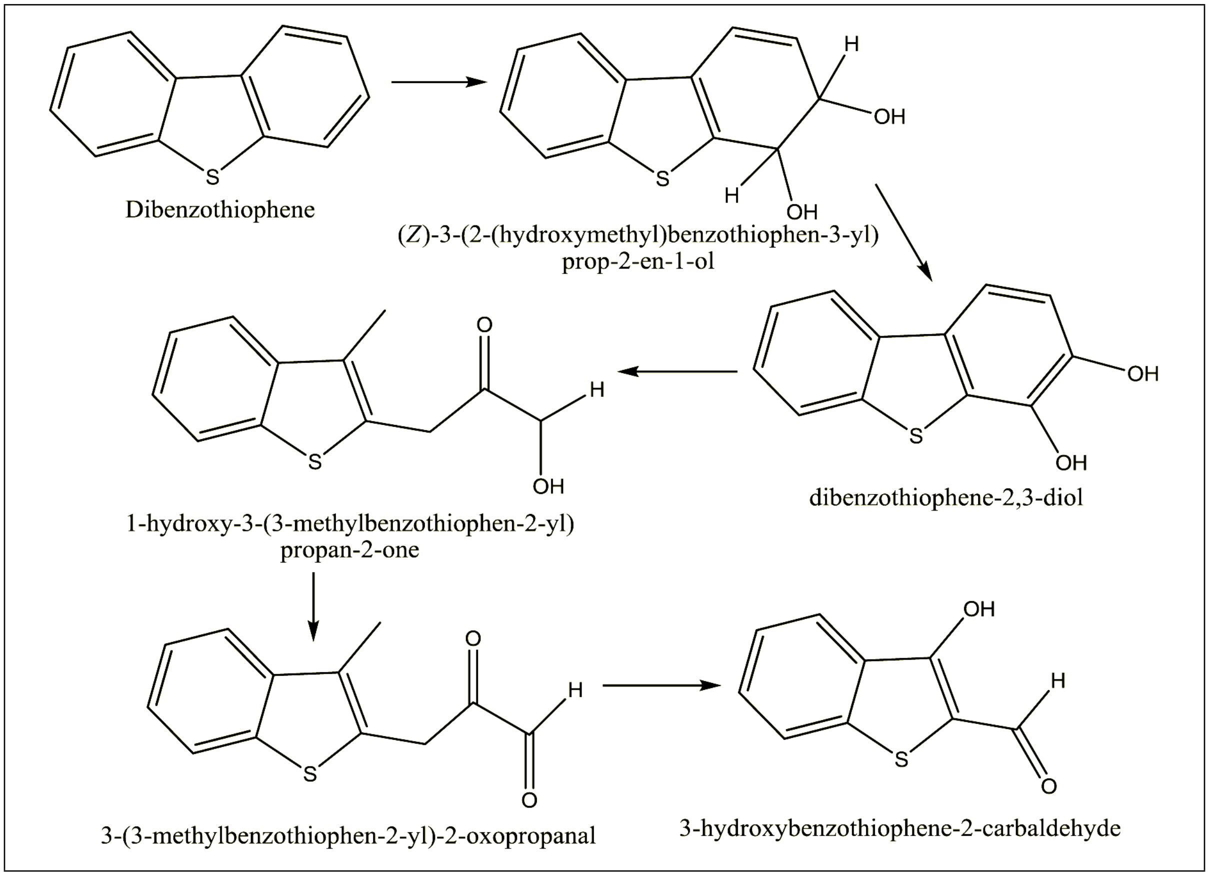
Ring Destructive Pathway

Rhodococcus erythropolis and *Pseudomonas stutzeri* bacteria strains are mostly employed for ring destructive biodesulfurization mechanistic process, also known as the 'Kodama pathway' (Scheme 1) (Campos-Martin *et al.* 2010 and Kodame *et al.* 1973), involves the initial dioxygenation of the peripheral aromatic ring of dibenzothiophene, followed by cleavage of the ring which finally leads to the accumulation of 3-hydroxybenzothiophene-2-carbaldehyde as a water-soluble end product with lower carbon content than dibenzothiophene. In this pathway, no desulfurization occurs; the dibenzothiophene (organosulfur compound) is converted to a more polar compound which can be stripped off.

Sulfur-Specific (Desulfurization) Pathway

The sulfur-specific desulfurization pathway can take place in the presence of isolated bacteria strain *Brevibacterium sp.* capable of using dibenzothiophene for growth as the sole source of carbon, sulfur and energy (Campos-Martin *et al.* 2010; Kodame *et al.* 1973). It involves the oxidation of dibenzothiophene (DBT) to dibenzothiophene sulfoxide (DBTO), dibenzothiophene sulfone ($DBTO_2$), sulfinate and hydroxybiphenyl in the presence of oxygen and water under ambient temperature and pressure conditions (Box 2). Enzymes also show potential in the desulfurization of DBT to $DBTO_2$ following a similar mechanistic pathway as the isolated bacteria strain (*Brevibacterium sp.*). Dibenzothiophene monooxygenase (DszC) catalyzes the conversion of dibenzothiophene (DBT) to dibenzothiophene sulfone ($DBTO_2$). The

Scheme 1. Kodama pathway of dibenzothiophene (DBT) degradation

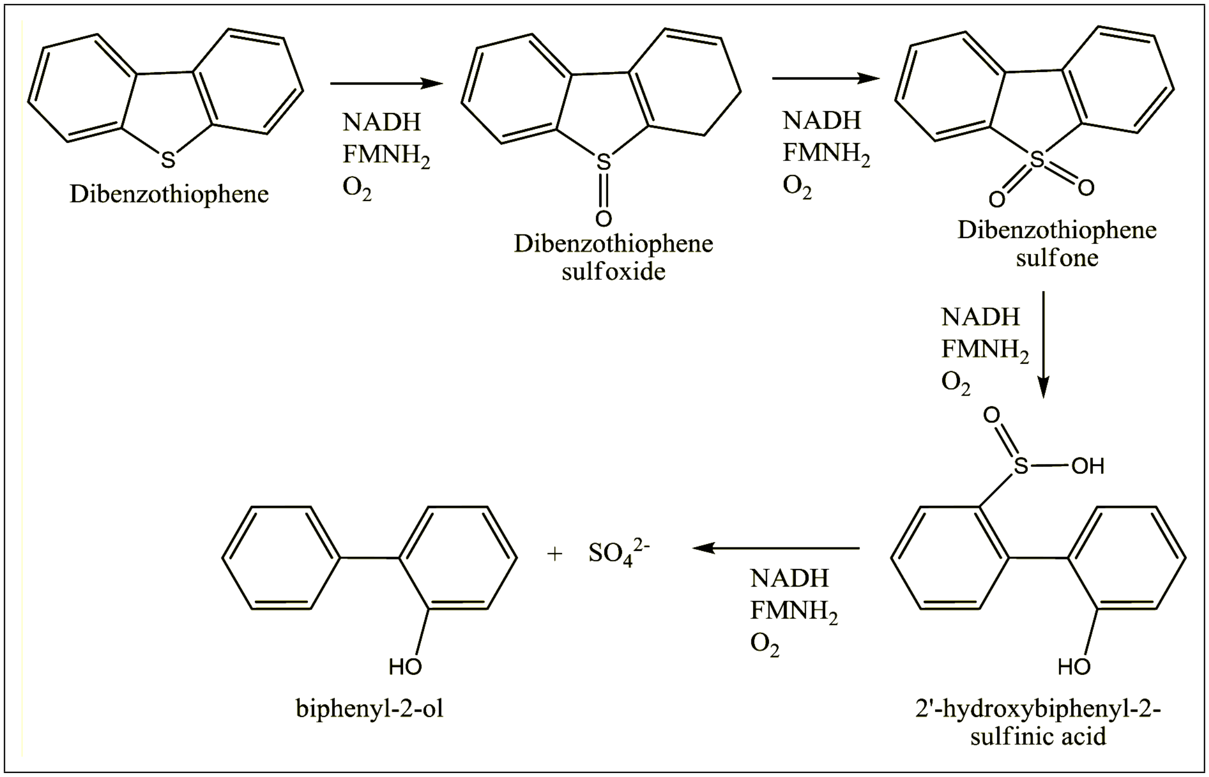


dszA gene encodes dibenzothiophene-5,5- dioxide monooxygenase (DszA) catalyzes the conversion of $DBTO_2$ into 2-hydroxybiphenyl-2-sulfinic acid. While dszB gene encodes 2-hydroxybiphenyl-2-sulfinate sulfinolyase (DszB) catalyzes the conversion of 2-hydroxybiphenyl-2-sulfinic acid into biphenyl-2-ol and sulphite (Campos-Martin *et al.* 2010; Kodame *et al.* 1973). Specific oxidative biodesulfurization of DBT degradation. catalyzes the conversion of HBPSi I nto 2-hydroxybiphenyl (2-HBP) and sulfite (Scheme 2), (Campos-Martin *et al.* 2010; Kodame *et al.* 1973).

In general, the bio-desulfurization process does not show very deep desulfurization, the maximum sulfur content limit of 50-200 ppm sulfur at best has been achieved (Barbara *et al.* 2011). However, the bio-desulfurization process suffers the following limitations:

1. Production of active resting cells (biocatalysts) with a high specific activity;
2. Preparation of a biphasic system containing oil fraction, aqueous phase and biocatalyst;
3. Bio-desulfurization of a wide range of organosulfur compounds at a suitable rate;
4. Separation of desulfurized oil fraction, and recovery of the biocatalyst and its return to the bioreactor; and
5. Efficient wastewater treatment (Booth *et al.* 2001).

Scheme 2. The pathway of biological desulfurization of DBT relies on biocatalysts for specificity. NADH is reduced nicotinamide adenosine dinucleotide; FMN is flavin mononucleotide.

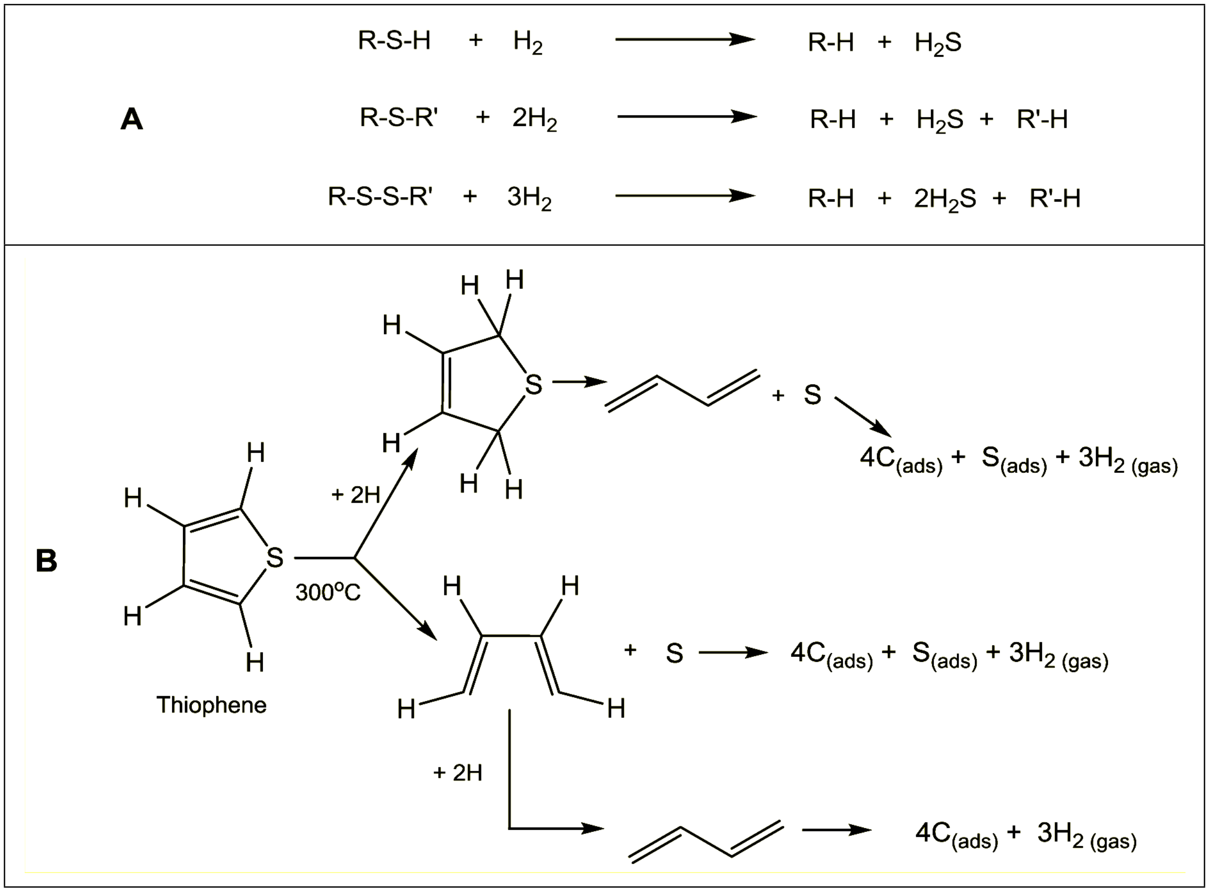


Hydro-Desulfurization

The hydro-desulfurization (HDS) process has been employed for the removal of sulfur compounds from as early as the 1930's. In the HDS process, crude oil is heated, mixed with hydrogen, and fed to a reactor packed with a pelleted CoMo/Al_2O_3 catalyst. The reactor temperatures range from 300 to 350°C in a pressure range of 15 to 90 bars to generate a mixture of the treated/desulfurized crude oil, hydrogen sulfides (H_2S) and hydrogen gas. H_2S is further recycled through a Claus process to recover the elemental sulfur (Song *et al.* 2003; Babich *et al.* 2003). HDS occurs directly through the hydrogenolysis pathway (Scheme 3a).

The addition of hydrogen to sulfur compounds at higher temperatures activates carbon-sulfur (C-S) bond cleavage as shown in the reaction Scheme 3b for the hydro-desulfurization of thiophene. Two mechanistic routes are presented in Scheme 3, and in the first route, hydrogenation of thiophene precedes by C-S bond scission, and in the second route, C-S bond scission occurs, before hydrogenation takes place. Both mechanistic routes produce carbon and sulfur, which can easily be absorbed into mesoporous aluminosilicate molecular sieves (Song *et al.* 2003; Song *et al.* 2003; Babich *et al.* 2003). Commercial hydrotreating catalysts are, typically, sulfides of Mo or tungsten (W) supported on Al_2O_3 and promoted by either Co or Ni.

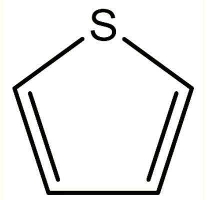
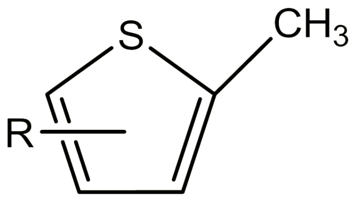
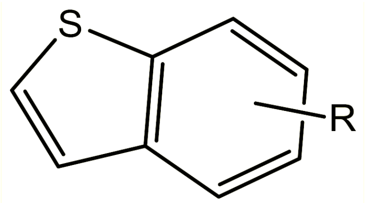
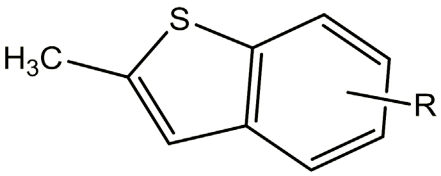
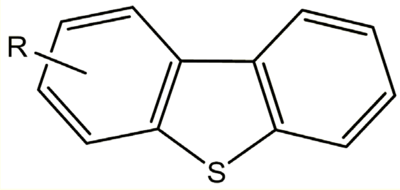
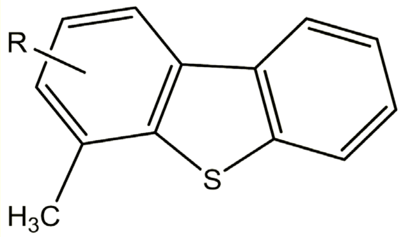
Scheme 3. (a) General HDS reaction scheme and (b) mechanistic routes for the hydro-desulfurization of thiophene



HDS process is however limited in treating refractory sulfur compounds such as dibenzothiophenes (DBTs) and especially the alkylated derivatives such as 4,6-dimethyldibenzothiophene (Song *et al.* 2003; Song *et al.* 2004; Schulz *et al.* 1999; Babich *et al.* 2003; Andersson *et al.* 2006, 2007; Nolte *et al.* 2013). These are the main non-reactive organosulfur compounds in the hydrogenation process. The HDS reactivity of various sulfur compounds decreases in the order of disulfides > sulfides, thiols > thiophenes > BTs (benzothiophenes), NTs (naphthothiophenes) > BNTs (benzonaphthothiophenes), DBTs (dibenzothiophenes) > DBTs with alkyl group(s) at the 4- and or 6-position(s) (Song *et al.* 2003, 2004). Table 1 lists some sulfur compounds found in crude oils, the order of reactivity of these sulfur compounds are governed by electron density of sulfur in the compounds mainly in the ODS process. The electron density is a representation of the probability of finding an electron in a specific location around an atom or molecule. In general, an electron is likely to be found in regions with high electron density than region low electron density, in so doing, influencing the reactivity of sulfur in the compounds (Song *et al.* 2003). Hence, the higher electron density results in decreased HDS activity.

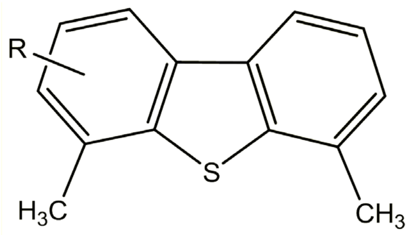
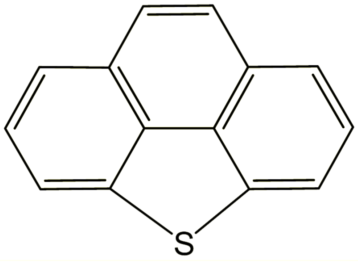
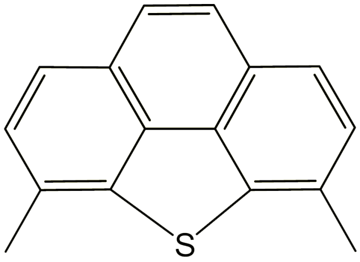
The production of ultra-low sulfur fuels (10-50 ppm) using HDS process therefore requires the application of extreme operating conditions, i.e. high temperatures and high hydrogen pressures, and the use of highly active catalysts at slow velocity pace (Schulz *et al.* 1999; Ma *et al.* 2001; Song *et al.* 1999).

Table 1. Some organosulfur compounds and their sulfur electron densities

Compound Names	Structures	Sulfur Electron Densities
Thiophene		5.696
Thiophenes with methyl at the 2 or 5 position		5.706-5.716
Benzothiophenes (BTs)		5.739
Benzothiophenes with methyl at the 2 or 7 position		5.746
Dibenzothiophenes (DBTs)		5.758
Dibenzothiophenes with methyl at 4 position		5.759

continued on following page

Table 1. Continued

Compound Names	Structures	Sulfur Electron Densities
Dibenzothiophenes with methyl at the 4 and 6 position		5.760
Phenanthro[4,5-*bcd*]thiophene		5.770
5,7-Dimethylphenanthro[4,5-*bcd*] thiophene		5.774

Under these conditions, the aromatics and polynuclear aromatics content would fall outside the requisite specification as they tend to be hydrogenated. The other fuel requirements such as oxygen content, vapor pressure and olefin content for petrol, and cetane number, density and T95 point for diesel would also be compromised. In addition, the high cost involved because of the use of excess hydrogen gas and energy therefore makes the end-product expensive. Alternative processes which can complement the HDS process under mild conditions to achieve ultra-low sulfur fuels are therefore essential and oxidative-desulfurization shows potential.

Oxidative-Desulfurization

Oxidative-desulfurization (ODS) has been considered as a new technology for desulfurization of fuel oils. The ODS process includes two stages:

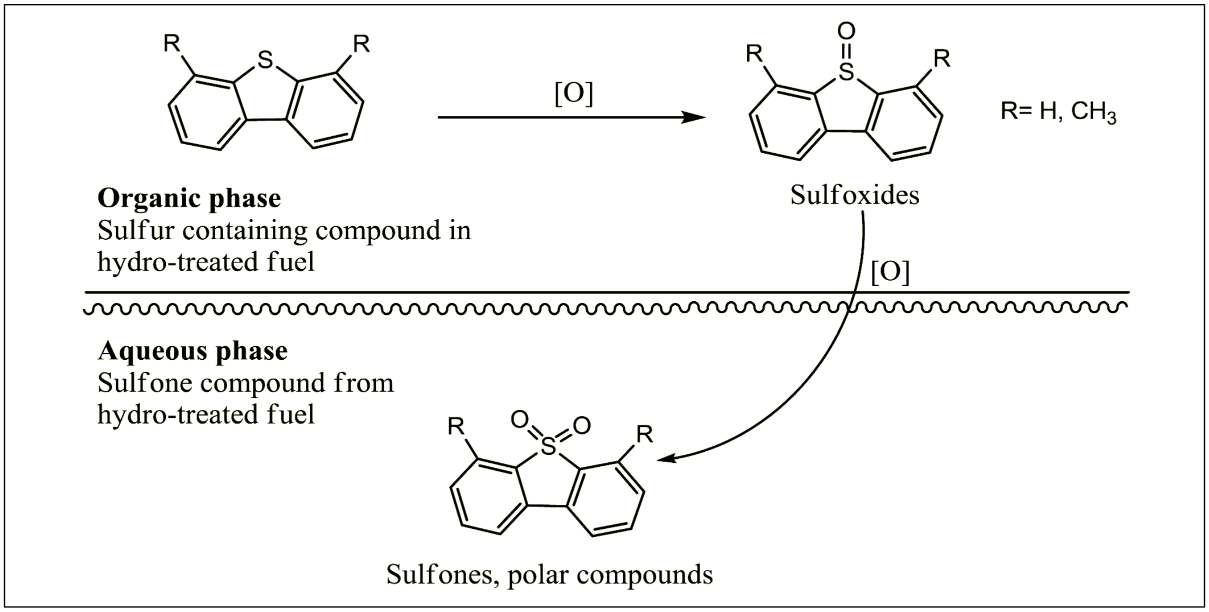
1. Oxidation of the sulfur atoms in the first step, and
2. Liquid extraction of the polar products at the final step.

The advantage of the ODS process is that the refractory sulfur-containing compounds can be oxidized and it operates at a low reaction temperature and pressure, and in the absence of hydrogen which is expensive. With HDS being able to desulfurize thiophene and acidic sulfur compounds at relatively moderate conditions and the ODS process being capable of desulfurizing refractory sulfur compounds, then the ODS process has great potential to be a complementary process to HDS for producing deeply desulfurized crude oil.

General Description of the ODS Process

In the ODS process, sulfur-containing compounds in fuel oils are oxidized using selective oxidants such as nitric acid and/or nitrogen oxides (Tam *et al.* 1984, 1990; Baxendale *et al.* 1946; Venturiello *et al.* 1983), organic hydroperoxides (Chica *et al.* 2006; Karas *et al.* 2004, 2008; Kocal *et al.* 2002; Mokhtar *et al.* 2014; Abdullah *et al.* 2015), peroxyacids (Zannikos *et al.* 1995; Aida *et al.* 1994), and hydrogen peroxide (Otsuki *et al.* 1999, 2000; Collins *et al.* 1997; Yazu *et al.* 2003; Paybarah *et al.* 1982). The use of hydrogen peroxide, a cheap aqueous oxidant, has been promoted for use in the oxidation of fuel oil by introducing surfactants which help to disperse oxidant in the form of small spherical droplets in the crude oil. The process is described as an emulsion catalysis system (Jiang *et al.* 2011). The ODS process generally takes place in the presence of a catalyst to produce sulfone compounds that can be preferentially extracted due to their increased relative polarity. For oxidation to take place, the oxidant needs to be in contact with fuel oils under optimum conditions, and the oxidant donates oxygen atoms to the sulfur in benzothiophenes, dibenzothiophenes and its derivatives to form sulfoxides and/or sulfones (Scheme 4). Some of the by-products generated by the oxidant influence the quality of the fuels; for example *tert*-butyl alcohol, which is a potential octane booster for fuels, is generated as by-products of *tert*-butylhydroperoxide (Karas *et al.* 2008).

Scheme 4. The ideal reaction in ODS process for dibenzothiophene and methyl substituted derivatives

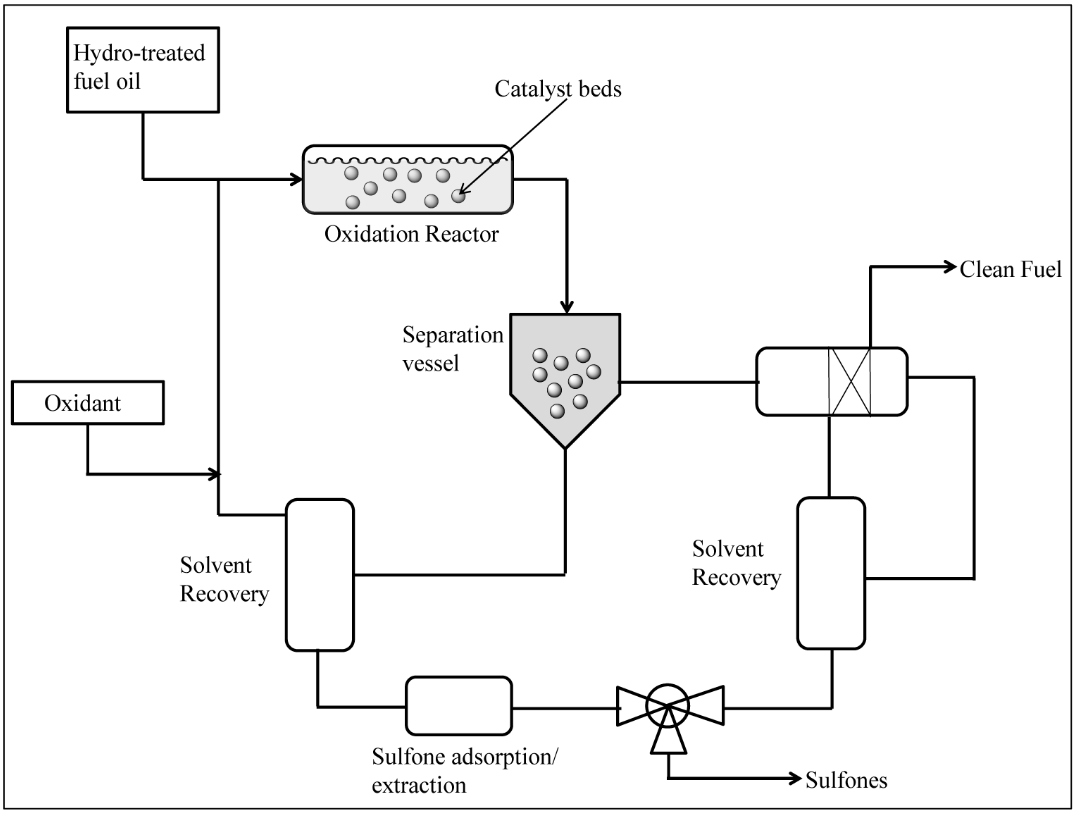


The oxidation of organosulfur compounds, which is the first step of the oxidative desulfurization process in hydro-treated fuel, takes place in the presence of metal catalyst(s) (Wang *et al*. 2003; Ishilara *et al*. 2005; Chica *et al*. 2006; Zhou *et al*. 2007; Kuznetsova *et al*. 2008; Prasad *et al*. 2008). A typical catalysed oxidation of hydro-treated fuel using vanadium as catalyst was conducted under batch and continuous flow processes at 40°C by using *tert*-butylhydroperoxide (*t*-BuOOH) as oxidant (Ogunlaja *et al*. 2013). The oxidation process showed high selectivity for organosulfones.

A practical industrial flow system for oxidative desulfurization of hydro-treated fuel (Figure 4), where catalyst in the hydro-treated is extracted and washed, un-used oxidant are also separated in the separator section before further oil processing can take place. Liquid-liquid extraction of the oxidized compounds (sulfones and sulfoxides) has been carried out by contacting the oxidized oil with a non-miscible solvent which is selective for the polar oxidized sulfur compounds (Hulea *et al*. 2001; Anisimov *et al*. 2003; Palomeque *et al*. 2002; Yazu *et al*. 2001; Djangkung *et al*. 2003; Shiraishi *et al*. 2003; Darian *et al*. 1988). The desulfurized oil is water washed to recover any traces of dissolved extraction solvent and then polished either by absorption using silica gel and alumina to produce high quality clean sulfur free oil (South African National standard, 2006).

Oxidative-desulfurization demonstrates that it is possible to remove sulfur compounds from fuels to meet strict regulatory limits (Tam *et al*. 1984, 1990; Baxendale *et al*. 1946; Venturiello *et al*. 1983; Chica *et al*. 2006; Karas *et al*. 2004, 2008; Kocal *et al*. 2002; Mokhtar *et al*. 2014; Abdullah *et al*. 2015),

Figure 4. Schematics of the oxidative-desulfurization (ODS) process



but a high oxidant-to-sulfur (O/S) ratio is required to oxidize sulfur compounds to their corresponding sulfoxides and sulfones. This drawback (i.e. the high oxidant constraint), however, can be avoided by use of suitable catalysts.

Adsorptive Desulfurization

Liquid Extraction

The choice of solvent for the extraction of sulfur and sulfone compounds in fuel oils is critical. For a solvent to be employed in the extraction process, it must be thermodynamically compatible with the compound to be extracted. Polar solvents such as *N,N*-dimethylformamide, dimethylsulfoxides, methanol, ethanol and acetonitrile are usually employed for the desulfurization of crude oils, mostly for the extraction of sulfur/sulfone compounds in the desulfurization process (Campos-Martin *et al.* 2010; Mokhtar *et al.* 2014, Abdullahi *et al.* 2015). Dimethylsulfoxides (DMSO) and *N,N*-dimethylformamide (DMF) are high boiling point solvents having high extractability for sulfones. These solvents holds similar boiling point with extracted sulfones compounds, and thus may not be easily separated from the extracted compounds hence discouraging solvent recovery by distillation. On the other hand, alcohols and acetonitrile are relatively low boiling point solvents, and are preferred for sulfone compound extraction, however, the high cost of these solvents and the high extraction of a large quantity of aromatics along with sulfones hamper its use in desulfurization.

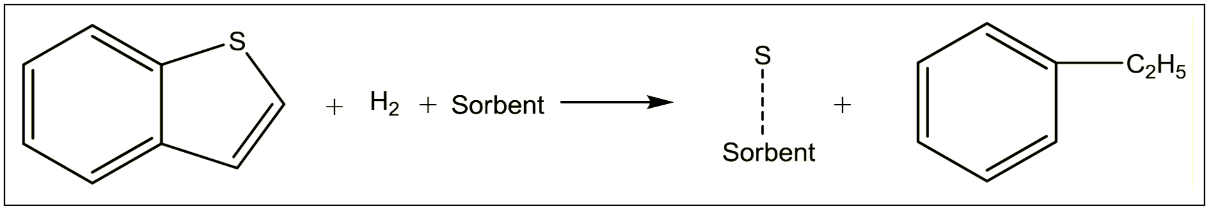
Liquid extraction of sulfur and organosulfone compounds has limitations since other aromatic compounds that influence fuel properties are extracted (Campos-Martin *et al.* 2010). This development has encouraged the use of solid adsorbent materials and a synthesis of stimuli-responsive materials that allow the formation of complexes with sulfur or sulfur compounds or from other types of bonding interactions with sulfone compounds in the presence of other aromatic compounds present in fuels.

Solid Sorbent Adsorption

Several reports on the removal of sulfur has been reported using of new adsorbent materials such as activated alumina, activated carbon, metal exchanged zeolites and metal oxides (Jeon *et al.* 2009; Bhandari *et al.* 2006; Hernandez *et al.* 2004; Kim *et al.* 2006; Liu *et al.* 2007; Blanco *et al.* 2011; Wang *et al.* 2007). Adsorption of sulfur on adsorbate molecules *via* the formation of complexes have been reported as a vital step for the removal of sulfur compounds. Metals such as nickel and copper impregnated on various adsorbents have been employed for deep adsorptive desulfurization of hydro-treated fuels (Hernandez *et al.* 2004, 2005; Yang *et al.* 2003, 2006; Zhang *et al.* 2008; King *et al.* 2006; Shan *et al.* 2008; Ania *et al.* 2006; Dasgupta *et al.* 2013; Velu *et al.* 2003).

In 2001, Phillips petroleum licensed a process called "S-Zorb" for the selective removal of sulfur. The adsorbent is based on zinc oxide, silica, alumina and nickel (Sughrue *et al.* 2001). The S-Zorb process is carried out in the presence of hydrogen and modified zinc oxide. Sulfur compounds are carried over to hydrogen sulfide, and the sulfur is bound by zinc oxide as zinc sulfide by the process known as chemisorption (Scheme 5). Metal organic framework (MOF) C300 has also been used for the adsorption of some organosulfur compounds in hydro-treated fuel (Blanco *et al.* 2013). However, these MOFs are expensive adsorbents, hence discouraging its application on an industrial scale (Blanco *et al.* 2013). The reported mode of binding between the adsorbent and sulfur compounds is known as π-complexation.

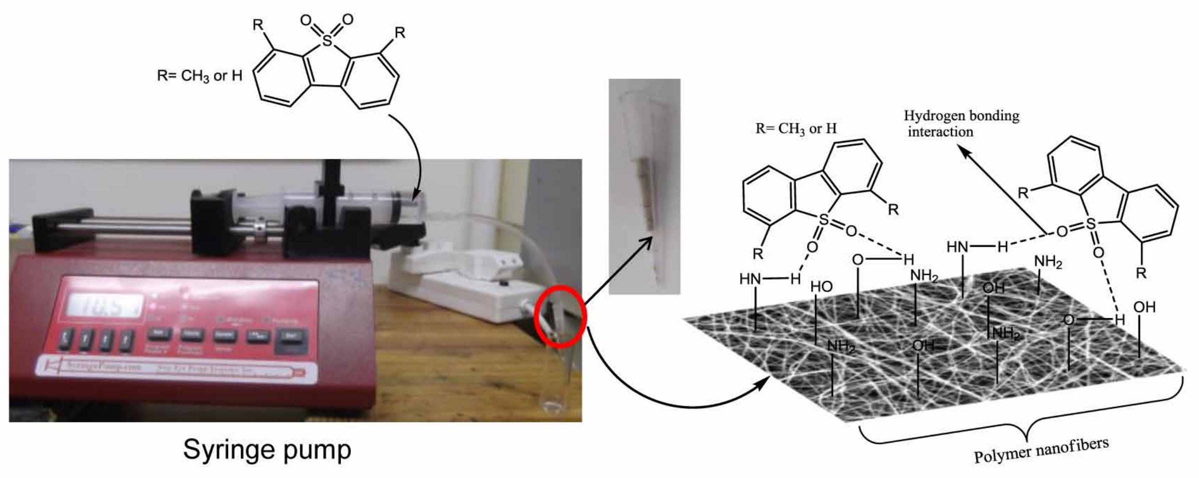
Scheme 5. Basic principle of the S-Zorb sulfur removal technology, process developed by Phillips petroleum for sulfur removal from liquid fuel at elevated temperatures under low H_2 pressure



Molecularly imprinted polymer materials have been employed for selective adsorption of oxidized refractory sulfur compounds in hydro-treated fuels (Ryu *et al*. 2002; Castro *et al*. 2001; Jorge *et al*. 2004; Ogunlaja *et al*. 2014). Template imprinting on polymers improves its absorptive properties and also provides selectivity due to polymer flexibility which makes accessing of the recognition site and removal of absorbed template easier. Polymer imprinting takes place through the formation of bonds/interactions such as hydrogen bonding, π-π interactions, van der Waals forces and electrostatic interactions (discussed in section 4.3) between the templates (organosulfones) and functional groups of the polymer network.

Most of the studies reported in the literature employed molecularly imprinted polymers in its powdery/monolithic form for the adsorption of refractory sulfur compounds in fuels. A low surface area and porosity of adsorbents are usually observed, and the accessibility of active sites on imprinted polymer sorbents are sometimes compromised. Due to these issues, the polymer adsorption properties can be improved by making them into nanofibers (Ogunlaja *et al*. 2014). The polymer nanofibers can readily be fabricated through a process known as electrospinning. Electrospinning process provides polymer nanofibers with controlled pore size as well as high surface-to-volume ratio, and this material decreases adsorption time and mass transfer constraints. Ogunlaja and co-workers employed a continuous flow adsorption process for the elimination of sulfone compounds in oxidized hydro-treated fuel by using a sulfone-imprinted polybenzimidazole nanofibers packed to the tip of a Teflon rubber tubing (Figure 5). The imprinted nanofibers show high selectivity in the adsorption of sulfone compounds from oxidized fuel.

Figure 5. Adsorption of dibenzothiophenes on imprinted polymer nanofibers



Adsorbent regeneration for re-use of spent adsorbent constitutes an important part of the overall feasibility and cost-effectiveness of the proposed oxidative desulfurization process. The following adsorbent regeneration strategies are possible:

1. Use of organic solvent to wash off the adsorbate under ambient pressure and at elevated temperature, and
2. Thermal regeneration at ambient pressure under vacuum.

A home-made pressurized hot water system was employed for the regeneration/desorption of sulfones from imprinted nanofibers (Figure 6) to demonstrate the effect of pressure and temeperature (Ogunlaja *et al*. 2014). Water was employed as a green solvent for extraction/desorption of sulfone compounds under pressurized subcritical conditions. Water was pressurized to 30 bars at 150°C, and in this subcritical state the dielectric constant of water is greatly decreased thus imitating the properties of organic solvents.

A combination of the HDS and ODS process is, however, proposed as a possible way for the reduction of sulfur in fuels to ultra-low levels as depicted in the schematic of the integrated HDS-ODS process (Figure 7). In this set-up, high sulfur fuel is taken through a hydro-treatment unit where less bulky sulfur compounds such as thiols, thioethers, alkylated disulfides and thiophenes are converted to H_2S as shown in Scheme 3a. In the Claus unit, H_2S reacts mostly with SO_2 to produce elemental sulfur and water. The resulting fuel (mildly hydro-treated fuel) will be transferred to the oxidative desulfurization chamber where refractory sulfur compounds are oxidized to organosulfone compounds. The removal of the organosulfones from fuel can be carried out by adsorption to produce an ultra-low sulfur fuel. Molecularly imprinted nanofibers show great promise (Ogunlaja *et al*. 2014), and they can be produced by a process called electrospinning.

Figure 6. A set-up of the home-made pressurized hot water for desorption of organosulfones from nanofibers

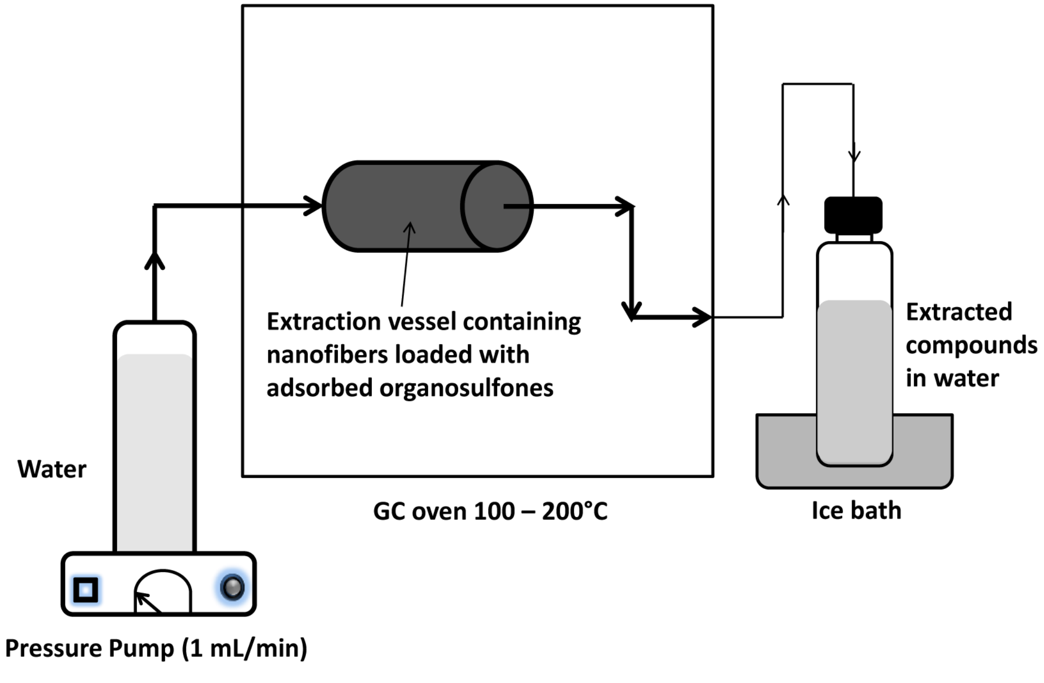
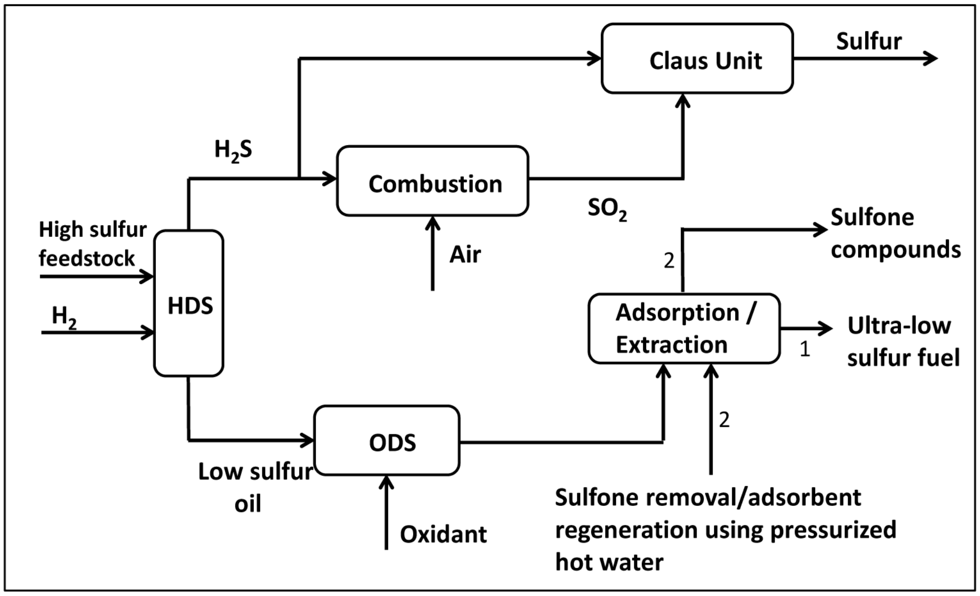


Figure 7. Integrated hydrodesulfurization-oxidative desulfurization (HDS-ODS) processes

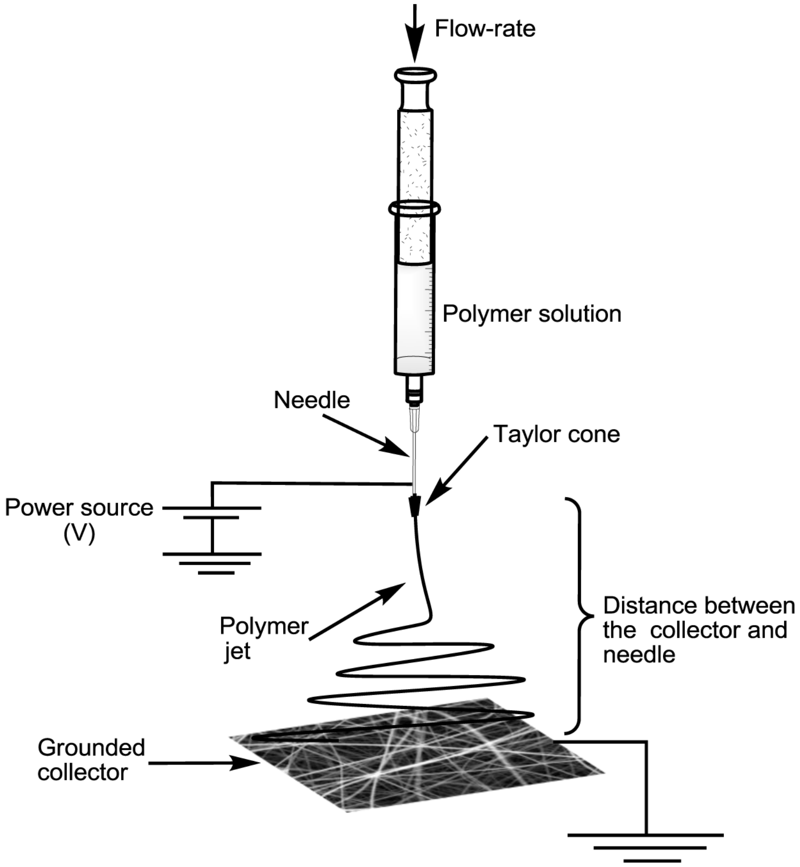


ELECTROSPINNING OF POLYMER SOLUTIONS

Electrospinning is a process whereby high voltage is applied to a polymer solution resulting in electrified jet that travels through the electric field until it lands on a collector (counter electrode) as nanofibers (Reneker *et al*. 2008). Potential applications of electrospun fibers include filtration membranes, adsorption sorbents, fiber-based sensors, tissue engineering scaffolds and catalytic nanofibers (Walmsley *et al*. 2012; Huang *et al*. 2003). The polymer can be dissolved in a suitable solvent (Reneker *et al*. 2008). A basic laboratory electrospinning set-up consists of a syringe pump, a high voltage and a collector (Figure 8), and it is a relatively simple and inexpensive set-up. During the electrospinning process, a polymer solution in a syringe is pumped to a needle tip attached to the syringe *via* tubing. The solution is held at the needle tip by surface tension, and the application of an electric field using a high-voltage source causes a positive charge to be induced within the polymer resulting in charge repulsion within the solution. This results in an electrostatic force, which opposes and eventually overcomes the surface tension of the polymer solution causing the initiation of a polymer jet. As the jet travels down to the collector that is negatively charged, the polymer solvent evaporates leaving the polymer nanofibers on the collector.

A stable electrospinning jet is known to be comprised of four regions (Reneker *et al*. 1996), and these are: the base, the jet, the splay, and the collection. In the base region, the jet emerges from the needle to form a cone known as the Taylor cone. The shape of the base depends upon the surface tension of the liquid and the force of the electric field. Jets can be ejected from surfaces that are essentially flat if the electric field is strong enough, and the solution spreads out evenly and it is collected on a grounded surface. Nanofiber properties such as mechanical properties, degradation rates and functional groups exposure on the surface can be improved by using innovative collectors and spinning techniques (Pham *et al*. 2006). Several electrospinning collectors have been made to improve and control nanofiber orienta-

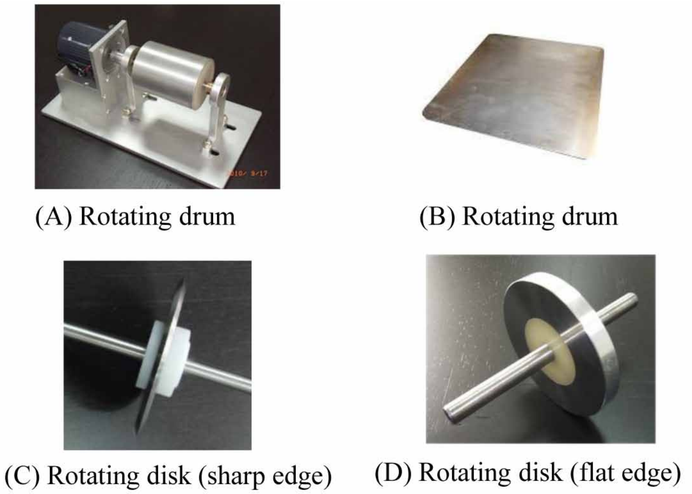
Figure 8. The electrospinning set-up used for the fabrication of polymer nanofibers in an ordinary laboratory



tion. Some of the commercially available collectors employed for electrospinning are presented in Figure 9. Controlled polymer electrospinning conditions can produce nanofibers with uniform morphology and diameters in the nanometer range. The latter property is sought after in order to improve the fiber functions by offering a fiber with high surface-to-volume ratio. Crosslinking of nanofibers enhances their mechanical stability and also prevents the material from dissolving in solvents of similar polarity. It is understood that crosslinking of imprinted polymers improves their adsorption properties by preserving cavities created by imprinted molecules. However, most crosslinking agents compete with reactive donor atoms on polymer nanofibers with respect to interacting molecules. This occurrence may result in the reduction of polymer active sites available for interaction. Polymer nanofibers sometimes become brittle and surface area compromised upon crosslinking (Ogunlaja *et al*. 2014). Hence, strategies are being sought to mediate against this problem.

A well-known limitation of the electrospinning process is the level of fiber production. A straightforward method of increasing the productivity of electrospinning in an ordinary laboratory is by increasing the number of spinnerets used in the process. Large-scale fiber production capabilities are important for achieving industrial requirements. Several technological advances have been explored to increase nanofiber production volume. Some of the modifications reported by Persano *et al*. 2013 are as follows:

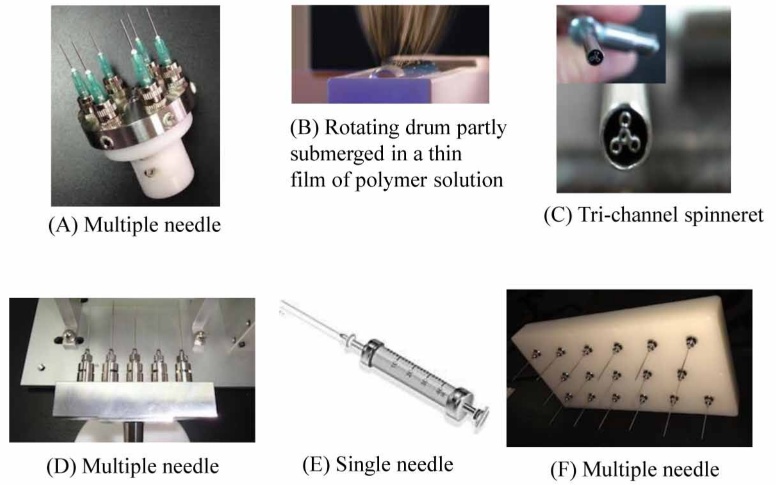
Figure 9. Some electrospinning collectors
(http://www.grafen.com.tr/product.php?id=293). Date accessed: 11/05/2015.


(A) Rotating drum
(B) Rotating drum
(C) Rotating disk (sharp edge)
(D) Rotating disk (flat edge)

1. The introduction of multi-spinneret components that allows parallel multiprocessing, and
2. The development of free surface electrospinning methods.

Electrospinning using multi-spinneret increases fiber mat thickness and quantity (Kidoaki *et al*. 2005; Ding *et al*. 2004; Varesano *et al*. 2009; Theron *et al*. 2005; Teo *et al*. 2005). Figure 10 shows some electrospinning spinnerets which mostly consist of needle(s). An innovative technology developed by Elmarco (Elmarco's Nanospider) and Stellenbosch Nanofiber Company employs a rotating drum/ball partly submerged in a thin film of polymer solution to produce nanofibers.

Figure 10. Images of some possible electrospinning spinnerets
(http://www.electro-spinning.com/multispinnerets.html and http://www.sncfibers.com). Date accessed: 11/05/2015.


(A) Multiple needle
(B) Rotating drum partly submerged in a thin film of polymer solution
(C) Tri-channel spinneret
(D) Multiple needle
(E) Single needle
(F) Multiple needle

The design and construction of process equipment for controllable, reproducible, continuous and mass electrospinning production has been advanced. The growing interest in electrospinning has already produced increased supply and competition among electrospinning equipment suppliers. Currently, a wide selection of industrial and laboratory-scale electrospinning equipment is available in the market. A list of representative companies that supply electrospinning equipment includes:

- Elmarco (www.elmarco.com),
- NaBond (www.electro-spinning.com),
- Holmarc Opto-Mechatronics (www.holmarc.com),
- E-Spin Nanotech (www.espinnanotech.com),
- Linari Engineering (www.linaribiomedical.com),
- Kato Tech (www.keskato.co.jp),
- Mecc Co. (www.mecc.co.jp),
- Toptec (www.toptec.co.kr),
- Electrospinz (www.electrospinz.co.nz),
- Electrospunra (www.electrospunra.com),
- IME Technologies (www.imetechnologies.nl),
- Yflow (www.yflow.com), and
- Inovenso (www.inovenso.com) (Persano *et al*. 2013), and
- Stellenbosch Nanofiber Company (www.sncfibers.com).

Some images of industrial and laboratory-scale mass electrospinning apparatus are presented in Figure 11.

Nanofibers show potential application in a wide range of fields comprising energy, environment, electronics, biotechnology, and pharmaceutics. Many companies in the field of nanofibers applications are small enterprises belonging to academic spin-offs, or pharmaceutical companies (Persano *et al*. 2013). A widely reported application of electrospun nanofibers is the area of biomedical sciences for wound dressing as well as hosts for drugs (Chong *et al*. 2007; Zhou *et al*. 2008; Heunis *et al*. 2011-2012; Zahedi *et al*. 2011). Some representative companies supplying electrospun products for different fields of application as reported by Persano *et al*. 2013 include:

- Stellenbosch Nanofiber Company (www.sncfibers.com),
- Donaldson (www.donaldson.com),
- DuPont (www.dupont.com),
- Ahlstrom Corporation (www.ahlstrom.com),
- Espin Technologies (www.espintechnologies.com),
- Esfil Tehno AS (www.esfiltehno.ee),
- Finetex Technology (www.finetextech.com),
- Hemcon Medical Technologies, Inc (www.hemcon.com),
- Hollingsworth and Vose Company (www.hollingsworth vose.com),
- Japan Vilene Company (www.vilene.co.jp),
- Johns Manville (www.jm.com),
- Kertak Nanotechnology (www.kertaknanotechnology.com),

Figure 11. (A) Elmarco laboratory-scale electrospinning apparatus; (B) industrial-scale electrospinning system, Nanospider produced by Elmarco (http://www.elmarco.com/nanofiber-equipment/electrospinning-machines-ns1ws500u/); (C) industrial-scale electrospinning system, Nanospinner416 produced by Inovenso Ltd. (http://www.inovenso.com/portfolio-view/nanospinner416/)

- Nanofiber Solutions (www.nanofibersolutions.com),
- Nano109 (www.nano109.com),
- NanoSpun (www.nanospuntech.com),
- Yflow (www.yflow.com),
- Polynanotec (www.polynanotec.com),
- SoftMaterials and Technologies s.r.l (www.smtnano.com), and
- SNS NanoFiber Technology (www.snsnano.com).

Parameters for Electrospinning

Several parameters are known to influence the formation of stable fibers in electrospinning. Doshi *et al.* 1995 classified these parameters as

1. Solution properties (viscosity, conductivity, surface tension, polymer molecular weight, dipole moment, and dielectric constant),
2. Controlled variables (distance between the needle tip and collector, voltage and flow-rate) and
3. Ambient parameters (temperature and humidity) (Dzenis 2004; Kumar 2010).

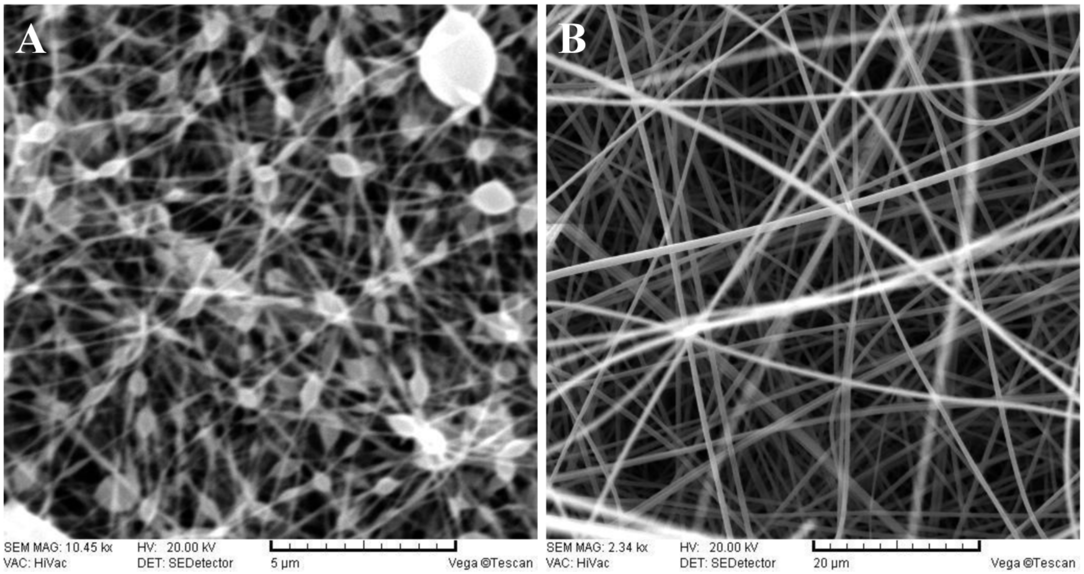
Viscosity

Low polymer solution concentrations result in low viscosity of solutions and tend to form beaded nanofibers when electrospun. Increasing the polymer solution concentration reduces the formation of beaded fibers. Fiber diameters increase with increasing concentration/viscosity (Ki *et al*. 2005; Jiang *et al*. 2004; Huang *et al*. 2001; Son *et al*. 2004; Fong *et al*. 1999; Koski *et al*. 2004; Zhang *et al*. 2005; Lee *et al*. 2004; Ding *et al*. 2002; Teo *et al*. 2006; Demir *et al*. 2002; Mit-Uppatham *et al*. 2004, Chen *et al*. 2004). Varying the concentration of polymer solution affects polymer fiber morphology, however, at a very high polymer solution concentration, charged solutions dries out at the tip of the needle hence preventing electrospining (Mit-Uppatham *et al*. 2004). SEM images of beaded and non-beaded polyvinyl chloride nanofibers are shown in Figure 12. Polymer weight also determines the morphology of fibers, most polymers with low molecular weight result in beaded fibers (Fong *et al*. 1999; Koski *et al*. 2004).

Solution Conductivity

Increasing polymer solution conductivity can produce more uniform nanofibers with fewer beads. A simple approach to increasing polymer solution conductivity is through the use of alcohols as dissolution solvents and also through the addition of a salt (Reneker *et al*. 1995; Mit-Uppatham *et al*. 2004, Chen *et al*. 2004; Geng *et al*. 2005; Kim *et al*. 2005; Lin *et al*. 2004; Liu *et al*. 2005; Zuo *et al*. 2005). The use of alcohols as solvents in the electrospinning of poly(hydroxybutyrate-co-valerate) (PHBV) produced

Figure 12. SEM images of beaded (A) and non-beaded (B) polyvinyl chloride (PVC) nanofibers; electrospinning conditions: (A) 20 wt% PVC, voltage = 18 kV, flow rate = 0.02 mL/h, distance = 18 cm, and (B) 50 wt% PVC, voltage = 20 kV, flow rate = 0.05 mL/h, distance = 18 cm



bead-free nanofibers (Zuo *et al*. 2005). In the electrospining of polybenzimidazole (PBI), lithium bromide salt was added in order to achieve polymer nanofibers (Figure 13). The salt allowed for the formation of uniform nanofibers rather than particles (Ogunlaja et al. 2014; Kim *et al*. 2005).

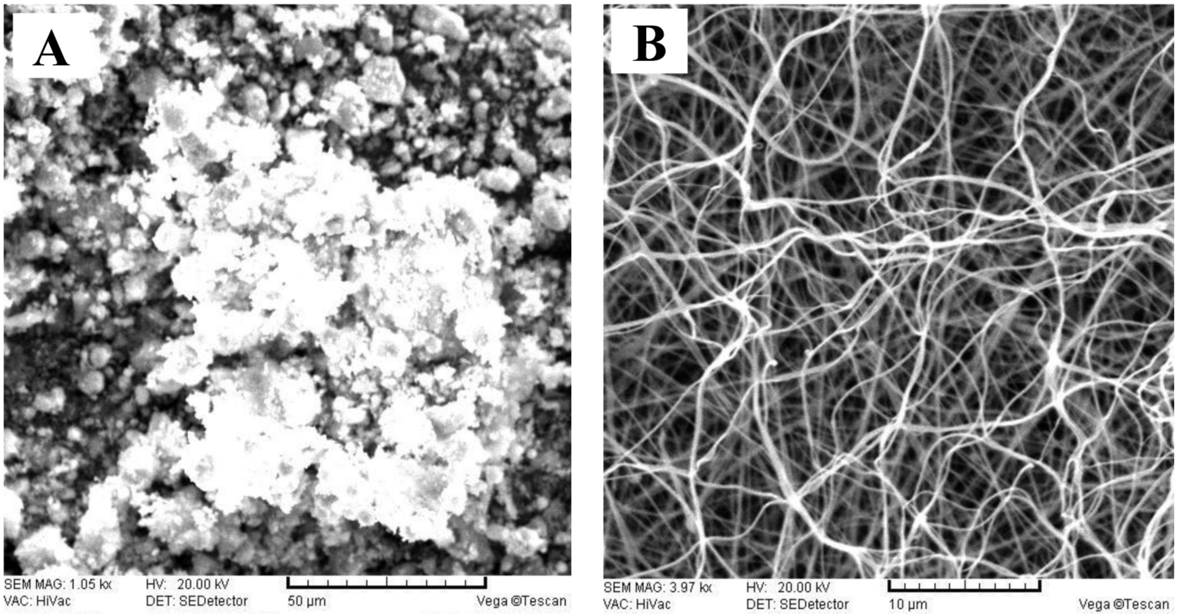
Flow Rate

Varying polymer electrospinning flow rate also affects the fiber size and morphology. Low flow-rates yielded nanofibers with smaller diameters, and this may be due to the longer time it takes for the travelling charged polymer to reach the collector. The long jet travelling time allows polymer solvent to evaporate, thus producing dry fibers. High flow-rates produced beaded nanofibers which do not dry upon reaching the collector due to short polymer jet travelling time (Zhang *et al*. 2005; Zuo *et al*. 2005; Gupta *et al*. 2005; Duan *et al*. 2004; Jarusuwannapoom *et al*. 2005; Wannatong *et al*. 2004; Zong *et al*. 2002; Yuan *et al*. 2004).

Distance between Needle Tip and Collector

Varying the distance between the needle tip and grounded collector has resulted in nanofibers having different diameters and morphology. The minimum distance required in obtaining smooth fibers is said to be a function of the fiber drying time and the volatility of the solvent. The shape and design of a collector do affect fiber morphology as porous fiber structures are obtained when a porous collector is employed. Also aligned fibers and yarns were obtained using a conductive frame, rotating drum, or a wheel-like bobbin collector (Walmsley *et al*. 2012; Huang *et al*. 2003; Fong *et al*. 1999; Teo *et al*. 2006).

Figure 13. SEM images of electrospun polybenzimidazole (PBI): (A) in the absence of lithium bromide (LiBr) and (B) in the presence of lithium bromide (LiBr)



Field Strength/Voltage

Voltage variation has been the most controlled parameter during electrospinning. A proper voltage or field strength produces a Taylor cone which gives rise to bead-free fibers. A Taylor cone refers to the cone observed in electrospinning processes from which a jet of charged particles originates above a threshold voltage. When a Taylor cone is formed, the force of the electric field has overcome the surface tension of the solution (Lee *et al*. 2004; Ding *et al*. 2002; Teo *et al*. 2006; Demir *et al*. 2002; Mit-Uppatham *et al*. 2004, Chen *et al*. 2004; Kim *et al*. 2005).

Ambient Parameters

Ambient conditions such as change in temperature and humidity during the polymer electrospinning process do affect nanofibers morphology and diameter (Mit-Uppatham *et al*. 2004). Reneker *et al.* 1996 electrospun polymer solutions under vacuum, and the fibers produced under this condition gave rise to large diameters.

Molecular Imprinting of Nanofibers

Molecular imprinting is a technique employed for the introduction of recognition sites into matrices (such as polymer) *via* the formation of an assembly between the imprinting template (molecule: organosulfones) and functional groups within the network (adsorbent). Template removal from the adsorbent creates molecular recognition sites on the spaces vacated within the adsorbent (Holmes *et al*. 1994, Sellergren 2001; Haupt 2003, Mosbach 1994, Wulff 1993, Ryu *et al*. 2002; Castro *et al*. 2001; Jorge *et al*. 2004; Ogunlaja *et al*. 2014). The molecular imprinting process for polymers is shown in Figure 14. However, for molecular imprinting of nanofibers we use pre-formed polymers and exploit the functionality on the backbone for recognition sites as the polymer strands fold around the template (Ogunlaja *at al.* 2014). This approach is relatively new and unexplored. Figure 14, therefore reflects the typical approach for molecular imprinting but if the polymer is formed first followed by the *in situ* molecular imprinting/electrospinning then that follows the new approach.

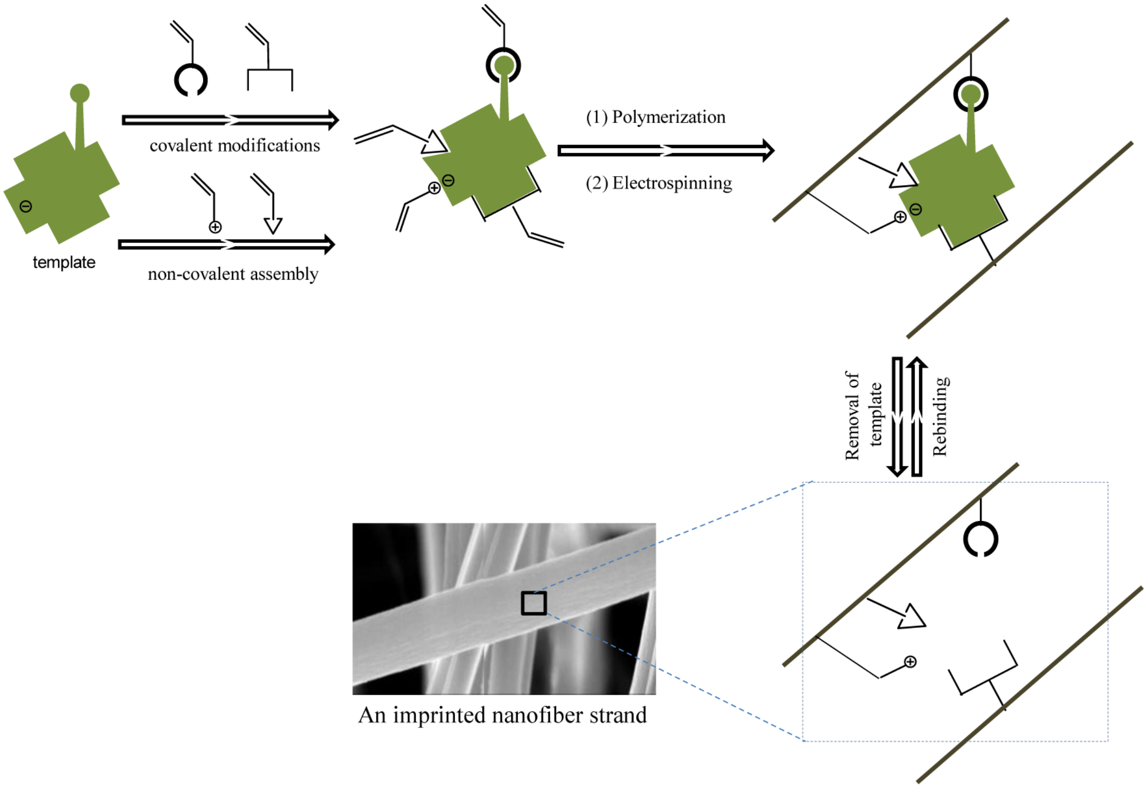
There are three known principal methodologies for assembling recognition site on polymers. These techniques are

1. Covalent binding approach,
2. Non-covalent approach and
3. Semi-covalent approach.

The Covalent Approach

Covalent bonding between molecules includes of interactions such as σ-bonding, π-bonding or metal ion bonding. In the covalent approach, templates (molecules) which can covalently bind to one or more groups in the polymer matrices are utilized. Compounds such as alcohols, aldehydes, ketones, amines, carboxylic acids and carboxylic ester linkage can be imprinted with this approach (Wulff 1993).

Figure 14. A schematic representation of the molecular imprinting process through the formation of reversible interactions between the template and polymerizable functionalities with the following possible interactions (A) reversible covalent bond(s), (B) covalently attached polymerizable binding groups that are activated for non-covalent interaction by template cleavage, (C) electrostatic interactions, (D) hydrophobic or van der Waals interactions



Non-Covalent Approach

Functional polymer and templates under a non-covalent interaction and this involves interactions such as hydrogen bonding, ion pairing and dipole-dipole interactions. Non-covalent imprinting approach is important because

1. The methodology is far easier than covalent methods, and
2. It produces higher affinity binding sites.

This method of imprinting most widely employed due to its simplicity (Mosbach 1994; Ogunlaja *et al.* 2014).

Semi-Covalent Approach

Semi-covalent imprinting produces a more uniform distribution of binding sites on the polymer by combining the technique of covalent and the non-covalent approach. In this approach, templates are covalently bound initially to a polymer group with known functionalities which is recovered after cleavage of the template. Re-binding of the template on the polymer takes place *via* non-covalent interactions without restrictions (Sellergren 2001).

Fabrication of Organosulfones Imprinted Nanofibers

Organosulfur compounds can be imprinted on polymers using the non-covalent molecular imprinting approach before polymers are electrospun into nanofibers. Interactions such as hydrogen bonding and dipole-dipole interactions occur between the functional polymer and organosulfones (templates) in the non-covalent imprinting approach. The method produces higher affinity binding sites. Several studies describing the fabrication of organosulfur and organosulfones imprinted nanofibers have been reported (Ryu *et al*. 2002; Castro *et al*. 2001; Jorge *et al*. 2004). In this chapter, we report on the experimental process for the fabrication of organosulfones imprinted polybenzimidazole nanofibers as described by Ogunlaja *et al*. 2014.

Polybenzimidazole (PBI) solution was prepared by dissolving 2.0 g of pristine PBI polymer in 10 mL *N,N*-dimethylacetamide containing 0.4 g (4% wt) LiBr. The dissolution was carried-out under reflux condition in a nitrogen atmosphere for 4 h. The resulting viscous solution was cooled, and filtered to remove any particulates. 1 mL (0.01 M) solution of organosulfone compound containing 40 μL of Triton X-114 (surfactant agent) was added to the dissolved PBI polymer, after which the mixture was further stirred at 50°C for 5 h to form a homogeneous mixture. The polymer solution was transferred into a 25 mL syringe and electrospun using the following optimised electrospinning conditions: a voltage of 25 kV at a flow-rate of 0.4 mL/h, with a distance between the needle tip and collector plate of 20 cm. The resulting nanofibers were then subjected to extensive washing using a mixture of acetonitrile and methanol (1:1) *via* Soxhlet extraction to remove residual *N,N*-dimethylacetamide and entrapped organosulfone compounds. The washed nanofibers were later dried overnight at an oven temperature of 60°C. This process leaves PBI nanofibers with cavities that recognise organosulfone compounds (Ogunlaja *et al*. 2014).

Materials Characterization

The following instrumental analysis techniques can be used to characterize polymer nanofibers or adsorbents:

Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) is currently being employed for the imaging of polymeric materials in the micro- (10^{-6}) to almost nano- (10^{-9}) scale region. SEM provides information on the surface morphologies and shapes of polymer microspheres. Fiber diameters can also be obtained from SEM images.

X-Ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a widely used technique to investigate the chemical composition of surfaces. XPS provides information on the following (Walmsley *et al*. 2012):

1. Identification of elements near the surface and surface composition,
2. Local chemical environments since this can cause small shifts in XPS peak positions
3. Oxidation states of elements

Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

Thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) are the most widely used techniques in the study of the degradation of polymer materials. TGA measures the stability and the decomposition pattern of the material. DSC on the other hand, measures the transition temperature and heat flow within an adsorbent, and the crystalline content of a polymer can be measured by using the DSC (Davis, 2004).

Composition Information

FT-IR is a light transmission technique which provides information about the functional groups present on an adsorbent. This technique can also be used to confirm the level of functionalization on adsorbent and can also detect the presence of impurities (Ogunlaja *et al*. 2014). Solid state NMR can also be used to confirm the presence of the functional groups on the polymer backbone.

Surface Area and Porosity Determination

The two common techniques for surface area measurements are (A) Mercury intrusion method and (B) Gas adsorption method (Davis, 2004; Ritter *et al*. 1945; Klobes *et al*. 2006; Washburn, 1921; Meyer *et al*. 1997).

Mercury Intrusion Method

Mercury porosimetry is a widely accepted method for determining total volume and pore size distribution in the meso- and macropore ranges. The total volume and pore size distribution can be measured by measuring the penetration of mercury into the pores (Ritter *et al*. 1945; Klobes *et al*. 2006).

Gas Adsorption Method

Gas adsorption measurements are widely used for the characterization of a variety of porous solids. Of particular importance is the application of physical adsorption for the determination of the surface area and pore size distribution. N_2, Ar, Kr and CO_2 gases are widely employed for measuring the adsorption/desorption isotherm (Davis, 2004). Brunauer-Emmett-Teller (BET) equation (Equation 1) is used to derive the surface area from physisorption isotherm data.

$$\frac{P}{n_a\left(P_o - P\right)} = \frac{1}{n_m C} + \frac{\left(C-1\right)}{n_m C}\cdot\frac{P}{P_o} \tag{1}$$

where n_a is the amount adsorbed at the relative pressure P/P_o, n_m is the monolayer capacity, and C is a constant that is dependent on the isotherm shape.

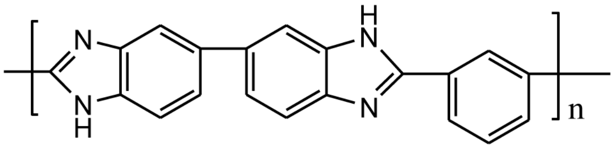
APPLICATION OF ORGANOSULFONES IMPRINTED NANOFIBERS FOR ADSORPTIVE DESULFURIZATION

In recent publications several solid absorbents have been employed as adsorbent for the desulfurization of fuel. The nanofibers show potential for the extraction of organosulfone compounds in the oxidative desulfurization process, a complimentary step to the hydrodesulfurization process. Herein, the focus is on the potential use of organosulfone-responsive nanofibers for the desulfurization of oxidized fuel using polymers such as chitosan and polybenzimidazole. These polymer adsorbents were employed under a continuous flow process to produce fuels with low sulfur content. The adsorption performance of these adsorbents depends on both the surface chemical properties such as active sites and physical properties including surface area, and pore size and distribution. The chemical interactions such as hydrogen bonding, π-π interactions, van der Waals forces and electrostatic interactions between organosulfone compounds and molecularly imprinted polymers have been discussed using DFT calculations. The potential use of poly alcohols such as polyvinyl alcohol (PVA), polyvinyl phenol (PVP) and polyvinyl benzyl alcohol (PVBA) for organosulfone adsorption has also been investigated by employing density functional theory calculations. The choice of a suitable polymer for adsorption has stimulated much debate, and with molecular modelling some issues such as polymer structure and polymer reactivity can be addressed. The subtle chemical interactions of the functional groups of the polymer with the reactive sites of the template molecules (in this case organosulfones) have been modelled computationally by our group of workers (Ogunlaja *et al.* 2014). We have observed some correlations between theory and experiments in the few polymer systems that we have tested up to date. This area of research requires further expansion but it must be guided by the computational approach.

Polybenzimidazole (PBI)

Polybenzimidazole (PBI) is a heterocyclic polymer which comprises of repeating units of benzimidazole (Figure 15). The -NH groups of the benzimidazole allows for hydrogen bonding interactions with polar compounds such as sulfones produced by the oxidation of organosulfur compounds in fuels (Ogunlaja *et*

Figure 15. Chemical structure of polybenzimidazole (PBI)



al. 2014). PBI provides excellent chemical and thermal stability properties (Walmsley *et al*. 2012). Polybenzimidazole (PBI) nanofibers were obtained by dissolving solid PBI powder in *N,N*-dimethylacetamide under reflux as explained in section 3.2, a representative SEM image of organosulfone-imprinted PBI nanofibers is shown in Figure 13.

Organosulfones-imprinted polybenzimidazole nanofibers were employed for the adsorption of organosulfone compounds in oxidized hydro-treated diesel, containing 394 ± 4.2 ppm S. A continuous flow process was employed in the adsorption process shown in Figure 5. Prior to adsorption, a 150 mg quantity of the respective organosulfone-imprinted PBI nanofibers was conditioned with a suitable solvent. The oxidized fuel was pumped through the nanofibers at a flow-rate of 1 $mL.h^{-1}$. The sulfur left within the hydro-treated fuel after the adsorption process was found to be below the limit of detection of the GC-AED (Figure 16). The saturated organosulfone adsorption capacity of the molecularly imprinted adsorbents from diesel fuel was 5.3 ± 0.4 mg/g. Polybenzimidazole showed excellent adsorption capacities, and this was attributed to the imprinting effect as well as other factors, mostly molecular interactions which were confirmed from the molecular modelling interactions between known organosulfone compounds and polybenzimidazole.

Chitosan (CHI)

Chitosan, an amino polysaccharide usually obtained by the deacetylation of chitin (Figure 17), has free amine and hydroxyl groups which allow for chemical modifications through the formation of hydrogen bonding interactions and has been investigated for the development of sorption systems (Ryu *et al*. 2002; Ruiz *et al*. 2000; Ngah *et al*. 1999; Xiaoliang *et al*. 2002. Chitosan also has the ability to swell when in contact with a thermodynamically compatible solvent which is another favourable property (Fariba *et al*. 2010; Monteiro *et al*. 1999.

Electrospinning of chitosan was achieved by dissolving 0.5 g of chitosan in a 10 mL of trifloroacetic acid/dichlomethane (7:3). A voltage of 30 kV was applied to the polymer solution which was pumped at a flow-rate of 1.2 mL/h, and the distance between the needle tip and collector plate was 17 cm (Ogunlaja *et al*. 2014). A representative SEM image of organosulfone-imprinted chitosan nanofibers is shown in Figure 18.

A similar adsorption process as reported for polybenzimidazole was also carried out by employing 300 mg of conditioned organosulfones-imprinted chitosan nanofibers. The adsorption process was also allowed to proceed at a flow-rate of 1 mL/h under room temperature. Sulfur analysis after the adsorption process indicated that a total of 62 ± 3.2 ppm S was left in the diesel (Figure 19). The saturated sulfur adsorption capacity of the molecularly imprinted adsorbents was 2.2 ± 0.2 mg/g. Molecular modelling was also employed in discussing the possible mode of binding between the organosulfone compounds and chitosan.

Poly Alcohols: Polyvinyl Alcohol (PVA), Polyvinyl Phenol (PVP) and Polyvinyl Benzyl Alcohol (PVBA)

Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer (Hallensbelen *et al*. 2000). It is resistant to oil and various solvents, and is therefore also an ideal polymer for use as adsorbent in fuel applications. Polyvinyl alcohol has high tensile strength with high melting point of between 180-230°C. The hydroxyl (-OH) functionalities on polyvinyl alcohol can be modified, and for example they can be cross-linked once

Figure 16. GC–AED chromatograms of carbon (A) at 179 nm, and sulfur (B) at 181 nm in hydrotreated diesel after oxidation, and chromatograms of carbon (C) at 179 nm and sulfur (D) at 181 nm in oxidized hydrotreated diesel after using organosulfones-imprinted polybenzimidazole nanofibers as adsorbent

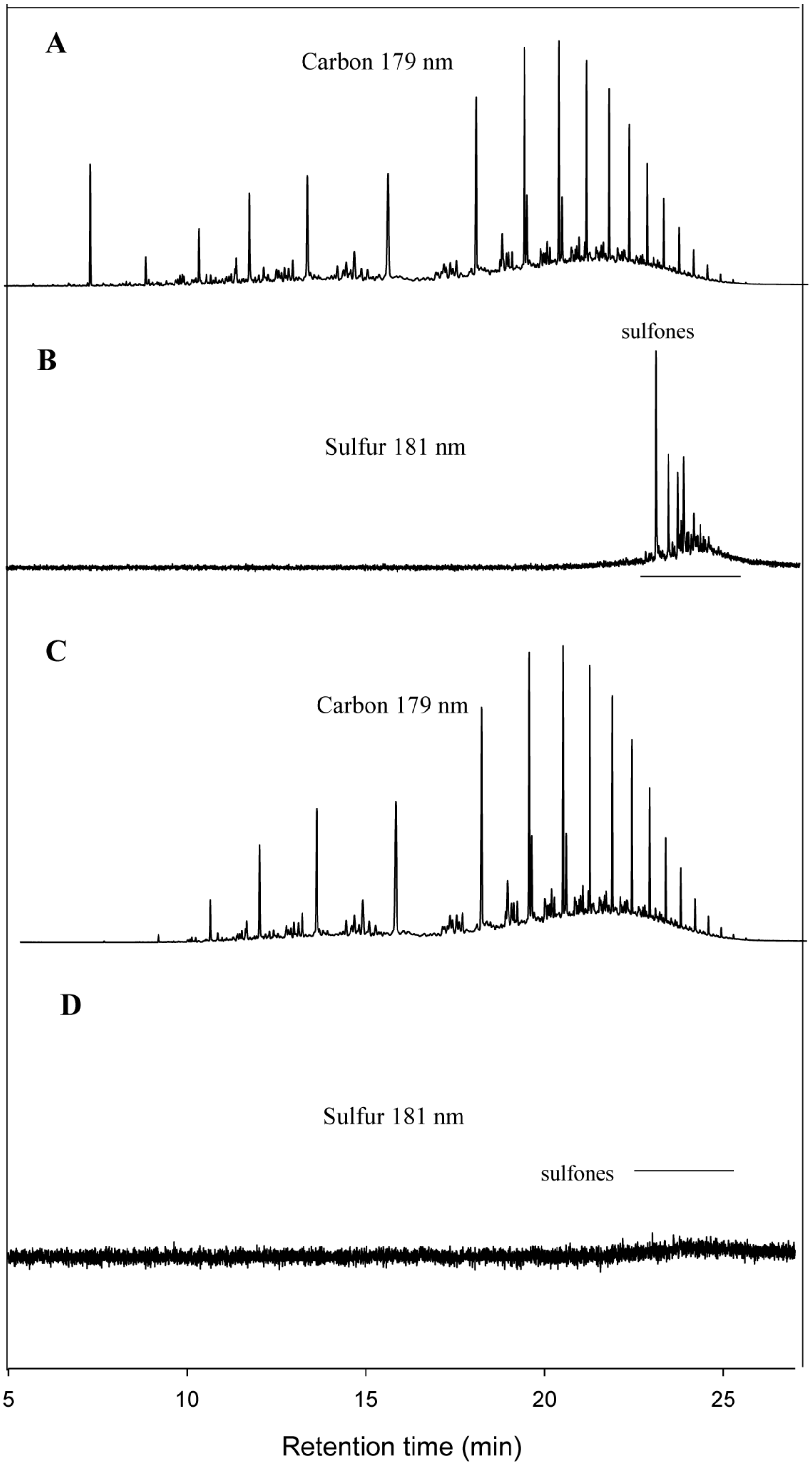


Figure 17. Chemical structure of chitosan

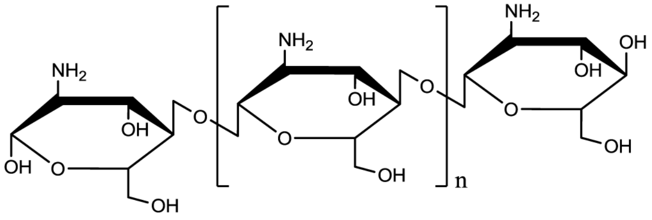
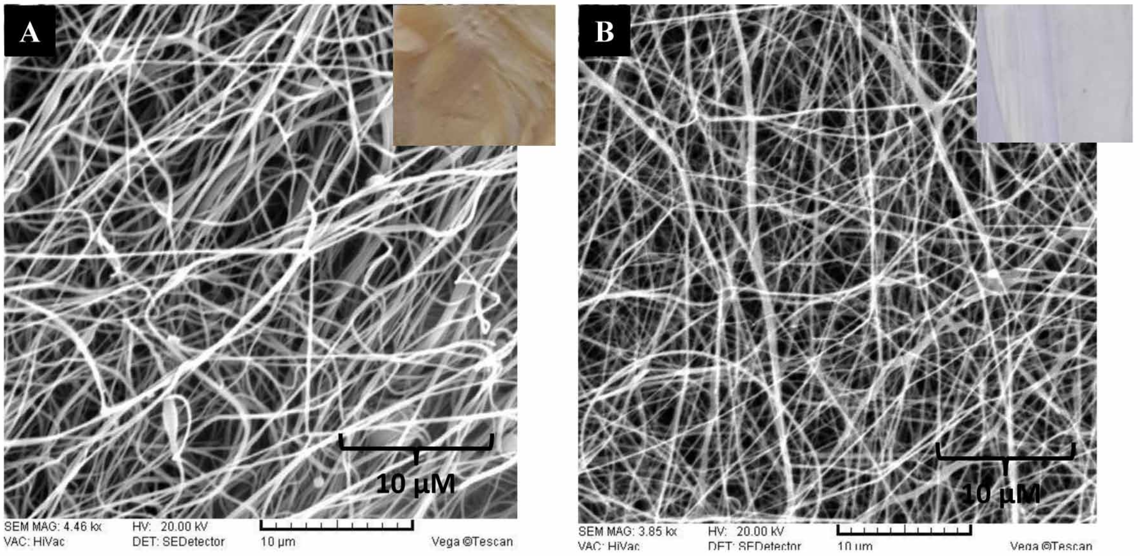


Figure 18. SEM images of (A) dibenzothiophene sulfone-imprinted polybenzimidazole and (B) dibenzothiophene sulfone-imprinted chitosan

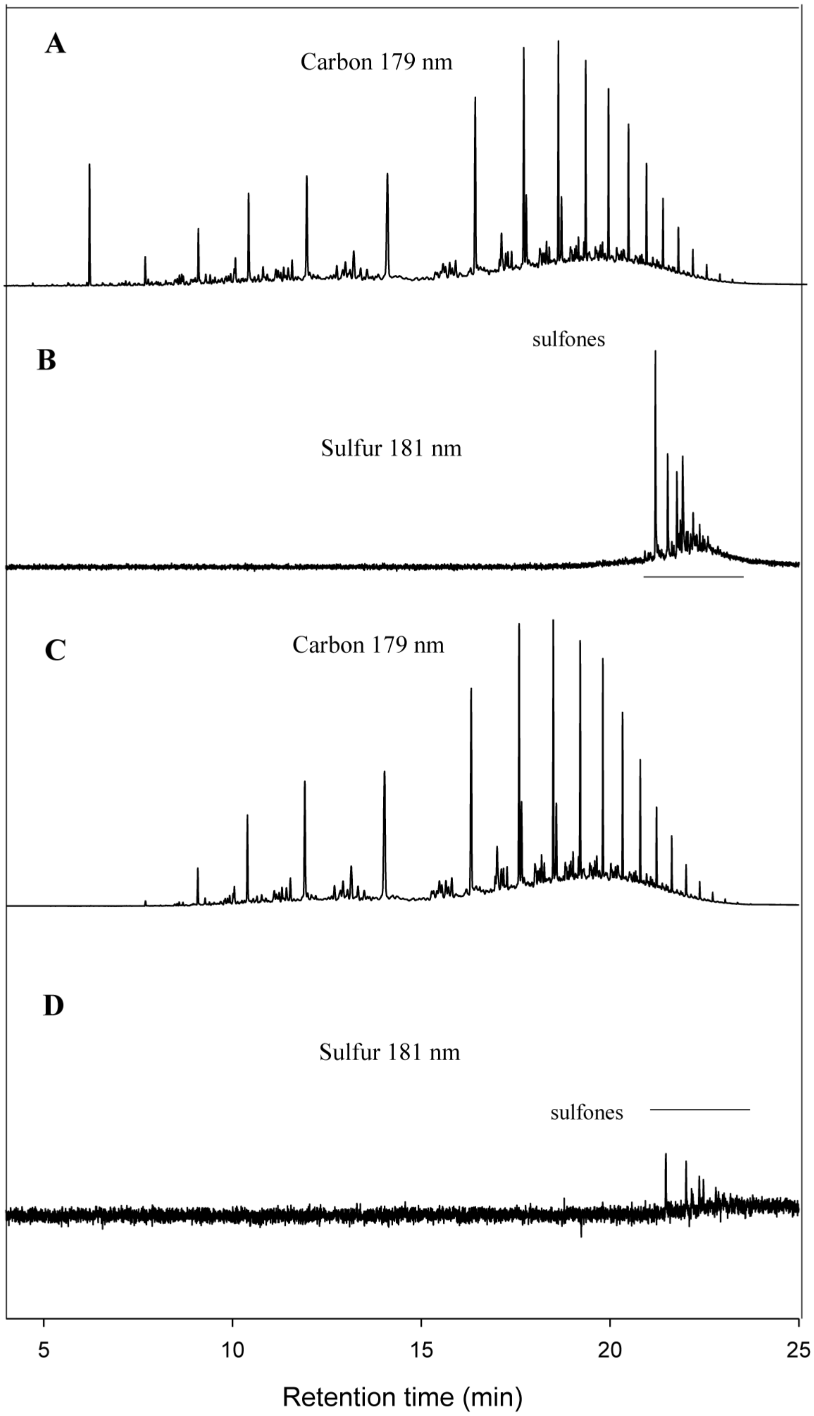


fibers are formed to strengthen the material (Miyazaki *et al.* 2010). Polyvinyl benzyl alcohol (PVBA) and polyvinyl phenol (PVP) can be synthesised from the polymerization of 4-vinylbenzyl alcohol and 4-vinyl phenol, respectively (Dekker *et al.* 1973). The benzene ring and hydroxyl (-OH) groups available on polyvinyl benzyl alcohol (PVBA) and polyvinyl phenol (PVP) can be explored for their π-π stacking and hydrogen bonding interactions properties with organosulfones respectively.

Molecular Modelling

The thermodynamic properties between template-polymer in the formation of an adduct have been reported as one of the major factors governing the binding performance of molecularly imprinted polymers (Nicholls *et al.* 2001). Therefore, to gain mechanistic insight into the binding performance and interactions which leads to adduct formation between imprinted nanofibers and organosulfone compounds,

Figure 19. GC–AED chromatograms of carbon (A) at 179 nm, and sulfur (B) at 181 nm in hydrotreated diesel after oxidation, and chromatograms of carbon (C) at 179 nm and sulfur (D) at 181 nm in oxidized hydrotreated diesel after using organosulfones-imprinted chitosan nanofibers as adsorbent



molecular simulation using density functional theory was performed. The emphasis of this chapter is on use of computational chemistry to design or choose relevant polymers for recognition of organosulfones. This approach should be transferable to other chemical systems that rely on subtle chemical interactions as drivers for molecular recognition.

Geometry optimizations and vibrational analyses of organosulfone-polymer adducts were performed using the Gaussian09 software. B3LYP functional was employed with a 6-31G(d) basis set. The enthalpies of formation ($\Delta\Delta H_{\text{adduct}}$), Gibb's free energies ($\Delta\Delta G_{\text{adduct}}$) and entropies of formation ($\Delta\Delta S_{\text{adduct}}$) for each adduct formed were calculated by using Equations 2 and 3.

$$\Delta\Delta H_{adduct} = \Delta H_{adduct} - \left(m\Delta H_{polymer} + t\Delta H_{organosulfone}\right) \tag{2}$$

where m and t are the stoichiometric amounts of polymer and organosulfone involved in adduct formation.

$$\Delta\Delta G_{adduct} = \Delta\Delta H_{adduct-} T\Delta\Delta S_{adduct} \tag{3}$$

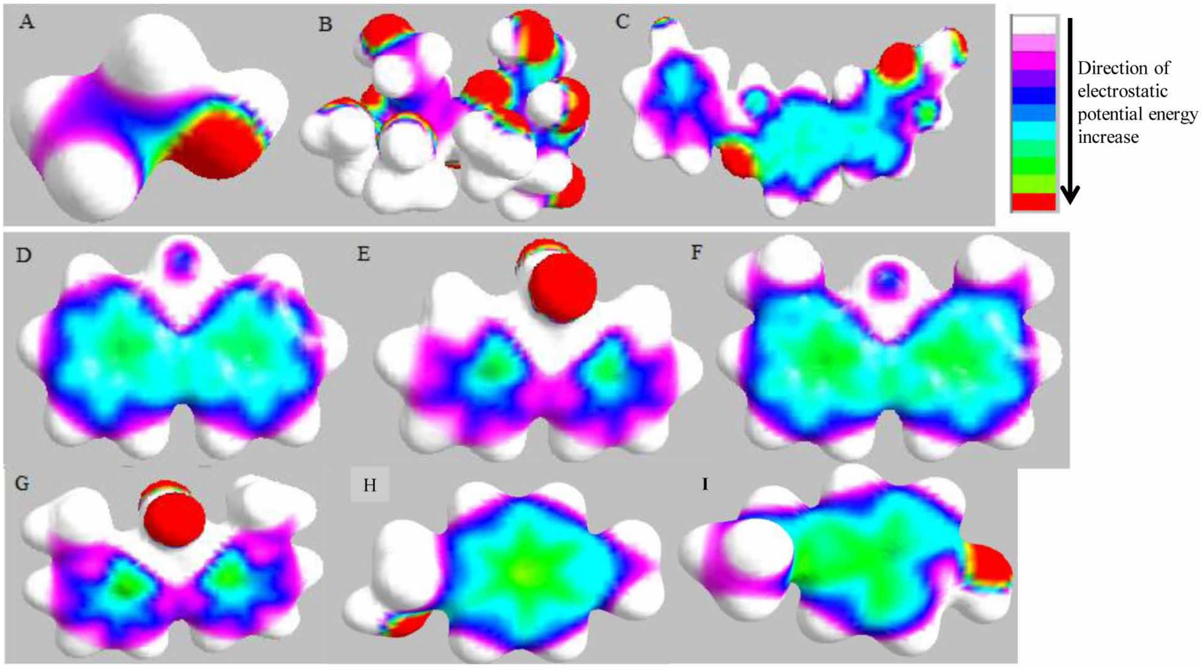
$\Delta\Delta$G, T and $\Delta\Delta$S are the Gibbs free energy for the adduct formation, temperature (298 K) and entropy for adduct formation at standard conditions (i.e. 1 molar concentration for solvents and 1 atm pressure) respectively. The Gibbs free energy (ΔG°) gives information about the feasibility of interaction (adduct formation); entropy (ΔS°) describes the spontaneous nature of interaction (adduct formation) whereas the sign of ΔH° reflects the endo- or exothermic nature of the process.

Electrostatic and Dipole Interactions

The strength of a dipole interaction depends on the size of each dipole, dipole energies and on their relative orientation. A molecule (polymer) with a permanent dipole moment will induce a dipole moment in a second molecule (organosulfone) that is located nearby in space, and this phenomenon is known as polarization (Kim *et al*. 2006). Polar molecules (a functional polymer and organosulfone compounds), do interact through dipole-dipole intermolecular forces and hydrogen bonds. The extent of charge separation within the imprinted polymers is characterized by its dipole moment which also explains their nature of polarity. Polarity prompted by dipole moment brings about a number of physical properties some of which are solubility (wettability), surface tension and boiling points (Kim *et al*. 2006). The dipole of the modelled polymer unit increases in the order of polyvinyl phenol (1.5630 Debye) < polyvinyl alcohol (1.5634 Debye) < polyvinylbenzyl alcohol (1.5638 Debye) < polybenzimidazole (4.0766 Debye) < chitosan (9.0372 Debye). Chitosan presented the highest dipole moment amongst the polymers modelled, and this confirms that the polymer shows better wettability properties from a neighbouring polar molecule.

Attractive and repulsive forces between interacting atoms and molecules, due to their electropositive and electronegative properties, were explained through electrostatic potential energies. The electrostatic potential for imprinted polymers, organosulfur and organosulfone compounds were color-mapped based on the electron density distribution of the various compounds (Figure 20). The color map shows the electrostatic potential energy (in hartrees) for the various colors. The red end of the spectrum (Figure 20) shows regions of highest stability for a positive test charge (more favorable to interactions), magenta/blue show the regions of least stability for a positive test charge (less favorable to interactions).

Figure 20. Electrostatic potential on electron density for the examined adsorbents (A) PVA, (B) Chitosan, (C) PBI, (D) dibenzothiophene, (E) dibenzothiophene sulfone, (F) 4,6-dimethyldibenzothiophene, (G) 4,6-dimethyldibenzothiophene sulfone, (H) polyvinylbenzyl alcohol (PVBA) and (I) polyvinyl phenol (PVP). Red colour indicate regions which have the highest negative domain



The negative characteristic electrostatic potential, represented in red color, are reactive as they are rich in electrons. With the imprinted polymers, negative electrostatic potential are distributed around the surface of the polymers, with PBI and chitosan being highly negative (mostly around the –OH and –NH functionalities). Organosulfur compounds show evidence that the negative electrostatic potentials are dominantly located on the two sides of the molecular plane. The methyl groups on the organosulfur and organosulfone compounds enhance the negative electrostatic potential on the aromatic molecular planes because of its positive inductive effect. Organosulfone compounds have the highest value of the negative electrostatic potential when compared to organosulfur compounds, and such negative domain is mainly located on the oxygen atoms of the compounds.

Orbital Energies

Interaction between atoms or molecules happens most likely between the HOMO of one molecule and the LUMO of the other molecule. The amount of energy required to add or remove electrons in a molecule can be obtained from the HOMO and LUMO energy values. HOMO characterizes the nucleophilicity of a species, i.e. its tendency to donate an electron, while LUMO characterizes the electrophilicity of a species, i.e. its tendency to receive an electron (Hizaddin *et al*. 2013).

Optimized geometries of polybenzimidazole, chitosan, polyvinyl alcohol, polyvinylbenzyl alcohol and polyvinyl phenol showing HOMO and LUMO positions are presented in Figures 21, 22, 23, 24 and

Figure 21. HOMO and LUMO locations of polybenzimidazole (PBI): (A) HOMO and (B) LUMO; blue and grey colours represent nitrogen and carbon atoms respectively.

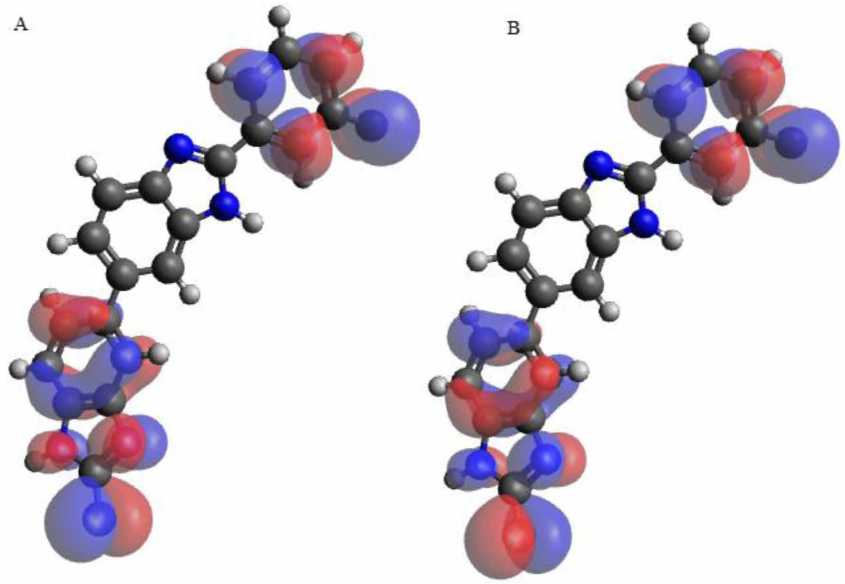
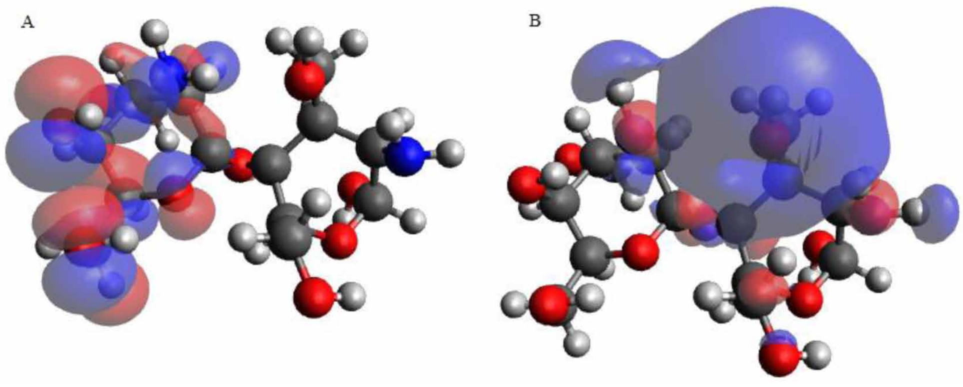


Figure 22. HOMO and LUMO locations of chitosan (unit): (A) HOMO and (B) LUMO; red, blue and grey colours represent oxygen, nitrogen and carbon atoms respectively.



25 respectively. Polymers with low HOMO energy values indicate a molecule with better electron donor and high ionization potential, while polymers with higher LUMO energy shows a molecule with high electron affinity, i.e. better electron acceptor (Table 2).

Orbital Energy Gap

From the HOMO and LUMO energy values, the HOMO-LUMO energy gap can be determined. Large HOMO-LUMO gap indicates high stability and resistance to charge transfer and changes in electron number and distribution. Therefore, hard molecules have a large HOMO-LUMO gap. Meanwhile, the small

Figure 23. HOMO and LUMO locations of polyvinyl alcohol (PVA) unit: (A) HOMO and (B) LUMO; red and grey colours represent oxygen and carbon atoms respectively.

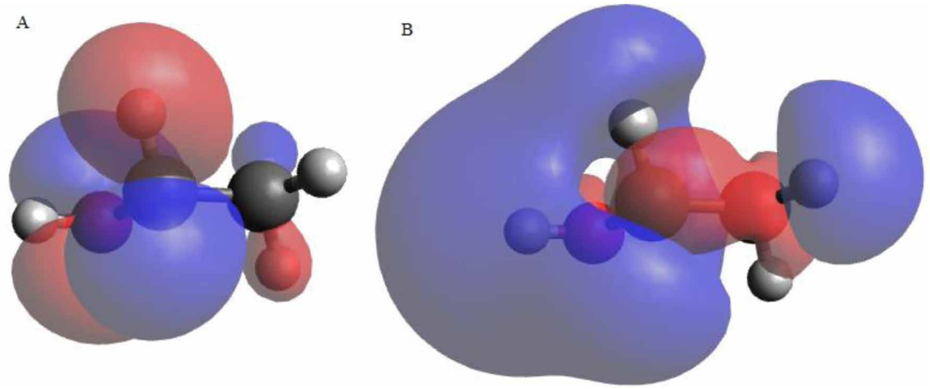
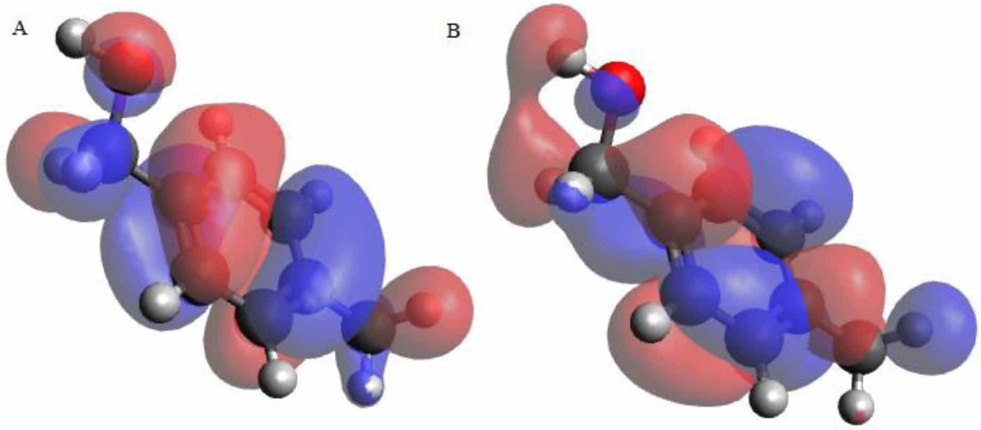


Figure 24. HOMO and LUMO locations of polyvinylbenzyl alcohol (PVBA) unit: (A) HOMO and (B) LUMO; red and grey colours represent oxygen and carbon atoms respectively.



HOMO-LUMO gap indicates high polarizability since they only require a small amount of energy to get them to the excited states. The small HOMO-LUMO gap is indicative of soft molecules (Pearson, 1986).

The HOMO-LUMO gaps of polybenzimidazole (PBI), chitosan, PVA, PVP and PVBA were 0.25606 eV, 6.77509 eV, 9.20017 eV, 5.83385 eV and 6.30461 eV. Polybenzimidazole (PBI) displayed the smallest HOMO-LUMO energy gap which is indicative of a soft molecule with better polarizability and reactivity while chitosan and PVA both presented high HOMO-LUMO energy gaps indicating hard molecules with low reactivity (Table 2). The optimization energies of polybenzimidazole (PBI), chitosan, PVA, PVP and PVBA were -66.7 × 10^4, -83.8 × 10^4, -9.7 × 10^4, -26.7× 10^4 and -24.2 × 10^4 kcal/mol respectively. Polymers with high energy have higher compactness/firmness, hence, making it difficult for incoming molecules (organosulfones) to reorganise around the polymer. Polymers with smaller energies have lower compactness, thus allowing facile association with incoming molecules (organosulfones). Polyvinyl alcohol (PVA) shows a much higher energy as compared to polyvinylbenzyl alcohol (PVBA), PVP, PBI and chitosan, confirming its less reactive environment (Isarankura *et al*. 2008; Nantasenamat *et al*. 2005, 2006, and 2007).

Figure 25. HOMO and LUMO locations of polyvinyl phenol (PVP) unit: (A) HOMO and (B) LUMO; red and grey colours represent oxygen and carbon atoms respectively.

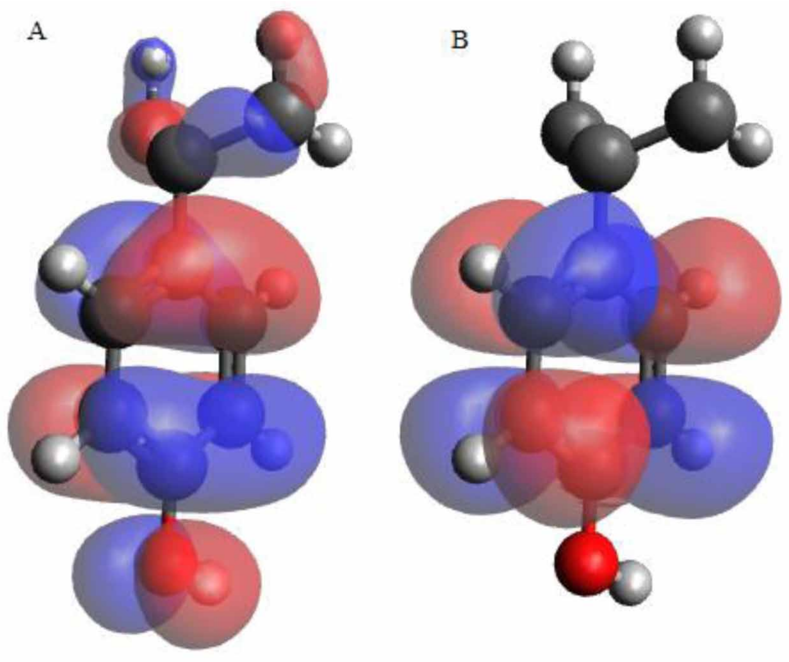


Table 2. Quantum chemical parameters; HOMO (E_H), LUMO (E_L) and band gap energies

Compounds	E_H (a.u.)	E_L (a.u.)	Orbital Energy Gap. (E_G) (a.u.)	[a]Orbital Energy Gap. (E_G) (eV)
PVA	-0.26154	0.07656	0.33810	9.20017
PBI	-0.15201	-0.14260	0.00941	0.25606
Chitosan	-0.22572	0.02326	0.24898	6.77509
PVBA	-0.23055	0.00114	0.23169	6.30461
PVP	-0.21398	-0.00041	0.21439	5.83385
$DBTO_2$	-0.24492	-0.06666	0.17826	4.85070
4,6-$DMDBTO_2$	-0.23826	-0.06235	0.17591	4.78676
PVA-$DBTO_2$	-0.24559	-0.06902	0.17657	4.80472
PVA-4,6$DMDBTO_2$	-0.23439	-0.05871	0.17568	4.78050
PBI-$DBTO_2$	-0.15304	-0.14387	0.00917	0.24953
PBI-4,6$DMDBTO_2$	-0.14548	-0.13604	0.00944	0.25688
Chitosan-$DBTO_2$	-0.14509	-0.06737	0.07773	2.11487
Chitosan-4,6$DMDBTO_2$	-0.13759	-0.06349	0.07410	2.01636
PVBA-$DBTO_2$	-0.22463	-0.07011	0.15452	4.20471
PVBA-4,6$DMDBTO_2$	-0.22345	-0.06944	0.15401	4.19083
PVP-$DBTO_2$	-0.20452	-0.07309	0.13143	3.57639
PVP-4,6$DMDBTO_2$	-0.20314	-0.06852	0.13462	3.66320

[a]The energies of HOMO, LUMO gaps energies were converted from a.u. to eV using the conversion factor of 27.2114.

Interaction Energies

Density functional theory (DFT) for molecular modelling was employed to understand the mode of interactions between polymers and organosulfones (Parr *et al.* 1989; Dreizler *et al.* 1990). The comparative strength for the formation of a given organosulfone-polymer adduct can be inferred from calculated interaction energy.

Molecular interactions between the dibenzothiophene sulfones and the various polymers caused a decrease in the HOMO-LUMO energy gap of PVA-DBTO$_2$ (4.80472 eV), PBI-DBTO$_2$ (0.24953 eV), Chitosan-DBTO$_2$ (2.01636 eV), PVP-DBTO$_2$ (3.57639 eV) and PVBA-DBTO$_2$ (4.20471 eV) as compared to the free dibenzothiophene (4.85070 eV) (Table 2). The HOMO-LUMO gap can be used as a relative index for the degree of interaction strength between organosulfones and polymers in which lower values indicate higher strengths of interaction. The observed HOMO-LUMO gaps suggest that the molecular interaction of PBI-DBTO$_2$ adduct is higher than that of PVA-DBTO$_2$ and Chitosan-DBTO$_2$, with Chitosan-DBTO$_2$ adduct formation more viable than PVBA-DBTO$_2$ and PVA-DBTO$_2$.

PBI-DBTO$_2$ adduct indicated that the HOMO and LUMO center around PBI, and this resulted in the formation of π-π interaction (π-π stacking) between polybenzimidazole (PBI) and dibenzothiophene sulfone (DBTO$_2$), hydrogen bonding interaction between -S=O of DBTO$_2$ and –NH of PBI was also visible (Figure 26). Chitosan-DBTO$_2$ adducts on the other hand, showed that the HOMO originates from chitosan while the LUMO comes from DBTO$_2$, this indicated that interactions took place *via* electron donation between HOMO and LUMO centers. Hydrogen bond interaction is also viable due to the presence of free –NH$_2$ and –OH groups on chitosan (Figure 27). The PVA-DBTO$_2$ adducts show that the HOMO is shared between PVA and DBTO$_2$ while the LUMO is centered on DBTO$_2$, and interactions can be said not to have taken place *via* electron donation between HOMO and LUMO centers but possibly through CH-π bond formation (Figure 28). Adducts (PVBA-DBTO$_2$) formed between polyvinylbenzyl alcohol (PVBA) and DBTO$_2$ indicate that HOMO is polyvinylbenzyl alcohol (PVBA) based while LUMO originated from DBTO$_2$, interaction also took place through hydrogen bonding between –OH group on polyvinylbenzyl alcohol and -S=O of DBTO$_2$ (Figure 29). PVP-DBTO$_2$ adduct (Figure 30) indicate that the HOMO and LUMO locations originate from polyvinyl phenol (PVP) and dibenzothiophene (DBTO$_2$) respectively, with possibility of hydrogen bonding interactions between –OH group of polyvinyl phenol and -S=O of DBTO$_2$.

Molecular interaction between 4,6-dimethyldibenzothiophene sulfone and the various polymers also caused a decrease in the HOMO-LUMO energy gap of PVA-4,6-DMDBTO$_2$ (4.78050 eV), PVP-4,6DMDBTO$_2$ (3.66320 eV), PBI-4,6-DMDBTO$_2$ (0.25688 eV), Chitosan-4,6-DMDBTO$_2$ (2.01636 eV) and PVBA-4,6-DMDBTO$_2$ (4.19083 eV) as compared to the free 4,6-dimethyldibenzothiophene (4.78676 eV) (Table 2). Unlike PVA-4,6-DMDBTO$_2$, PVBA-4,6-DMDBTO$_2$, PVP-4,6DMDBTO$_2$ and Chitosan-4,6-DMDBTO$_2$, the HOMO–LUMO gap in PBI-4,6-DMDBTO$_2$ adduct displayed excellent molecular interactions.

PBI-4,6-DMDBTO$_2$ adduct indicated that the HOMO and LUMO centre on PBI, and this resulted in the formation of π-π stacking between polybenzimidazole (PBI) and 4,6-dimethyldibenzothiophene sulfone (4,6-DMDBTO$_2$), in a similar manner to the interaction observed with DBTO$_2$. Hydrogen bonding formation between -S=O of 4,6-DMDBTO$_2$ and –NH of PBI was however not observed, and this might be due to the steric hindrance caused by the methyl groups in 4,6-DMDBTO$_2$ (Figure 31). Chitosan-4,6-DMDBTO$_2$ adducts also showed that the HOMO originates from chitosan while the LUMO

Figure 26. HOMO and LUMO locations of PBI-dibenzothiophene (PBI-DBTO$_2$) adduct: (A) HOMO and (B) LUMO; red, yellow and grey colours represent oxygen, sulfur and carbon atoms respectively.

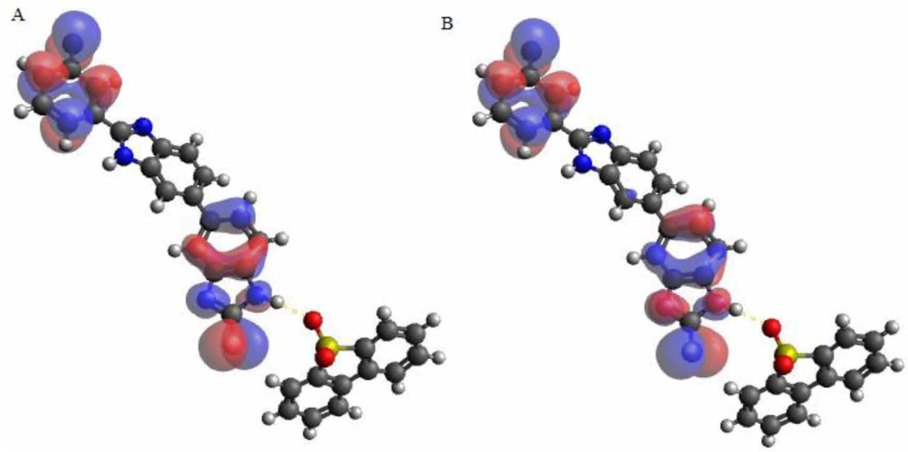
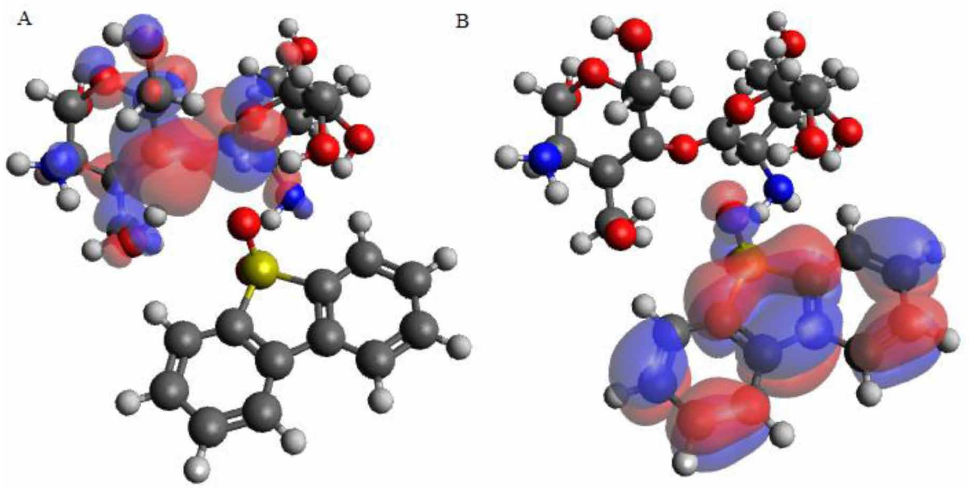
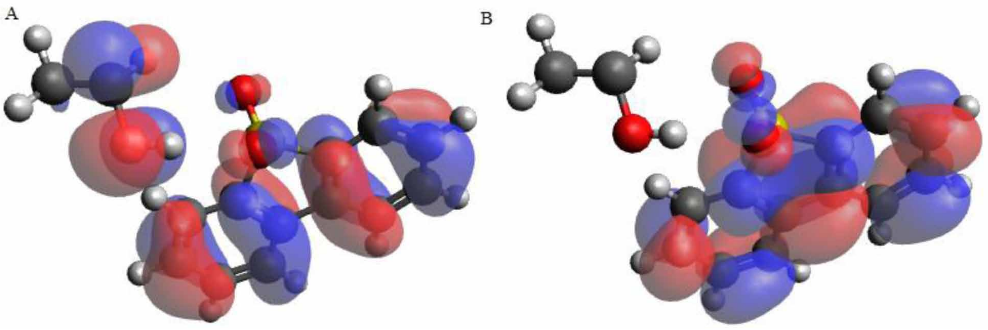


Figure 27. HOMO and LUMO locations of chitosan-dibenzothiophene (chitosan-DBTO$_2$) adduct: (A) HOMO and (B) LUMO; red, yellow and grey colours represent oxygen, sulfur and carbon atoms respectively.



comes from 4,6-DMDBTO$_2$, and this is similar to the results obtained with Chitosan-DBTO$_2$ adduct confirming that interaction took place *via* electron donation between chitosan and 4,6-DMDBTO$_2$ (Figure 32). PVA-4,6-DMDBTO$_2$ adducts showed that both the HOMO and LUMO of the adduct originates from 4,6-DMDBTO$_2$, in which little or no interactions take place (Figure 33). PVBA-4,6-DMDBTO$_2$ adduct indicate that HOMO initiates from polyvinylbenzyl alcohol (PVBA) while LUMO comes from 4,6-DMDBTO$_2$, hydrogen bonding interactions between –OH group on polyvinylbenzyl alcohol and

Figure 28. HOMO and LUMO locations of PVA-dibenzothiophene sulfone (PVA-DBTO$_2$) adduct: (A) HOMO and (B) LUMO; red, yellow and grey colours represent oxygen, sulfur and carbon atoms respectively.



-S=O of 4,6-DMDBTO$_2$ was also possible (Figure 34). The HOMO and LUMO locations of PVP-4,6-DMDBTO$_2$ adduct (Figure 35) are in similar positions as reported for the PVBA-4,6-DMDBTO$_2$ adduct.

Thermodynamic parameters such as enthalpy (ΔΔH), entropy (ΔΔS) and free energies (ΔΔG) are presented in Table 3. Gibbs free energy is known as the most useful thermochemical parameter for understanding chemical reactions at constant temperature and pressure, a $\Delta G < 0$ is indicative of a spontaneous reaction while $\Delta G > 0$ shows that a reaction is possibly non-spontaneous. Polybenzimidazole (PBI) displayed –Gibbs free energies for adduct formation with DBTO$_2$ and 4,6-DMDBTO$_2$. Negative enthalpies and positive entropies indicate that interactions are possibly favourable at low temperatures hence leading to adduct formation between organosulfones and imprinted polymers (Table 3). Polybenzimidazole (PBI), Chitosan and polyvinylbenzyl alcohol (PVBA) all show possibility for interaction with organosulfone compounds at low temperature (298 K), going by the molecular modelling condition. PVA and PVP both displayed positive ΔΔH and ΔΔG, hence external energy would be required for adduct formation. PBI displayed the most favourable energetics for adduct formation, and this was in agreement with what was observed from experiments (Ogunlaja *et al.* 2014).

Figure 29. HOMO and LUMO locations of PVBA-dibenzothiophene (PVBA-DBTO$_2$) adduct: (A) HOMO and (B) LUMO; red, yellow and grey colours represent oxygen, sulfur and carbon atoms respectively.

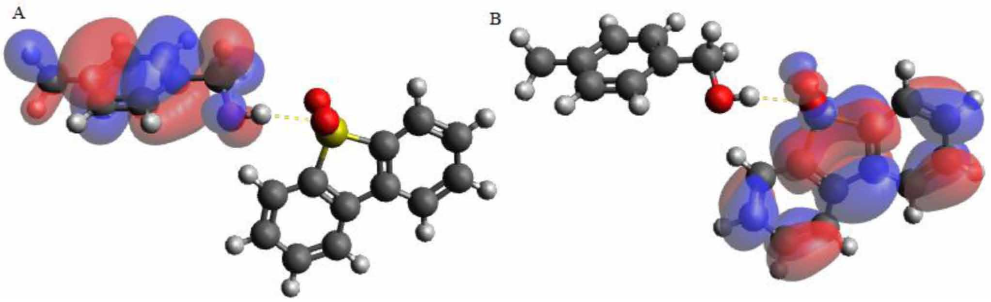
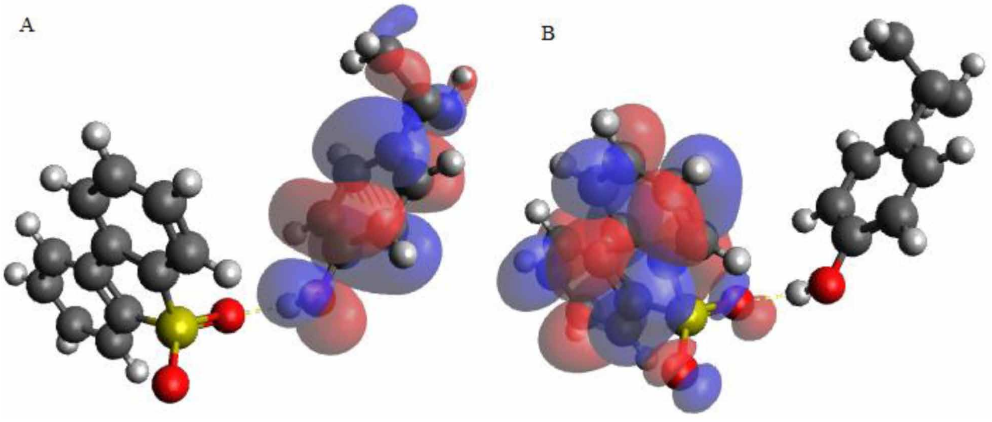


Figure 30. HOMO and LUMO locations of PVP-dibenzothiophene (PVP-DBTO$_2$) adduct: (A) HOMO and (B) LUMO; red, sulfur and grey colours represent oxygen, yellow and carbon atoms respectively.



NOTES AND PERSPECTIVES

The heightened concerns for cleaner fuel and the increasingly strict regulations on sulfur contents in fuels have made the desulfurization process progressively more important. The sulfur problem is becoming more serious as most of the oil reserves are sourer, i.e. they possess a high sulfur content. Researchers are continually exploring possible ways of removing organosulfur compounds in fuels without compromising the fuel properties. Sulfur compounds in fuel are mostly hydro-treated but this is not sufficient to achieve the ultra-low levels without compromising the fuel properties. In recent studies, refractory organosulfur compounds in fuels are oxidized by employing a heterogeneous catalyst followed by separation of the oxidized sulfur compounds using imprinted polymers, metal organic frameworks (MOFs) or solvents to remove the organosulfones. This process is termed oxidative desulfurization, and it shows great promise for the future of the fuel industry. Progress has also been made in the use of bacteria to

Figure 31. HOMO and LUMO locations of PBI-4,6-dimethyldibenzothiophene (PBI-4,6-DMDBTO$_2$) adduct: (A) HOMO and (B) LUMO; red, blue, yellow and grey colours represent oxygen, nitrogen, sulfur and carbon atoms respectively.

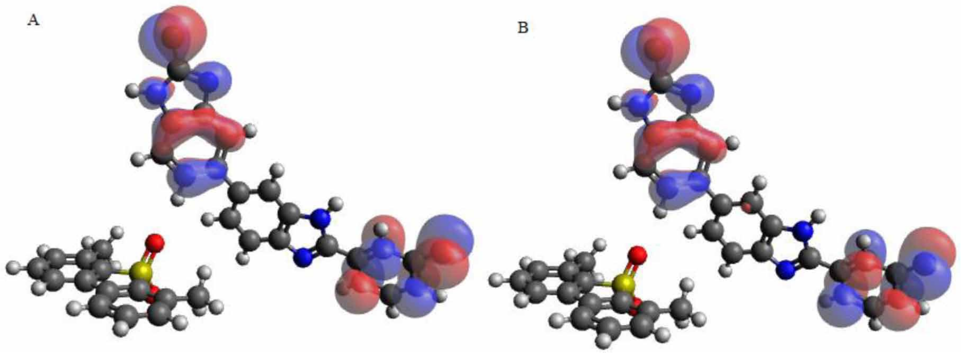


Figure 32. HOMO and LUMO locations of chitosan-4,6-dimethyldibenzothiophene (chitosan-4,6-DMDBTO$_2$*) adduct: (A) HOMO and (B) LUMO; red, blue, yellow and grey colours represent oxygen, nitrogen, sulfur and carbon atoms respectively.*

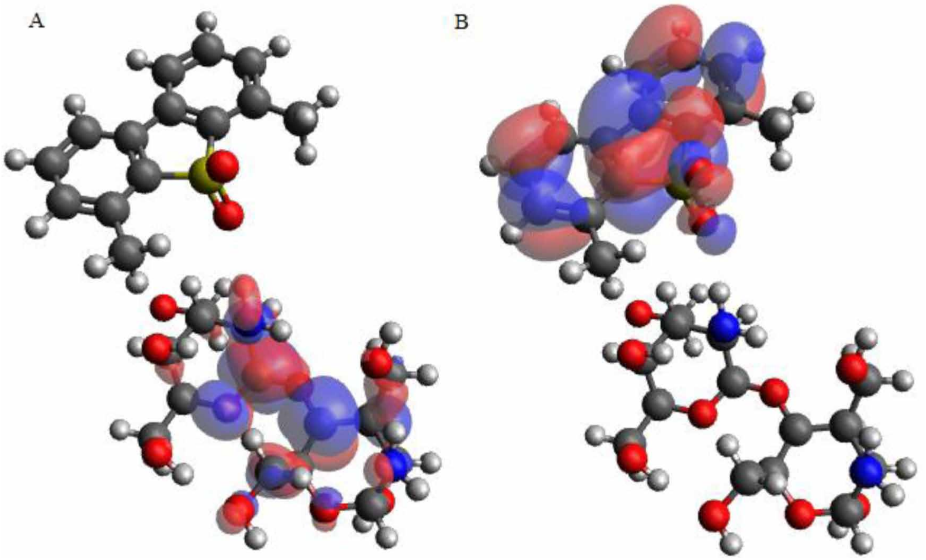
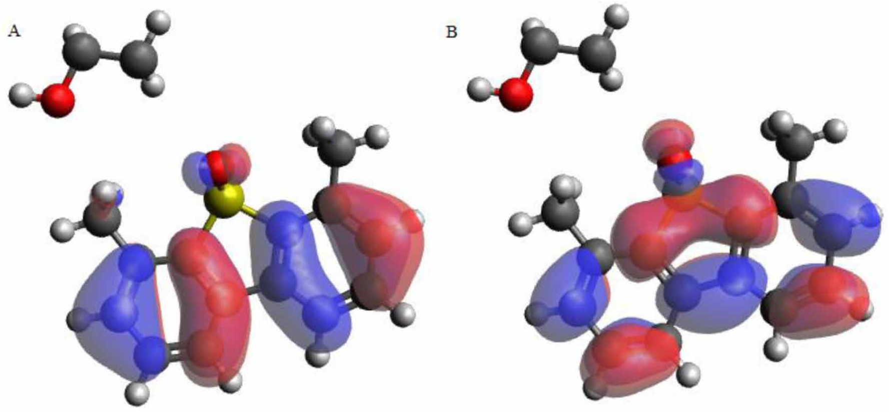


Figure 33. HOMO and LUMO locations of PVA-4,6-dimethyldibenzothiophene (PVA-4,6-DMDBTO$_2$*) adduct: (A) HOMO and (B) LUMO; red, yellow and grey colours represent oxygen, sulfur and carbon atoms respectively.*



remove sulfur from fossil fuels *via* a process known as biodesulfurization. New approaches, for example those applying nanomaterials such as molecularly imprinted nanofibers for selective adsorptive removal of organosulfur compounds in fuels, are necessary for production of affordable ultraclean transportation fuels. However, research in this area is at its infancy stages and requires more extensive investigations. A systematic approach in selecting a suitable polymer for the adsorptive removal of oxidized refractory organosulfur compounds from fuel can be addressed *via* DFT calculations in order to understand the underlying chemical interactions. This chapter has demonstrated the positive aspects of this approach.

Figure 34. HOMO and LUMO locations of PVBA-4,6-dimethyldibenzothiophene (PVBA-4,6-DBTO$_2$) adduct: (A) HOMO and (B) LUMO; red, sulfur and grey colours represent oxygen, yellow and carbon atoms respectively.

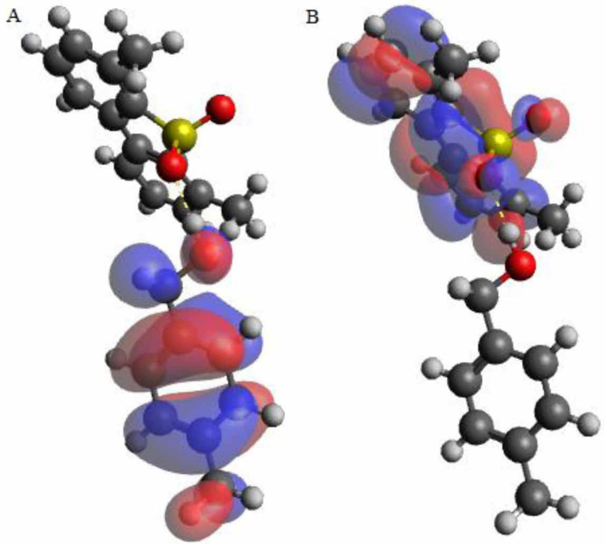
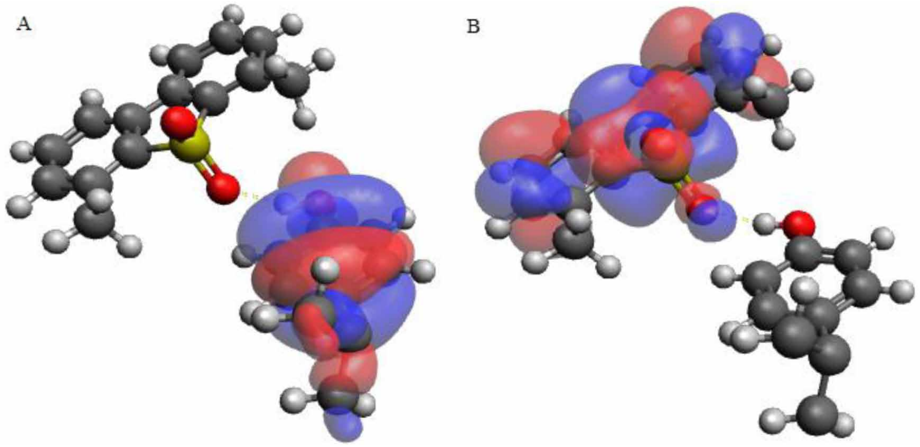


Figure 35. HOMO and LUMO locations of PVP-4,6-dimethyldibenzothiophene (PVP-4,6-DBTO$_2$) adduct: (A) HOMO and (B) LUMO; red, sulfur and grey colours represent oxygen, yellow and carbon atoms respectively.



However, from a technology transfer point of view, the development and implementation of the ODS process as an alternative for production of ultra-low sulfur fuel is still a challenge for both academia and industry. The cost of the additional units for ODS (for the oxidation and adsorption steps) to complement HDS presents a major challenge for the fuel industry. This will also have a negative effect on fuel prices for the ordinary consumer. It remains a challenge for academia to convince the conservative fuel industry of the possibilities of the technologies discussed in this chapter. The nanofiber production houses have provided a space for developments in the area of large scale fabrication of functional nanofibers,

Table 3. DFT modelling studies on the formation of adducts between organosulfone compounds with imprinted polymers (ΔΔH, ΔΔG and ΔΔS adduct)

Polymer	ΔΔH (kcal.Mol^{-1})		ΔΔG (kcal.Mol^{-1})		ΔΔS (Cal.Mol^{-1})	
	$DBTO_2$	4,6-$DMDBTO_2$	$DBTO_2$	4,6-$DMDBTO_2$	$DBTO_2$	4,6$DMDBTO_2$
PBI	-13.3	-13.6	-2.7	-2.5	-35.4	-37.5
Chitosan	-5.6	-4.7	4.8	5.9	-34.9	-35.7
PVA	0.1	12.6	0	43.9	0.1	0
PVP	1.3	17.3	21.4	57.2	-0.6	0.2
PVBA	-11.7	-26.2	0.1	20.5	-11.8	-57.1

and the medical applications have dominated this space. It is desirable that the fuel industry can find possibilities for this technology, and it will be the role of academia to present attractive solutions in this regard. This chapter, therefore, attempts to introduce the chemical and materials development aspect of the molecularly imprinted nanofiber technology and to present it as a prospective alternative for extraction of polar organosulfones from oxidized hydrotreated fuel.

REFERENCES

Abdullah, W., Nazwanie, W., Bakar, W. A., Azelee, W., Rusmidah, A., & Zaidi, E. (2015). Oxidative desulfurization of commercial diesel catalyzed by *tert*-butyl hydroperoxide polymolybdate on alumina: Optimization by Box-Behnken design. *Clean Technologies and Environmental Policy*, *17*(2), 433–441. doi:10.1007/s10098-014-0797-5

Aida, T., & Yamamoto, D. (1994). Annual book of ASTM standards, 2005. Standard test method for determination of sulfur compounds in natural gas and gaseous fuels by gas chromatography and chemiluminescence. *Preprints of Papers- American Chemical Society. Division of Fuel Chemistry*, *39*(5), 623.

Andersson, J. T., Panda, S. K., & Schrader, W. (2007). Analysis of large sulfur aromatic compounds in fossil fuels by FT-ICR MS. In O. R. Koseoglu & S. Kasztelan (Eds.), *Hydrotreating/Hydrocracking Processing*. Washington, D.C.: American Chemical Society.

Andersson, J. T., & Schade, T. (2006). Speciation of alkylated dibenzothiophenes in a deeply desulfurized diesel fuel. *Energy & Fuels*, *20*(4), 1614–1620. doi:10.1021/ef0502507

Ania, C. O., & Bandosz, T. J. (2006). Metal-loaded polystyrene-based activated carbons as dibenzothiophene removal media via reactive adsorption. *Carbon*, *44*(12), 2404–2412. doi:10.1016/j.carbon.2006.05.016

Anisimov, A. V., Fedorova, E. V., Lesnugin, A. Z., Senyavin, V. M., Aslanov, L. A., Rybakov, V. B., & Tarakanova, A. V. (2003). Vanadium peroxocomplexes as oxidation catalysts of sulfur organic compounds by hydrogen peroxide in bi-phase systems. *Catalysis Today*, *78*(1-4), 319–325. doi:10.1016/S0920-5861(02)00311-5

Babich, V. I., & Moulijn, J. A. (2003). Science and technology of novel processes for deep desulfurization of oil refinery streams: A review. *Fuel*, *82*(6), 607–631. doi:10.1016/S0016-2361(02)00324-1

Barbara, P., Rufino, M. N., Campos-Martin, J. M., & Fierro, J. L. G. (2011). Towards near zero-sulfur liquid fuels: A perspective review. *Catalysis Science & Technology*, *1*(1), 23–42. doi:10.1039/c0cy00049c

Baxendale, J. H., Evans, M. G., & Park, G. S. (1946). The mechanism and kinetics of the initiation of polymerisation by systems containing hydrogen peroxide. *Transactions of the Faraday Society*, *42*, 155–169. doi:10.1039/tf9464200155

Bhandari, V. M., Ko, C. H., Park, J. G., Han, S., Cho, S., & Kim, J. (2006). Desulfurization of diesel using ion-exchanged zeolites. *Chemical Engineering Science*, *61*(8), 2599–2608. doi:10.1016/j.ces.2005.11.015

Blanco-Brieva, G., Campos-Martin, J. M., Al-Zahrani, S. M., & Fierro, J. L. G. (2011). Effectiveness of metal–organic frameworks for removal of refractory organo-sulfur compound present in liquid fuels. *Fuel*, *90*(1), 190–197. doi:10.1016/j.fuel.2010.08.008

Blanco-Brieva, G., Campos-Martin, J. M., Al-Zahrani, S. M., & Fierro, J. L. G. (2013). Thermal regeneration of the metal organic frameworks used in the adsorption of refractory organosulfur compounds from liquid fuels. *Fuel*, *105*, 459–465. doi:10.1016/j.fuel.2012.08.003

Booth, B., Buglass, J. G., & Unsworth, J. F. (2001). Tailoring fuels for the new millennium. *Topics in Catalysis*, *16-17*(1/4), 39–46. doi:10.1023/A:1016670528451

Campestrini, S., Conte, V., Di Furia, F., Modena, G., & Bortolini, O. (1988). Metal catalysis in oxidation by peroxides. 30. Electrophilic oxygen transfer from anionic, coordinatively saturated molybdenum peroxo complexes. *The Journal of Organic Chemistry*, *53*(24), 5721–5724. doi:10.1021/jo00259a021

Campos-Martin, J. M., Capel-Sanchez, M. C., Perez-Presas, P., & Fierro, J. L. G. (2010). Oxidative processes of desulfurization of liquid fuels. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *85*(7), 879–890. doi:10.1002/jctb.2371

Castro, B., Whitcombe, M. J., Vulfson, E. N., Vazquez-Duhalt, R., & Barzana, E. (2001). Molecular imprinting for the selective adsorption of organosulfur compounds present in fuels. *Analytica Chimica Acta*, *435*(1), 83–90. doi:10.1016/S0003-2670(01)00799-1

Chang, J. H., Chang, Y. K., Cho, K. S., & Chang, H. N. (2000). Desulfurization of model and diesel oils by resting cells of Gordona sp. *Biotechnology Letters*, *22*(3), 193–196. doi:10.1023/A:1005637013879

Chang, J. H., Rhee, S. K., Chang, Y. K., & Chang, H. N. (1998). Desulfurization of diesel oils by a newly isolated dibenzothiophene-degrading Norcadia sp. strain CYKS2. *Biotechnology Progress*, *14*(6), 851–855. doi:10.1021/bp9800788 PMID:9841646

Chen, H., & Hsieh, Y. L. (2004). Ultrafine hydrogel fibers with dual temperature- and pH-responsive swelling behaviors. *Journal of Polymer Science. Part A, Polymer Chemistry*, *42*(24), 6331–6339. doi:10.1002/pola.20461

Chica, A., Corma, A., & Dómine, M. E. (2006). Catalytic oxidative desulfurization (ODS) of diesel fuel on a continuous fixed-bed reactor. *Journal of Catalysis*, *242*(2), 299–308. doi:10.1016/j.jcat.2006.06.013

Chica, A., Gatti, G., Moden, B., Marchese, L., & Iglesia, E. (2006). Selective catalytic oxidation of organosulfur compounds with *tert*-butylhydroperoxide. *Chemistry (Weinheim an der Bergstrasse, Germany)*, *12*(7), 1960–1967. doi:10.1002/chem.200500858 PMID:16385590

Chong, E. J., Phan, T. T., Lim, I. J., Zhang, Y. Z., Bay, B. H., Ramakrishna, S., & Lim, C. T. (2007). Evaluation of electrospun PCL/gelatin nanofibrous scaffold for wound healing and layered dermal reconstitution. *Acta Biomaterialia*, *3*(3), 321–330. doi:10.1016/j.actbio.2007.01.002 PMID:17321811

Collins, F. M., Lucy, A. R., & Sharp, C. (1997). Oxidative desulfurization of oils via hydrogen peroxide and heteropolyanion catalysis. *Journal of Molecular Catalysis A Chemical*, *117*(1-3), 397–403. doi:10.1016/S1381-1169(96)00251-8

Crude oil reserves and spatial distribution. (n. d.). Retrieved from http://web2.mendelu.cz/af_291_projekty2/vseo/stranka.php?kod=312

Darian, S. T., & Arabshshi, S. H. (1988). Process for upgrading diesel oils. US Patent 4746420.

Dasgupta, S., Gupta, P., Anshu, A., Nanoti, A. N., Goswami, M. O., Garg, E. T., & Stöcker, M. et al. (2013). Adsorptive desulfurization of diesel by regenerable nickel based adsorbents. *Fuel*, *108*, 184–189. doi:10.1016/j.fuel.2012.12.060

Davis, F. J. (2004). Polymer chemistry-A practical approach. Oxford University Press, Great Clarendon Street, Oxford OX2 6DP. pp 19-21

Dekker, M., Yocum, R.H., & Nyquist, E.B. (1973). Functional monomers; their preparation, polymerization, and application. Michigan, USA. ISBN-0824718100, 9780824718107.

Demir, M. M., Yilgor, I., Yilgor, E., & Erman, B. (2002). Electrospinning of polyurethane fibers. *Polymer*, *43*(11), 3303–3309. doi:10.1016/S0032-3861(02)00136-2

Di-Giuseppe, A., Crucianelli, M., De Angelis, F., Crestini, C., & Saladino, R. (2009). Efficient oxidation of thiophene derivatives with homogeneous and heterogeneous MTO/H_2O_2 systems: A novel approach for, oxidative desulfurization (ODS) of diesel fuel. *Applied Catalysis B: Environmental*, *89*(1-2), 239–245. doi:10.1016/j.apcatb.2009.02.009

Ding, B., Kim, H. Y., Lee, S. C., Shao, C. L., Lee, D. R., Park, S. J., & Choi, K. J. et al. (2002). Preparation and characterization of a nanoscale poly(vinyl alcohol) fiber aggregate produced by an electrospinning method. *Journal of Polymer Science. Part B, Polymer Physics*, *40*(13), 1261–1268. doi:10.1002/polb.10191

Ding, B., Kimura, E., Sato, T., Fujita, S., & Shiratori, S. (2004). Fabrication of blend biodegradable nanofibrous nonwoven mats via multi-jet electrospinning. *Polymer*, *45*(6), 1895–1902. doi:10.1016/j.polymer.2004.01.026

Djangkung, S., Murti, S., Yang, H., Choi, K., Kora, Y., & Mochida, I. (2003). Influences of nitrogen species on the hydrodesulfurization reactivity of a gas oil over sulfide catalysts of variable activity. *Applied Catalysis A, General*, *252*(2), 331–346. doi:10.1016/S0926-860X(03)00468-X

Doshi, J., & Reneker, D. H. (1995). Electrospinning process and applications of electrospun fibers. *Journal of Electrostatics*, *35*(2-3), 151–160. doi:10.1016/0304-3886(95)00041-8

Dreizler, R. M., & Gross, E. K. U. (1990). *Density functional theory*. Berlin: Springer. doi:10.1007/978-3-642-86105-5

Duan, B., Dong, C. H., Yuan, X. Y., & Yao, K. D. (2004). Electrospinning of chitosan solutions in acetic acid with poly(ethylene oxide). *Journal of Biomaterials Science. Polymer Edition*, *15*(6), 797–811. doi:10.1163/156856204774196171 PMID:15255527

Dzenis, Y. (2004). Spinning continuous fibers for nanotechnology. *Science*, 304, 1917-1919. EPA sulfur distribution. Retrieved January 28, 2013, from http://www.eia.gov/todayinenergy/detail.cfm?id=7110

El-Newehy, M.H., Al, D.S.S., Kenawy, E.R., & Abdel, M.A. (2011) Nanospider technology for the production of nylon 6-nanofibers for biomedical applications. *Journal of Nanomaterial* 1-8.

Fariba, G., Vasheghani-Farahani, S., & Vasheghani-Farahani, E. (2010). Theoretical description of hydrogel swelling: A review. *Iranian Polymer Journal*, *19*, 375–398.

Fong, H., Chun, I., & Reneker, D. H. (1999). Beaded nanofibers formed during electrospinning. *Polymer*, *40*(16), 4585–4592. doi:10.1016/S0032-3861(99)00068-3

Geng, X. Y., Kwon, O. H., & Jang, J. H. (2005). Electrospinning of chitosan dissolved in concentrated acetic acid solution. *Biomaterials*, *26*(27), 5427–5432. doi:10.1016/j.biomaterials.2005.01.066 PMID:15860199

Gupta, P., Elkins, C., Long, T. E., & Wilkes, G. L. (2005). Electrospinning of linear homopolymers of poly(methyl methacrylate): Exploring relationships between fiber formation, viscosity, molecular weight and concentration in a good solvent. *Polymer*, *46*(13), 4799–4810. doi:10.1016/j.polymer.2005.04.021

Hallensleben, M. L. (2000). *Polyvinyl compounds*, others. In *Ullmann's encyclopedia of industrial chemistry*. Weinheim: Wiley-VCH; doi:10.1002/14356007.a21_743

Haupt, K. (2003). Molecularly imprinted polymers: The next generation. *Analytical Chemistry*, *75*(17), 376A–383A. doi:10.1021/ac031385h PMID:14632031

Hernandez-Maldonado, A. J., Qi, G., & Yang, R. T. (2005). Desulfurization of commercial fuels by p-complexation monolayer CuCl/g-Al_2O_3. *Applied Catalysis B: Environmental*, *61*(3-4), 212–218. doi:10.1016/j.apcatb.2005.05.003

Hernańdez-Maldonado, A. J., Stamatis, S. D., Yang, R. T., He, A. Z., & Cannella, W. (2004). New sorbents for desulfurization of diesel fuels via p-complexation: Layered beds and regeneration. *Industrial & Engineering Chemistry Research*, *43*(3), 769–776. doi:10.1021/ie034108+

Hernańdez-Maldonado, A. J., & Yang, R. T. (2004). Desulfurization of diesel fuels via π-complexation with nickel(II)-exchanged X- and Y-zeolites. *Industrial & Engineering Chemistry Research*, *43*(4), 1081–1089. doi:10.1021/ie034206v

Hernandez-Maldonado, A. J., & Yang, R. T. (2004). Desulfurization of diesel fuels by adsorption *via* π-complexation with vapor-phase exchanged Cu(I)-Y zeolites. *Journal of the American Chemical Society*, *126*(4), 992–993. doi:10.1021/ja039304m PMID:14746446

Heunis, T., Bshena, O., Klumperman, B., & Dicks, L. (2011). Release of bacteriocins from nanofibers prepared with combinations of poly(D,L-lactide) (PDLLA) and poly(ethylene oxide) (PEO). *International Journal of Molecular Sciences*, *12*(12), 2158–2173. doi:10.3390/ijms12042158 PMID:21731433

Heunis, T. D. J., Botes, M., & Dicks, L. M. T. (2010). Encapsulation of *Lactobacillus plantarum* 423 and its bacteriocin in nanofibers. *Probiotics and Antimicrobial Proteins*, *2*(1), 46–51. doi:10.1007/s12602-009-9024-9

Heunis, T. D. J., & Dicks, L. M. T. (2010). Nanofibers offer alternative ways to the treatment of skin infections. *Journal of Biomedicine & Biotechnology*, *2010*, 1–10. doi:10.1155/2010/510682 PMID:20798871

Hizaddin, H. F., Hashim, M. A., & Anantharaj, R. (2013). Evaluation of molecular interaction in binary mixture of ionic liquids+ heterocyclic nitrogen compounds: Ab Initio method and COSMORS model. *Industrial & Engineering Chemistry Research*, *52*(50), 18043–18058. doi:10.1021/ie403032t

Holmes, A. B., & Stephenson, G. R. (1994). Molecular imprinting. *Chemistry & Industry*, *18*, 304.

Huang, L., Nagapudi, K., Apkarian, R. P., & Chaikof, E. L. (2001). Engineered collagen-PEO nanofibers and fabrics. *Journal of Biomaterials Science. Polymer Edition*, *12*, 979–993. doi:10.1163/156856201753252516 PMID:11787524

Huang, Z. M., Zhang, Y. Z., Kotaki, M., & Ramakrishna, S. (2003). A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Composites Science and Technology*, *63*(15), 2223–2253. doi:10.1016/S0266-3538(03)00178-7

Hulea, V., Fajula, F., & Bousquet, J. (2001). Mild oxidation with H_2O_2 over Ti-containing molecular sieves-a very efficient method for removing aromatic sulfur compounds from fuels. *Journal of Catalysis*, *198*(2), 179–186. doi:10.1006/jcat.2000.3149

Isarankura-Na-Ayudhya, C., Nantasenamat, C., Buraparuangsang, P., Piacham, T., Ye, L., Bülow, L., & Prachayasittikul, V. (2008). Computational insights on sulfonamide imprinted polymers. *Molecules (Basel, Switzerland)*, *13*(12), 3077–3091. doi:10.3390/molecules13123077 PMID:19078850

Ishihara, A., Wang, D. H., Dumeignil, F., Amano, H., Qian, E. W. H., & Kabe, T. (2005). Oxidative desulfurization and denitrogenation of a light gas oil using an oxidation/adsorption continuous flow process. *Applied Catalysis A, General*, *279*(1-2), 279–287. doi:10.1016/j.apcata.2004.10.037

Jarusuwannapoom, T., Hongroijanawiwat, W., Jitjaicham, S., Wannatong, L., Nithitanakul, M., Pattamaprom, C., & Supaphol, P. et al. (2005). Effect of solvents on electro-spinnability of polystyrene solutions and morphological appearance of resulting electrospun polystyrene fibers. *European Polymer Journal*, *41*(3), 409–421. doi:10.1016/j.eurpolymj.2004.10.010

Jeon, H., Ko, C. H., Kim, S. H., & Kim, J. (2009). Removal of refractory sulphur compounds in diesel using activated carbon with controlled porosity. *Energy & Fuels*, *23*(5), 2537–2543. doi:10.1021/ef801050k

Jiang, H. L., Fang, D. F., Hsiao, B. S., Chu, B., & Chen, W. L. (2004). Optimization and characterization of dextran membranes prepared by electrospinning. *Biomacromolecules*, *5*(2), 326–333. doi:10.1021/bm034345w PMID:15002991

Jiang, Z., Lu, H., Zhang, Y., & Li, C. (2011). Oxidative desulfurization of fuel oils. *Chinese Journal of Catalysis*, *32*(5), 707–715. doi:10.1016/S1872-2067(10)60246-X

Jorge, A., & Le Borgne, S. (2004). Selective adsorption of dibenzothiophene sulfone by an imprinted and stimuli-responsive chitosan hydrogel. *Macromolecules*, *37*(8), 2938–2943. doi:10.1021/ma049961e

Karas, L. J., Grey, R. A., & Lynch, M. W. (2008). *Desulfurization process*. US Patent 2008047875.

Karas, L. J., Han, Y. Z., & Leyshon, D. W. (2004). *Organosulfur oxidation process*. US Patent 2004178122.

Ki, C. S., Baek, D. H., Gang, K. D., Lee, K. H., Um, I. C., & Park, Y. H. (2005). Characterization of gelatin nanofiber prepared from gelatin-formic acid solution. *Polymer*, *46*(14), 5094–5102. doi:10.1016/j.polymer.2005.04.040

Kidoaki, S., Kwon, I. K., & Matsuda, T. (2005). Mesoscopic spatial designs of nano- and micron-fiber meshes for tissue-engineering matrix and scaffold based on newly devised multilayering and mixing electrospinning techniques. *Biomaterials*, *26*(1), 37–46. doi:10.1016/j.biomaterials.2004.01.063 PMID:15193879

Kim, B., Park, H., Lee, S. H., & Sigmund, W. M. (2005). Poly(acrylic acid) nanofibers by electrospinning. *Materials Letters*, *59*(7), 829–832. doi:10.1016/j.matlet.2004.11.032

Kim, H. S., Kim, K., Jin, H. J., & Chin, I. J. (2005). Morphological characterization of electrospun nanofibrous membranes of biodegradable poly(L-lactide) and poly(lactideco-glycolide). *Macromolecular Symposia*, *224*(1), 145–154. doi:10.1002/masy.200550613

Kim, J., Ma, X., Zhou, A., & Song, C. (2006). Ultra-deep desulfurization and denitrogenation of diesel fuel by selective adsorption over three different adsorbents: A study on adsorptive selectivity and mechanism. *Catalysis Today*, *111*(1-2), 74–83. doi:10.1016/j.cattod.2005.10.017

Kim, J. H., Ma, X., Zhou, A., & Song, C. (2006). Ultra-deep desulfurization and denitrogenation of diesel fuel by selective adsorption over three different adsorbents: A study on adsorptive selectivity and mechanism. *Catalysis Today*, *111*(1-2), 74–83. doi:10.1016/j.cattod.2005.10.017

King, D. L., & Li, L. (2006). Removal of sulfur components from low sulfur gasoline using copper exchanged zeolite Y at ambient temperature. *Catalysis Today*, *116*(4), 526–529. doi:10.1016/j.cattod.2006.06.026

Klobes, P., Meyer, K., & Munro, R. G. (2006). Porosity and specific surface area measurements for solid materials. *National Institute of Standards and Technology Special Publication*, *89*, 960–917.

Kocal, J. A., & Branvold, T. A. (2002). *Removal of sulfur-containing compounds from liquid hydrocarbon streams*. US Patent 6368495.

Kodama, K., Umehara, K., Shimizu, K., Nakatani, S., Minoda, Y., & Yamada, K. (1973). Identification of microbial products from dibenzothiophene and its proposed oxidation pathway. *Agricultural and Biological Chemistry*, *37*(1), 45–50. doi:10.1271/bbb1961.37.45

Koski, A., Yim, K., & Shivkumar, S. (2004). Effect of molecular weight on fibrous PVA produced by electrospinning. *Materials Letters*, *58*(3-4), 493–497. doi:10.1016/S0167-577X(03)00532-9

Kumar, A. (2010). *Nanofibers*. Vukovar: Intech. doi:10.5772/45660

Kuznetsova, L., Detusheva, L., Kuznetsov, N., Duplyakin, V., & Likholobov, V. (2008). Liquid-phase oxidation of benzothiophene and dibenzothiophene by cumyl-hydroperoxide in the presence of catalysts based on supported metal oxides. *Kinetics and Catalysis*, *49*(5), 644–652. doi:10.1134/S002315840805008X

Lee, J. S., Choi, K. H., Do Ghim, H., Kim, S. S., Chun, D. H., Kim, H. Y., & Lyoo, W. S. (2004). Role of molecular weight of a tactic poly(vinyl alcohol) (PVA) in the structure and properties of PVA nanofabric prepared by electrospinning. *Journal of Applied Polymer Science*, *94*(4), 1638–1646. doi:10.1002/app.20602

Lin, T., Wang, H. X., Wang, H. M., & Wang, X. G. (2004). The charge effect of cationic surfactants on the elimination of fibre microspheres in the electrospinning of polystyrene. *Nanotechnology*, *15*(9), 1375–1381. doi:10.1088/0957-4484/15/9/044

Liu, B. S., Xu, D. F., Chu, J. X., Liu, W., & Au, C. T. (2007). Deep desulfurization by the adsorption process of fluidized catalytic cracking (FCC) diesel over mesoporous Al-MCM- 41 materials. *Energy & Fuels*, *21*(1), 250–255. doi:10.1021/ef060249n

Liu, J., & Kumar, S. (2005). Microscopic polymer cups by electrospinning. *Polymer*, *46*(10), 3211–3214. doi:10.1016/j.polymer.2004.11.116

Ma, X., Lu, S., Yin, Z., & Song, C. (2001). New approaches to deep desulfurization of diesel fuel, jet fuel, and gasoline by adsorption for ultra-clean fuels and for fuel cell applications. *American Chemical Society. Division of Fuel Chemistry*, *46*(2), 648–649.

Ma, X., Sakanishi, K., Isoda, T., & Mochida, I. (1995). Quantum chemical calculation on the desulfurization reactivities of heterocyclic sulfur compounds. *Energy & Fuels*, *9*(1), 33–37. doi:10.1021/ef00049a005

Ma, X., Sakanishi, K., & Mochida, I. (1994). Hydrodesulfurization reactivities of various sulfur compounds in diesel fuel. *Industrial & Engineering Chemistry Research*, *33*(2), 218–222. doi:10.1021/ie00026a007

Ma, X., Sakanishi, K., & Mochida, I. (1996). Hydrodesulfurization reactivities of various sulfur compounds in vacuum gas oil. *Industrial & Engineering Chemistry Research*, *35*(8), 2487–2494. doi:10.1021/ie960137r

Meyer, K., Klobes, P., & Röhl-Kuhn, B. (1997). Certification of reference material with special emphasis on porous solids. *Crystal Research and Technology*, *32*(1), 173–183. doi:10.1002/crat.2170320118

Mit-Uppatham, C., Nithitanakul, M., & Supaphol, P. (2004). Ultrafine electrospun polyamide-6 fibers: Effect of solution conditions on morphology and average fiber diameter. *Macromolecular Chemistry and Physics*, *205*(17), 2327–2338. doi:10.1002/macp.200400225

Miyazaki, T., Takeda, Y., Akane, S., Itou, T., Hoshiko, A., & En, K. (2010). Role of boric acid for a poly (vinyl alcohol) film as a cross-linking agent: Melting behaviors of the films with boric acid. *Polymer*, *51*(23), 5539–5549. doi:10.1016/j.polymer.2010.09.048

Mokhtar, W. N. A. W., Bakar, W. A. W. A., Ali, R., & Abdul-Kadir, A. A. (2014). Deep desulfurization of model diesel by extraction with *N,N*-dimethylformamide: Optimization by Box–Behnken design. *Journal of the Taiwan Institute of Chemical Engineers*, *45*(4), 1542–1548. doi:10.1016/j.jtice.2014.03.017

Monteiro, O. A. C. Jr, & Airoldi, C. (1999). Some studies of crosslinking chitosan–glutaraldehyde interaction in a homogeneous system. *International Journal of Biological Macromolecules*, *26*(2-3), 119–128. doi:10.1016/S0141-8130(99)00068-9 PMID:10517518

Mosbach, K. (1994). Molecular imprinting. *Trends in Biochemical Sciences*, *19*(1), 9–14. doi:10.1016/0968-0004(94)90166-X PMID:8140624

Nantasenamat, C., Isarankura-Na-Ayudhya, C., Naenna, T., & Prachayasittikul, V. (2007). Quantitative structure-imprinting factor relationship of molecularly imprinted polymers. *Biosensors & Bioelectronics*, *22*(12), 3309–3317. doi:10.1016/j.bios.2007.01.017 PMID:17317143

Nantasenamat, C., Naenna, T., Isarankura Na Ayudhya, C., & Prachayasittikul, V. (2005). Quantitative prediction of imprinting factor of molecularly imprinted polymers by artificial neural network. *Journal of Computer-Aided Molecular Design*, *19*(7), 509–524. doi:10.1007/s10822-005-9004-4 PMID:16244792

Nantasenamat, C., Tantimongcolwat, T., Naenna, T., Isarankura-Na-Ayudhya, C., & Prachayasittikul, V. (2006). Prediction of selectivity index of pentachlorophenol-imprinted polymers. *EXCLI Journal*, *5*, 150–163.

Ngah, W. S. W., & Liang, K. H. (1999). Adsorption of gold(III) ions onto chitosan and *N*-carboxymethyl chitosan: Equilibrium studies. *Industrial & Engineering Chemistry Research*, *38*(4), 1411–1414. doi:10.1021/ie9803164

Nicholls, I. A., Adbo, K., Andersson, H. S., Andersson, P. O., Ankarloo, J., Hedin-Dahlström, J., & Wikman, S. et al. (2001). Can we rationally design molecularly imprinted polymers? *Analytica Chimica Acta*, *435*(1), 9–18. doi:10.1016/S0003-2670(01)00932-1

Nolte, T., Posch, T. N., Huhn, C., & Andersson, J. T. (2013). Desulfurized fuels from Athabasca bitumen and their polycyclic aromatic sulfur heterocycles. Analysis based on capillary electrophoresis coupled with TOF MS. *Energy & Fuels*, *27*(1), 97–107. doi:10.1021/ef301424d

Ogunlaja, A. S., Coombes, M. J., Torto, N., & Tshentu, Z. R. (2014). The adsorptive extraction of oxidised sulfur-containing compounds from fuels by using molecularly imprinted chitosan materials. *Reactive & Functional Polymers*, *81*, 61–76. doi:10.1016/j.reactfunctpolym.2014.04.006

Ogunlaja, A. S., du Sautoy, C. W., Torto, N., & Tshentu, Z. R. (2014). Design, fabrication and evaluation of intelligent sulfone-selective polybenzimidazole nanofibers. *Talanta*, *126*, 61–72. doi:10.1016/j.talanta.2014.03.035 PMID:24881535

Ogunlaja, A. S., Khene, S., Antunes, E., Nyokong, T., Torto, N., & Tshentu, Z. R. (2013). The development of catalytic oxovanadium(IV)-containing microspheres for the oxidation of various organosulfur compounds. *Applied Catalysis A, General*, *462-463*, 157–167. doi:10.1016/j.apcata.2013.05.004

Ogunlaja, A. S., Walmsley, R. S., du Sautoy, C. W., Torto, N., & Tshentu, Z. R. (2013). Development of a continuous flow system for the oxidative desulfurization of refractory organosulfur compounds in hydrotreated diesel. *Energy & Fuels*, *27*(12), 7714–7723. doi:10.1021/ef401708f

Otsuki, S., Nonaka, T., Qian, W., Ishihara, A., & Kabe, T. (1999). Oxidative desulfurization of middle distillate using ozone. *Journal of the Japan Petroleum Institute*, *42*(5), 315–320. doi:10.1627/jpi1958.42.315

Otsuki, S., Nonaka, T., Takashima, N., Qian, W., Ishihara, A., Imai, T., & Kabe, T. (2000). Oxidative desulfurization of light gas oil and vacuum gas oil by oxidation and solvent extraction. *Energy & Fuels*, *14*(6), 1232–1239. doi:10.1021/ef000096i

Palomeque, J., Clacens, J. M., & Figueras, F. (2002). Oxidation of dibenzothiophene by hydrogen peroxide catalysed by solid bases. *Journal of Catalysis*, *211*(1), 103–108. doi:10.1016/S0021-9517(02)93721-8

Parr, R. G., & Yang, W. (1989). *Density functional theory of atoms and molecules*. Oxford: Oxford University Press.

Paybarah, A., Bone, R. L., & Corcoran, W. H. (1982). Selective oxidation of dibenzothiophene by peroxybenzoic acid formed in situ. *Industrial & Engineering Chemistry Product Research and Development*, *21*(3), 426–431. doi:10.1021/i200018a014

Pearson, R. G. (1986). Absolute electronegativity and hardness correlated with molecular orbital theory. *Proceedings of the National Academy of Sciences of the United States of America*, *83*(22), 8440–8441. doi:10.1073/pnas.83.22.8440 PMID:16578791

Persano, L., Camposeo, A., Tekmen, C., & Pisignano, D. (2013). Industrial upscaling of electrospinning and applications of polymer nanofibers: A review. *Macromolecular Materials and Engineering*, *298*(5), 504–520. doi:10.1002/mame.201200290

Pham, Q. P., Sharma, U., & Mikos, A. G. (2006). Electrospinning of polymeric nanofibers for tissue engineering applications: A review. *Tissue Engineering*, *12*(5), 1197–1211. doi:10.1089/ten.2006.12.1197 PMID:16771634

Prasad, V. V. D. N., Jeong, K. E., Chae, H. J., Kim, C. U., & Jeong, S. Y. (2008). Oxidative desulfurization of 4,6-dimethyl dibenzothiophene and light cycle oil over supported molybdenum oxide catalysts. *Catalysis Communications*, *9*(10), 1966–1969. doi:10.1016/j.catcom.2008.03.021

Reneker, D. H., & Chun, I. (1996). Nanometre diameter fibres of polymer, produced by electrospinning. *Nanotechnology*, *7*(3), 216–223. doi:10.1088/0957-4484/7/3/009

Reneker, D. H., & Yarin, A. L. (2008). Electrospinning jets and polymer nanofibers. *Polymer*, *49*(10), 2837–2425. doi:10.1016/j.polymer.2008.02.002

Ritter, H. L., & Drake, L. C. (1945). Pore size distribution in porous materials. *Industrial & Engineering Chemistry Fundamentals*, *17*, 782–787.

Ruiz, M., Sastre, A. M., & Guibal, E. (2000). Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin. *Reactive & Functional Polymers*, *45*, 155–173. doi:10.1016/S1381-5148(00)00019-5

Ryu, K., Heo, J., & Yoo, I. K. (2002). Removal of dibenzothiophene and its oxidized product in anhydrous water-immiscible organic solvent by immobilized cytochrome c. *Biotechnology Letters*, *24*(2), 143–146. doi:10.1023/A:1013806830105

Sami, M., & Hatch, L. F. (1994). Chemistry of petrochemical processes, Gulf publishing company, Houston, Texas, p11-17.Monticello, D.J. (2000). Biodesulfurization and the upgrading of petroleum distillates. *Current Opinion in Biotechnology*, *11*, 540–546.

Schulz, H., Böhringer, W., Ousmanov, F., & Waller, P. (1999). Refractory sulfur compounds in gas oils. *Fuel Processing Technology*, *61*(1-2), 5–41. doi:10.1016/S0378-3820(99)00028-4

Schulz, H., Böhringer, W., Waller, P., & Ousmanov, F. (1999). Gas oil deep hydrodesulfurization: Refractory compounds and retarded kinetics. *Catalysis Today*, *49*(1-3), 87–97. doi:10.1016/S0920-5861(98)00412-X

Sellergren, B. (2001). *In molecularly imprinted polymers: man-made mimics of antibodies and their applications in analytical chemistry, techniques and instrumentation in analytical chemistry* (Vol. 23, pp. 113–184). Amsterdam: Elsevier.

Shan, J. H., Liu, X. Q., Sun, L. B., & Cui, R. (2008). Cu-Ce Bimetal ion-exchanged Y-Zeolites for selective adsorption of thiophenic sulfur. *Energy & Fuels*, *22*(6), 3955–3959. doi:10.1021/ef800296n

Si, X., Cheng, S., Lu, Y., Gao, G., & He, M. Y. (2008). Oxidative desulfurization of model oil over Au/Ti-MWW. *Catalysis Letters*, *122*(3-4), 321–324. doi:10.1007/s10562-007-9380-6

Sing, K. S. W., Everett, D. H., Haul, R. A., Moscou, L., Pierotti, R. A., Rouquerol, J., & Siemieniewska, T. (1985). Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure and Applied Chemistry*, *57*(4), 603–619. doi:10.1351/pac198557040603

Soleimani, M., Bassi, A., & Margaritis, A. (2007). Biodesulfurization of refractory organic sulfur compounds in fossil fuels. *Biotechnology Advances*, *25*(6), 570–596. doi:10.1016/j.biotechadv.2007.07.003 PMID:17716849

Son, W. K., Youk, J. H., Lee, T. S., & Park, W. H. (2004). The effects of solution properties and polyelectrolyte on electrospinning of ultrafine poly(ethylene oxide) fibers. *Polymer*, *45*(9), 2959–2966. doi:10.1016/j.polymer.2004.03.006

Song, C. (1999). Designing sulfur-resistant, noble-metal hydrotreating catalysts. *Chemtech*, *29*(3), 26–30.

Song, C. (1999). Sulfur-resistant noble metal catalysts based on shape-selective exclusion and hydrogen spillover. In C. Song, J.M. Garces, Y. Sugi, (Eds.), Shape-selective catalysis, chemicals synthesis and hydrocarbon processing (ACS Symposium Series 738), American Chemical Society, Washington, DC (pp. 381-390).

Song, C., & Ma, X. L. (2003). New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization. *Applied Catalysis B: Environmental*, *41*(1-2), 207–238. doi:10.1016/S0926-3373(02)00212-6

Song, C., & Reddy, K. M. (1999). Mesoporous molecular sieve MCM-41 supported Co-Mo catalyst for hydrodesulfurization of dibenzothiophene in distillate fuels. *Applied Catalysis A, General*, *176*(1), 1–10. doi:10.1016/S0926-860X(98)00230-0

Song, C., Turaga, U. T., & Ma, X. (2006) Desulfurization. Encyclopedia of Chemical Processing pp. 651-661 Doi:10.1081/E-ECHP-120007732

Song, C. S. (2003). An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel. *Catalysis Today*, *86*(1-4), 211–263. doi:10.1016/S0920-5861(03)00412-7

Song, C. S., & Ma, X. L. (2004). Ultra-deep desulfurization of liquid hydrocarbon fuels: Chemistry and process. *International Journal of Green Energy*, *1*(2), 167–191. doi:10.1081/GE-120038751

Stellenbosch Nanofiber Company. (n. d.). Retrieved from http://www.sncfibers.com/#!products/c1jm9

Sughrue, E. L., Khare, G. P., Bertus, B. J., & Johnson, M. M. (2001). US Patent 6.254.766.

Tam, P. S., & Kittrell, J. R. (1984). *Process for purifying hydrocarbonaceous oils*.U.S. Patent 4, 485, 007.

Tam, P. S., Kittrell, J. R., & Eldridge, J. W. (1990). Desulfurization of fuel oil by oxidation and extraction. 1. Enhancement of extraction oil yield. *Industrial & Engineering Chemistry Research*, *29*(3), 321–324. doi:10.1021/ie00099a002

Tam, P. S., Kittrell, J. R., & Eldridge, J. W. (1990). Desulfurization of fuel oil by oxidation and extraction. 2. Kinetic modeling of oxidation reaction. *Industrial & Engineering Chemistry Research*, *29*(3), 324–329. doi:10.1021/ie00099a003

Teo, W. E., & Ramakrishna, S. (2005). Electrospun fibre bundle made of aligned nanofibres over two fixed points. *Nanotechnology*, *16*(9), 1878–1884. doi:10.1088/0957-4484/16/9/077

Teo, W. E., & Ramakrishna, S. (2006). A review on electrospinning design and nanofibre assemblies. *Nanotechnology*, *17*(14), 89–106. doi:10.1088/0957-4484/17/14/R01 PMID:19661572

Theron, S. A., Yarin, A. L., Zussman, E., & Kroll, E. (2005). Multiple jets in electrospinning: Experiment and modelling. *Polymer*, *46*(9), 2889–2899. doi:10.1016/j.polymer.2005.01.054

Topsoe, H., Clausen, B. S., & Massoth, F. E. (1996). Hydrotreating catalysis. In *Science and Technology* (p. 310). Berlin: Springer-Verlag.

Torres-García, E., Galano, A., & Rodriguez-Gattorno, G. (2011). Oxidative desulfurization (ODS) of organosulfur compounds catalysed by peroxo-metallate complexes of WOx–ZrO_2: Thermochemical, structural, and reactivity indexes analyses. *Journal of Catalysis*, *282*(1), 201–208. doi:10.1016/j.jcat.2011.06.010

Varesano, A., Carletto, R. A., & Mazzuchetti, G. (2009). Experimental investigations on the electrospinning process. *Journal of Materials Processing Technology*, *209*(11), 5178–5185. doi:10.1016/j.jmatprotec.2009.03.003

Velu, S., Ma, X., & Song, C. (2003). Selective adsorption for removing sulfur from jet fuel over zeolite-based adsorbents. *Industrial & Engineering Chemistry Research*, *42*(21), 5293–5304. doi:10.1021/ie020995p

Venturiello, C., Alneri, E., & Ricci, M. (1983). A new effective catalytic system for epoxidation of olefins by hydrogen peroxide under phase-transfer conditions. *The Journal of Organic Chemistry*, *48*(21), 3831–3833. doi:10.1021/jo00169a052

Walmsley, R. S., Hlangothi, P., Litwinski, C., Torto, N., Nyokong, T., & Tshentu, Z. R. (2012). Catalytic oxidation of thioanisole using oxovanadium(IV)-functionalized electrospun polybenzimidazole nanofibers. *Journal of Applied Polymer Science*, *127*(6), 4719–4725. doi:10.1002/app.38067

Walmsley, R. S., Ogunlaja, A. S., Coombes, M. J., Chidawanyika, W., Litwinski, C., Torto, N., & Tshentu, Z. R. et al. (2012). Imidazole-functionalized polymer microspheres and fibers – useful materials for immobilization of oxovanadium(IV) catalysts. *Journal of Materials Chemistry*, *22*(12), 5792–5800. doi:10.1039/c2jm15485d

Wang, D. H., Qian, E. W. H., Amano, H., Okata, K., Ishihara, A., & Kabe, T. (2003). Oxidative desulfurization of fuel oil - Part I. Oxidation of dibenzothiophenes using *tert*-butylhydroperoxide. *Applied Catalysis A, General*, *253*(1), 91–99. doi:10.1016/S0926-860X(03)00528-3

Wang, Y., & Yang, R. T. (2007). Desulfurization of liquid fuels by adsorption on carbon-based sorbents and ultrasound-assisted sorbent regeneration. *Langmuir*, *23*(7), 3825–3831. doi:10.1021/la063364z PMID:17315903

Wannatong, L., Sirivat, A., & Supaphol, P. (2004). Effects of solvents on electrospun polymeric fibers: Preliminary study on polystyrene. *Polymer International*, *53*(11), 1851–1859. doi:10.1002/pi.1599

Washburn, E. W. (1921). The dynamics of capillary flow. *Physical Review*, *17*(3), 273–283. doi:10.1103/PhysRev.17.273

Whitehurst, D. D., Isoda, T., & Mochida, I. (1998). Present state of the art and future challenges in the hydrodesulfurization of polyaromatic sulfur compounds. *Advances in Catalysis*, *42*, 345–471. doi:10.1016/S0360-0564(08)60631-8

Wulff, G. (1993). The role of binding-site interactions in the molecular imprinting of polymers. *Trends in Biotechnology*, *11*(3), 85–87. doi:10.1016/0167-7799(93)90056-F PMID:7763512

Xiaoliang, M., Lu, S., & Song, C. (2002). A new approach to deep desulfurization of gasoline, diesel fuel and jet fuel by selective adsorption for ultra-clean fuels and for fuel cell applications. *Catalysis Today*, *77*(1-2), 107–116. doi:10.1016/S0920-5861(02)00237-7

Yang, R. T., Hernandez-Maldonado, A. J., & Yang, F. H. (2003). Desulfurization of transportation fuels with zeolites under ambient conditions. *Science*, *301*(5629), 79–81. doi:10.1126/science.1085088 PMID:12843388

Yang, X., Erickson, L. E., Hohn, K. L., Jeevanandam, P., & Klabunde, K. K. (2006). Sol-gel Cu-Al_2O_3 adsorbents for selective adsorption of thiophene out of hydrocarbon. *Industrial & Engineering Chemistry Research*, *45*(18), 6169–6174. doi:10.1021/ie060559t

Yazu, K., Furuya, T., Miki, K., & Ukegawa, K. (2003). Tungstophosphoric acid-catalysed oxidative desulfurization of light oil with hydrogen peroxide in a light oil/acetic acid biphasic system. *Chemistry Letters*, *32*(10), 920–921. doi:10.1246/cl.2003.920

Yazu, K., Yamamoto, Y., Furuya, T., Miki, K., & Ukegawa, K. (2001). Oxidation of dibenzothiophenes in an organic biphasic system and its application to oxidative desulfurization of light oil. *Energy & Fuels*, *15*(6), 1535–1536. doi:10.1021/ef0101412

Yuan, X. Y., Zhang, Y. Y., Dong, C. H., & Sheng, J. (2004). Morphology of ultrafine polysulfone fibers prepared by electrospinning. *Polymer International*, *53*(11), 1704–1710. doi:10.1002/pi.1538

Zahedi, P., Rezaeian, I., Ranaei-Siadat, S. O., Jafari, S. H., & Supaphol, P. (2010). A review on wound dressings with an emphasis on electrospun nanofibrous polymeric bandages. *Polymers for Advanced Technologies*, *21*, 77–95.

Zannikos, F., Lois, E., & Stournas, S. (1995). Desulfurization of petroleum fractions by oxidation and solvent extraction. *Fuel Processing Technology*, *42*(1), 35–45. doi:10.1016/0378-3820(94)00104-2

Zhang, C. X., Yuan, X. Y., Wu, L. L., Han, Y., & Sheng, J. (2005). Study on morphology of electrospun poly(vinyl alcohol) mats. *European Polymer Journal*, *41*(3), 423–432. doi:10.1016/j.eurpolymj.2004.10.027

Zhang, Z. Y., Shi, T. B., Jia, C. Z., Ji, W. J., Chen, Y., & He, M. Y. (2008). Adsorptive removal of aromatic organosulfur compounds over the modified Na-Y zeolites. *Applied Catalysis B: Environmental*, *82*(1-2), 1–10. doi:10.1016/j.apcatb.2008.01.006

Zhou, X. R., Zhao, C. X., Yang, J. Z., & Zhang, S. F. (2007). Catalytic oxidation of dibenzothiophene using cyclohexanone peroxide. *Energy & Fuels*, *21*(1), 7–10. doi:10.1021/ef060441p

Zhou, Y., Yang, D., Chen, X., Xu, Q., Lu, F., & Nie, J. (2008). Electrospun water-soluble carboxyethyl chitosan/poly(vinyl alcohol) nanofibrous membrane as potential wound dressing for skin regeneration. *Biomacromolecules*, *9*(1), 349–354. doi:10.1021/bm7009015 PMID:18067266

Zong, X. H., Kim, K., Fang, D. F., Ran, S. F., Hsiao, B. S., & Chu, B. (2002). Structure and process relationship of electrospun bioabsorbable nanofiber membranes. *Polymer*, *43*(16), 4403–4412. doi:10.1016/S0032-3861(02)00275-6

Zuo, W. W., Zhu, M. F., Yang, W., Yu, H., Chen, Y. M., & Zhang, Y. (2005). Experimental study on relationship between jet instability and formation of beaded fibers during electrospinning. *Polymer Engineering and Science*, *45*(5), 704–709. doi:10.1002/pen.20304

Chapter 11

Flue Gas Desulfurization:

Processes and Technologies

Ricardo del Valle-Zermeño
University of Barcelona, Spain

Josep Maria Chimenos
University of Barcelona, Spain

Joan Formosa
University of Barcelona, Spain

ABSTRACT

Most of the total quantity of sulfur oxides (SOx) emitted to the atmosphere come from the combustion of fossil fuels, whose preponderance in the energy mix is expected to prevail in the years to come. In order to avoid the damaging consequences that this supposes, the improvement of the removal methods has been the topic of many researches. In this sense, the majority of abatement processes have always been based on wet Flue Gas Desulfurization (wFGD) technologies. In this chapter, the origin, development, deployment and enhancement of the wFGD processes is thoroughly revised. From the early studies on sulfur absorption for commercial purposes to the maturing of the technology fostered by environmental regulations, the chapter covers the aspects that have accompanied FGD research, including the reaction mechanism studies, the main types and configurations, and extending the analysis on the variables, parameters and technical aspects conditioning the process.

INTRODUCTION

The 80% of the total quantity of sulfur oxides (SO_x) are regarded to be emitted from anthropogenic sources through the combustion of fossil fuels during energy production processes (Pandey & Malhotra, 1999). In this sense, the predictions from the Energy Information Administration (EIA), the World Energy Council (WEC) and the International Energy Agency (IEA) agree that fossil fuels will play a key role in the energy consumption mix in the future (EIA, 2013; WEC, 2013; IEA, 2014). Particularly for oil, the EIA reference case shows that the total primary energy consumption is going to grow a 0.4% per year until 2040. As for coal, its consumption is expected to increase at 0.3% per year, remaining the second-largest energy source worldwide (EIA, 2013). Therefore, the continued great dependency

DOI: 10.4018/978-1-4666-9545-0.ch011

on fossil fuels entails damaging consequences to the environment and the global climate (IEA, 2014). In order to overcome these prejudicial effects, Air Pollution Control Policies have aid fostering the research on SO_2 removal at a worldwide level since the 1970s (Chang, Song, & Wang, 2011). Today, the techniques to reduce SO_2 emissions can be divided in three categories (Crnkovic, Milioli, & Pagliuso, 2006; Lee & Huffman, 2007):

1. Pre-combustion technologies (including fuel desulfurization and coal gasification or liquefaction);
2. Simultaneous combustion of coal and limestone mixtures (removal is carried out during combustion); and
3. Post-combustion technologies or flue gas desulfurization (FGD).

For more than 50 years, the majority of removal methods have been based on FGD technologies, which are scrubbing processes where the flue gas at the outlet of the combustion process is put into contact with an alkaline component (Siagi & Mbarawa, 2009; Taylor, Rubin, & Hounshell, 2005; Y. Wu, Li, & Li, 2007). Furthermore, FGD methods can be classified as once-through or regenerable (Mathieu et al., 2013). In the former type, the SO_2 is predominantly bound to the sorbent, which must be managed as a waste or by-product. As for the latter, no waste is generated as the substances produced can be reused as absorbents after a proper treatment. Once-through and regenerable FGD methods can be of the wet or dry type depending on the quantity of water used in the process as well as on the moisture content of the residue obtained (Taerakul et al., 2007). Wet FGD technologies have been predominantly selected over the dry type because of their high desulfurization efficiency, low investment, compact flow sheet and less land occupied, rare fouling, high utilization rate of reagents and a stable operating environment (Chang et al., 2011; Frandsen et al., 2001; Tomas Hlincik & Buryan, 2013; Kiil, Michelsen, & Dam-johansen, 1998; Shen et al., 2013; Taerakul et al., 2007). Limestone is used as the alkaline component in more than 90% of the installed desulfurization capacity in the world because of its natural abundance and low cost (Hrastel, Gerbec, & Stergaršek, 2007; Kallinikos, Farsari, Spartinos, & Papayannakos, 2010; Kiil et al., 1998; Ryu, Grace, & Lim, 2006). During the last years, the research over more efficient removal technologies has been fostered by the tightening of emission control policies and the expected increase in fossil fuels. The aim of this chapter is to summarize the main aspects and characteristics of FGD processes: from the description of the particular nature of SO_2 that has historically promoted environmental legislation to the revision of the basic concepts concerning the abatement techniques and the management of the effluents obtained. By this manner, the reader would be able to obtain an overall description of the FGD process before go in depth with the subsequent chapters.

THE PROBLEM OF SO_2

SO_2 Effects

The negative effects of SO_2 are both to human health and the environment. Once in the atmosphere, a series of photochemical or catalytic reactions promote its oxidation to SO_3 before being hydrated and again oxidized by air humidity into sulfuric acid (H_2SO_4) (Electric Power Research Institute [EPRI], 2006b; Phillips, Canagaratna, Goodfriend, & Leopold, 1995):

$$SO_2 + OH^- \rightarrow HSO_3 \quad (1)$$

$$HSO_3 + O_2 \rightarrow HO_2 + SO_3 \quad (2)$$

$$SO_3 + H_2O \rightarrow SO_3 - H_2O \quad (3)$$

$$SO_3 - H_2O \rightarrow H_2SO_4 \quad (4)$$

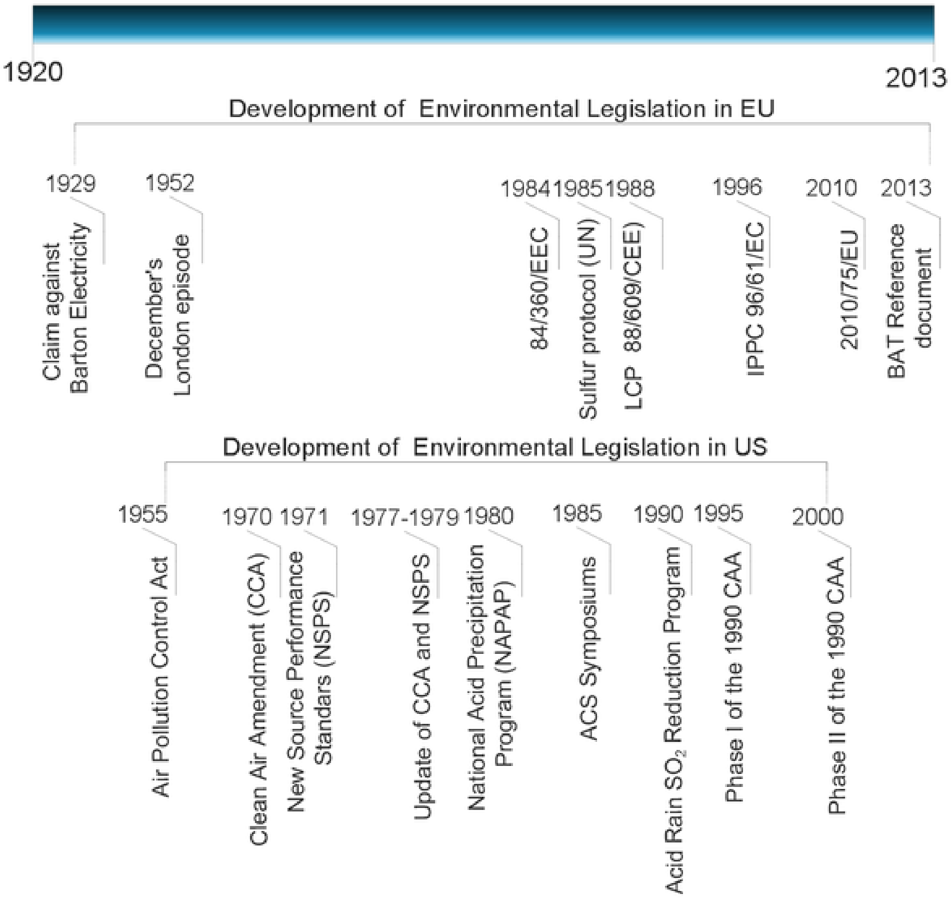
This process is commonly known as acid rain and its consequences are varied. From the adverse effects on the wildlife of aquatic ecosystems, forests and soils to the acidification of soils, easing the release of toxic metals into lakes and streams while provoking root damage, and plant and nutrient leaching (IEA, 2013; Biswas, Devotta, Chakrabarti, & Pandey, 2005; Brasseur, Guy P., Orlando, John J., Tyndall, Geoffrey, 1999; EEA, 2013; Frandsen et al., 2001; Gómez, Fueyo, & Tomás, 2007; Tomas Hlincik & Buryan, 2013; Johnson, 1987; Siagi & Mbarawa, 2009). Likewise, it also serves as a precursor for certain reactions that favor ozone depletion in the stratosphere (Brogren & Karlsson, 1997; Li, Zhu, & Ma, 2013). The main consequences for human health are related to the irritation of eye, nose and throat that in extreme cases might be linked to the formation of fine particles that might lead to broncho-constriction (Lippmann, 2009; Taylor, Rubin & Hounshell, 2005). Damages to materials are caused by SO_2 deposition over the surface either through gas dissolution in the moisture film or by dry deposition, fostering corrosion of the calcareous stone and marble surfaces of buildings and historic monuments (Lipfert, 1984; Malaga-Starzec, Panas, & Lindqvist, 2004; Mathieu et al., 2013; Pandey & Malhotra, 1999).

Development of the Environmental Legislations through History

When the adverse effects over the environment and the human health began to be realized, several legislations started to be introduced, firstly in the United Kingdom (UK) and then in the United States (USA) and Japan, which served as models for the many countries that followed, as it can be summarized in Figure 1 ("A history of flue gas desulfurization systems since 1850. Research, development and demonstration," 1977; Soud, 2000).

The initial environmental directives and control policies were aimed at reducing the emissions from power and thermal plants, as these industries were regarded as the primary source. The first measures included switching from high to low sulphur fuels (Álvarez-Ayuso, Querol, & Tomás, 2006). But the need of imposing SO_2 controls began in 1929 when the House of Lords (UK) upheld the claim of a landowner against the Barton Electricity Works of the Manchester Corporation for damages to his land by the SO_2 emissions from the power plant ("A history of flue gas desulfurization systems since 1850. Research, development and demonstration," 1977). Later on, the sharp increase in the weekly mortality in central London and the surroundings during December of 1952 warned about the SO_2 emissions from the inefficient burning of coal in domestic open grates (Lipfert, 1984). Nevertheless, it was not until June 28th

Figure 1. Timeline of the environmental legislations in the EU and the United States



of 1984 that the first emission control on an EU level was imposed for combating the air pollution from industrial plants through the Air Framework Directive 84/360/EEC. It managed to achieve a dramatic reduction in SO_2 discharges and therefore supposed a preliminary step to the further implemented Directive of Large Combustion Plants (LCP) of 1988 (88/609/CEE), where Emission Limit Values (ELVs) were set for the first time. The measures announced were addressed to those plants built after July 1987, although some restrictions for the already existing plants were also included. A little bit earlier, the first Sulfur Protocol was signed in 1985 under the United Nation's Economic Commission for Europe Convention on Long Transboundary Air Pollution (Brasseur, Guy P., Orlando, John J., Tyndall, Geoffrey, 1999). Almost 20 years after, in 2001, the LCP directive (2001/80/CEE) and the associated ELVs were updated and considered to be necessary but not sufficient for complying with the requirements of the Directive (96/61/EC) of Integrated Pollution Prevention and Control (IPPC). This directive accounted for the first time the Best Available Techniques (BAT) reference documents. Furthermore, new standards for were again updated in 2010 by the EU to ELVs as stringent as 35 mg/Nm^3 to new large combustion plants above 300 MWth using gaseous fuels and 150 mg/Nm^3 for liquid and solid fuels (Mathieu et al., 2013). Apart from this, the new BAT reference document of 2013 is exhorting all type of burning-fuels industries to reutilize the by-products and residues from the emission production process itself, in accordance with the EU energy policy of sustainability and competitiveness (CEC, 2006).

Similarly to what happened in Europe, nine major federal legislative/regulatory events fostered the development of FGD systems in the United States (Taylor, Rubin, & Hounshell, 2005). The first action occurred on 1955 when the Air Pollution Control Act was the first federal approach for controlling emissions of the industry. However, it was not until 1967 that the Air Quality Control Act allowed attracting national attention on the FGD technology market. In 1970, the Clean Air Act Amendment (CAA) of the Environmental Protection Agency (EPA) required every state to develop adequate control technologies for SO_2 control, resulting in a 20% annual reduction (Brasseur, Guy P., Orlando, John J., Tyndall, Geoffrey, 1999). Analogous to the European BAT reference document that would appear later, the New Source Performance Standards (NSPS) document of 1971 listed the necessary removal methods available to the industry. In 1977 and 1979 the CAA and the NSPS were respectively updated in order to promote the implementation of scrubbing methods at new plants, inherently preventing their building. In 1980, the US Congress authorized the National Acid Precipitation Assessment Program (NAPAP), a 10-year study that pretended to assess the causes and effects of acidic deposition. The effects were reflected in The American Chemical Society's Symposium "Materials Degradation Caused by Acid Rain" and the Electrochemical Society's Symposium "Corrosion Effects of Acid Deposition" of 1985. These events are considered to be great contributors in the spreading the effects of SO_2 on materials damage (Baboian, 1986; Brasseur, Guy P., Orlando, John J., Tyndall, Geoffrey, 1999; Mackenzie, L. Davis, 1998; Mansfeld, F., Haagenrud, S., Kucera, V., Haynie, F., Sinclair, 1986). The NAPAP was reauthorized in 1990 in the form of the 1990 CAA, where an emission-allowance trading program was added for attaining a reduction of 8.12 million tonnes of SO_2 per year until 2010 (Brasseur et al., 1999). Title IV of the 1990 CAA covered two phases of the Acid Rain SO_2 Reduction Program. The first phase (1995-1999) applied an aggregate emission limit of 4.5 kg·Gcal^{-1} of SO_2 per MBtu heat input of coal and Phase II (2000-2010) set an emission limit of 2.2 kg·Gcal^{-1} (Nelli & Rochelle, 1998; R. K. Srivastava & Jozewicz, 2001; Taylor et al., 2005). Additionally, the EPA issued the Clean Air Interstate Rule (CAIR) that incorporated a cap-and-trade program for annual emissions of SO_2 in order to solve the problem of power plant drifting from one state to another (EIA, 2014). Like the EU IPPC/BAT, the CAIR is scheduled to be tightened in 2015.

Worldwide, the World Health Organization (WHO) has also developed Air Quality Guidelines for SO_2 to assist member states in establishing their own standards (Lippmann, 2009). In this sense, China announced in 2011 stringent emission standards for thermal power plants, similar to the EU IPPC/BAT (Wu et al., 2014). Therefore, companies at both sides of the ocean will have to assess the technological and economic implications that the more and more stringent environmental legislations will suppose. The existing pollution control devices are not fully satisfactory and/or cost effective to meet the above-mentioned pollution control regulations (Meikap, Kundu, & Biswas, 2002).This explains the interest of many power and fossil-fuel combustion industries in getting better yields for their existing FGD plants (Gutiérrez Ortiz et al., 2006). The next sections deal with the origin and development of FGD processes, the main types of available technologies and the most important aspects and parameters.

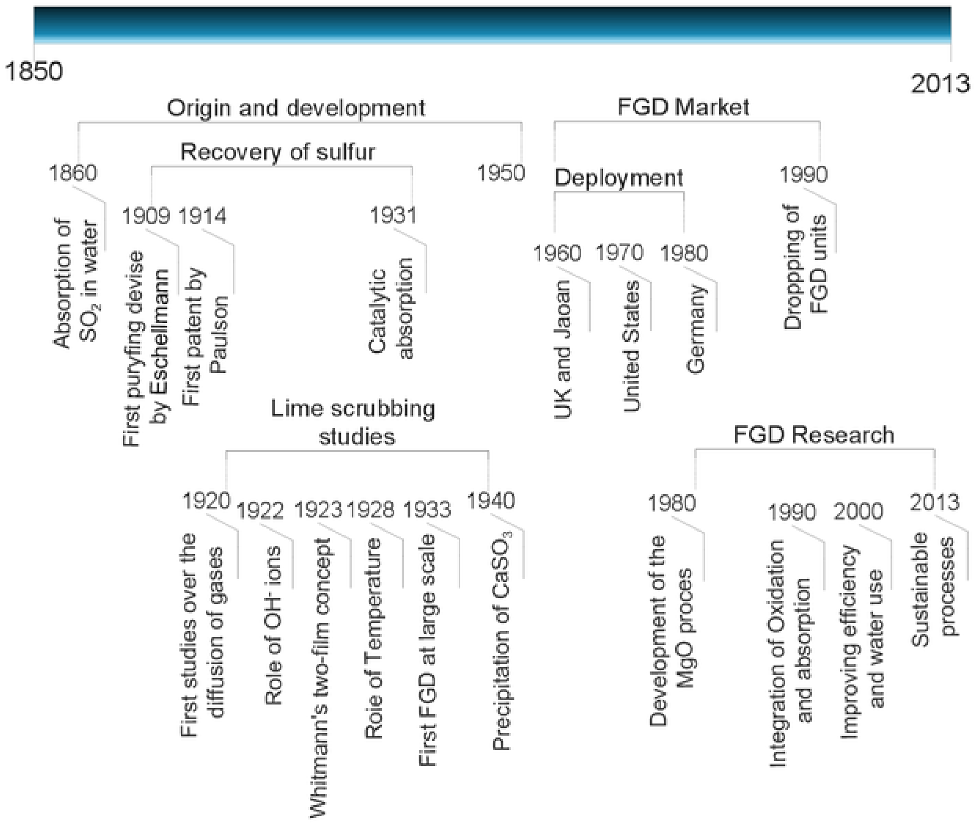
FGD PROCESSES

Origin and Development

The highlights of the origin and development of FGD technologies through history are summarized in Figure 2.

Although the deployment of FGD processes took place from the 1960s until 2009, the early studies carried out between 1850-1950 allowed establishing the theoretical basis for the main principles and concepts, which were especially important for the further design of modern scrubbers (Markusson, 2012). The studies on the absorption of SO_2 by water began in the 1860s with the aim of finding a suitable method for the recovery of sulfur and its use as a commodity reagent for sulfuric acid production ("A history of flue gas desulfurization systems since 1850. Research, development and demonstration," 1977). The first studies focused on the maximum amount of absorption as a function of pressure and temperature (Freese, 1920; Johnstone & Leppla, 1934; T.K. Sherwood, 1925; Sims, 1861; Watts, 1864) before exploring the possibility of using several catalysts for increasing the rate of absorption (Johnstone, 1931). On the early 1900s, several reactions of reduction were proposed for also recovering elemental sulfur (Lamoreaux, 1916; Lepsoe, 1938, 1940; Wells, 1917; Young, 1931). In 1909, Eschellmann devised a method for purifying burner gases using a suspension of lime and later in 1914 Paulson patented a

Figure 2. Timeline of the FGD technology



method (H.F. Johnstone, 1931). These processes were carried out by the pulp industry and were proposed for the production of sulfite acid cooking ("A history of flue gas desulfurization systems since 1850. Research, development and demonstration," 1977). In the framework of this issue, in 1922, Thompson Smith and Parkhurst focused on the chemistry of the lime scrubbing process, reporting the importance of the role of the hydroxide ion in the absorption process (Thompson Smith & Parkhurst, 1922). Rioux and Berard (1928) complemented these findings and pointed out that the rate of absorption increases in lime concentration until precipitation and by decreasing the temperature of the process (Rioux & Berard, 1928). Therefore, Johnstone and Singh (1940) proposed adding lime for easing the precipitation of calcium sulfite before recirculating the sulfite-bisulfite solution (Johnstone & Singh, 1940). Besides the chemical and physical aspects at laboratory scale, the required theoretical basis for the up-scaling to the industry began by the early studies of the diffusion of two gases (Hanks & McAdams, 1929; Lewis & Chang, 1928). The two-film concept proposed by Whitman is considered a cornerstone on which the further scrubbing technology was later based on (Whitman, 1923). According to this model, the gas must diffuse through both films before being absorbed into the liquid and the type of liquid plays an important role in the absorption rate. The next modifications to the model included unsteady conditions and transport of the absorbed gas to the bulk of the liquid (Higbie, 1935; Sherwood, 1952). The flourishing of the FGD technology was later driven by regulation, technology suppliers, organized knowledge sharing events and the emergence of the coal mining industry (Markusson, 2012). Thus, the first experimental FGD at full-scale commenced operation in London in 1933 (Bettelheim, Kyte, & Littler, 1981). It consisted in scrubbing the flue gases with water from the Thames river and adding chalk or alkaline waste sludge. Other large-scale FGD installations in the UK such as the Battersea Station, Swansea Station and Fulham Station served as precursors of subsequent larger installations ("A history of flue gas desulfurization systems since 1850. Research, development and demonstration," 1977). In Japan, the earliest FGD units on power plants also served as benchmarks for early US investments, from a few systems in the late 1960s to around 70 systems in the 1970s (Lefohn, Husar, & Husar, 1999; Markusson, 2012; Taylor et al., 2005). Despite the deployment of the German market in the 1980s, by the late of that decade the build of FGD units dramatically dropped because the reduced rate of building coal-fired power plants caused in part by the higher environmental compliance costs (Bellas, 1998). During this period, the research on FGD was aim at reducing scaling while improving removal efficiency and the integration of oxidation and absorption was proposed was a partial solution (Markusson, 2012). Thus far, wet FGD has been the most widespread method for removing SO_2 and is nowadays considered a mature technology (Biswas et al., 2005; Du et al, 2011). The research and development over the last years has focused on improving the removal efficiency while minimizing the water consumption and the effluents produced (Chen, Ge, Dou, Pan, & Zhou, 2009). The next sections address the mechanism of reaction involved in the absorption process and the different configurations that arise from it.

MECHANISM OF ABSORPTION AND MAIN FGD CONFIGURATIONS

The Absorption of SO_2: A Mass-Transfer Process

The absorption of SO_2 into alkaline solutions has been the topic of many studies and researches for decades and nowadays is widely known that the reactions are considered instantaneous and the mass transfer process of the species involved is the limiting and most important physical step (Brogren & Karlsson, 1997; Dragan & Ozunu, 2012).

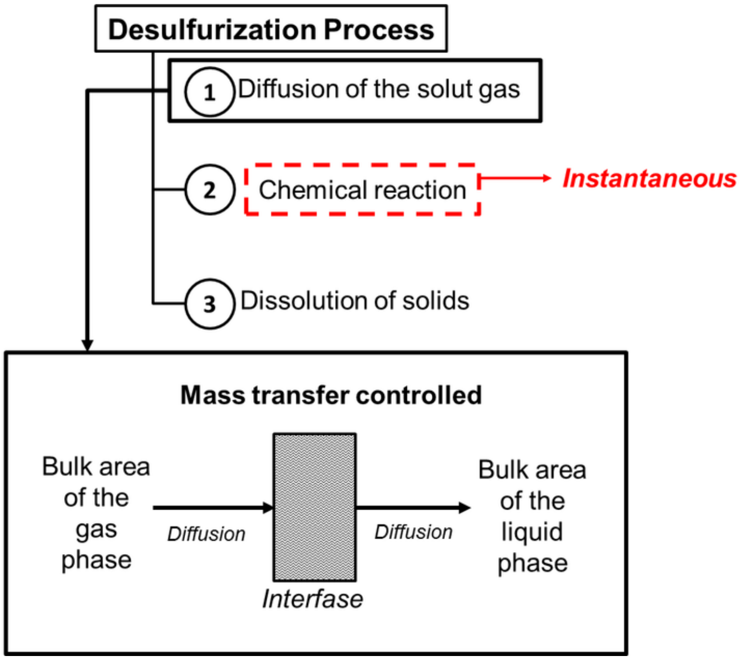
Ramachandran and Sharma (1969) were the first to theoretically discuss the problem of gas absorption with chemical reaction and proposed a two-film model, depending on whether the solid dissolution in the liquid film was important or not (Ramachandran & Sharma, 1969). Based on this two-film model, Hikita et al. (1972) later proposed a penetration theory while Rochelle and King (1977) focused on the absorption in limestone slurries considering the effect of additives. These and other subsequent studies contributed to the understanding of the three main stages of the desulfurization process (Figure 3): diffusion of the solute gas in the film, chemical reaction, and dissolution of the solids (Liu & Xiao, 2006).

Taking into account that the chemical reactions between the dissolved reactants are considered instantaneous and irreversible, the mass-transfer becomes particularly important and hence the main controlling step among the three main stages (Dou, Byun, & Hwang, 2008). This mass transfer operation is influenced by both a gas and a liquid film resistance taking place in three steps (Hansen, Fogh, Knudsen, & Kiil, 2011; Sada, Kumazawa, & Butt, 1979b):

1. Diffusion from the bulk area of the gas phase to the gas-liquid interface;
2. Transfer across the gas-liquid interface;
3. Diffusion into the bulk area of the liquid.

This diffusion-transfer-diffusion progression mainly depends on the coefficient rates in both phases although the dissolution of solids may also influence (Sada, Kumazawa, & Butt, 1979). Therefore the research over desulfurization enhancement has been directed towards improving the contact between the gas and liquid phases and the dissolution of the alkaline solids. The contact of both phases, depicted

Figure 3. The three stages of the desulfurization process



by the ratio of gas to liquid film resistance, is considered to be determined by the concentration of SO_2 in the flue gas and its solubility in the liquid, the liquid to gas (L/G) ratio, the contacting pattern, the reactant used, and the potential use of additives in the slurry (Dou, Pan, Jin, Wang, & Li, 2009; Hansen et al., 2011; Hansen, Kiil, Johnsson, & Sonder, 2008; Krammer, Brunner, Khinast, & Staudinger, 1997). In practical terms, the enhancement of SO_2 absorption in FGD processes require the improvement of three technical aspects directly related to mass transfer: interfacial area, mixing and residence time (Lee & Huffman, 2007). The interfacial area has been usually improved by using fine particles of suspended solids as their size affects the absorption rate despite their alkaline nature (Kakaraniya, Kari, Verma, & Mehra, 2007; V. Dagaonkar, A.C.M. Beenackers, & G. Pangarkar, 2001). As for the mixing and the residence time, these are related to how well the contact between phases take place and hence to the mass transfer process. Other important aspects that have also attracted research interest are those related to operation, such as plugging and scaling, reagent utilization and corrosion among others (Karlsson & Rosenberg, 1980). Based on the abovementioned reaction mechanism, the next section deals with the most important FGD configurations aimed at improving the mass transfer process.

Main FGD Configurations

FGD systems are comprised of absorption units and are attached to the end of the combustion process (Bellas, 1998; T Hlincik & Buryan, 2013). The wet type dominates an estimated 84% of the market share and therefore deserve a special analysis (Frandsen, Kiil, & Johnsson, 2001; Kaminski, 2003). This technology can be divided according to the method of contact between both phases and further into several subcategories depending on specific chemical reactions and flow conditions (B B Hansen, Kiil, Johnsson, & Sonder, 2008; Nygaard et al., 2004; Zhao, Jin, & Zhong, 2007). The process of absorption takes places in scrubbing towers where both phases are brought into contact by means of different contact methods such as spraying or forcing through a pool (Kallinikos, Farsari, Spartinos, & Papayannakos, 2010; Lee & Huffman, 2007). The contact method is aimed at favoring the mass-transfer process by increasing or renovating the active interfacial area. On this aspect, Brauer (1984) classified the absorbers by the form of generating the active interfacial area in (Brauer, 1984):

1. Packed columns;
2. Jet absorbers;
3. Bubble and drop absorbers like tray columns;
4. Bubble columns and various types of spray columns.

Other types of absorbers can be considered a further modification of the existing configurations, like moving-bed tray and spray towers (Mackenzie & Cornwell, 1998). Therefore, the mass transfer medium is usually a combination of liquid droplets from spray headers, sieve trays or other flue gas straightening devises (Smith, Booth, & Crevecoeur, n.d.). Increasing the number of spray headers, perforated trays, liquid distribution rings, baffles and dual direction nozzles or any other contact enhancement device is meant to increase the desulfurization performance (Smith, Booth, & Crevecoeur, n.d.).

The spray towers without packing, with grid-type packing, or with rods are regarded as the best alternatives because of their simple design and small risk of scaling and other technical problems (Karlsson & Rosenberg, 1980).

Although wet FGD technologies are more effective in terms of SO_2 removal rate than the dry processes, they are more expensive because of the larger amounts of wastewater that need to be treated and hence the larger facilities and investments costs required (T Hlincik & Buryan, 2013; Warych & Szymanowski, 2001; J. Wu, Iizuka, Kumagai, Yamasaki, & Yanagisawa, 2008; Zhang, You, Zhao, Chen, & Qi, 2008).

There are nine commercial non-regenerative systems that are considered the most important wet FGD systems: Lime-limestone ($CaO/CaCO_3$) methods, caustic soda (NaOH), soda ash (Na_2CO_3), or ammonia (NH_3) (Lee, Huffman, & Chang, 2007; Mackenzie & Cornwell, 1998). As for the regenerable type, the most important processes are those based in using magnesium oxide, citrate salts and the Wellman-Lord process. The main characteristics of the most used wet FGD configurations are presented below.

Spray Towers

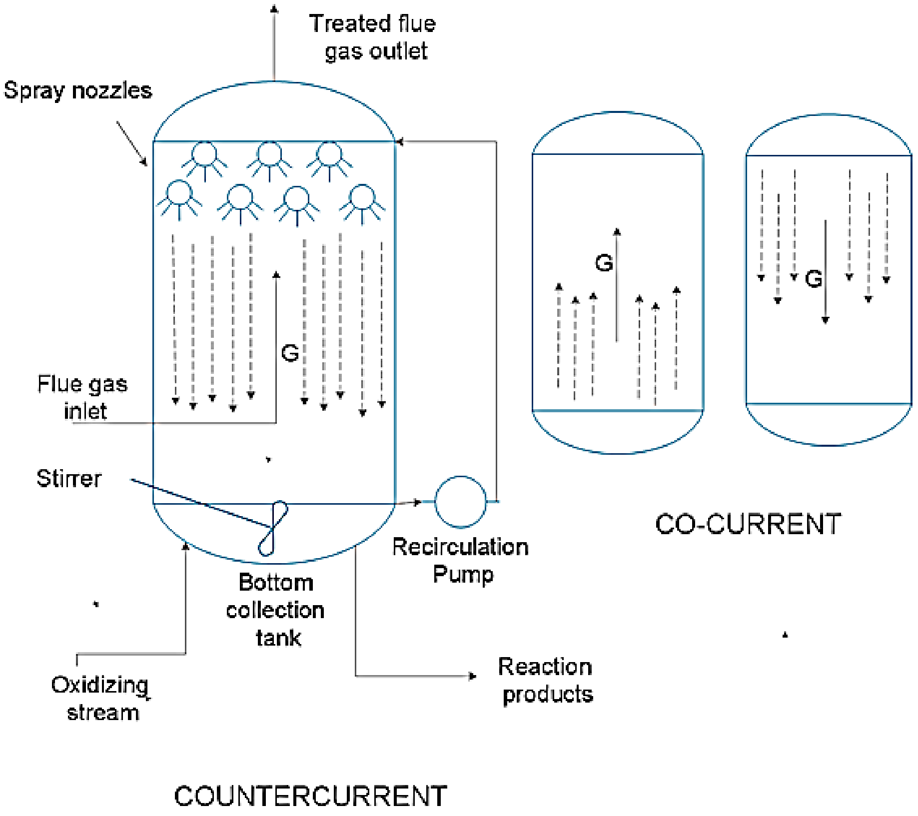
They consist on an empty tower with a set of nozzles for spraying the absorbing liquid placed at the top. They can be classified as countercurrent or co-current depending on the relative direction between the liquid flow and the gas stream (Figure 4).

In a countercurrent absorber, the stream gas moving upwards from the bottom contacts the absorbing slurry that is sprayed by the spray heads from the top. A large number of spray nozzles for covering the whole cross section of the tower can be added. The scrubbing slurry loaded with the reaction products is collected at the bottom of the scrubber and pumped to the top of the absorber for recirculation (Eden & Luckas, 1998). The reaction products are constantly stirred in order to maintain suspension and the precipitated solids are extracted from the bottom and further dewatered for treatment or commercial purposes. Several parameters such as the initial velocity of the droplets, their size and the liquid-to-gas (L/G) ratio are regarded to be a function of the scrubber aerodynamics (Lee & Huffman, 2007; Michalski, 1997, 1999). Taking this into account, the modeling of spray towers has been the topic of many studies (Table 1).

Table 1. Several modelling for spray towers

Model Objective and Parameters Considered	Remarks	References
Dynamic absorption rate SO_2 into a droplet limestone slurry	The mass-transfer process before the outlet of the absorber is to a large extent liquid-side controlled	Brogren & Karlsson (1997)
The pressure drop, the slurry or the liquid residence time, the droplet concentration along the scrubber and the parameters describing droplets and gas flow	Increasing the gas flow rate decreases the pressure drop in the concurrent type while increasing it in the countercurrent configuration.	Michalski (1997)
Semi-empirically or empirically correlations describing the scrubber hydraulics, efficiency, and by-product crystallization based on the model of the single spray bank FGD scrubber.	The model is able to predict the scrubber efficiency for very fast and very slow reaction rates in the slurry.	Michalski (1999)
A model based on the Whitman film theory that considered the internal circulation of suspended solids inside the drop, which accounted for solid dissolution, chemical reaction and molecular diffusion.	• For large droplets, internal circulation enhanced the mass-transfer with respect to a stagnant droplet. • The liquid circulation that exists near the gas–liquid interface, enhances the absorption rate	Muginstein, Fichman, & Gutfinger (2001)
A model for counter-current limestone spray scrubber using the dual-film theory and considering the pressure drop and removal efficiency as a function of the number of the operating spray levels.	The best positioning of the spraying nozzles, the distance between the spray levels, the size of the wall rings, the number of operating spray levels and other critical parameters can be evaluated numerically.	Marocco (2010)

Figure 4. Main features on a spray scrubber and the two types of flow configurations. G: gas phase; S: absorbing slurry



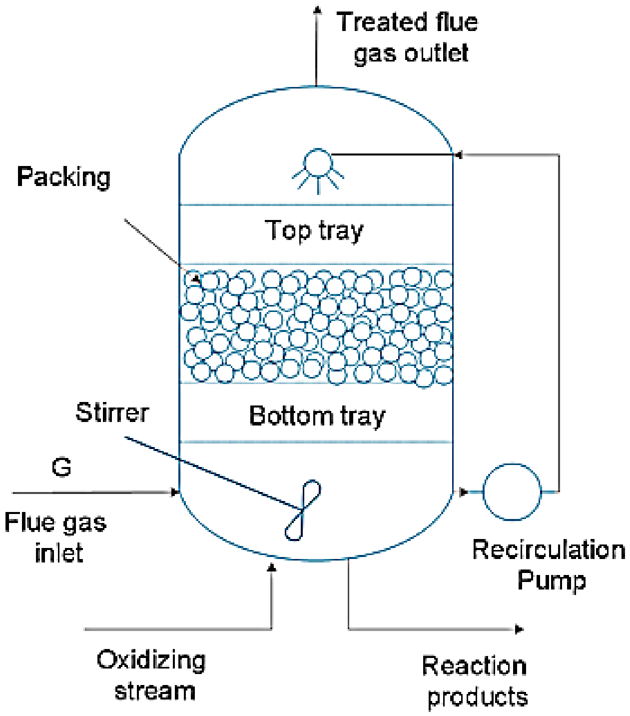
Some innovative approaches have been recently reported with the aim of improving the desulfurization efficiency of spray towers by enhancing the contact between phases. Rajmohan et al (2008) developed a new spray scrubber with a twin fluid and an air blast atomizer and reported that increasing removal efficiencies can be obtained by increasing the spray liquid flow rate and the concentration of SO_2 in the gas. Dou et al. (2007) based their studies on the research reported by Wang et al. (1993) and Carleson and Berg (1983) with respect the effect of applying voltages on limestone water spray. The charged droplets of $Ca(OH)_2$ become smaller with an applied voltage and therefore the contact area with SO_2 can be increased by means of electrostatic spraying (Dou, Byun, & Hwang, 2008).

Packed Towers

Developed by Mitsubishi Heavy Industries, in this configuration (Figure 5) the liquid is sprayed over a packing material that is collected between support trays (top and bottom), thus providing a large contact area, sufficient resident time as well easing a turbulent mixing of the phases (Muramatsu, Shimizu, Shinoda, & Tatani, 1984).

The packing material, made of numerous geometric shapes and sizes and commonly made of high-density thermoplastics, is considered the largest material cost. This fact can be reduced by placing the packing material randomly, at the cost of assuming a higher pressure drop and worse liquid distribution

Figure 5. Main features of a packed tower



(Lee & Huffman, 2007). Choosing between co-current and countercurrent flow depends on the solids dissolution although the latter is the most preferred choice as the most diluted gas in contact with the purest absorbing slurry supposed the maximum concentration difference (Karlsson & Rosenberg, 1980). The most important controlling parameters are reported to be the pressure drop, column flooding point, and liquid holdup in the column (Chen, Yates, Neathery, & Liu, 2012; Muramatsu et al., 1984).

Fluidized Bed Scrubber

The main difference of this type of absorber is the packing section, which is comprised of mobile packing spheres (polypropylene or polyethyle) placed that rotate and moved by the effect of the gas, which enhances the mixing of phases while acting as a self-cleaning mechanism (Lee & Huffman, 2007).

Jet Bubbling Reactor (JBR)

This configuration allows improving the efficiency of conventional scrubbers by vigorously bubbling the flue gas through the absorbing liquid in a single reaction tank (denominated the “jet bubbling zone”). This zone increases the gas/liquid interfacial area for SO_x absorption (Hansen et al., 2008; Yuanjing Zheng, Kiil, & Johnsson, 2003). The JBR process avoids the use of large recycle pumps and spray heads but it usually presents high pressure drops. The enhancement of the absorption is based on the froth zone created by the fine bubble bed, where the bubbles are continuously collapsing and renovating the interfacial area for mass-transfer (Zheng et al., 2003).

Bubble Column

Bubble columns are designed to disperse the flue gases by bubbling them in a deep pool of liquid. The most important parameter of the removal efficiency is the bursting of bubbles (Meikap, Kundu, & Biswas, 2002a, 2002b). These devices are commonly used as particulate scrubbers in the industry because they are simple to build, easy to operate, high liquid phase content for reaction, excellent heat transfer properties, and low initial costs (Meikap et al., 2002; Mohan, Biswas, & Meikap, 2008). The columns must be operated in series or in multiple stages in order to obtain high removal efficiencies (Meikap et al., 2002). In this aspect, Meikap et al. (2002) reported experimental results with 100% SO_2 removal efficiency using water as absorbing agent. A combination with a spray tower has also been reported, with removal efficiencies in the 62.54-97.58% range from a lean air-SO_2 mixture of 400-1200 ppm of SO_2 (Raj Mohan & Meikap, 2010).

FGD SYSTEMS

Lime and Limestone Based Processes

The use of lime and limestone in FGD systems has prevailed since the 1970s because they are regarded as the most cost effective and reliable method, nowadays representing over 90% of the installed desulfurization capacity worldwide (Brogren & Karlsson, 1997; Hrastel et al., 2007; Kiil et al., 1998; Nolan, 2000; Taylor et al., 2005). The main advantages can be summarized as follows (Dragan & Ozunu, 2012; Bravo, Camacho, Moya, & García, 2002):

1. Both minerals are abundant and present a low cost.
2. Their use allows obtaining gypsum as reaction product, which can be reuse or sell as a product.
3. The absorption rate can be enhanced by altering the characteristics (shape, diameter and composition) of the limestone/lime particles.

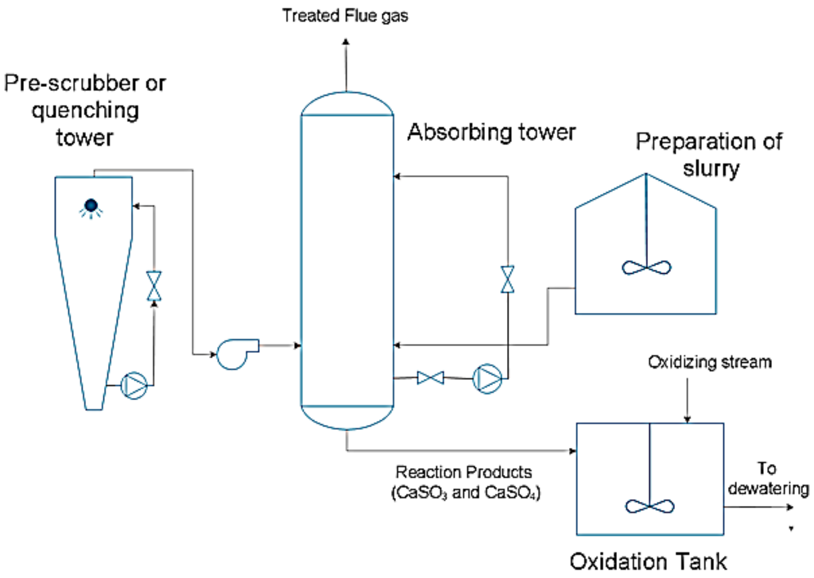
However, the literature has also highlighted three major issues related to limestone wet FGD processes (Yan et al., 2014):

1. The large quantity of limestone that is required.
2. The large quantity of gypsum that is generated might not be absorbed by the market.
3. The problems related to fouling, wear and corrosion.

The most common configuration is the counter current spray scrubber because of its reliability (Brogren & Karlsson, 1997). The system is formed by three units (Figure 6a): pre-scrubber for cooling and dust-removal, absorber and the oxidation unit (Kikkawa, Nakamoto, Morishita, & Yamada, 2002). The slurry leaving the second tower can be also collected in a reaction tank at the bottom of the scrubber, allowing eliminating the third unit (Figure 6b) (Brogren & Karlsson, 1997; Kikkawa et al., 2002).

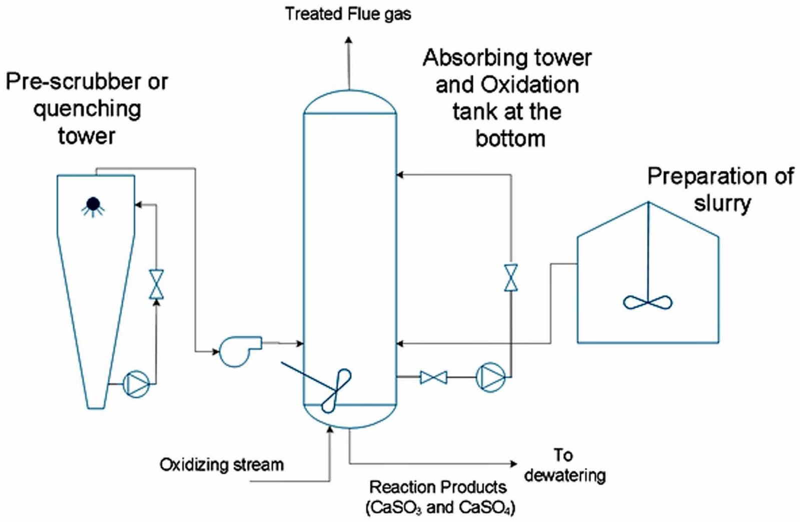
The complex chemistry of the process has been the topic of my researches (Frandsen et al., 2001; Lancia, Musmarra, & Pepe, 1997; Nygaard et al., 2004; Olausson, Wallin, & Bjerle, 1993). The reac-

Figure 6a. Units involved in the lime and limestone FGD process: a three units system



tions taking place in the absorber are a function of choosing between lime and limestone, the type of limestone, and the calcining and slaking methods (Mackenzie and Cornwell, 1998). Even though the use of lime allows to achieve a better pH stability in the absorber, limestone is preferred because its 5 to 10 times cheaper, although it requires a prior treatment process (calcination, transportation, and slaking) (Chen et al., 2009; EPRI, 2006; Karlsson, Klingspor, Linne, & Bjerle, 1983; Karlsson & Rosenberg, 1980; Lancia et al., 1997).

Figure 6b. Units involved in the lime and limestone FGD process: integration of the oxidation and absorption units



The overall process can be divided into four stages:

1. SO_2 absorption
2. Oxidation of HSO_3^-,
3. Dissolution of limestone, and
4. Crystallization of the reaction products (gypsum) (Kiil et al., 1998).

Absorption of SO_2 and Oxidation of HSO_3^-

Once the SO_2 diffuses through the gas film towards the gas-liquid interface and dissolves in the liquid phase, the first and second dissociations take place (Sada et al., 1979; Uchida, Moriguchi, Maejima, Koide, & Kageyama, 1978; Warych & Szymanowski, 2001):

$$\mathrm{SO_2 + 2OH- \rightarrow SO_3^{2-} + H_2O} \quad (5)$$

$$\mathrm{SO_2 + SO_3^{2-} + H_2O \rightarrow 2HSO_3^-} \quad (6)$$

Enabling the subsequent reaction of HSO_3^- with OH- to form SO_3^{2-}.

$$\mathrm{HSO_3{}^- + OH^- \rightarrow SO_3^{2-} + H_2O} \quad (7)$$

The SO_3^{2-} generated further react with the cations from the dissolution of $CaCO_3$/CaO.

Dissolution

Uchida et al (1978) early pointed out that the dissolution process plays a very important role in the absorption of SO_2 (Uchida et al., 1978). Nowadays it is widely known that dissolution taking place both at the scrubber and the feed tank is very important for the desulfurization process (Carletti et al., 2013; Gutiérrez Ortiz et al., 2006; Siagi & Mbarawa, 2009; Bravo, Camacho, Moya, & García, 2002; Warych & Szymanowski, 2001).Unlike lime, limestone hardly dissolves in the scrubber system but its reactivity can be increased by decreasing the particle size and by decreasing the pH of the media, at the cost of inhibiting the dissociation of SO_2 (Carletti et al., 2013; Shengyu, Wende, Pei, & Zhixiang, 2008; Wallin & Bjerle, 1989). In this aspect, particle size is regarded as the most important reactivity characteristic of ground limestone of reasonable purity (Brogren & Karlsson, 1997). After being ground, the slurry is formed in the slurry tank by suspending the lime-based solids in water to a 25-30 wt % proportion (EPRI, 2006).

Gypsum Crystallization

The main product from the reaction between sulfur dioxide and calcium carbonate is hydrated calcium sulfite ($CaSO_3$) (Brogren & Karlsson, 1997; EPRI, 2006; Hansen & Kiil, 2012):

$$SO_2 + CaCO_3 + \frac{1}{2}H_2O \rightarrow CaSO_3 \cdot \frac{1}{2}H_2O + CO_2 \tag{8}$$

However, if the pH is below 3, $Ca(HSO_3)_2$ rather than $CaCO_3 + \frac{1}{2}H_2O$ is reported to be precipitated (Brogren & Karlsson, 1997; Olausson et al., 1993). Once precipitated, the hydrated calcium sulfite can be oxidized to gypsum by blowing air into the system (forced oxidation), before being extracted and dewatered for commercial purposes (Álvarez-Ayuso et al., 2006). An uncontrolled crystallization of gypsum can lead to scaling and therefore when saleable gypsum is not required, emulsified sulfur or sodium thiosulfate can be added as inhibitors of oxidation or scaling control agents (Nolan, 2000).

Magnesium Oxide Process

Karlsson and Rosenberg (1980) were the first to be interested in the enhancing effect of magnesium on the SO_2 absorption rate (Karlsson & Rosenberg, 1980). Nowadays the magnesium-based wet FGD process has been reported to be more suitable for low SO_2 concentration FGD systems because of the low investment required, compact flow sheet and less land occupied, its high efficiency, reliable operation and rare fouling. However, the lack of magnesium resources and the high cost of MgO are the main drawbacks (Yan et al., 2014). The small additions of MgO (to a 3-8%) for enhancing the conventional limestone/lime process has been preferred (Biswas et al., 2005). The absorption process proceeds as follows (Chen et al., 2009):

$$MgO + H_2O \rightarrow Mg(OH)_2 \tag{9}$$

$$SO_2 + Mg(OH)_2 + 5H_2O \rightarrow MgSO_3 \cdot 6H_2O \tag{10}$$

$$SO_2 + MgSO_3 \cdot 6H_2O \rightarrow Mg(HSO_3)_2 + 5H_2O \tag{11}$$

$$Mg(HSO_3)_2 + MgO + 5H_2O \rightarrow 2MgSO_3 \cdot 6H_2O \tag{12}$$

The suspended $Mg(OH)_2$ paticles yield a high scrubbing capacity because the reaction product magnesium sulfite posses a high solubility, allowing to maintain alkalinity much longer than the calcium based process and resulting in a larger SO_2 absorption (Kakaraniya, Kari, Verma, & Mehra, 2007; Sada, Kumazawa, & Butt, 1977; Sada et al., 1979; V. Dagaonkar et al., 2001). In this aspect, inhibitors of oxidation, such as sodium thiosulfate can be also added for improving the process (Shen et al., 2013). The final product can be regenerated by means of thermal decomposition (Chen et al., 2009).

The Seawater Process

Bromley (1972) was the first to suggest the use of seawater as desulfurization agent because of its alkaline nature, large neutralizing capacity, great availability in coastal zones and the fact that no solid residues are produced (Bromley, 1972). However, the large space needed for treating and neutralizing the large amounts of seawater before discharged are the main drawbacks (Tokumura et al., 2006; Vidal B., Ollero, Gutiérrez Ortiz, & Villanueva, 2007). The removal rate can be further enhanced by adjusting the water temperature and the salt concentration, which exert a great influence over SO_2 solubility (Al-Enezi, Ettouney, El-Dessouky, & Fawzi, 2001; Douabul & Riley, 1979).

The most cost effective configuration is the packed tower with recirculation of the flow of seawater (Caiazzo, Di Nardo, Langella, & Scala, 2012; Vidal B et al., 2007). Nowadays the systems installed account for 0.6% of the total systems used (Nyman, 1991; Srivastava, 2000). Alternatively, the use of seawater for preparing the lime slurry has also been reported to be effective, as the presence of sodium chloride and other salts enhances absorption (Ollero, Salvador, & Cañadas, 1997).

Other Alternative and New Processes

Inorganic and Organic Absorbents

Sun et al (2010) reported the use of sodium humate (HA-Na) solutions with a 99% removal efficiency. These solutions are polydisperse heterogeneous molecules that can be extracted from low-rank coals and other natural materials for desulfurization purposes (Zhiguo Sun, Zhao, Gao, & Hu, 2010).

The addition of citric acid-sodium citrate solutions was firstly proposed by Erga (1975) for improving SO_2 absorption (Erga, 1980). The process possesses several advantages such as the simplicity, the regenerative and non-toxic nature of the absorbent and reciclability of the citrate buffer (Bekassy-Molnar, Marki, & Majeed, 2005; Mondal, Chelluboyana, & Rao, 2013). The increase in water solubility from the buffering effect of the citrate enhances the reaction with SO_2 (Bekassy-Molnar et al., 2005):

$$3SO_2 + 3H_2O + 2Na_3Ci \rightarrow 3Na_2SO_3 + 2H_3Ci \tag{13}$$

Removal efficiencies are reported to reach to up to 85-90% (Bekassy-Molnar et al., 2005).

The use of NaOH as absorbing agent was studied by Pourmohammadbaher et al (2011) when assessing the simultaneous absorption of SO_2 and NO (Pourmohammadbagher, Jamshidi, Ale-Ebrahim, Dabir, & Mehrabani-Zeinabad, 2011) and the use of mixtures have also been considered: NaOH + sodium citrate solutions (Mondal et al., 2013) and NaOH+ $KMnO_4$ (Chu, Chien, & Li, 2001). Potassium and sodium carbonate solvents have been also proposed in a wide range of configurations with significant efficiencies (Bandyopadhyay & Biswas, 2006; Ebrahimi, Picioreanu, Kleerebezem, Heijnen, & van Loosdrecht, 2003; Wappel et al., 2009). Additionally, sulphuric and acetic acid solutions along with ClO_2 have been also suggested (Adewuyi, He, Shaw, & Lolertpihop, 1999; Colle, Thomas, & Vanderschuren, 2005; Colle, Vanderschuren, & Thomas, 2004, 2008, 2005; Jin, Deshwal, Park, & Lee, 2006; Thomas, Colle, & Vanderschuren, 2003a, 2003b; Xia, Rumpf, & Maurer, 1999; Yang & Shaw, 1998).

The use of organic compounds has also attracted interest. The studies carried out by Hwang et al (2009) and Choi et al (2009) focused in the simultaneous absorption of CO_2 and SO_2 into aqueous 1,8-Diamino-p-menthane and mixtures of NH_3/amines respectively (Choi, Seo, Cho, Park, & Oh, 2009; Hwang et al., 2009).

The main disadvantages of these non-conventional absorbents are the costs associated and the limited experience on a large scale.

Reutilization of Residues as Desulfurization Agents

Many industrial alkaline wastes contain significant amounts of CaO and other alkaline oxides that could be reused as SO_2 absorbents in a sustainable FGD process (Del Valle-Zermeño et al., 2014; B. Zheng & Lu, 2009). In this aspect, the residual $Ca(OH)_2$ and $CaCO_3$ in the spray dry absorption product (SDAP) has been reported to be feasible for desulphurization at both laboratory and pilot plant scale (Hjuler & Dam-Johansen, 1994; Y Zheng, Kiil, Johnsson, & Zhong, 2002). Del Valle-Zermeño et al (2014) also reported the reutilization of several MgO by-products from the calcination of natural magnesite in a closed-loop desulfurization process with a 100% removal efficiency.

CONTROL VARIABLES AND PARAMETERS

Identifying the optimum operating parameters is aim for achieving a high degree of SO_2 removal with minimum operation costs (Dou, Pan, Jin, Wang, & Li, 2009). The variables affecting the desulfurization performance of a given technology can be categorized as a function of the stage of the process and are described below.

The Scrubbing Performance

Desulfurization Efficiency (η)

It can be expressed by the difference in SO_2 concentration at the inlet ($[SO_2]$inlet) and outlet ($[SO_2]$ outlet) of the process (Gao et al., 2011; Kikkawa et al., 2002; Matsushima et al., 2004; Meikap, Kundu, & Biswas, 2002a, 2002b; Shen et al., 2013; Zhiguo Sun et al., 2010; Wu, Li, & Li, 2007; Zhao, Jin, & Zhong, 2007):

$$\eta = 1 - \frac{\left[\mathrm{SO_2}\right]_{outlet}}{\left[\mathrm{SO_2}\right]_{inlet}} \times 100 \tag{1}$$

It depends on the rest of parameters as well as on the FGD configuration (Gutiérrez Ortiz et al., 2006; Warych & Szymanowski, 2001). Although the enhancement of the desulfurization efficiency was the primary goal at the early researches, nowadays the aim is to improve it while enhancing other parameters in a trade-off between environmental legislation and process economy. The efficiency can be assessed experimentally at lab-scale by using breakthrough points such as those reported by Hlincik and Buryan

(2013) and del Valle-Zermeño et al (2014). Table 2 presents the desulfurization efficiency ranges of several technologies using different absorbents and methods.

Ca/S Ratio

This ratio applied to calcium-based processes as it is defined as the moles calcium (either in the form of lime or limestone) supplied per mole of SO_2 in the flue gas. Its value can give an idea of the con-

Table 2. Desulfurization efficiency ranges for several technologies and absorbents

Technology	Absorbing Agent	η (%)	Reference
Mobile bed	$CaO/Ca(OH)_2$	70	(Joseph & Beachler, 1998)
Sieve tray		90	
Countercurrent spray		80-91	
Venturi		86-95	
Mobile bed		85.7-90	
Sieve tray	$CaCO_3$	80	
Countercurrent spray		52-90	
Weir crosscurrent spray		82	
Venturi/sieve tray		90	
Packed tower		85-97	
Mobile bed		75.5-87	
Sieve plates	Double-alkali	94.2	
Venturi		85-90.5	
Mobile bed		90	
Sieve plate	Sodium based	90-91.2	
Trays		90-96	
Plates		90-98	
Venturi		85-95	
Packed tower		94	
Packed-bed reactor	$Ca(OH)_2/CaSiO_3$	50-90	(Nelli & Rochelle, 1998)
Countercurrent absorber	$CaCO_3$ + adipic acid	48-97	(Eden & Luckas, 1998)
Coaxial cylinders with impinging streams	$Ca(OH)_2$	94-96	(Berman, Tanklevsky, Oren, & Tamir, 2000a
	$Ca(OH)_2$ + NaOH	99	(Berman, Tanklevsky, Oren, & Tamir, 2000b)
Absorbing towers	Mg enhanced $Ca(OH)_2$	98	(Nolan, 2000)
Packed tower	$CaCO_3$ + adipic acids	80-90	(Frandsen et al., 2001)
	Chalk + adipic acids	87-95	
Circulating fluidized-bed absorber	$CaO/Ca(OH)_2$	95-97	(Ollero, Gutiérrez Ortiz, Cabanillas, & Otero, 2001)
Cocurrent packed tower	Spray dry absorption product	75-78	(Y Zheng et al., 2002)

continued on following page

Table 2. Continued

Technology	Absorbing Agent	η (%)	Reference
Multistage bubble column	H_2O	70-71 (one stage)	(Meikap et al., 2002a)
		82-89 (three stages)	
Countercurrent absorber	Seawater	91-97	(Oikawa, Yongsiri, Takeda, & Harimoto, 2003)
Jet Bubbling reactor	$CaCO_3$	69.4-99	(Yuanjing Zheng, Kiil, & Johnsson, 2003)
Wet scrubber with forced oxidation	$CaCO_3$	90	(Kaminski, 2003)
Wet scrubber (gypsum wallboard)			
Wet scrubber with inhibited oxidation			
Wet scrubber using dibasic acid			
Wet scrubber Mg enhanced	$Ca(OH)_2$		
Bubbling reactor	ClO_2	~100	(Jin et al., 2006)
Countercurrent packed tower	$CaCO_3$	58.6-99.3	(Gutiérrez Ortiz et al., 2006)
Impinging stream FGD system	$Ca(OH)_2$	88.5-96.00	(Wu et al., 2007)
Packed tower	Catalytic seawater	55.2-99.7	(Vidal B. et al., 2007)
Spray scrubber	$CaCO_3$	64.3-94.7	(Zhao et al., 2007)
Bubbling reactor	$CaCO_3$ + acetic acid	95	(Shengyu et al., 2008)
Twin fluid air-assisted atomizer	H_2O	~99.99	(Rajmohan, Reddy, & Meikap, 2008)
Bubbling reactor	Magnesia	92-97	(L. Wang, Ma, Yuan, & Hao, 2009)
Spraying reactor	$CaCO_3$	85-95	(Dou et al., 2009)
Bubbling reactor	Sodium humate solution	98-99	(Z Sun, Zhao, Gao, & Hu, 2010)
Spray tower + bubble column	H_2O	62.54-97.58	(Raj Mohan & Meikap, 2010)
Cocurrent grid absorber	$CaCO_3$	91-99	(Hansen et al., 2011)
PCF device	$CaCO_3$	82.1-84.8	(Gao et al., 2011)
Dense phase tower	$CaO/Ca(OH)_2$	95.2-97	(Chang et al., 2011)
Swirl wet scrubber system	NaOH solution (2% w/v)	100	(Pourmohammadbagher et al., 2011)
Tray tower	$CaCO_3/CaMg(CO_3)_2$	98	(Carletti et al., 2013)
Spray scrubber	Magnesia + $Na_2S_2O_3$	85.4-91.9	(Shen et al., 2013)
Bubble column reactor	NH_4CO_3	100	(Qin, Hansen, & Kiil, 2014)
	$CaCO_3$ + foaming agents	73-90	(Qin, Hansen, & Kiil, 2014)
	NaOH + foaming agents	93	

sumption of the alkaline component for a given efficiency and therefore it is considered an important indicator of the process economy (Berman et al., 2000a). The removal rate increases with an increasing Ca/S ratio although it can be kept constant after a certain critical value, dependent on several factors such as the coal suflur content and the type of method employed (Matsushima et al., 2004; Nolan, 2000; Ollero et al., 2001; Wu et al., 2007). At large scale it is controlled by adjusting the feed of fresh slurry although it has also been reported that a difference between the internal ratio with respect the outside should be taken into account: when part of the solid product with unconverted lime is recirculated, the internal Ca/S ratio is greater (Ollero et al., 1997). The recirculated slurry may not be as effective as the fresh one because of the layer of reaction products formed over the surface that induces diffusion. Table 3 summarizes several range Ca/S values of different technologies. For the sake of comparison, other technologies apart from the wet type were included.

Range of pH

The pH value in the absorber depends on the SO_2 absorption and the availability and rate of dissolution of the alkaline reagent (Qin, Hansen, & Kiil, 2014). It is a very important operation parameter because it affects the dissolution of the solids, the relative concentration of HSO_3^- and SO_3^{2-}, and the dissolution equilibrium of SO_2 (Zheng, Kiil, & Johnsson, 2003). Its range is limited by two extreme values (Figure 7).

1. Low pH values accelerate the dissolution of limestone and magnesium compounds, as it is mass-transfer controlled, at the expense of giving higher concentrations of HSO_3 that inhibite the dissociation of SO_2 (Carletti et al., 2013; Guo, Pan, Zhang, Xu, & Ren, 2011; Shengyu et al., 2008; Wallin & Bjerle, 1989). Moreover, absorption at low pH favores the elimination of sulfite ions, the dissolution of $CaSO_3$ and the crystallization of $CaSO_4$ in the bottom tank, all of which reduce the risk of scaling and plugging and therefore suppose lower operating and maintenance costs (Dou, Pan, Jin, Wang & Li, 2009; Shengyu et al., 2008).

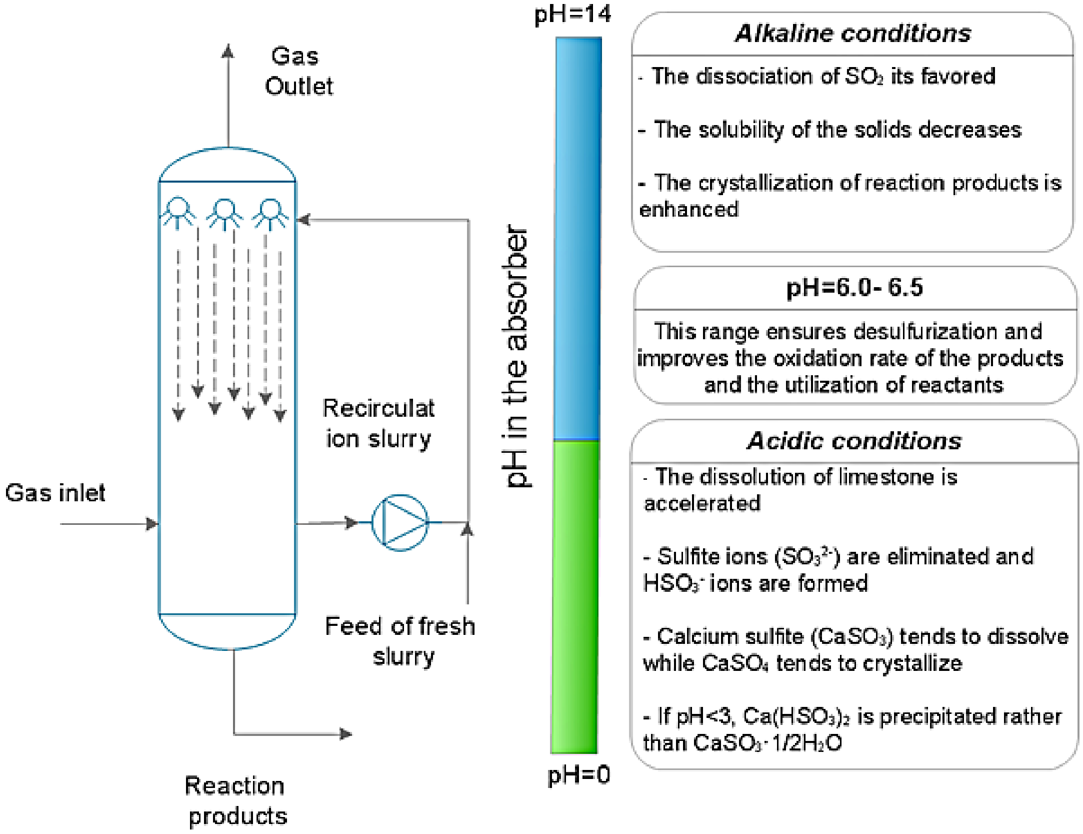
Table 3. Ranges of Ca/S ratio for several technologies including others than the wet type

FGD Technology	Ca/S (mol/mol)	Ref.
Pilot packed absorber using limestone	1.0-1.5	(Gutiérrez Ortiz et al., 2006)
Gas-continuous impinging stream gas-liquid reactor using lime	1.0-1.6	(Wu, Li, & Li, 2007)
Double coaxial cylinders with impinging streams using lime	1.8	(Berman et al., 2000)
Spray tower using limestone	1.03	(Carletti et al., 2013)
Semi-dray FGD with multifluid lime spray generator	1.5	(Y. Zhou, Zhang, Wang, & Wang, 2005)
Oxy-fuel CFB combustor using limestone and different kinds of coals	2.5-4.0	(Duan, Sun, Zhao, Zhou, & Chen, 2014)
Semi-dry DPT using lime mesh	1.0-1.8	(Chang et al., 2011)
Electrostatic Spray using limewater	0.8-1.3	(Z. Wang & Luo, 2009)
DSI using lime	0.8-2.52	(Gutiérrez Ortiz & Ollero, 2001)
DSI using activated lime	0.7-2.3	(Gutiérrez Ortiz & Ollero, 2003)
COOLSIDE process: Injection of lime in a humidified flue gas	2	(Stouffer, Yoon, & Burke, 1989; Yoon, Stouffer, Rosenhoover, Withum, & Burke, 1988)
LIMB	2	(Goots, T.R., DePero, M.J.M Nolan, 1992; Nola, P.S., Becker, 1992; Nolan, 2000)

COOLSIDE process: In-duct injection technology applied during the combustion of coals developed by CONSOL Inc. and the U.S. Department of Energy (DOE) (Stouffer, Rosenhoover, & Withum, 1993); LIMB process: "The Limestone Injection Multistage Burner Demonstration" (Nolan, 2000).

CFB: Circulating Fluidized Bed; DPT: Dense Phase Tower; DSI: Duct Sorbent Injection;

Figure 7. The pH regime of a limestone wet absorber. Main features at both alkaline and acidic conditions.



2. High pH values reduce the solids solubility while benefitting the absorption of SO_2. When it is maintained above 4, the liquid-side resistance can be neglected and the gas film mass transport resistance dominates the absorption process (Frandsen et al., 2001; Lancia et al., 1997).

In the actual industrial running, the slurry pH value should be maintained in the 6.0-6.5 range in order to ensure the desulfurization efficiency, improve the utilization of the absorbent and hence reduce costs and improve the oxidation rate of the reaction products (Shen et al., 2012, 2013).

In the case of magnesium enhanced processes, the dissolution of magnesium compounds (both the magnesium hydroxide as reagent and magnesium sulfite as the product) are also controlled by pH (Shen et al., 2012; Wang, Keener, Li, & Khang, 1998).

Therefore, pH control at the absorber is essential for a reliable scrubber operation and its value is controlled by the addition of feed mixture (Carletti et al., 2013; Frandsen et al., 2001).

The Contact between Phases: The Liquid-to-Gas (L/G) Ratio

The liquid-to-gas (L/G) ratio is defined as the quotient between the flow rate of the recycle slurry (liters per time units) and the flow rate (m^3 per time units) of the flue gas and is determinant of the recycle's pump power in a scrubber (Gutiérrez Ortiz et al., 2006). Its importance lies in the fact that the absorption of SO_2 is a mass transfer process that is favored by a large interface area and the effectivity of the contact between phases. As more slurry droplets contact with the flue gas,the mass transfer process improves, although leading to more energy consumption and thus operation costs (Gao et al., 2011; Shen et al., 2013). Although increasing the L/G ratio improves the removal efficiency, increasing beyond a limit strengths the cohesion of droplets and ends up decreasing the effective gas-liquid interface, resulting in smaller mass-transfer rate (Gao et al., 2011; Wu, Li, & Li, 2007). Therefore, there's a trade-off between the desulfurization efficiency, the operation costs and the L/G ratio. Table 4 presents different values of L/G reported in the literature corresponding to different technologies.

Different authors have addressed the influence of different parameters and variables when optimizing this ratio (Gutiérrez Ortiz et al., 2006; Kikkawa et al., 2002; Warych & Szymanowski, 2001; Zhao, Jin, & Zhong, 2007):

- A good design can minimize the L/G ratio and hence optimize the operation.
- At a constant flow rate, the decrease in the L/G ratio will lead to lower power consumption due to the induced-draft fan.
- Along with pH, the L/G ratio influences the sorbent consumption
- The height of the absorption tower and the diameter of the slurry drop exert a great influence over L/G.

The goal of economical optimization is the combination of pH and L/G ratio for a required desulfurization efficiency at minimum operation costs.

Reactivity: Particle Size Distribution and Dissolution of the Solids

The effects of particle size distribution (PSD) near the gas-liquid interface are highly significant (Mehra, 1996). The enhancement of the SO_2 removal rate by limestone slurries has been commonly addressed by

Table 4. Ranges of the L/G ratio corresponding different FGD technologies

FGD Technology	L/G (L/m^3)	Ref.
Magnesium-based spray scrubber	8-10	(Shen et al., 2013)
Lime-based impingin stream gas-liquid reactor	0.85-1.0	(Wu et al., 2007)
Limestone spraying absorber	9-13	(Dou et al., 2009)
Spray tower	15	(Carletti et al., 2013)
Spray tower	8-15	(Warych & Szymanowski, 2001)
Limestone packed tower	15.5	(Kiil et al., 1998)
Limestone PCF device	10	(Gao et al., 2011)
Spray tower	~17	(Kallinikos, Farsari, Spartinos, & Papayannakos, 2010)
Co-current packed tower using limestone and several additives	13.1-13.5	(Hansen, Kiil, Johnsson, & Sonder, 2008)
Co-current packed tower using limestone/chalk	14.24-14.28	(Frandsen et al., 2001)
Countercurrent pilot-scale packed tower	7.5-15	(Gutiérrez Ortiz et al., 2006)
Spray sieve tray scrubber using $NaClO_2$/NaOH solution	5-10	(Chien & Chu, 2000)

reducing the size of the solids for accelerating dissolution and hence reduce the volume of the holding tank (Frandsen et al., 2001; Kiil et al., 1998; V. Bravo, F. Camacho, M. Moya, & A. I. García, 2002). In this aspect, the process of dissolution takes place both at the absorption tower and the feed tank of the FGD system. Besides PSD, other factors such as the source of origin of the solids, the pH of the liquid phase and the sulfite ion concentration have also been reported to be influential to the dissolution (Dragan & Ozunu, 2012; Eden & Luckas, 1998; Kallinikos et al., 2010). Dissolution is a mass transfer process controlled by diffusion through the liquid film surrounding the particles (A Lancia, Musmarra, Pepe, & Volpicelli, 1994; Amedeo Lancia et al., 1997; Shih, Lin, & Shiau, 2000). However, at pH > 5 the surface kinetics becomes more important (Brogren & Karlsson, 1997; A Lancia et al., 1994). Related to this, higher sulfite ion concentrations in the suspension inhibit the dissolution process because of the crystallization taking place over the calcium carbonate surface (Dragan & Ozunu, 2012).

Besides playing an important role in the absorption, limestone dissolution is also determinant for the quality of the gypsum that can be obtained as a byproduct of the process (A Lancia et al., 1994).

The dissolution of other alkaline solids has been also subject of study. For instance, the dissolution rate of magnesium hydrate increases with increasing stirring speed due to the enhancement of the mass transfer process (Guo et al., 2011). On the contrary, the slow dissolution of dolomite is controlled by chemical reaction, which makes it suitable for the neutralization of acid soils in agriculture (Ahlbeck, Engman, Fältén, & Vihma, 1995).

TECHNICAL CONSIDERATIONS

Corrosion, Scaling, and Foaming

The phenomenon of corrosion occurs at low pH and is highly exacerbated in the presence of chloride ions from coal, water and lime/limestone (Karlsson & Rosenberg, 1980). This problem is scarcely reported in the literature as it is commonly dealt by selecting adequate materials for the FGD system. On the other hand, scaling is a complex phenomenon that depends on design parameters as well as on the chemistry and variables of the process. There are three types of scaling:

1. Carbonate scaling,
2. Sulfite scaling,
3. Sulfate scaling.

Carbonate and sulfite scaling can be controlled by keeping the pH below 9 (Karlsson & Rosenberg, 1980). Controlling sulfate scaling requieres the regulation of the oxidation rate of sulfite to sulfate, by bubbling compressed air (air forced oxidation) and enabling the precipitation at the bottom of the scrubber (Two-units FGD system) or at a separate reaction tank (Three-units FGD system). An alternative is to avoid precipitation in the pipeline by adding inhibition agents such as emulsified sulfur or sodium thiosulfate (Nolan, 2000; Ryu, Grace, & Lim, 2006). The recirculation of large amounts of gypsum also eases the deposition of newly formed $CaSO_4$ particles over the already formed crystals, reducing the risk of scaling (Karlsson & Rosenberg, 1980).

Foaming is caused by adipic acids, small particles/electrolytes, and microbiology. It can cause interference with the online measurements of the slurry level and its density, it can favor gypsum scaling in the demister and ease cavitation in recycle pumps as well as overflow in the slurry tank (Hansen et al., 2008). However, it has also been described as beneficial, as it implies an increase in the liquid/gas interfacial area (Frandsen et al., 2001).

Management of the Effluents

After depleting the alkaline potential of the slurry, the reaction products are taken to dewatering. Two kinds of dewatering systems are reported: hydrocyclones for the first step of dewatering and centrifugal separator or thickener and belt filter for the second (EPRI, 2006; Warych & Szymanowski, 2001). Either way, two streams are finally produced: the dewatered or residual solids and the wastewater effluents.

The potential reutilization or disposal of the residual solids is a dependent on their composition, which in turn is influenced by the type of coal used during the combustion process, the type of alkaline absorbent used in FGD system, and the presence of any other air emission control device (EPRI, 2007). Alternatively to landfill, they can be reused in different fields according to their quality and characteristics. The main fields of reutilization are in building (95% - wallboard and cement production) and agricultue (5%) (EPRI, 2001).

The reutilization as construction material must take into consideration the change of color promoted by several compounds that might affect the commercialization as wallboard gypsum characteristics (EPRI, 2001; Tokalic, Marinkovic, & Trifunovic, 2012). The presence of soluble salts can as well reduce the required calcination temperature during gypsum preparation and promote corrosion and efflorescence once is put in service (EPRI, 2001).

The unreacted alkalinity, the presence of required plant nutrients, suitable solubility and high levels of available Ca allows to consider FGD residual solids a great promise for the agricultural field (EPRI, 2007). Their benefits can be summarized as follows (Clark, Ritchey, & Baligar, 2001):

1. They posses an amendment capacity to mitigate low soil pH problema.
2. Can provide a source of nutrients to plants and animals (e.g. Mg, Ca and S).
3. They can improve sodic soil problems.
4. They can reduce the phosphorus availability/transport.

However, the constraints are the excessive presence of soluble salts and other compounds such as Al, B, F, Se and other trace elements (Clark et al., 2001; EPRI, 2006).

The disposal in either a landfill or pit/quarry also require the assessment of the long-term environmental impact of the leachate generated (Zhou & Dayal, 1990). The parameters of concern in the leachates and the FGD wastewater are the total solids (TSS) and the concentration of several anions such as Fl^-, Cl^- and SO_4^{2-}, trace metals (Se, Hg, Al, Sb, Be and Ta) and NH_3 (EPRI, 2006).

CONCLUSION

During the last years, the research over more efficient removal technologies of SO_2 has been fostered by the tightening of emission control policies and the expected increase in coal and fossil fuels in the years to come. In this chapter, the aspects related to the origin, development and deployment of Flue Gas Desulfurization (FGD) technologies have been summarized in order to provide an overall description of the process and allow the reader to go in depth with other aspects in the next chapters. A general depiction on the early studies over SO_2 removal and the absorption mechanisms was presented in the first sections as a prelude for understanding the current status of FGD processes. The understanding of the chemistry involved enabled to develop the different configurations that nowadays are available. Because of their importance, a detailed analysis was performed on the benefits and constraints of the lime and limestone FGD systems, which nowadays represent over 90% of the installed desulfurization capacity worldwide. The magnesium-based wet FGD process was also described, together with other alternative processes that are gaining popularity, such as the use of seawater and other inorganic/organic absorbents. The analysis of the variables and parameters affecting the desulfurization performance showed that their optimizing is aimed at achieving a high degree of SO_2 removal with minimum operation costs. The most important parameters such as the PSD have been described as a preamble for understanding how the nanotechnology could play an important role. Moreover, an assessment of the main technical considerations and the aspects influencing the management of effluents is necessary for successfully carried out a FGD process.

REFERENCES

A history of flue gas desulfurization systems since 1850. Research, development and demonstration. (1977). *Journal of Air Pollution Control Association*, *27*, 948–61.

Adewuyi, Y. G., He, X., Shaw, H., & Lolertpihop, W. (1999). Simultaneous absorption and oxidation of NO and SO_2 by aqueous solutions of sodium chlorite. *Chemical Engineering Communications*, *174*(1), 21–51. doi:10.1080/00986449908912788

Ahlbeck, J., Engman, T., Fältén, S., & Vihma, M. (1995). Measuring the reactivity of limestone for wet flue-gas desulfurization. *Chemical Engineering Science*, *50*(7), 1081–1089. doi:10.1016/0009-2509(94)00482-7

Al-Enezi, G., Ettouney, H., El-Dessouky, H., & Fawzi, N. (2001). Solubility of sulfur dioxide in seawater. *Industrial & Engineering Chemistry Research*, *40*(5), 1434–1441. doi:10.1021/ie9905963

Álvarez-Ayuso, E., Querol, X., & Tomás, A. (2006). Environmental impact of a coal combustion-desulphurisation plant: Abatement capacity of desulphurisation process and environmental characterisation of combustion by-products. *Chemosphere*, *65*(11), 2009–2017. doi:10.1016/j.chemosphere.2006.06.070 PMID:16890268

Baboian, R. (1986). Materials Degradation Caused by Acid Rain. Proceedings of the *American Chemical Society Symposium Series*, 318. doi:10.1021/bk-1986-0318

Bandyopadhyay, A., & Biswas, M. N. (2006). Prediction of the removal efficiency of a novel two-stage hybrid scrubber for flue gas desulfurization. *Chemical Engineering & Technology*, *29*(1), 130–145. doi:10.1002/ceat.200500160

Bekassy-Molnar, E., Marki, E., & Majeed, J. G. (2005). Sulphur dioxide absorption in air-lift-tube absorbers by sodium citrate buffer solution. *Chemical Engineering and Processing: Process Intensification*, *44*(9), 1039–1046. doi:10.1016/j.cep.2005.02.001

Bellas, A. S. (1998). Empirical evidence of advances in scrubber technology. *Resource and Energy Economics*, *20*(4), 327–343. doi:10.1016/S0928-7655(97)00039-0

Berman, Y., Tanklevsky, A., Oren, Y., & Tamir, A. (2000). Modeling and experimental studies of SO_2 absorption in coaxial cylinders with impinging streams: Part I. *Chemical Engineering Science*, *55*(5), 1009–1021. doi:10.1016/S0009-2509(99)00380-2

Berman, Y., Tanklevsky, A., Oren, Y., & Tamir, A. (2000b). Modeling and experimental studies of SO_2 absorption in coaxial cylinders with impinging streams: Part II. *Chemical Engineering Science*, *55*(5), 1023–1028. doi:10.1016/S0009-2509(99)00381-4

Bettelheim, J., Kyte, W.S. and Littler, A. (1981). Fifty years experience of flue gas desulphurisation at power stations in the United Kingdom. *The Chemical Engineer*, 275-277(284).

Biondo, S. J., & Marten, J. C. (1977). A History Of Flue Gas Desulfurization Systems Since 1850. *Journal of the Air Pollution Control Association*, *27*(10), 948–961. doi:10.1080/00022470.1977.10470518

Biswas, R., Devotta, S., Chakrabarti, T., & Pandey, R. A. (2005). Flue Gas Desulfurization: Physicochemical and Biotechnological Approaches. *Critical Reviews in Environmental Science and Technology*, *35*(6), 571–622. doi:10.1080/10643380500326374

Brasseur, G. P., Orlando, J. J., & Tyndall, G. S. (Eds.). (1999). *Atmospheric Chemistry and Global Change*. New York: Oxford University Press.

Brauer, H. (1984). Air Pollution Control Equipment. In O. Hutzinger (Ed.), The handbook of environmental chemistry (Volume 4, part B, pp. 188–252).

Bravo, V., R., F. Camacho, R., M. Moya, V., & A. I. García, L. (. (2002). Desulphurization of SO_2–N_2 mixtures by limestone slurries. *Chemical Engineering Science*, *57*(11), 2047–2058. doi:10.1016/S0009-2509(02)00095-7

Brogren, C., & Karlsson, H. T. (1997). Modeling the absorption of SO_2 in a spray scrubber using the penetration theory. *Chemical Engineering Science*, *52*(18), 3085–3099. doi:10.1016/S0009-2509(97)00126-7

Bromley, L. A. (1972). Use of sea water to scrub sulfur dioxide from stack gases. *Int. J. Sulfur Chem. Part B*, *7*(1), 77–84.

Caiazzo, G., Di Nardo, A., Langella, G., & Scala, F. (2012). Seawater scrubbing desulfurization: A model for SO_2 absorption in fall-down droplets. *Environmental Progress and Sustainable Energy*, *31*(2), 277–287. doi:10.1002/ep.10541

Carleson, T. E., & Berg, J. C. (1983). The effect of electric fields on the absorption of pure sulfur dioxide by water drops. *Chemical Engineering Science*, *38*(6), 871–876. doi:10.1016/0009-2509(83)80008-6

Carletti, C., Bjondahl, F., De Blasio, C., Ahlbeck, J., Järvinen, L., & Westerlund, T. (2013). Modeling limestone reactivity and sizing the dissolution tank in wet flue gas desulfurization scrubbers. *Environmental Progress and Sustainable Energy*, *32*(3), 663–672. doi:10.1002/ep.11683

Chang, G., Song, C., & Wang, L. (2011). A modeling and experimental study of flue gas desulfurization in a dense phase tower. *Journal of Hazardous Materials*, *189*(1-2), 134–140. doi:10.1016/j.jhazmat.2011.02.009 PMID:21377795

Chen, H., Ge, H., Dou, B., Pan, W., & Zhou, G. (2009). Thermogravimetric Kinetics of $MgSO_3·6H_2O$ Byproduct from Magnesia Wet Flue Gas Desulfurization. *Energy & Fuels*, *23*(5), 2552–2556. doi:10.1021/ef900083f

Chen, Z., Yates, D., Neathery, J. K., & Liu, K. (2012). The effect of fly ash on fluid dynamics of CO_2 scrubber in coal-fired power plant. *Chemical Engineering Research & Design*, *90*(3), 328–335. doi:10.1016/j.cherd.2011.07.024

Chien, T.-W., & Chu, H. (2000). Removal of SO_2 and NO from flue gas by wet scrubbing using an aqueous $NaClO_2$ solution. *Journal of Hazardous Materials*, *80*(1-3), 43–57. doi:10.1016/S0304-3894(00)00274-0 PMID:11080568

Choi, W.-J., Seo, J.-B., Cho, S.-W., Park, S.-W., & Oh, K.-J. (2009). Simultaneous absorption of CO_2 and SO_2 into aqueous AMP/NH_3 solutions in binary composite absorption system. *Korean Journal of Chemical Engineering*, *26*(3), 705–710. doi:10.1007/s11814-009-0118-6

Chu, H., Chien, T. W., & Li, S. Y. (2001). Simultaneous absorption of SO_2 and NO from flue gas with $KMnO_4$/NaOH solutions. *The Science of the Total Environment*, *275*(1–3), 127–135. doi:10.1016/S0048-9697(00)00860-3 PMID:11482398

Clark, R. B., Ritchey, K. D., & Baligar, V. C. (2001). Benefits and constraints for use of FGD products on agricultural land. *Fuel*, *80*(6), 821–828. doi:10.1016/S0016-2361(00)00162-9

Colle, S., Thomas, D., & Vanderschuren, J. (2005). Process simulations of sulphur dioxide abatement with hydrogen peroxide solutions in a packed column. *Chemical Engineering Research and Design*, 83(1 A), 81–87.

Colle, S., Vanderschuren, J., & Thomas, D. (2004). Pilot-scale validation of the kinetics of SO2 absorption into sulphuric acid solutions containing hydrogen peroxide. *Chemical Engineering and Processing: Process Intensification*, *43*(11), 1397–1402. doi:10.1016/j.cep.2004.04.005

Colle, S., Vanderschuren, J., & Thomas, D. (2005). Simulation of SO2 absorption into sulfuric acid solutions containing hydrogen peroxide in the fast and moderately fast kinetic regimes. *Chemical Engineering Science*, *60*(22), 6472–6479. doi:10.1016/j.ces.2005.04.076

Colle, S., Vanderschuren, J., & Thomas, D. (2008). Effect of temperature on SO2 absorption into sulphuric acid solutions containing hydrogen peroxide. *Chemical Engineering and Processing: Process Intensification*, *47*(9-10), 1603–1608. doi:10.1016/j.cep.2007.08.014

Comission of the European Communities. (2006). *Green Paper – A European Strategy for Sustainable*. Brussels: Competitive and Secure Energy.

Crnkovic, P. M., Milioli, F. E., & Pagliuso, J. D. (2006). Kinetics study of the SO_2 sorption by Brazilian dolomite using thermogravimetry. *Thermochimica Acta*, *447*(2), 161–166. doi:10.1016/j.tca.2006.05.023

Dagaonkar, V., M., A.C.M. Beenackers, A., & G. Pangarkar, V. (. (2001). Absorption of sulfur dioxide into aqueous reactive slurries of calcium and magnesium hydroxide in a stirre cell. *Chemical Engineering Science*, *56*(3), 1095–1101. doi:10.1016/S0009-2509(00)00326-2

Del Valle-Zermeño, R., Formosa, J., Aparicio, J. A., & Chimenos, J. M. (2014). Reutilization of low-grade magnesium oxides for flue gas desulfurization during calcination of natural magnesite: A closed-loop process. *Chemical Engineering Journal*, *254*, 63–72. doi:10.1016/j.cej.2014.05.089

Del Valle-Zermeño, R., Niubó, M., Formosa, J., Guembe, M., Aparicio, J. A., & Chimenos, J. M. (2015). Synergistic effect of the parameters affecting wet flue gas desulfurization using magnesium oxides by-products. *Chemical Engineering Journal*, *262*, 268–277. doi:10.1016/j.cej.2014.09.085

Dou, B., Byun, Y.-C., & Hwang, J. (2008). Flue gas desulfurization with an electrostatic spraying absorber. *Energy & Fuels*, *22*(2), 1041–1045. doi:10.1021/ef700646c

Dou, B., Pan, W., Jin, Q., Wang, W., & Li, Y. (2009). Prediction of SO_2 removal efficiency for wet Flue Gas Desulfurization. *Energy Conversion and Management*, *50*(10), 2547–2553. doi:10.1016/j.enconman.2009.06.012

Douabul, A., & Riley, J. (1979). Solubility of Sulfur Dioxide in distilled water and decarbonated sea water. *Journal of Chemical & Engineering Data*, *24*(4), 274–276. doi:10.1021/je60083a014

Dragan, S., & Ozunu, A. (2012). Characterization of calcium carbonates used in wet flue gas desulphurization processes. *Central European Journal of Chemistry*, *10*(5), 1556–1564. doi:10.2478/s11532-012-0068-4

Du, Q., Zhao, H., Ming, L., Gao, J., Zhao, G., & Wu, S. (2011). Experimental Investigation on the Kinetics of NO Complex Absorption through Fe II EDTA Solvent in a Double-Stirred Reactor. *Industrial & Engineering Chemistry Research*, *50*(8), 4425–4431. doi:10.1021/ie102501h

Duan, L., Sun, H., Zhao, C., Zhou, W., & Chen, X. (2014). Coal combustion characteristics on an oxy-fuel circulating fluidized bed combustor with warm flue gas recycle. *Fuel*, *127*, 47–51. doi:10.1016/j.fuel.2013.06.016

Ebrahimi, S., Picioreanu, C., Kleerebezem, R., Heijnen, J. J., & van Loosdrecht, M. C. M. (2003). Rate-based modelling of SO_2 absorption into aqueous $NaHCO_3$/Na_2CO_3 solutions accompanied by the desorption of CO_2. *Chemical Engineering Science*, *58*(16), 3589–3600. doi:10.1016/S0009-2509(03)00231-8

Eden, D., & Luckas, M. (1998). A heat and mass transfer model for the simulation of the wet limestone flue gas scrubbing process. *Chemical Engineering & Technology*, *21*(1), 56–60. doi:10.1002/(SICI)1521-4125(199801)21:1<56::AID-CEAT56>3.0.CO;2-9

Electric Power Research Institute (EPRI). (2001). *Alternative By-Products from Flue Gas Desulfurization Systems: Utilization of Clean Coal By-Products from SO_2 Control Process*. Retrieved from www.epri.com/abstracts/Pages/ProductAbstract.aspx?ProductId=000000000001004611

Electric Power Research Institute (EPRI). (2006). *Flue Gas Desulfurization (FGD) Wastewater Characterization: Screening Study*. Retrieved from http://www.epri.com/abstracts/Pages/ProductAbstract.aspx?ProductId=000000000001010162

Electric Power Research Institute (EPRI). (2006). *SO_3 Mitigation: Current Utility Operating Experience*. Retrieved from http://www.epri.com/abstracts/Pages/ProductAbstract.aspx?ProductId=000000000001010754

Electric Power Research Institute (EPRI)EPRI. (2007). *Use of Flue Gas Desulfurization Products in Agricultural Applicatio*ns. Retrieved from http://www.epri.com/abstracts/Pages/ProductAbstract.aspx?ProductId=000000000001012698

Erga, O. (1980). SO_2 Recovery by a sodium citrate solution scrubbing. *Chemical Engineering Science*, *35*(1-2), 162–169. doi:10.1016/0009-2509(80)80083-2

European Environment Agency. (2014). *Air Quality in Europe*, Retrieved from http://www.eea.europa.eu/publications/air-quality-in-europe-2013

Frandsen, J. B. W., Kiil, S., & Johnsson, J. E. (2001). Optimisation of a wet FGD pilot plant using fine limestone and organic acids. *Chemical Engineering Science*, *56*(10), 3275–3287. doi:10.1016/S0009-2509(01)00010-0

Freese, E. (1920). Absorption of sulfur dioxide by water. *Wochbl. Papierfabr.*, 51(861).

Gao, H., Li, C., Zeng, G., Zhang, W., Shi, L., & Fan, X. et al. (2011). Experimental study of wet flue gas desulphurization with a novel type PCF device. *Chemical Engineering and Processing: Process Intensification*, *50*(2), 189–195. doi:10.1016/j.cep.2010.12.011

Gómez, A., Fueyo, N., & Tomás, A. (2007). Detailed modelling of a flue-gas desulfurisation plant. *Computers & Chemical Engineering*, *31*(11), 1419–1431. doi:10.1016/j.compchemeng.2006.12.004

Goots, T. R., De Pero, M. J., & Nolan, P. S. (1992). *Demonstration Project Extension and Coolside Demonstration*. Retrieved from http://netl.doe.gov/File%20Library/Research/Coal/major%20demonstrations/cctdp/Round1/000000A7.pdf

Guo, R.-T., Pan, W.-G., Zhang, X.-B., Xu, H.-J., & Ren, J.-X. (2011). Dissolution rate of magnesium hydrate for wet flue gas desulfurization. *Fuel*, *90*(1), 7–10. doi:10.1016/j.fuel.2010.08.016

Gutiérrez Ortiz, F. J., & Ollero, P. (2001). A pilot plant technical assessment of an advanced in-duct desulphurisation process. *Journal of Hazardous Materials*, *83*(3), 197–218. doi:10.1016/S0304-3894(00)00364-2 PMID:11348732

Gutiérrez Ortiz, F. J., & Ollero, P. (2003). Flue-Gas Desulfurization in an Advanced in-Duct Desulfurization Process: An Empirical Model from an Experimental Pilot-Plant Study. *Industrial & Engineering Chemistry Research*, *42*(25), 6625–6637. doi:10.1021/ie030185t

Gutiérrez Ortiz, F. J., Vidal, F., Ollero, P., Salvador, L., Cortés, V., & Giménez, A. (2006). Pilot-plant technical assessment of wet flue gas desulfurization using limestone. *Industrial & Engineering Chemistry Research*, *45*(4), 1466–1477. doi:10.1021/ie051316o

Hanks, W. V., & McAdams, W. H. (1929). Studies in absorption. I-Very soluble gases. *Industrial & Engineering Chemistry*, *21*(1034).

Hansen, B. B., Fogh, F., Knudsen, N. O., & Kiil, S. (2011). Performance of a wet flue gas desulfurization pilot plant under oxy-fuel conditions. *Industrial & Engineering Chemistry Research*, *50*(8), 4238–4244. doi:10.1021/ie1022173

Hansen, B. B., & Kiil, S. (2012). Investigation of Parameters affecting Gypsum Dewatering Properties in a Wet Flue Gas Desulphurization Pilot Plant. *Industrial & Engineering Chemistry Research*, *51*(30), 10100–10107. doi:10.1021/ie3005435

Hansen, B. B., Kiil, S., Johnsson, J. E., & Sonder, K. B. (2008). Foaming in wet flue gas desulfurization plants: The influence of particles, electrolytes, and buffers. *Industrial & Engineering Chemistry Research*, *47*(9), 3239–3246. doi:10.1021/ie071660g

Higbie, R. (1935). The rate of absorption of a pure gas into a still liquid during short periods of exposure. *Transactions of American Institute of Chemical Engineers*, *31*, 365–389.

Hikita, H., Asai, S., & Takatsuka, T. (1972). Gas absorption with a two-step instantaneous chemical reaction. *The Chemical Engineering Journal*, *4*(1), 31–40. doi:10.1016/0300-9467(72)80050-9

Hjuler, K., & Dam-Johansen, K. (1994). Wet oxidation of residual product from spray absorption of sulphur dioxide. *Chemical Engineering Science*, *49*(2424 PART A), 4515–4521. doi:10.1016/S0009-2509(05)80037-5

Hlincik, T., & Buryan, P. (2013). Desulfurization of boiler flue gas by means of activated calcium oxide. *Fuel Processing Technology*, *111*(0), 62–67. doi:10.1016/j.fuproc.2013.01.018

Hlincik, T., & Buryan, P. (2013). Evaluation of limestones for the purposes of desulphurisation during the fluid combustion of brown coal. *Fuel*, *104*(0), 208–215. doi:10.1016/j.fuel.2012.09.074

Hrastel, I., Gerbec, M., & Stergaršek, A. (2007). Technology Optimization of Wet Flue Gas Desulfurization Process. *Chemical Engineering & Technology*, *30*(2), 220–233. doi:10.1002/ceat.200600314

Hwang, K.-S., Kim, D.-W., Park, S.-W., Park, D.-W., Oh, K.-J., & Kim, S.-S. (2009). Simultaneous absorption of carbon dioxide and sulfur dioxide into aqueous 1,8-diamino-p-menthane. *Separation Science and Technology*, *44*(16), 3888–3910. doi:10.1080/01496390903338444

International Energy Agency. (2014). *World Energy Investment Outlook*. Retrieved from http://www.iea.org/publications/freepublications/publication/world-energy-investment-outlook---special-report---.html

Jin, D.-S., Deshwal, B.-R., Park, Y.-S., & Lee, H.-K. (2006). Simultaneous removal of SO2 and NO by wet scrubbing using aqueous chlorine dioxide solution. *Journal of Hazardous Materials*, *135*(1-3), 412–417. doi:10.1016/j.jhazmat.2005.12.001 PMID:16442222

Johnson, R. W., Gordon, G. E., Calkins, W., & Elzerman, A. Z. (Eds.). (1987). *The Chemistry of Acid Rain: Sources and Atmospheric Processes*. Washington, D.C.: American Chemical Society. doi:10.1021/bk-1987-0349

Johnstone, H. F. (1931). Metallic ions as catalysts for the Removal of Sulfur Dioxide from Boiler Furnace Gases. *Industrial & Engineering Chemistry*, *23*(5), 559–561. doi:10.1021/ie50257a022

Johnstone, H. F., & Leppla, P. W. (1934). The solubility of sulfur dioxide at low partial pressures. The ionization constant and heat of ionization of sulfurous acid. *Journal of the American Chemical Society*, *56*(11), 2233–2238. doi:10.1021/ja01326a009

Johnstone, H. F., & Singh, A. D. (1940). Recovery of Sulfur Dioxide from Waste Gases. Regeneration of the Absorbent by Treatment with Zinc Oxide. *Industrial & Engineering Chemistry*, *32*(8), 1037–1048. doi:10.1021/ie50368a007

Joseph, G., & Beachler, D. (1998). *Scrubber Systems Operation Review. Flue Gas Desulfurization (Acid Gas Removal) Systems*. Retrieved from http://yosemite.epa.gov/oaqps/eogtrain.nsf/b81bacb527b016d785256e4a004c0393/d4ec501f07c0e03a85256b6c006caf64/$FILE/si412c_lesson9.pdf

Kakaraniya, S., Kari, C., Verma, R., & Mehra, A. (2007). Gas absorption in slurries of fine particles: SO_2-$Mg(OH)_2$-$MgSO_3$ system. *Industrial & Engineering Chemistry Research*, *46*(7), 1904–1913. doi:10.1021/ie061461h

Kallinikos, L. E., Farsari, E. I., Spartinos, D. N., & Papayannakos, N. G. (2010). Simulation of the operation of an industrial wet flue gas desulfurization system. *Fuel Processing Technology*, *91*(12), 1794–1802. doi:10.1016/j.fuproc.2010.07.020

Kaminski, J. (2003). Technologies and costs of SO_2-emissions reduction for the energy sector. *Applied Energy*, *75*(3-4), 165–172. doi:10.1016/S0306-2619(03)00029-1

Karlsson, H. T., Klingspor, J., Linne, M., & Bjerle, I. (1983). Activated wet-dry scrubbing of SO_2. *Journal of the Air Pollution Control Association*, *33*(1), 23–28. doi:10.1080/00022470.1983.10465543

Karlsson, H. T., & Rosenberg, H. S. (1980). Technical aspects of lime/limestone scrubbers for coal-fired power plants. I. Process chemistry and scrubber systems. *Journal of the Air Pollution Control Association*, *30*(6), 710–714. doi:10.1080/00022470.1980.10465999

Kiil, S., Michelsen, M. L., & Dam-johansen, K. (1998). Experimental Investigation and Modeling of a Wet Flue Gas Desulfurization Pilot Plant. *Industrial & Engineering Chemistry Research*, *37*(7), 2792–2806. doi:10.1021/ie9709446

Kikkawa, H., Nakamoto, T., Morishita, M., & Yamada, K. (2002). New wet FGD process using granular limestone. *Industrial & Engineering Chemistry Research*, *41*(12), 3028–3036. doi:10.1021/ie0109760

Krammer, G., Brunner, C., Khinast, J., & Staudinger, G. (1997). Reaction of $Ca(OH)_2$ with SO_2 at Low Temperature. *Industrial & Engineering Chemistry Research*, *36*(5), 1410–1418. doi:10.1021/ie960628b

Lamoreaux, W. F. (1916, May 16). *Recovering elemental sulfur from sulfurous gases*. U. S. Patent 1,182,915. CA 10:1918.

Lancia, A., Musmarra, D., & Pepe, F. (1997). Modeling of SO_2 Absorption into Limestone Suspensions. *Industrial & Engineering Chemistry Research*, *36*(1), 197–203. doi:10.1021/ie9602365

Lancia, A., Musmarra, D., Pepe, F., & Volpicelli, G. (1994). Characteristic times for limestone particle dissolution in the production of gypsum from the wet flue gas desulfurization process. *Environmental Science & Technology*, *28*(6), 1031–1036. doi:10.1021/es00055a011 PMID:22176227

Lee, C. C., & Huffman, G. L. (2007). Wet and Dry Scrubbers for Emission Control. In C. C. Lee & S. Dar Lin (Eds.), *Handbook of Environmental Engineering Calculations* (pp. 3103–3140). New York: McGraw-Hill.

Lee, C. C., Huffman, G. L., & Chang, J. C. S. (2007). Air Emission Control. In C. C. Lee & S. Dar Lin (Eds.), *Handbook of Environmental Engineering Calculations*. New York: McGraw-Hill.

Lefohn, A. S., Husar, J. D., & Husar, R. B. (1999). Estimating historical anthropogenic global sulfur emission patterns for the period 1850-1990. *Atmospheric Environment*, *33*(21), 3435–3444. doi:10.1016/S1352-2310(99)00112-0

Lepsoe, R. (1938). Chemistry of Sulfur Dioxide Reduction. Thermodynamics. *Industrial & Engineering Chemistry*, *30*(1), 92–100. doi:10.1021/ie50337a019

Lepsoe, R. (1940). Chemistry of Sulfur Dioxide Reduction. *Industrial & Engineering Chemistry*, *32*(7), 910–918. doi:10.1021/ie50367a011

Lewis, W. K., & Chang, K. C. (1928). Distillation III. The mechanism of rectification. Trans. *AlChE.*, *21*, 127.

Li, X., Zhu, C., & Ma, Y. (2013). Removal of SO_2 using ammonium bicarbonate aqueous solution as absorbent in a bubble column reactor. *Frontiers of Chemical Science and Engineering*, *7*(2), 185–191. doi:10.1007/s11705-013-1326-5

Lipfert, F. W. (1984). Mortality and Air Pollution. In O. Hutzinger (Ed.), The Handbook of Environmental Chemistry. Volume 4, part B: Air Pollution. Berlin, Springer-Verlag.

Lippmann, M. (2009). Sulfur Oxides-SO_2, H_2SO_4, NH_4HSO_4, and $(NH_4)2SO_4$. In M. Lippmann (Ed.), *Environmental Toxicants: Human Exposures and Their Health Effects*. United States: Wiley. doi:10.1002/9780470442890.ch25

Liu, S.-Y., & Xiao, W.-D. (2006). Modeling and simulation of a bubbling SO_2 absorber with granular limestone slurry and an organic acid additive. *Chemical Engineering & Technology*, *29*(10), 1167–1173. doi:10.1002/ceat.200600101

Mackenzie, L. D., & Cornwell, D. A. (1998). *Introduction to Environmental Engineering*. McGraw-Hill.

Malaga-Starzec, K., Panas, I., & Lindqvist, O. (2004). Model study of initial adsorption of SO_2 on calcite and dolomite. *Applied Surface Science*, *222*(1-4), 82–88. doi:10.1016/j.apsusc.2003.08.019

Mansfeld, F., Haagenrud, S., Kucera, V., Haynie, F., & Sinclair, J. (1986). *Proceedings of the Symposia on Corrosion Effects of Acid Deposition and Corrosion of Electronic Materials. The Electrochemical Society*, 86(6), 108–154.

Markusson, N. (2012). *Scaling up and deployment of FGD in the US (1960s-2009)*. Retrieved from www.geos.ed.ac.uk/homes/nmarkuss/CaseScaling.pdf

Marocco, L. (2010). Modeling of the fluid dynamics and SO_2 absorption in a gas-liquid reactor. *Chemical Engineering Journal*, *162*(1), 217–226. doi:10.1016/j.cej.2010.05.033

Mathieu, Y., Tzanis, L., Soulard, M., Patarin, J., Vierling, M., & Molière, M. (2013). Adsorption of SOx by oxide materials: A review. *Fuel Processing Technology*, *114*(0), 81–100. doi:10.1016/j.fuproc.2013.03.019

Matsushima, N., Li, Y., Nishioka, M., Sadakata, M., Qi, H., & Xu, X. (2004). Novel dry-desulfurization process using $Ca(OH)_2$/fly ash sorbent in a circulating fluidized bed. *Environmental Science & Technology*, *38*(24), 6867–6874. doi:10.1021/es035373p PMID:15669351

Mehra, A. (1996). Gas absorption in reactive slurries: Particle dissolution near gas-liquid interface. *Chemical Engineering Science*, *51*(3), 461–477. doi:10.1016/0009-2509(95)00259-6

Meikap, B. C., Kundu, G., & Biswas, M. N. (2002). A novel modified multi-stage bubble column scrubber for SO2 removal from industrial off gases. *Separation Science and Technology*, *37*(15), 3421–3442. doi:10.1081/SS-120014435

Meikap, B. C., Kundu, G., & Biswas, M. N. (2002). Modeling of a novel multi-stage bubble column scrubber for flue gas desulfurization. *Chemical Engineering Journal*, *86*(3), 331–342. doi:10.1016/S1385-8947(01)00226-1

Meikap, B. C., Kundu, G., & Biswas, M. N. (2002c). Scrubbing of fly-ash laden SO_2 in modified multistage bubble column scrubber. *AIChE Journal. American Institute of Chemical Engineers*, *48*(9), 2074–2083. doi:10.1002/aic.690480920

Michalski, J. (1999). The influence of aerodynamic characteristics on mass exchange efficiency in FGD scrubbers. *Chemical Engineering & Technology*, *22*(4), 343–351. doi:10.1002/(SICI)1521-4125(199904)22:4<343::AID-CEAT343>3.0.CO;2-T

Michalski, J. A. (1997). Aerodynamic characteristics of FGD spray towers. *Chemical Engineering & Technology*, *20*(2), 108–117. doi:10.1002/ceat.270200208

Michalski, J. A. (1998). The influence of spraying angle on aerodynamic characteristics of FGD spray towers. *Chemical Engineering Communications*, *165*(1), 17–40. doi:10.1080/00986449808912368

Mohan, B. R., Biswas, S., & Meikap, B. C. (2008). Performance characteristics of the particulates scrubbing in a counter-current spray-column. *Separation and Purification Technology*, *61*(1), 96–102. doi:10.1016/j.seppur.2007.09.018

Mondal, M. K., Chelluboyana, V. R., & Rao, J. S. (2013). Solubility of SO2 in aqueous blend of sodium citrate and sodium hydroxide. *Fluid Phase Equilibria*, *349*, 56–60. doi:10.1016/j.fluid.2013.03.025

Muginstein, A., Fichman, M., & Gutfinger, C. (2001). Gas absorption in a moving drop containing suspended solids. *International Journal of Multiphase Flow*, *27*(6), 1079–1094. doi:10.1016/S0301-9322(00)00063-X

Muramatsu, K., Shimizu, T., Shinoda, N., & Tatani, A. (1984). Development of Mitsubishi wet flue gas desulfurization system. *Chem. Econ. Eng. Rev*, *16*(11), 15–22.

Nelli, C. H., & Rochelle, G. T. (1998). Simultaneous sulfur dioxide and nitrogen dioxide removal by calcium hydroxide and calcium silicate solids. *Journal of the Air & Waste Management Association*, *48*(9), 819–828. doi:10.1080/10473289.1998.10463728 PMID:9775761

Nolan, P. S. (2000). *Flue Gas Desulfurization Technologies for Coal-Fired Power Plants*. Retrieved from http://www.babcock.com/library/Documents/br-1709.pdf

Nolan, P. S., Becker, T. W., Rodemeyer, P. O., & Prodesky, E. J. (1992). *Demonstration of Sorbent Injection Technology on a Wall-Fired Utility Boiler (Edgewater LIMB Demonstration)*. Retrieved from http://nepis.epa.gov/

Nygaard, H. G., Kiil, S., Johnsson, J. E., Jensen, J. N., Hansen, J., Fogh, F., & Dam-Johansen, K. (2004). Full-scale measurements of SO_2 gas phase concentrations and slurry compositions in a wet flue gas desulphurisation spray absorber. *Fuel*, *83*(9), 1151–1164. doi:10.1016/j.fuel.2003.12.007

Nyman, G. B. G. (1991). Seawater scrubbing removes SO_2 from refinery flue gases. *Oil & Gas Journal*, *89*(26), 51–55.

Ochoa González, R., Díaz-Somoano, M., López Antón, M. A., & Martínez-Tarazona, M. R. (2012). Effect of adding aluminum salts to wet FGD systems upon the stabilization of mercury. *Fuel*, *96*(0), 568–571. doi:10.1016/j.fuel.2012.01.054

Oikawa, K., Yongsiri, C., Takeda, K., & Harimoto, T. (2003). Seawater flue gas desulfurization: Its technical implications and performance results. *Environment and Progress*, *22*(1), 67–73. doi:10.1002/ep.670220118

Olausson, S., Wallin, M., & Bjerle, I. (1993). A model for the absorption of sulphur dioxide into a limestone slurry. *Chemical Engineering Journal*, *51*(2), 99–108. doi:10.1016/0300-9467(93)80016-H

Ollero, P., Gutiérrez Ortiz, F. J., Cabanillas, A., & Otero, J. (2001). Flue-gas desulfurization in circulating fluidized beds: An empirical model from an experimental pilot-plant study. *Industrial & Engineering Chemistry Research*, *40*(23), 5640–5648. doi:10.1021/ie010152i

Ollero, P., Salvador, L., & Cañadas, L. (1997). An experimental study of flue gas desulfurization in a pilot spray dryer. *Environment and Progress*, *16*(1), 20–28. doi:10.1002/ep.3300160116

Pandey, R. A., & Malhotra, S. (1999). Desulfurization of gaseous fuels with recovery of elemental sulfur: An overview. *Critical Reviews in Environmental Science and Technology*, *29*(3), 229–268. doi:10.1080/10643389991259236

Phillips, J. A., Canagaratna, M., Goodfriend, H., & Leopold, K. R. (1995). Microwave Detection of A Key Intermediate in the Formation of Atmospheric Sulfuric Acid: The Structure of H20-SO3. *Journal of Physical Chemistry*, *99*(2), 501–504. doi:10.1021/j100002a008

Poon, C. S., Kou, S. C., Lam, L., & Lin, Z. S. (2001). Activation of fly ash/cement systems using calcium sulfate anhydrite ($CaSO_4$). *Cement and Concrete Research*, *31*(6), 873–881. doi:10.1016/S0008-8846(01)00478-1

Poon, C. S., Qiao, X. C., & Lin, Z. S. (2004). Effects of flue gas desulphurization sludge on the pozzolanic reaction of reject-fly-ash-blended cement pastes. *Cement and Concrete Research*, *34*(10), 1907–1918. doi:10.1016/j.cemconres.2004.02.027

Pourmohammadbagher, A., Jamshidi, E., Ale-Ebrahim, H., Dabir, B., & Mehrabani-Zeinabad, M. (2011). Simultaneous removal of gaseous pollutants with a novel swirl wet scrubber. *Chemical Engineering and Processing: Process Intensification*, *50*(8), 773–779. doi:10.1016/j.cep.2011.06.001

Qin, S., Hansen, B. B., & Kiil, S. (2014). Effects of foaming and antifoaming agents on the performance of a wet flue gas desulfurization pilot plant. *AIChE Journal. American Institute of Chemical Engineers*, *60*(7), 2382–2388. doi:10.1002/aic.14428

Raj Mohan, B., & Meikap, B. C. (2010). Control of so2 from industrial effluents by a spray-cum bubble column scrubber. *Journal of Applied Sciences*, *10*(24), 3277–3282. doi:10.3923/jas.2010.3277.3282

Rajmohan, B., Reddy, S. N., & Meikap, B. C. (2008). Removal of SO2 from industrial effluents by a novel twin fluid air-assist atomized spray scrubber. *Industrial & Engineering Chemistry Research*, *47*(20), 7833–7840. doi:10.1021/ie800712a

Ramachandran, P. A., & Sharma, M. M. (1969). Absorption with fast reaction in a slurry containing sparingly soluble fine particles. *Chemical Engineering Science*, *24*(11), 1681–1686. doi:10.1016/0009-2509(69)87033-8

Rioux, P., & Berard, P. A. (1928). The rate of absorption of sulfur dioxide in alkaline solutions. *Compt. Rend.*, 186(1433).

Rochelle, G. T., & King, C. J. (1977). The effect of additives on mass transfer in $CaCO_3$ or CaO slurry scrubbing of SO_2 from waste gases. Industrial & Engineering Chemistry Fundamentals, *16*(1), 67–75. doi:10.1021/i160061a015

Ryu, H.-J., Grace, J. R., & Lim, C. J. (2006). Simultaneous CO_2/SO_2 capture characteristics of three limestones in a fluidized-bed reactor. *Energy & Fuels*, *20*(4), 1621–1628. doi:10.1021/ef050277q

Sada, E., Kumazawa, H., & Butt, M. A. (1977). Single gas absorption with reaction in a slurry containing fine particles. *Chemical Engineering Science*, *32*(10), 1165–1170. doi:10.1016/0009-2509(77)80048-1

Sada, E., Kumazawa, H., & Butt, M. A. (1979a). Chemical absorption into a finite slurry. *Chemical Engineering Science*, *34*(5), 715–718. doi:10.1016/0009-2509(79)85118-0

Sada, E., Kumazawa, H., & Butt, M. A. (1979b). Single and simultaneous absorptions of lean SO_2 and NO_2 into aqueous slurries of $Ca(OH)_2$ or $Mg(OH)_2$ particles. *Journal of Chemical Engineering of Japan*, *12*(2), 111–117. doi:10.1252/jcej.12.111

Shen, Z., Chen, X., Tong, M., Guo, S., Ni, M., & Lu, J. (2013). Studies on magnesium-based wet flue gas desulfurization process with oxidation inhibition of the byproduct. *Fuel*, *105*(0), 578–584. doi:10.1016/j.fuel.2012.07.050

Shen, Z., Guo, S., Kang, W., Zeng, K., Yin, M., Tian, J., & Lu, J. (2012). Kinetics and Mechanism of Sulfite Oxidation in the Magnesium-Based Wet Flue Gas Desulfurization Process. *Industrial & Engineering Chemistry Research*, *51*(11), 4192–4198. doi:10.1021/ie300163v

Shengyu, L., Wende, X., Pei, L., & Zhixiang, Y. (2008). Feasibility study of new limestone flue gas desulfurization process. *Clean - Soil, Air. Water (Basel)*, *36*(5-6), 482–487.

Sherwood, T. K. (1925). Solubilities of sulfur dioxide and ammonia in water. *Industrial & Engineering Chemistry*, *19*(745).

Sherwood, T. K. (1952). *Absorption and Extraction*. New York: McGraw-Hill, Inc.

Shih, S.-M., Lin, J.-P., & Shiau, G.-Y. (2000). Dissolution rates of limestones of different sources. *Journal of Hazardous Materials*, *79*(1-2), 159–171. doi:10.1016/S0304-3894(00)00253-3 PMID:11040393

Siagi, Z. O., & Mbarawa, M. (2009). Dissolution rate of South African calcium-based materials at constant pH. *Journal of Hazardous Materials*, *163*(2–3), 678–682. doi:10.1016/j.jhazmat.2008.07.014 PMID:18703281

Sims, T. H. (1861). Contributions to the knowledge of the laws of gas-absorption, sulfurous acid in water. *Journal of the Chemical Society*, *14*(1).

Smith, K., Booth, W., & Crevecoeur, S. *Evaluation of Wet FGD Technologies to Meet Requirements for Post CO_2 Removal of Flue Gas Streams*. Retrieved from http://www.mass.gov/eea/docs/dep/air/priorities/hazeapd25.pdf

Solem-Tishmack, J. K., McCarthy, G. J., Docktor, B., Eylands, K. E., Thompson, J. S., & Hassett, D. J. (1995). High-calcium coal combustion by-products: Engineering properties, ettringite formation, and potential application in solidification and stabilization of selenium and boron. *Cement and Concrete Research*, *25*(3), 658–670. doi:10.1016/0008-8846(95)00054-G

Sound, H. N. (2000). *Developments in FGD*. London: IEA Coal Research Centre.

Srivastava, R. K. (2000). *Controlling SO_2 emissions: a Review of Technologies*. Washington, United States: U.S. Environmental Protection Agency.

Srivastava, R. K., & Jozewicz, W. (2001). Flue Gas Desulfurization: The State of the Art. *Journal of the Air & Waste Management Association*, *51*(12), 1676–1688. doi:10.1080/10473289.2001.10464387 PMID:15666473

Stouffer, M. R., Rosenhoover, W. A., & Withum, J. A. (1993). Advanced coolside desulfurization process. *Environment and Progress*, *12*(2), 133–139. doi:10.1002/ep.670120211

Stouffer, M. R., Yoon, H., & Burke, F. P. (1989). An investigation of the mechanisms of flue gas desulfurization by in-duct dry sorbent injection. *Industrial & Engineering Chemistry Research*, *28*(1), 20–27. doi:10.1021/ie00085a005

Sun, Z., Zhao, Y., Gao, H., & Hu, G. (2010). Removal of SO_2 from Flue Gas by Sodium Humate Solution. *Energy & Fuels*, *24*(2), 1013–1019. doi:10.1021/ef901052r

Taerakul, P., Sun, P., Golightly, D. W., Walker, H. W., Weavers, L. K., Zand, B., & Fan, L.-S. (2007). Characterization and re-use potential of by-products generated from the Ohio State Carbonation and Ash Reactivation (OSCAR) process. *Fuel*, *86*(4), 541–553. doi:10.1016/j.fuel.2006.08.012

Taylor, M. R., Rubin, E. S., & Hounshell, D. A. (2005). Control of SO_2 emissions from power plants: A case of induced technological innovation in the U.S. *Technological Forecasting and Social Chan*ge, 72(6 SPEC. ISS.), 697–718.

Taylor, M. R., Rubin, E. S., & Hounshell, D. A. (2005). Regulation as the mother of innovation: The case of SO_2 control. *Law & Policy*, *27*(2), 348–378. doi:10.1111/j.1467-9930.2005.00203.x

Thomas, D., Colle, S., & Vanderschuren, J. (2003a). Designing wet scrubbers for SO_2 absorption into fairly concentrated sulfuric acid solutions containing hydrogen peroxide. *Chemical Engineering & Technology*, *26*(4), 497–502. doi:10.1002/ceat.200390074

Thomas, D., Colle, S., & Vanderschuren, J. (2003b). Kinetics of SO_2 absorption into fairly concentrated sulphuric acid solutions containing hydrogen peroxide. *Chemical Engineering and Processing: Process Intensification*, *42*(6), 487–494. doi:10.1016/S0255-2701(02)00070-3

Thompson Smith, W. M., & Parkhurst, R. B. (1922). The solubility of sulfur dioxide in suspensions of calcium and magnesium hydroxides. *Journal of the American Chemical Society*, *44*(9), 1918–1927. doi:10.1021/ja01430a010

Tokalic, R., Marinkovic, S., Trifunovic, P., Devic, G., & Zildzovic, S. (2013). Preliminary Examination of the System Fly Ash-Bottom Ash-Flue Gas Desulphurization Gypsum-Portland Cement-Water for Road Construction. *Journal of Chemistry*, *2013*, 421480. doi:10.1155/2013/421480

Tokumura, M., Baba, M., Znad, H. T., Kawase, Y., Yongsiri, C., & Takeda, K. (2006). Neutralization of the acidified seawater effluent from the flue gas desulfurization process: Experimental investigation, dynamic modeling, and simulation. *Industrial & Engineering Chemistry Research*, *45*(18), 6339–6348. doi:10.1021/ie0603619

Uchida, S., Moriguchi, H., Maejima, H., Koide, K., & Kageyama, S. (1978). Absorption of Sulfur Oxide into limesone slurry in a stirred tank reactor. *Canadian Journal of Chemical Engineering*, *56*(6), 690–697. doi:10.1002/cjce.5450560607

Ukawa, N., Okino, S., Iwaki, T., Oshima, M., & Watanabe, Y. (1992). The effects of fluoride complexes in wet limestone flue gas desulfurization. *Journal of Chemical Engineering of Japan*, *25*(2), 146–152. doi:10.1252/jcej.25.146

U.S. Energy Information Administration. (2013). *International Energy Outlook 2014*. Retrieved from http://www.eia.gov/forecasts/ieo/

U.S. Energy Information Administration. (2014). *Annual Energy Outlook*. Retrieved from http://www.eia.gov/forecasts/aeo/

Vidal, B., Ollero, F., Gutiérrez, P., Ortiz, F. J., & Villanueva, A. (2007). Catalytic seawater flue gas desulfurization process: An experimental pilot plant study. *Environmental Science & Technology*, *41*(20), 7114–7119. doi:10.1021/es0706899 PMID:17993156

Wallin, M., & Bjerle, I. (1989). A mass transfer model for limestone dissolution from a rotating cylinder. *Chemical Engineering Science*, *44*(1), 61–67. doi:10.1016/0009-2509(89)85233-9

Wang, J., Keener, T. C., Li, G., & Khang, S.-J. (1998). The dissolution rate of $Ca(OH)_2$ in aqueous solutions. *Chemical Engineering Communications*, *169*(1), 167–184. doi:10.1080/00986449808912726

Wang, L., Ma, Y., Yuan, G., & Hao, J. (2009). Study on the reaction characteristics of flue gas desulfurization by magnesia. Proceedings of the *3rd International Conference on Bioinformatics and Biomedical Engineering, iCBBE 2009*. Department of Environmental Science and Engineering, Tsinghua University, Beijing, China. doi:10.1109/ICBBE.2009.5163522

Wang, S. H., Chang, J. S., & Berezin, A. A. (1993). Atomization characteristics of electrohydrodynamic limestone-water slurry spray. *Journal of Electrostatics*, *30*(C), 235–246. doi:10.1016/0304-3886(93)90078-L

Wang, Z., & Luo, T. (2009). Experimental investigation on flue gas desulfurization by electrostatic spray. Proceedings of the *2009 International Conference on Energy and Environment Technology, ICEET 2009* (Vol. 3, pp. 44–47).

Wappel, D., Khan, A., Shallcross, D., Joswig, S., Kentish, S., & Stevens, G. (2009). The Effect of SO2 on CO2 Absorption in an Aqueous Potassium Carbonate Solvent. In Energy Procedia (Vol. 1, pp. 125–131).

Warych, J., & Szymanowski, M. (2001). Model of the wet limestone flue gas desulfurization process for cost optimization. *Industrial & Engineering Chemistry Research*, *40*(12), 2597–2605. doi:10.1021/ie0005708

Watts, W. M. (1864). On the absorption of mixed gases in water; II. Sulfurous acid and carbonic acid in water. *Journal of the Chemical Society*, *17*(98).

Wells, A. E. (1917). An Investigation of the Wet Thiogen Process. *Journal of Industrial and Engineering Chemistry*, *9*(9), 872–873. doi:10.1021/ie50093a019

Whitman, W. G. (1923). Preliminary experimental confirmation of the two-film theory of gas absorption. *Chemical and Metallurgical Engineering*, *29*, 146–148.

World Energy Council. (2014). *World Energy Insight*. Retrieved from http://www.worldenergy.org/publications/2013/world-energy-insight-2013/

Wu, J., Iizuka, A., Kumagai, K., Yamasaki, A., & Yanagisawa, Y. (2008). Desulfurization Characteristics of Waste Cement Particles as a Sorbent in Dry Desulfurization. *Industrial & Engineering Chemistry Research*, *47*(24), 9871–9877. doi:10.1021/ie8009654

Wu, X.-C., Zhao, H.-F., Zhang, Y.-X., Zheng, C.-H., & Gao, X. (2014). Measurement of slurry droplets in coal-fired flue gas after WFGD. *Environmental Geochemistry and Health*, Sept., 25. PMID:25252634

Wu, Y., Li, Q., & Li, F. (2007). Desulfurization in the gas-continuous impinging stream gas–liquid reactor. *Chemical Engineering Science*, *62*(6), 1814–1824. doi:10.1016/j.ces.2006.01.027

Xia, J., Rumpf, B., & Maurer, G. (1999). Solubility of sulfur dioxide in aqueous solutions of acetic acid, sodium acetate, and ammonium acetate in the temperature range from 313 to 393 K at pressures up to 3.3 MPa: Experimental results and comparison with correlations/predictions. *Industrial & Engineering Chemistry Research*, *38*(3), 1149–1158. doi:10.1021/ie980529t

Yan, L., Lu, X., Wang, Q., Kang, Y., Xu, J., & Chen, Y. (2014). Research on sulfur recovery from the byproducts of magnesia wet flue gas desulfurization. *Applied Thermal Engineering*, *65*(1-2), 487–494. doi:10.1016/j.applthermaleng.2014.01.032

Yang, C.-L., & Shaw, H. (1998). Aqueous Absorption of Nitric Oxide Induced by Sodium Chlorite Oxidation in the Presence of Sulfur Dioxide. *Environment and Progress*, *17*(2), 80–85. doi:10.1002/ep.670170213

Yang, W., & Carleson, T. E. (1990). Several effects of electric fields on liquid extraction. *IEEE Transactions on Industry Applications*, *26*(2), 366–373. doi:10.1109/28.54265

Yoon, H., Stouffer, M. R., Rosenhoover, W. A., Withum, J. A., & Burke, F. P. (1988). Pilot Process Variable Study of Coolside Desulfurization. *Environment and Progress*, *7*(2), 104–111. doi:10.1002/ep.3300070211

Young, G. J. (1931). Reduction of sulfur dioxide. *Engineering and Mining Journal*, *131*(7).

Zhang, J., You, C., Zhao, S., Chen, C., & Qi, H. (2008). Characteristics and reactivity of rapidly hydrated sorbent for semidry flue gas desulfurization. *Environmental Science & Technology*, *42*(5), 1705–1710. doi:10.1021/es702208e PMID:18441824

Zhao, J., Jin, B., & Zhong, Z. (2007). The degree of desulphurization of a limestone/gypsum wet FGD spray tower using response surface methodology. *Chemical Engineering & Technology*, *30*(4), 517–522. doi:10.1002/ceat.200600347

Zheng, B., & Lu, C. (2009). Desulphurization Characteristic of Industry Alkaline Wastes during Coal Combustion. *Journal of Electromagnetic Analysis & Applications*, *1*(01), 36–41. doi:10.4236/jemaa.2009.11007

Zheng, Y., Kiil, S., & Johnsson, J. E. (2003). Experimental investigation of a pilot-scale jet bubbling reactor for wet flue gas desulphurisation. *Chemical Engineering Science*, *58*(20), 4695–4703. doi:10.1016/j.ces.2003.07.002

Zheng, Y., Kiil, S., Johnsson, J. E., & Zhong, Q. (2002). Use of spray dry absorption product in wet flue gas desulphurisation plants: Pilot-scale experiments. *Fuel*, *81*(15), 1899–1905. doi:10.1016/S0016-2361(02)00133-3

Zhou, Y., Zhang, M., Wang, D., & Wang, L. (2005). Study on a novel semidry flue gas desulfurization with multifluid alkaline spray generator. *Industrial & Engineering Chemistry Research*, *44*(23), 8830–8836. doi:10.1021/ie050457n

Zhou, Z., & Dayal, R. (1990). Characterization and leaching studies of FGD waste by-products. *Waste Management (New York, N.Y.)*, *10*(1), 53–59. doi:10.1016/0956-053X(90)90069-W

KEY TERMS AND DEFINITIONS

Best Available Techniques (BAT): A reference document that provides a set of sustainable directives and that is attached to several environmental legislations.

Ca/S Ratio: Ratio of the moles of calcium contained in the alkaline slurry with respect the moles of sulfur that are neutralized. It is usually used as a parameter for assessing the consumption and effectiveness during desulfurization.

Desulfurization Efficiency: The most common parameter for expressing the effectiveness of a SO_2 removal process. It is defined as the ratio of the difference in the concentration of SO_2 in the flue gases at the inlet and outlet of the FGD process with respect the concentration at the inlet.

Flue Gas Desulfurization (FGD): An abatement technique of SO_2 emissions that is applied after the fuel is burned and hence is catalogued as a post-combustion technology.

L/G Ratio: In a scrubber, the ratio of liters of recirculation slurry per cubic meters of inlet gas. Along with the desulfurization efficiency, it is one of the most important parameters for expressing the performance of a given desulfurization methods. It expresses the effectiveness of the mass transfer process.

Wet FGD: A type of FGD method in which a suspension or slurry is used as absorbing agent in the form of droplets or spray.

Chapter 12

Nanotechnology Applied to the Biodesulfurization of Fossil Fuels and Spent Caustic Streams

Danai Montalvan-Sorrosa
National Autonomous University of Mexico, Mexico

Daniel de los Cobos-Vasconcelos
National Autonomous University of Mexico, Mexico

Armando Gonzalez-Sanchez
National Autonomous University of Mexico, Mexico

ABSTRACT

The use of nanostructured materials in combination with desulfurizing microorganisms is a promising technique that would improve the desulfurization processes of gaseous fuels, oil, and some wastewater. Nanoparticles are highly versatile and tunable depending on the necessities of each particular contaminated media. The chapter shows the current technological options for the biodesulfurization of natural gas, oil and wastewater produced from the petroleum refining, where the application of nano-sized materials combined with desulfurizing microorganisms would improve the desulfurization capacities. In addition, advantages, disadvantages and opportunities of this hybrid technology are presented.

INTRODUCTION

Sulfur in Gaseous Fuels

The world's energy requirements have strongly increased due to the growing industrialization, especially in emerging economies. Fossil fuels still represent the main energy source around the world. Among these various energy sources, gaseous fuels have been increasingly used because of their easier exploitation and their somewhat more environmentally friendly impact (i.e. natural gas). However, these gaseous fuels

DOI: 10.4018/978-1-4666-9545-0.ch012

commonly contain significant concentrations of hydrogen sulfide (H_2S), and other sulfur species such as carbon disulfide (CS_2), carbonyl sulfide (COS) and organic sulfides (see Table 1). On the other hand, non-fossil fuels used such as coal, oil, peat, wood, and other organic materials contain sulfur, which is released as SO_2 after combustion. In combination with the humidity of the atmosphere, SO_2 produce the recurrent problem of acid rain that can cause severe damage to ecosystems. Sulfur poisoning of chemical catalyzer is another frequent problem during cracking and refining of crude petroleum.

Spent Caustic Streams

The spent caustic streams are wastewater originated from petroleum refining process. In petroleum refining, H_2S is removed from fuel gases by scrubbing into a sodium hydroxide solution, producing sulfides (HS^- and S^{2-}). The resulting sulfidic caustic aqueous solution can contain sulfide concentrations exceeding 2 - 3 w/w (0.6 – 0.9 mol L^{-1}), at pH greater than 12 and even other organic sulfur and aromatic compounds (Sipma, *et al.* 2004). Maintaining these streams under alkaline conditions would limit the emission of foul sulfide odorants. Olmos, et al. (2004) reported a characterization (Table 2) of spent caustic and sour waters produced in a Mexican petroleum refinery.

The aim of this chapter is to show the current technological options for the biodesulfurization of fossil fuels such as natural gas, oil and wastewater produced from the petroleum refining, where the application of nano-sized materials combined with desulfurizing microorganisms would improve the desulfurization capacities. In addition, advantages, disadvantages and opportunities of this hybrid technology are presented.

BACKGROUND

Conventional Desulfurization Methods

Several inorganic materials have been used for effective sorption of sulfur related compounds from fossil fuels in the recent years. Metal oxides of Fe, Zn, Mn, Mo, V, Ca, Sr, Ba, Co, Cu, Si and W have been particularly used for sulfur scavenging (Meng, *et al.* 2009). The general equation for desulfurization reactions is:

Table 1. Typical compositions of various gaseous fuels

	Composition (% v/v)							
Gaseous Fuels	**Other S***	**H_2S**	**H_2**	**CO_2**	**CH_4**	**N_2**	**CO**	**HC****
Natural gas	≈0.25	3.8–8.6	≈0.3	2–18	36–71	54–58	—	≈3.0
Distillery Biogas	≈0.003	1.2–2.5	≈0.04	22–28	58–64	1.5–5	—	—
Refinery fuel gas	≈0.03	4.5–7.5	≈20	11–15	≈ 1.5	50–59	≈18	≈ 2
Coke oven gases	≈0.03	0.3–4.8	≈15.0	24–28	≈ 50	≈0.15	≈10	≈0.02
Coal gasification	≈0.017	0.6–2.0	≈21	15–26	5–26	≈27	9-22	≈0.6

(González-Sánchez & Revah, 2006).

*CS_2, Mercaptans, and thiophene, **HC Hydrocarbons.

Table 2. Characterization of spent caustic and sour waters

Parameter (g/L)	Spent Caustic		Sour Waters	
	Average	**Std. Dev.**	**Average**	**Std. Dev.**
	9 Sample		**10 Samples**	
pH	13	0.2	10	0.8
Total chemical oxygen demand	364.1	53	1.56	0.26
Total organic carbon	53.9	27	0.31	0.04
Phenol	30.6	27.4	0.12	0.04
O-cresol	6	3.2	0.02	0.005
P-cresol	17.9	6	0.06	0.01
3,4-dimethylphenol	1.4	0.6	<0.0001	
2,5-dimethylphenol	2.9	0.3	<0.0001	
2-ethylphenol	0		<0.0001	
Total Kjeldahl nitrogen	1.1	0.4	5.49	3.95
NH_4^+	0.003	0.002	0.71	0.59
Sulfides	48.5	18.4	0.32	0.09
Sulfates	20.3	3	0.3	0.16
Chloride	37.9	18	0.4	0.22
Nitrate	<0.0001		0.001	
Nitrite	<0.0001		0.063	0.03
Phosphate	4.6	3.7	0.53	0.15
Carbonate	15.5	11.4	1.04	0.08
Sodium	27.2	5.5	0.002	$8.5\text{x}10^{-4}$
Potassium	0.08	0.01	0.0003	$2.1\text{x}10^{-5}$
Calcium	0.03	0.005	$9\text{x}10^{-5}$	$7\text{x}10^{-6}$
Iron(II)	0.05	0.001	$2.1\text{x}10^{-4}$	$5.7\text{x}10^{-6}$

From the Tula Refinery. Olmos, *et al.* (2004).

$$MO + H_2S \rightarrow MS + H_2O \tag{1}$$

where M corresponds to a divalent metal (Dolan, Ilyushechkin, & Mclennan, 2012).

Sulfides in aqueous streams are usually removed by chemical methods that requires high-energy inputs and produce secondary contaminants (Pandey, *et al.* 1999). However, recently biological processes have been proposed to overcome these issues (Gonzalez-Sanchez & Revah, 2006).

Biodesulfurization

Biodesulfurization is a not highly energy demanding process that consists on the biological transformation of sulfur containing compounds under mild conditions (temperature, pressure and pH around 20°C, 1 atm and 7 respectively). Specialized bacteria (Gonzalez-Sanchez & Revah, 2006) are the key factor as they perform these conversions as part of their metabolism. H_2S and organic sulfur compounds (i.e.

dibenzothiophene DBT) are inconvenient components of oil petroleum and natural gas (see above). The biodesulfurization process begins with the removal of the sulfur compounds from the natural gas or oil petroleum by through their interfacial mass transfer to the aqueous bulk phase (i.e. by absorption) where the microorganisms grow, then the sulfur compounds become bioavailable for their consequent biotransformation.

For the case of H_2S, the kinetics and stoichiometry (pathway) of the biological oxidation depend mainly on the extracellular conditions such as nutrients supply, where the dissolved oxygen concentration usually defines the selectivity, the yield and rates of the bioreactions showed in equations 2 and 3.

$$2H_2S + O_2 \rightarrow 2S^{\circ} \downarrow + 2H_2O \quad \Delta G^{\circ} = -129.50 \text{ kJ mol}^{-1} \tag{2}$$

$$2H_2S + 4O_2 \rightarrow 2SO_4^{2-} + 2H^{+} \quad \Delta G^{\circ} = -772.43 \text{ kJ mol}^{-1} \tag{3}$$

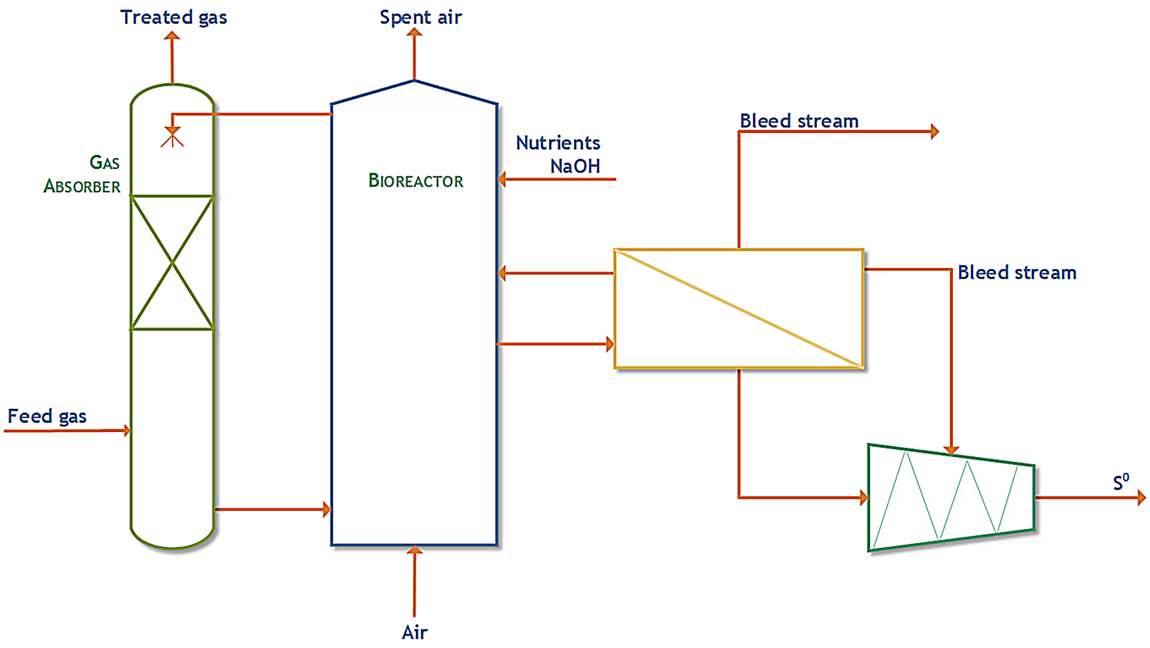
Biological based technologies are more environmental friendly and cheaper than traditional methods. Nevertheless, they are restricted to ambient and acidic or neutral conditions (Alcántara, *et al.* 2004; Gonzalez-Sanchez & Revah, 2006). Biological H_2S removal processes from fuel gases require an initial absorption or adsorption in to an aqueous phase or solid superficies where specialized microorganisms catalyze its oxidation either under limiting or excess oxygen conditions (Janssen, *et al.* 1995).

Alcántara, *et al.* (2004) investigated the formation and the recovery of elemental sulfur in a bioreactor-settler system some details, it had a dynamic flow zone and a static zone, which allowed sulfur sedimentation because the liquid phase aeration and the sulfide oxidation were spatially separated. Steady state sulfide oxidizing cultures were established at different O_2/S^{2-} molar ratios. At $O_2/S^{2-} > 1.0$, sulfate was the main product while with an O_2/S^{2-} of 0.5, elemental sulfur formed attaining 85% of the theoretical value shown in Equation 2. With this system, most of the sulfate formed was in the aeration vessel, and a dual oxygen-sulfide limitation was observed in the settler (Velasco *et al.* 2004; Gonzalez-Sanchez *et al.* 2005).

Krishnakumar *et al.* (2005) reported on an aerobic bioreactor called reverse fluidized loop reactor (RFLR), which recovered elemental sulfur from aqueous sulfide. The RFLR contained buoyant carrier particles (in the scale of millimeters) on which sulfide-oxidizing bacteria formed a biofilm. The process allowed the elemental sulfur to be efficiently separated from the aqueous phase.

A bioscrubbing system employed by Thiopaq® (Janssen *et al.* 2000) consists of a gas absorber and a bioreactor. (Figure 1). In the gas absorber, gaseous H_2S is scrubbed using an alkaline solution (pH 8.0 to 8.5). The dissolved sulfide is then oxidized by microorganisms in the bioreactor to elemental sulfur and sulfate according to Equations 2 and 3. The Thiopaq® desulfurization process has been applied to the removal of H_2S from high-pressure natural gas. In a demonstration plant, natural gas with a H_2S content of up to 8% vol. was desulfurized at high gas pressures (between 5 and 53 bar) without any negative effect on the bacteria. A drawback of the system is that sodium bicarbonate can precipitate at high CO_2 partial pressures. To avoid this, low CO_2 partial pressures should be present. Alternately, lower pH can be used in the absorber but higher liquid flows or larger scrubbers would likely be required to get similar absorption capacity.

Figure 1. Diagram of the bioscrubber system for the treatment of H_2S containing gas streams (Thiopaq® process)



In the petroleum refining processes, after the hydrodesulfurization of oil petroleum, high amounts of DBT remain, which is one of the most recalcitrant sulfur compounds to remove from fossil fuels even after hydrodesulfurization. Olson, & Stanley (1993) reports the ability of the bacterial strain *Rhodococcus rhodochrous IGTS8* to transform DBT to sulfite (SO_3^{2-}) or sulfate (SO_4^{2-}) by the 4S desulfurization pathway (see Figure 2), that had been also reported to occur in other bacteria strains (Zhang, et al., 2010, Derikvand, et al. 2014). The sulfur ions produced after the degradation of the DBT molecule can be separated using an aqueous solution (i.e. water).

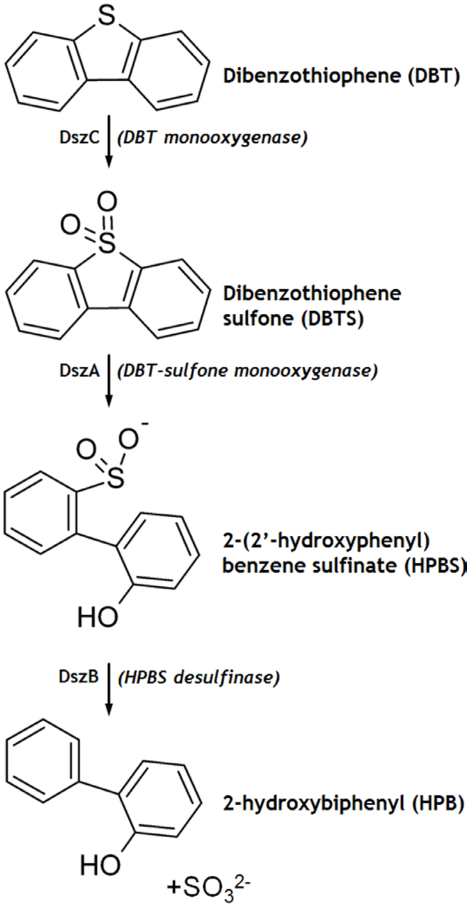
One of the bottlenecks of the biological desulfurization is the transference of the DBT to the microorganisms due to the immiscibility of organic and aqueous phases, this disadvantage could be overtaken by the deployment of functionalized nanoparticles as explained in Figure 2.

NANOMATERIALS AND DESULFURIZATION

Nanomaterials have been applied extensively in desulfurization processes as adsorbents due their high adsorption capacity and surface area. Nanomaterials have been recently incorporated in the traditional methods for desulfurization, particularly in adsorptive desulfurization and in a less extent in hydrodesulfurization processes.

Among the common materials used in adsorption desulfurization are silica gel, activated alumina and carbon and metal organic framework sorbents. The chemical functionalities in the surface of this materials allow to incorporate nanomaterial that enhance the desulfurization process, particularly when d-block metals (Ag, Cu, Ni and Zn) are used (Chandra Srivastava, 2012).

Figure 2. The main 4S biodesulfurization pathway for the degradation of DBT
Modified from Nuhu, (2013).



FeO nanoparticles possess one of the higher adsorptivities and specificity towards sulfur compounds among other nanomaterials. The removal of sulfur by adsorptive methods requires the presence of substrates with a high adsorption capacity as activated carbon, silica or alumina (zeolites) (Liu, *et al.* 2010). Major concerns about the desirable properties of these materials are a high porosity and tunable surface chemical properties. Pores with sizes similar to the sulfur compounds in fossil fuels increase the capacity of retention.

Reactive adsorption is a technique that combines catalytic hydrodesulfurization and adsorption, sulfur-containing molecules which react in the presence of a H_2 stream (Chandra Srivastava, 2012). The Ni/ZnO is the most common catalyst used in reactive desulfurization. Metallic Ni acts as the catalytic site in which hydrodesulfurization takes place while ZnO adsorbs the produced H_2S generating ZnS (Zhao, *et al.* 2010) and (Ito & van Veen, 2006). By different methods, the sorbent can be regenerated and reused or simply discarded.

A more friendly and sustainable version of nanodesulfurization is nanobiodesulfurization, a method that combines nanostructured adsorbents and microorganisms (i.e. bacteria, microalgae).

NANOBIODESULFURIZATION

Microorganisms capable of metabolizing recalcitrant organosulfur molecules have been used as free cell cultures or immobilized in different substrates. Immobilization may facilitate the separation of the cell from the product and may enhance the biocatalytic activity. The term nanobiodesulfurization refers to desulfurization methods in which nanomaterials and bacteria that metabolizes organosulfur molecules and by-products are used.

One of the first applications of nanomaterials in desulfurization processes was the use of magnetic nanoparticles attached to the surface membrane of *Pseudomonas delafieldii* R-8 (Shan, *et al.* 2005). In this work, Liu *et al.* (2010) show that cells coated with Fe_3O_4 nanoparticles have the same desulfurization activity as the uncoated cells. The coating process only requires the mixing of both nanoparticles and cells in aqueous saline solution and then the cells can be recovered by applying a magnetic field (Figure 3). In addition, coated cells can be reused at least five times, in contrast with free cells that do not show activity if they are used again. Even though the nanoparticles do not directly contribute to the desulfurization process, their use facilitates the recuperation of the biocatalytic biomass.

Biodesulfurization usually occurs in organic phases; therefore, the transference of organosulfur molecules to the cell membrane is limited. The cell membrane needs to be not only resistant but also permeable enough to capture the sulfur-containing molecules. This issue may be overcame with the use of genetically modified bacteria that are stable in oil phases or by using sorbents of organosulfur molecules. For example, when *P. delafieldii* R-8 are assembled with the nanosorbent γ-Al_2O_3 the desulfurization rate of the cells increased at least two times than that of the cells alone (Guobin, *et al.* 2005). The nano γ-Al_2O_3 in the cell membrane adsorbs dibenzothiophene (DBT), which increases the transference rate of the sulfur compound from the media to the cell membrane (Figure 4). In a two phase procedure, DBT is first adsorbed in a Cu modified zeolite and then degraded by *P. delafieldii* R-8 to 2-hydroxybiphenyl (HBP), the nanosorbent is then bioregenerated and may be reused (Li, *et al.* 2006).

Figure 3. Magnetic immobilization and separation of biodesulfurizing bacteria; bacteria are decorated with magnetic Fe_3O_4 nanoparticles (NP's), and they can be separated from the media by using a magnetic field.

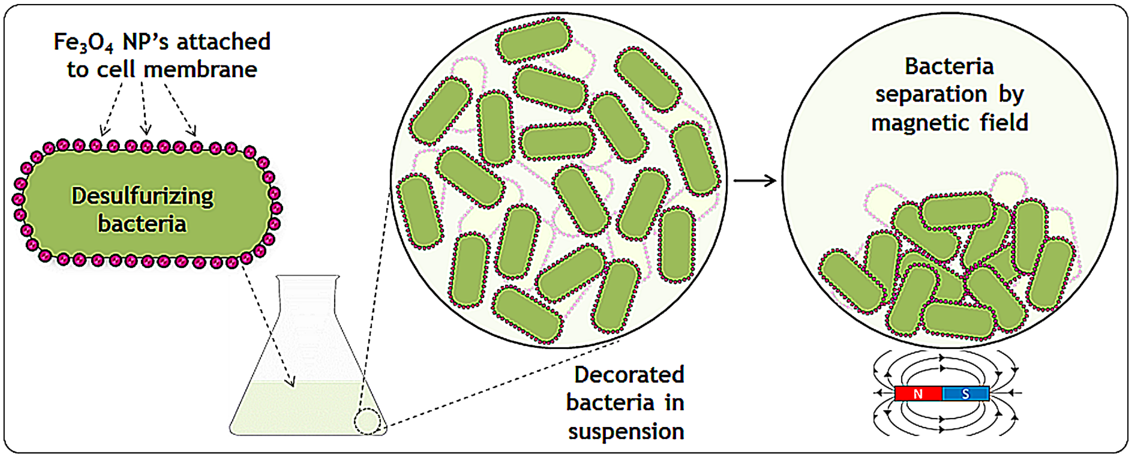
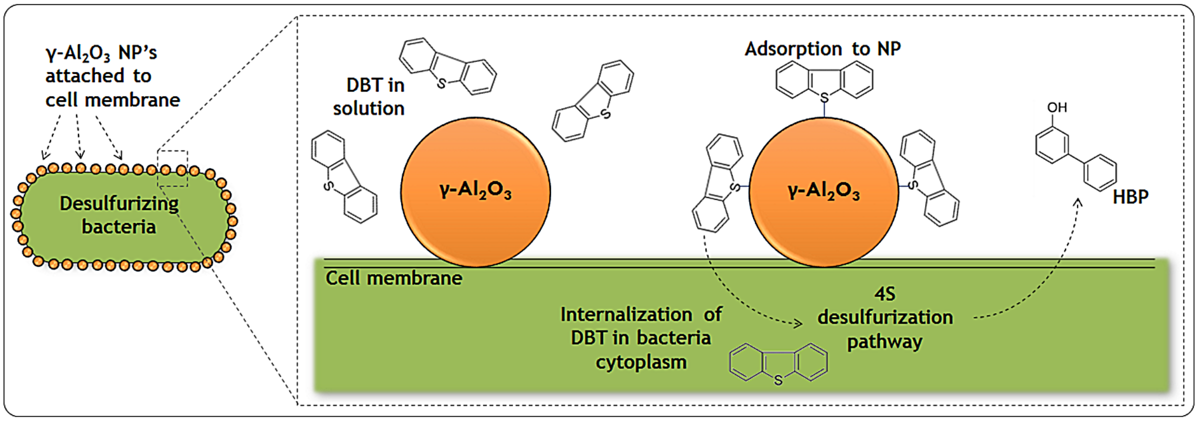


Figure 4. Biodesulfurization can be enhanced by using sulfur adsorbent nanoparticles as γ-Al_2O_3. Organosulfur compounds are more easily biodegraded by desulfurizing bacteria when they are attached to NP's in the bacteria cell membrane. Once in the NP's, DBT is internalized in the bacteria cytoplasm, where the desulfurization pathway takes place. 2-hydroxybiphenyl (HBP) is the final product of the 4S metabolic pathway, is secreted to the media and can be used to monitor DBT degradation.



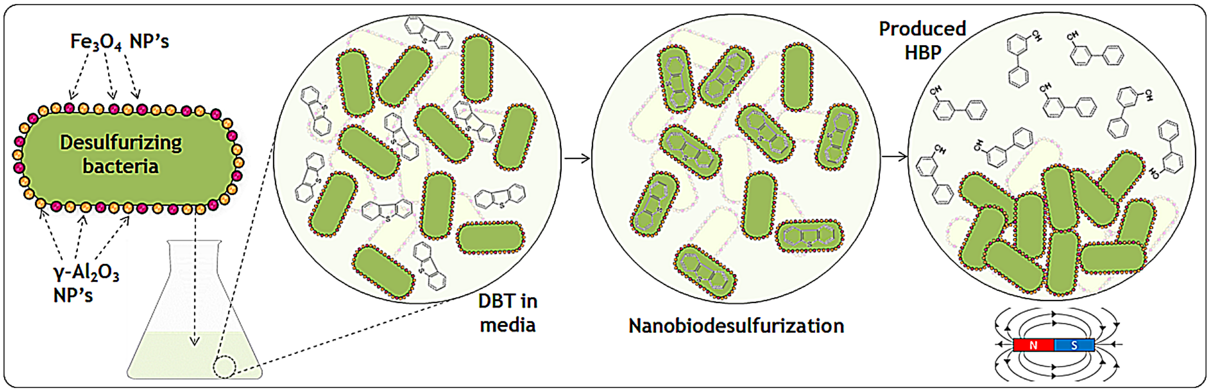
Magnetic nanoparticles not only allow recovery of bacterial cells but also may have an important role in cell membrane permeabilization. Ansari *et al.* (2009) clearly demonstrate that Fe_3O_4 nanoparticles actually facilitate transport of DBT from the media to the cytoplasm of *Rhodococcus erythropolis* IGST8. This facilitation has been argued to be due to self-assembly of the nanoparticles inside the membrane, which may forms pore-like structures that increases the surface conductance. Moreover, the size and stability of the nanoparticles in a suspension are important issues that need deep investigation since they could influence the process performance. According with Bardania, *et al.* (2013), attachment of nanoparticles on the cell membrane of *R. erythropolis* IGTS8 is more uniform when smaller nanoparticles of Fe_3O_4 (<5 nm) are deployed.. Additionally, the use of glycine decreases the aggregation tendency of the nanoparticles, which may lead to a higher adsorption of DBT by each cell.

Zhang, *et al*., (2010) combined two strategies for the degradation of a mixture of DBT, n-octane and water using *R. erythropolis* LSSE8-1-vgb: coating the cells with both Fe_3O_4 and γ-Al_2O_3 nanoparticles (Figure 5). The biodesulfurization activity was higher with the coated cells, it was knowledge by using a high porosity nano-γ-Al_2O_3 that adsorption and desulfurization increases.

Polymeric matrices with immobilized cells can be optimized by adding nanoparticles. Derikvand, *et al.* (2014) achieved DBT degradation by using *R. erythropolis* R1 decorated with γ-Al_2O_3 and immobilized in alginate beds. The addition of nicotinamide and riboflavin to the media (Figure 5) improved the desulfurization rate, because these biomolecules are precursors in the 4S pathway (Derikvand *et al.*, 2014). The use of polymeric matrices as alginate can be useful in combination with nanobiodesulfurization, as the recovery and reuse of the immobilized biomass is easier. Polyvinyl alcohol has also been used as immobilizing support for the desulfurizing bacteria *Sphingomonas subarctica* T7b.

Even though inorganic materials have been used as bacterial supports, and they enhance the desulfurization rates, it is very likely that the nanostructured version of these materials could improve even more the metabolism of organosulfur compounds. Nanostructured materials can bind to the bacterial membrane more easily than the non-nanostructured counterpart. For example, in the case of γ-Al_2O_3 it

Figure 5. Bacteria decorated with magnetic and sulfur-adsorbent nanoparticles increase the rate of biodesulfurization of fossil fuels. Nanobiodesulfurization occurs when DBT is bound to the γ-Al_2O_3 nanoparticles, DBT is degraded in the bacteria cytoplasm and HBP is released. By applying a magnetic field, the desulfurized fuel and the bacteria can be recover separately.



was observed that its nano-sized version works much better than γ-Al_2O_3 of regular sizes (Zhang *et al.*, 2008). The capture of DBT from the oil phase by the bacteria is easier when nanoparticles are attached in the cell membrane, this increases the biodesulfurization rate.

Nanobiodesulfurization is a still growing field of investigation. Many other materials that includes noble metal, Cu, Ti, Ce and Ni/Zn nanoparticles, silica nanospheres, carbon nanotubes, and even graphene are prone to be used in combination with desulfurizing bacteria. In addition, the optimization of different polymeric matrices for immobilization and bioreactor configuration are necessary for the improvement of desulfurizing methods.

Nanomaterials are used in many environmental processes as waste water treatment, energy production, filtration, and removal of different compounds as metal ions, pharmaceuticals, biocides and other organic pollutants. For an excellent review of environmental applications of nanostructured materials and microorganisms we recommend the work of Alvarez & Cervantes, (2011).

Additionally, there are many microorganisms and microbial communities that can be applied in biodesulfurization. In contrast with other methods as hydrodesulfurization, which is carried on at temperatures around 300 °C, biodesulfurization can proceed at temperatures as low as 30-50 °C. Alkylated dibenzothiophenes and other recalcitrant organosulfur molecules are difficult to remove by hydrodesulfurization (HDS) but not by nanobiodesulfurization in which organosulfur compounds are adsorbed on nanomaterials.

PERSPECTIVES AND CONCLUSION

The use of nanostructured materials in combination with microorganisms for the desulfurization of petroleum related streams are denominated a nano-biodesulfurization process, it represents a new opportunity for improving the desulfurization capacities of gaseous and oil fossil fuels besides of their wastewater produced. Nanoparticles are highly versatile and tunable depending on the necessities of each particular biodesulfurization case. Some issues like low transference rate of sulfured compounds from the gas and organic phases to the interior of the cell membrane may be overcome by using desulfurizing bacteria coated with nanoparticles. Full-scale desulfurization would deploy the concept of nano-biodesulfurization but at the moment further developments must be conducted, mainly about the optimal growing of the desulfurizing bacteria and the nanoparticles coating on their surface, where in the upstream process is desirable that the nanoparticles would be recovered for their posterior recycling.

REFERENCES

Alcántara, S., Velasco, A., Muñoz, A., Cid, J., Revah, S., & Razo-Flores, E. (2004). Hydrogen sulfide oxidation by a microbial consortium in a recirculation reactor system: Sulfur formation under oxygen limitation and removal of phenols. *Environmental Science & Technology*, *38*(3), 918–923. doi:10.1021/es034527y PMID:14968883

Alvarez, L. H., & Cervantes, F. J. (2011). (Bio)nanotechnologies to enhance environmental quality and energy production. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *86*(11), 1354–1363. doi:10.1002/jctb.2697

Ansari, F., Grigoriev, P., Libor, S., Tothill, I. E., & Ramsden, J. J. (2009). DBT Degradation Enhancement by Decorating Rhodococcus erythropolis IGST8 with Magnetic Fe_3O_4 Nanoparticles. *Biotechnology and Bioengineering*, *102*(5), 1505–1512. doi:10.1002/bit.22161 PMID:19012265

Bardania, H., Raheb, J., Mohammad-Beigi, H., Rasekh, B., & Arpanaei, A. (2013). Desulfurization activity and reusability of magnetite nanoparticle-coated Rhodococcus erythropolis FMF and R. erythropolis IGTS8 bacterial cells. *Biotechnology and Applied Biochemistry*, *60*(May), 323–329. doi:10.1002/bab.1090 PMID:23656694

Chandra Srivastava, V. (2012). An evaluation of desulfurization technologies for sulfur removal from liquid fuels. *RSC Advances*, *2*(3), 759–783. doi:10.1039/C1RA00309G

Derikvand, P., & Etemadifar, Z. (2014). Improvement of biodesulfurization rate of alginate immobilized *Rhodococcus erythropolis* R1. *Jundishapur Journal of Microbiology*, *7*(3), 1–7. doi:10.5812/jjm.9123 PMID:25147685

Derikvand, P., Etemadifar, Z., & Biria, D. (2014). Taguchi optimization of dibenzothiophene biodesulfurization by *Rhodococcus erythropolis* R1 immobilized cells in a biphasic system. *International Biodeterioration & Biodegradation*, *86*, 343–348. doi:10.1016/j.ibiod.2013.10.006

Dolan, M. D., Ilyushechkin, A. Y., Mclennan, K. G., & Sharma, S. D. (2012). Sulfur removal from coal-derived syngas : Thermodynamic considerations and review. *Asia-Pacific Journal of Chemical Engineering*, *7*(1), 1–13. doi:10.1002/apj.528

Gallagher, J. R., Olson, E. S., & Stanley, D. C. (1993). Microbial desulfurization of dibenzothiophene: A sulfur-specific pathway. *FEMS Microbiology Letters*, *107*(1), 31–35. doi:10.1111/j.1574-6968.1993.tb05999.x PMID:8467997

Gonzalez-Sanchez, A., & Revah, S. (2006). Product recovery from H_2S containing gases. In P. N. L. Lens, C. Kennes, P. LeCloirec, & M. Deshusses (Eds.), *Waste gas treatment for resource recovery* (pp. 399–406). London, UK: IWA Publishing.

Gray, K. A., Mrachko, G. T., & Squires, C. H. (2003). Biodesulfurization of fossil fuels. *Current Opinion in Microbiology*, *6*(3), 229–235. doi:10.1016/S1369-5274(03)00065-1 PMID:12831898

Guobin, S., Huaiying, Z., Weiquan, C., Jianmin, X., & Huizhou, L. (2005). Improvement of biodesulfurization rate by assembling nanosorbents on the surfaces of microbial cells. *Biophysical Journal*, *89*(6), L58–L60. doi:10.1529/biophysj.105.073718 PMID:16258046

Ito, E., & van Veen, J. (2006). On novel processes for removing sulfur from refinery streams. *Catalysis Today*, *116*(4), 446–460. doi:10.1016/j.cattod.2006.06.040

Janssen, A., Sleyster, R., van der Kaa, C., Jochemsen, A., Bontsema, J., & Lettinga, G. (1995). Biological sulphide oxidation in a fed-batch reactor. *Biotechnology and Bioengineering*, *47*(3), 327–333. doi:10.1002/bit.260470307 PMID:18623408

Li, W., Xing, J., Xiong, X., Huang, J., & Liu, H. (2006). Feasibility study on the integration of adsorption/bioregeneration of π-complexation adsorbent for desulfurization. *Industrial & Engineering Chemistry Research*, *45*(8), 2845–2849. doi:10.1021/ie051125l

Li, Y.-G., Gao, H.-S., Li, W.-L., Xing, J.-M., & Liu, H.-Z. (2009). In situ magnetic separation and immobilization of dibenzothiophene-desulfurizing bacteria. *Bioresource Technology*, *100*(21), 5092–5096. doi:10.1016/j.biortech.2009.05.064 PMID:19541480

Liu, Y., Bisson, T. M., Yang, H., & Xu, Z. (2010). Recent developments in novel sorbents for flue gas clean up. *Fuel Processing Technology*, *91*(10), 1175–1197. doi:10.1016/j.fuproc.2010.04.015

Meng, X. M., De Jong, W., & Verkooijen, A. H. M. (2009). Thermodynamic Analysis and Kinetics Model of H 2 S Sorption Using Different Sorbents. *Environmental Progress and Sustainable Energy*, *28*(3), 360–371. doi:10.1002/ep.10386

Nuhu, A. A. (2013). Bio-catalytic desulfurization of fossil fuels: A mini review. *Reviews in Environmental Science and Biotechnology*, *12*(1), 9–23. doi:10.1007/s11157-012-9267-x

Olmos, A., Olguin, P., Fajardo, C., Razo, E., & Monroy, O. (2004). Physicochemical characterization of spent caustic from the OXIMER process and sour waters from Mexican oil refineries. *Energy & Fuels*, *18*(2), 302–304. doi:10.1021/ef030053c

Sipma, J., Svitelskaya, A., van der Mark, B., Hulshoff Pol, L. W., Lettinga, G., Buisman, C. J. N., & Janssen, A. J. H. (2004). Potentials of biological oxidation processes for the treatment of spent sulfidic caustics containing thiols. *Water Research*, *38*(20), 4331–4340. doi:10.1016/j.watres.2004.08.022 PMID:15556208

Shan, G., Xing, J., Zhang, H., & Liu, H. (2005). Biodesulfurization of Dibenzothiophene by Microbial Cells Coated with Magnetite Nanoparticles. *Applied and Environmental Microbiology*, *71*(8), 4497–4502. doi:10.1128/AEM.71.8.4497-4502.2005 PMID:16085841

Zhang, H., Liu, Q., Li, Y., Li, W., Xiong, X., Xing, J., & Liu, H. (2008). Selection of adsorbents for in-situ coupling technology of adsorptive desulfurization and biodesulfurization. *Science in China Series B: Chemistry*, *51*(1), 69–77. doi:10.1007/s11426-007-0118-5

Zhang, T., Li, W.-L., Chen, X.-X., Tang, H., Li, Q., Xing, J.-M., & Liu, H.-Z. (2010). Enhanced biodesulfurization by magnetic immobilized Rhodococcus erythropolis LSSE8-1-vgb assembled with nano-γ-Al2O3. *World Journal of Microbiology & Biotechnology*, *27*(2), 299–305. doi:10.1007/s11274-010-0459-7

Zhao, L., Chen, Y., Gao, J., & Chen, Y. (2010). Desulfurization mechanism of FCC gasoline: A review. *Frontiers of Chemical Engineering in China*, *4*(3), 314–321. doi:10.1007/s11705-009-0271-9

Chapter 13

Advances in the Reduction of the Costs Inherent to Fossil Fuels' Biodesulfurization towards Its Potential Industrial Application

Susana M. Paixão
Laboratório Nacional de Energia e Geologia, Portugal

Bruno F. Arez
Laboratório Nacional de Energia e Geologia, Portugal

Tiago P. Silva
Laboratório Nacional de Energia e Geologia, Portugal

Luís Alves
Laboratório Nacional de Energia e Geologia, Portugal

ABSTRACT

Biodesulfurization (BDS) process consists on the use of microorganisms for the removal of sulfur from fossil fuels. Through BDS it is possible to treat most of the organosulfur compounds recalcitrant to the conventional hydrodesulfurization (HDS), the petroleum industry's solution, at mild operating conditions, without the need for molecular hydrogen or metal catalysts. This technique results in lower emissions, smaller residue production and less energy consumption, which makes BDS an eco-friendly process that can complement HDS making it more efficient. BDS has been extensively studied and much is already known about the process. Clearly, BDS presents advantages as a complementary technique to HDS; however its commercial use has been delayed by several limitations both upstream and downstream the process. This study will comprehensively review and discuss key issues, like reduction of the BDS costs, advances and/or challenges for a competitive BDS towards its potential industrial application aiming ultra low sulfur fuels.

DOI: 10.4018/978-1-4666-9545-0.ch013

INTRODUCTION

The combustion of fossil fuel generates emissions of sulfur as sulfur dioxide (SO_2), which is corrosive and toxic, and as fine particulate matter of metal sulfates. These emissions are responsible for damage in many different areas. Gaseous chemical compounds of sulfur constitute a major health hazard when present in the air: the large-ring thiophenes, such as dibenzothiophene, abundant in crude oil, are toxic to mammals (Murphy, Amin, Coletta, & Hoffman, 1992); SO_2 gas at high levels can cause bronchial irritation and trigger asthma attacks in susceptible individuals and long-term exposure to combustion-related one particulate air pollution is an important risk factor for cardio-pulmonary and lung cancer mortality (Pope et al., 2002; Mohebali & Ball, 2008). In addition, incomplete burning of liquid fossil fuels causes emissions of aromatic sulfur compounds to the air (Ho & Li, 2002), and the oxidation of sulfur compounds in the atmosphere eventually leads to aerosol of sulphuric acid. This aerosol causes acid rains, which are responsible for the corrosion of many infrastructures and monuments, and even affect several living organisms including agricultural crops, thus causing direct damage to the economy (Bender & Weigel, 2011). The aerosol is also harmful to the stratospheric ozone contributing to the hole on the Earth's protective ozone layer (Denis, 2010). Lastly, sulfur compounds even prevent functioning of all major pollution control technologies such as automobile catalytic converters (Maricq, Chase, Xu, & Laing, 2002), making it more difficult to fight against pollution.

Since gasoline, diesel and non-transportation fuels account for 75 to 80% of the total refinery products (Babich & Moulijn, 2003), it is only natural that countries find the reductions of sulfur concentration in fuels as the most effective way to decrease the amount of SO_2 emitted in to the air and limit its prejudicial effects (Mohebali, Ball, Kaytash, & Rasekh, 2008).

Therefore, in response to the increasing concerns with environmental and health and effects of the SO_x molecules, several countries have started to impose strict limits on the levels of sulfur present in the fossil fuels. This forced the petroleum industry to develop techniques which remove the sulfur from the fuels, such as hydrodesulfurization (HDS), a process that combines high temperatures and pressures with molecular hydrogen in the presence of complex metal catalysts. However, this process is not very effective at removing heterocyclic sulfur compounds, which can account to up to 70% of the sulfur in petroleum (Borgne & Quintero, 2003), requiring harsher conditions to meet the strict EU sulfur regulations (10 ppm). This deeper desulfurization, with even higher temperatures and pressures, results in an increase of pollution (with > CO_2 release), a rise of production costs (resulting from higher energy consumption) and, sometimes, a loss of octane value (Khedkar & Shanker, 2014; Mohebali & Ball, 2008; Srivastava, 2012).

For this reason, oil desulfurization has become an increasingly studied area, and there have been many different approaches to solve these problems, such as the development of new combinations of metal catalysts for HDS, the study of techniques such as catalytic oxidation, desulfurization by adsorption, chemical desulfurization, physical desulfurization, photochemical desulfurization, photocatalytic desulfurization, and biodesulfurization (Srivastava, 2012).

The biodesulfurization (BDS) process consists on the use of microorganisms for the removal of sulfur from fossil fuels. Through BDS it is possible to treat most of the compounds recalcitrant to HDS at mild operating conditions, without the need for molecular hydrogen, or metal catalysts (Mohebali & Ball, 2008). If successfully implemented, it will result in lower environmental costs, with a reduction of 70–80% of CO_2 emissions, smaller residue production, and reduced energy consumption, which in turn translates in reduced capital (two thirds of HDS) and operational costs (10-15% lower) (Kaufman et al., 1997; McFarland et al., 1998; Tuli & Kumar, 2008; Vazquez-Duhalt, Torres, Brenda, & Le Borgne, 2002). This makes BDS an eco-friendly process that can complement the traditional methods of desulfurization making them more efficient (Kaufman, Harkins, & Borole, 1998; Linguist & Pacheco, 1999; Pacheco et al., 1999).

BDS has been extensively studied in the last decades, and much is already known about the process. Its efficiency is traditionally determined by following the degradation of model compounds, either on aqueous medium, or on model oils composed of organic solvents. When using complex substrates such as real oil derivatives, BDS efficiency can also be determined by measuring the reduction in total sulfur concentration.

The most commonly used molecule for BDS studies is dibenzothiophene (DBT). This model compound consists of two benzene rings fused with a central thiophene ring, and has a great variety of alkyl derivatives which are very abundant in crude oil (Figure 1). Among all the organosulfur compounds present in petroleum and its refined products, DBT and its derivatives present the greatest challenge to the desulfurization process (Rivera, Navarro-Santos, Guerra-Gonzalez, & Lima, 2014), because their structure makes it very hard to remove the sulfur atom contained in the thiophene ring without damaging the benzene structure, making them ideal to study.

Many microorganisms are able to use DBT as a sulfur source, and there are several pathways described for DBT desulfurization. However, most of the known BDS metabolic pathways involve the mineralization of the sulfur atom and complete or partial destruction of the benzene ring which makes them unappealing for the biodesulfurization process (Aggarwal, Karimi, Kilbane, & Lee, 2012; Gupta, Roychoudhury, & Deb, 2005; Lee, Senius, & Grossman, 1995).

The most studied and widely used pathway in BDS is the "4S pathway" (Kilbane, 2006). Through it, microorganisms are able to remove the sulfur atom under aerobic conditions while maintaining both benzene rings intact (Figure 2). This results in little loss of calorific potential making it an industrially interesting process (Mcfarland, 1999; Mohebali & Ball, 2008).

The "4S pathway" is composed of four enzymes (Ohshiro & Izumi, 1999). Two are monooxygenases: a DBT-monooxygenase (DBT-MO or DszC, encoded by the *dszC* gene) and a DBT-sulfone monooxygenase (DBTO2-MO or DszA, encoded by the *dszA* gene), which are flavin-dependent and require a third enzyme, the flavin reductase (DszD, encoded by the *dszD* gene) for activity. The last enzyme, hydroxyphenyl benzene sulfonate-desulfinase (DszB, encoded by the *dszB* gene), completes the reaction sequence, which results in the production of 2-hydroxybiphenyl (2-HBP), released into the culture medium, and SO_3^{2-} that is metabolized by the cell (Boniek, Figueiredo, dos Santos, & Stoianoff, 2014; Gray, Mrachko, & Squires, 2003).

Figure 1. Dibenzothiophene and two of its alkyl derivatives, 4-methyl dibenzothiophene and 4,6-dimethyl dibenzothiophene

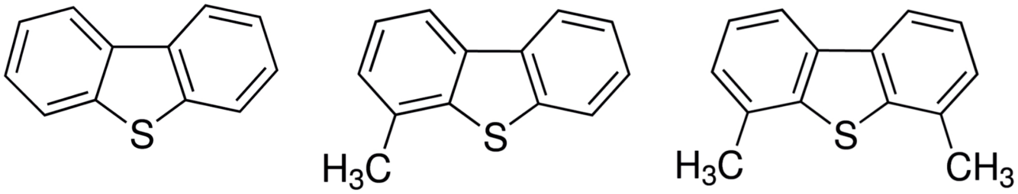
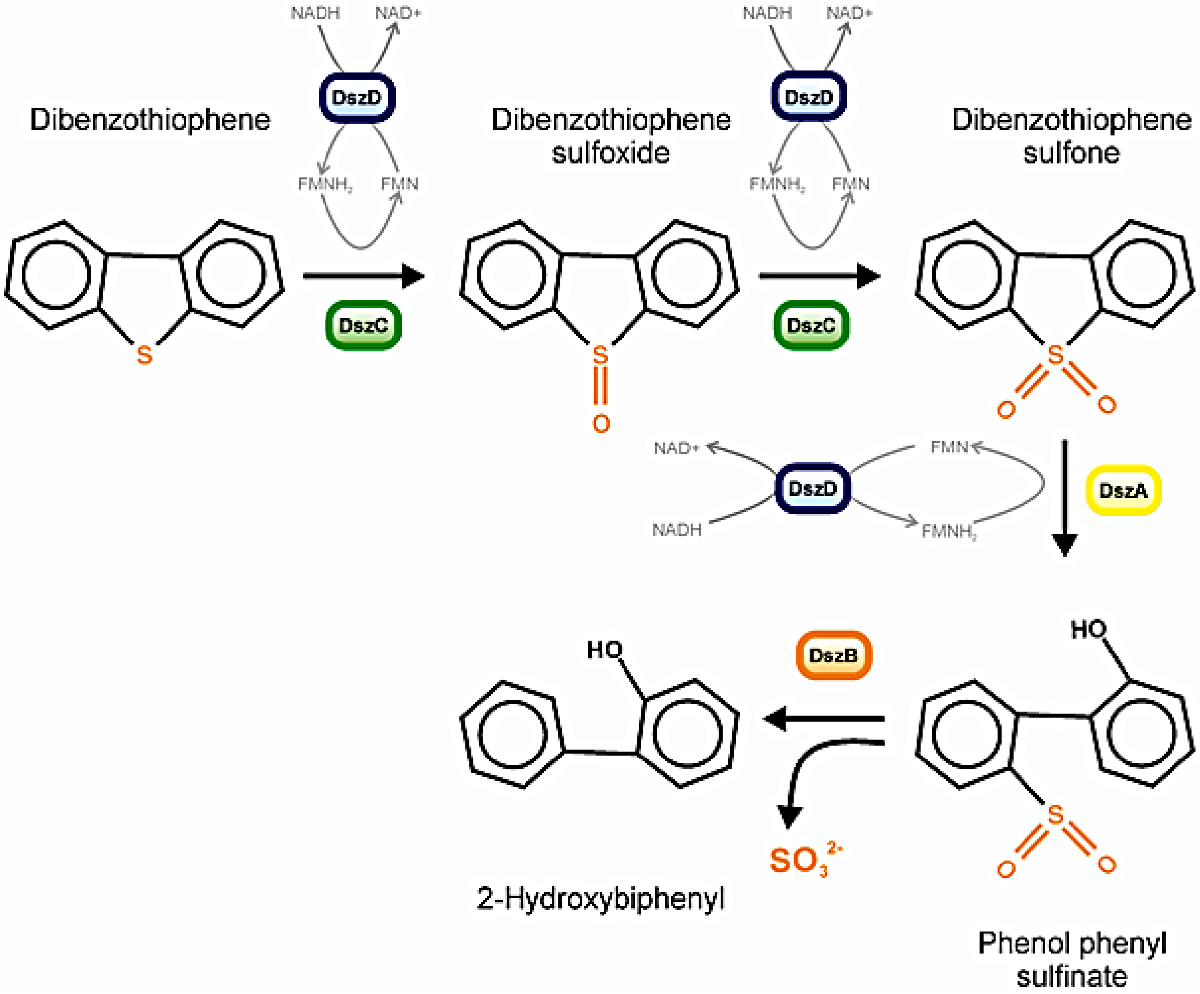


Figure 2. Scheme of the 4S pathway for DBT microbial desulfurization. The sulfur atom is removed from DBT keeping C-C structure.



This metabolic pathway is widespread throughout several genera of microorganisms, such as *Arthrobacter*, *Agrobacterium*, *Brevibacterium*, *Klebsiella*, *Mycobacterium*, *Nocardia*, *Paenibacillus*, *Pseudomonas*, *Xanthomonas*, *Gordonia* and *Rhodococcus*, with these two last ones being the most promising.

Using biocatalysts, researchers have successfully been able to remove sulfur from such different substrates as gasoline, kerosene, diesel, HDS diesel, and light and heavy crude oil. The desulfurization values described range from ~30 to ~100%, using different microorganisms and on different distillates, being achieved ultra-low sulfur fuels (Bhatia & Sharma, 2012; Guchhait, Biswas, Bhattacharya & Chowdhury, 2005a; Kilbane, 2006; Nuhu, 2013). As can be observed from Table 1, which summarizes the best desulfurizing strains studied with the respective BDS activity achieved, the highest desulfurization was obtained with a genetically modified strain of *R. erythropolis* KA 2-5-1. This strain has achieved the

Table 1. Cultures with the highest desulfurization activities

Microbial Strain	Specific Activity (μmol g^{-1} (DCW) h^{-1})	References
Rhodococcus erythropolis KA 2-5-1, wild type	74	Kobayashi et al., 2000
Rhodococcus erythropolis KA 2-5-1, cloned dsz genes	280	Hirasawa, Ishii, Kobayashi, Koizumi, & Maruhashi, 2001
Rhodococcus erythropolis KA 2-5-1, cloned *dsz* genes	250	M. Konishi et al., 2005
Rhodococcus erythropolis IGTS8	72	Kilbane & LeBorgne, 2004
Mycobacterium sp. G3, wild type	178	Takada et al., 2005
Mycobacterium sp. G3, hsp60 promoter	211	

(Adapted from Kilbane, 2006).

maximal biodesulfurization activity observed until nowadays (280 μmol g^{-1} h^{-1} on DBT). However, this value is still much lower than the estimated for a successful commercial process, which would require a biocatalyst with desulfurization activity on petroleum of 1.2 mmol g^{-1} h^{-1} to 3 mmol g^{-1} h^{-1} (Kilbane, 2006; Kirimura et al., 2004; Monticello, 2000; Okada et al., 2003).

Within a biological desulfurization process, the microorganism must first be cultivated in order to produce large amounts of highly active biomass. This biomass is then used in a bioreactor to desulfurize an organic phase. At the end of the process, biomass, water and organic phase must be separated. So, even if the levels of biodesulfurization activity are brought up to industrial levels there are other bottlenecks to the implementation of a cost appealing BDS process.

BDS COST REDUCTION

To make the BDS process economically competitive with the deep hydrodesulfurization process that is currently used by petroleum industry, it is necessary to improve several factors, including the cost of producing the biocatalyst, and its biocatalytic activity (Mohebali & Ball, 2008).

At the present, there is no economically suitable method for large-scale production of biocatalysts (Ma et al., 2006), and a crucial limitation, common within many other biotechnological processes, is the cost of the culture medium, which represents 30 to 40% of the total production costs (Silva, Silva, Kamida, Goes-Neto, & Koblitz, 2014). So, an important line of work to turn BDS scale-up less costly is the optimization of the culture medium aiming to reduce expenses with maximal biocatalyst production.

Cost-Effective Culture Media

In the last years, culture media for the BDS process have been greatly optimized, targeting a reduction in overall components for minimum costs, and the elimination of all possible inhibitors. Aiming for a cost-effective culture medium for biocatalyst production within the BDS process, three main aspects must be considered: sulfur source, BDS promoters and carbon source.

Sulfur Source

It is a well-known fact that the nature and concentration of the sulfur source used for the growth of the biocatalyst greatly influences the biodesulfurization activity (M. Z. Li, Squires, Monticello, & Childs, 1996; Oldfield, Pogrebinsky, Simmonds, Olson, & Kulpa, 1997). The promoter and regulatory regions of the *dsz* operon are strongly repressed in the presence of readily bioavailable sulfur, *i.e.*, sulfate, sulfide, methionine and cysteine, (M. Z. Li et al., 1996), because desulfurization enzymes are sulfate-starvation-induced proteins (Tanaka, Yoshikawa, Maruhashi, & Kurane, 2002). Also, in the presence of sulfate other enzymes such as sulfite oxiredutase have their activities leading to a preferential consumption of sulfate instead of DBT as the source of sulfur to support cell growth (Aggarwal et al., 2012).

In fact, even small concentrations of sulfate or other easy access sulfur sources produce an inhibitory effect on BDS. Mohebali & Ball (2008) describe that for *G. alkanivorans* strain RIPI90A 14.4 mg l^{-1} sulfate repressed the Dsz phenotype. Silva, Paixão, Teixeira, Roseiro, & Alves (2013) reported 50% inhibition at 13.6 ± 0.6 mg l^{-1}sulfate and complete repression at 60 mg l^{-1} on growing cells. Moreover, the bacteria have very low sulfur requirements. In *Rhodococcus sp.*, the cells were found to require 0.1 mM of sulfur for normal growth (Reichmuth, Hittle, Blanch, & Keasling, 2000). Only 1% of bacterial dry weight is sulfur (Stoner et al., 1990), which implies a very low need of this element. Therefore, it is important to take into account the nature of the sulfur source used when preparing the medium for the biocatalyst.

In order to avoid BDS inhibition, most studies are performed using DBT as the sulfur source for biocatalysts production (Mohebali & Ball, 2008). This however becomes an impractical method for large-scale production of biocatalysts because of DBT high price, low water solubility, and the growth inhibition caused by the 2-HBP, the end product of DBT desulfurization (Guobin et al., 2006; Honda, Sugiyama, Saito, & Kobayashi, 1998; Kilbane & Le Borgne, 2004; Ohshiro, Suzuki, & Izumi, 1996; Yoshikawa et al., 2002). So, to achieve a commercially efficient method of avoiding repression it becomes important to explore alternatives.

Mixed Sources

One alternative that could slightly decrease the cost of the sulfur source is the use of small concentrations of sulfate mixed with DBT. If the concentration of sulfate is limiting, the biocatalyst will consume sulfate until it is spent and it will then turn towards the DBT. Silva et al. (2013) demonstrated that *G. alkanivorans* strain 1B cells cultivated with 0.063 mM of sulfate and 0.4 mM of DBT were able to express desulfurization activity, despite a reduction of 22.4% when compared with the DBT control. Also, Ma et al. (2006) were able to obtain increased desulfurization activity of *Rhodococcus* sp. cells cultured with mixed sulfur sources. A maximum activity of 39 μmol g^{-1} h^{-1} was achieved when the concentrations of DBT and sulfate were 0.16 mM and 0.04 mM, respectively, which is very similar to what was observed with 0.20 mM DBT. This method allows a small reduction on DBT concentration while maintaining some BDS activity.

Induction

Another alternative is to use sulfate, which is cheap, as the sulfur source to produce large amounts of high-density bacterial culture with no desulfurization abilities, then wash the biocatalyst to remove the sulfate, and finally proceed with the induction of the expression of the *dsz* operon, by exposing the cells to DBT. This translates in a reduction of the amount of DBT necessary to produce an active catalyst, leading to a less costly biocatalyst production. Ma et al. (2006) were able to obtain *Rhodococcus* sp. biomass with a maximum value of the desulfurization activity of about 15.6 μmol g^{-1} h^{-1} after about 8 h of induction. Longer induction lowered the desulfurization activity, probably due to the accumulation of toxic metabolites in the medium (Chang et al., 2001; Honda et al., 1998; Monticello & Finnerty, 1985).

Alternative Sulfur Sources

The best option towards a cheaper biocatalyst production would probably be to use alternative sulfur sources, which do not inhibit the Dsz phenotype expression, unlike sulfate, and are not as expensive as DBT. In this context, several sulfur sources have been tested. In 2002, Yoshikawa et al. tested different water-soluble sulfur compounds such as dimethyl-sulfoxide (DMSO), 2-aminoethanesulfonic acid, methanesulfonic acid, cysteic acid, p-aminobenzene sulfonic acid, or sodium sulfate as the sole sulfur source for the cultivation of *R. erythropolis* KA 2-5-1. It was found that 2-aminoethanesulfonic acid was the most effective to produce a high density of cells, even when compared with DBT. Its use resulted in a BDS activity of 111 μmol (2-HBP) g^{-1} h^{-1}, with a high growth rate ($\mu_{max} = 0.37$ h^{-1}) and a final cell concentration of 20 g dry cells weight (DCW) after 89 h.

Many researchers have reported that DMSO can be used as an alternative sulfur substrate that does not repress desulfurization activity. (Abbad-Andaloussi, Lagnel, Warzywoda, & Monot, 2003; M. Z. Li et al., 1996; Luo et al., 2003; Ma et al., 2006; Mohebali, Ball, Kaytash, & Rasekh, 2007, 2008; Oldfield et al., 1997; Olmo, Santos, Alcon, & Garcia-Ochoa, 2005; Tang & Hong, 2014). This happens because DMSO is not a substrate for the DBT desulfurizing enzymes (M. Z. Li et al., 1996). So, in the presence of DMSO there is a de-repression of the *dsz* operon in the absence of more readily bioavailable sulfur sources (M. Z. Li et al., 1996; Oldfield et al., 1997). Ma et al. (2006) used 1 mM of DMSO as the single sulfur source to grow *Rhodococcus* sp. cells and obtained a cell density of 4.0 g l^{-1} and desulfurization activity of 51.6 μmol g^{-1} h^{-1}. Based on the cell density and desulfurization activity and comparing with results using DBT and Na_2SO_4, DMSO proved to be the cheapest sulfur source for preparing the biocatalyst for oil desulfurization.

Mohebali et al. (2008) showed that the Dsz phenotype was expressed through the 4S pathway in the presence of DMSO as the sulfur source for the growth of *G. alkanivorans* strain RIPI90A. When using DMSO the growth rate was higher than with DBT, however concentrations higher than 200 μg ml^{-1} induced inhibition. This study also concluded that DMSO should be used as the sulfur source for mass production of *G. alkanivorans* RIPI90A, and there should be an induction step with DBT to increase resting cell activity. Prior to induction, the specific activity detected was 1.4 μmol (2-HBP) g^{-1} h^{-1}, and following incubation (5 h) the highest specific activity observed was 5.11 μmol (2-HBP) g^{-1} h^{-1}.

Another option is the use of hydrodesulfurized oil or waste engine oil as the sulfur source. This method employed by Mukhopadhyaya, Chowdhury, & Bhattacharya (2005), consists on the supplementation of the culture medium with an oil or derivative rich in sulfur, as a way of stimulating desulfurization activity of the biocatalyst, while promoting pre-adaptation of the culture to the BDS conditions. These sulfur sources are cheap, and/or easily available in a refinery making them very interesting for the BDS process. However these oils are very complex and could have inhibitors that limit high density microbial growth. Moreover, the emulsification resulting from the interaction of water, bacteria and oil should difficult the separation of the biomass making it impractical for some processes.

Biodesulfurization Promoters

Nitrogen Source

Glutamic acid can be both a carbon and nitrogen source, so Martin, Alcon, Santos, & Garcia-ochoa (2004) tested the importance of the presence of an inorganic nitrogen source for the growth and desulfurization by *Pseudomonas putida* CECT5279. They determined that the presence or absence of NH_4Cl in the culture medium with glutamic acid did not influence the growth of the microorganism. But, when both nitrogen sources were present the desulfurization rate was 10 to 20% higher. So, the optimal conditions for desulfurization were determined to be an initial concentration of 20 g l^{-1} glutamic acid supplemented with 670 ppm of NH_4Cl.

NADH Promoting Substances

The 4S pathway is NADH dependent, since this molecule is necessary to regenerate the DszA and DszC enzymes. Moreover, the regeneration of NADH also implies the use of other key cofactors, such as ATP, the basic source of energy for most metabolic reactions. ATP may be even more important since it seems to be implicated in the uptake of DBT (Z. Wang et al., 2011), and in the formation and consumption of sulfite and sulfate for biomass production during DBT metabolism (Aggarwal et al., 2012).

The industrial BDS process will depend on the reuse of the biocatalyst, for economic efficiency. However, in long-term use of the biocatalyst there is a loss of BDS activity that is associated with a loss in redox potential and energy. So, in order to allow the greater reuse of the bacterial cells, it became important to study ways to regenerate molecules such as NADH, FMNH and ATP. In this context, Martinez, Santos, Alcon, & Garcia-Ochoa (2014) studied some of the compounds related to the Krebs cycle dehydrogenases able of producing NADH from NAD^+ as possible co-substrates to enhance the BDS process. Citric and succinic acids were used in order to study both extremes of the Krebs cycle, and acetic acid was selected due to the metabolic importance of its active derivative, acetyl-CoA. The results obtained from this work showed that the addition of these cofactors resulted in an increase of the yield and rate of biodesulfurization by *P. putida* CECT5279 cells. Amongst the three co-substrates tested, acetic acid proved to be the most influential, at a concentration of 1.5% the yield of the process increased up to 140% when using single-aged cells in a batch process and to 122% using an optimized mixture of cells in a fed-batch process.

Besides NADH, FMNH is also a fundamental cofactor for the regeneration of the 4S pathway. So, some works on how to maintain the levels of intercellular cofactors of the biocatalyst during the BDS process have been carried out. Nicotinamide and riboflavin are precursors of $NADH_2$ and $FMNH_2$, respectively. As a consequence, to reduce the loss of BDS efficiency due to immobilization and excessive reuse of the biocatalyst, Derikvand, Etemadifar, & Biria (2014) applied the two co-factor precursors and recorded a reduced loss in cell viability and desulfurization activity after each step, enhancing the BDS efficiency by more than 30% after four reuse steps. Therefore, by providing essential co-factors in 4S pathway, it is possible to increase the efficiency of the biocatalyst, allowing for more cycles of BDS for each batch of cells produced, thus effectively lowering the cost of the process.

Carbon Sources

Alongside the sulfur source, carbon is probably the most important component of a culture medium. Depending on the chosen carbon source the biocatalyst may present great changes on BDS efficiency and growth rate. Traditionally, most microbial biotechnological studies were performed with glucose as the single carbon source to demonstrate the biocatalysts activity. Since most microorganisms are glucophilic, it is common sense that this will result in a better expression of the strains metabolic properties (Alves & Paixão, 2014b; Alves et al., 2005; Mohebali et al., 2008; Nuhu, 2013).

However, in recent years, there have been some BDS studies which have revealed that other carbon sources might be better suited for this process. In this context, some theoretical studies were performed based on the sequenced genomes of *R. erithropolis and G. alkanivorans*. These studies analyzed the effects on growth rate and desulfurization efficiency of several carbon sources, such as acetate, citrate, ethanol, formate, fructose, fumarate, gluconate, glucose, glutamate, glycerol, lactate, malate, oxaloacetate, oxoglutarate, pyruvate, and succinate.

According to results presented by Aggarwal, Karimi, & Ivan (2013) and Aggarwal, Karimi, & Lee (2011), ethanol appears to be the best for both growth and desulfurization on both genera. For *G. alkanivorans* the carbon sources as compared to ethanol have the 100% basis rank as follows: fumarate (80%) > oxoglutarate (78.79%) > pyruvate (78.43%) > glutamate (78.24%) > succinate (78%) > acetate > fructose=glucose=lactate (76.86%) > glycerol (75%) > citrate (71.88%) > oxaloacetate (69.70%) > malate (69.11%) > formate (50%). Aggarwal et al. (2013) proceeded to explain that NADH production and usage could justify why ethanol is the best carbon source. Since the desulfurization activity requires high levels of NADH (4 moles for each 1 of DBT), and the cell still requires NADH to grow, priority should be given to a carbon source that provides more NADH during its metabolism. And this was the case for ethanol, since it led to the production of two additional moles of NADH for each one of its own mol. This was the highest among all tested substrates, and thus it seems to be the best substrate for both growth and desulfurization.

However, Alves & Paixão (2014b) reported a novel behavior of a strain isolated in 2005. *G. alkanivorans* strain 1B has now been described as fructophilic bacterium. This means that, contrary to what was predicted, this strain prefers fructose to glucose for both growth and desulfurization. In fact the lowest values for the growth rate (0.025 h^{-1}), 2-HBP production rate (1.80 $\mu M\ h^{-1}$) and specific production rate ($q_{2\text{-HBP}} = 1.22\ \mu mol\ g^{-1}\ h^{-1}$) were obtained in glucose grown cultures. When cultivated with an equal mix of glucose and fructose as carbon source, the value of $q_{2\text{-HBP}}$ increased to 1.90 $\mu mol\ g^{-1}\ h^{-1}$. The highest values for cell growth ($\mu = 0.091\ h^{-1}$), 2-HPB production (9.29 $\mu M\ h^{-1}$) and specific production ($q_{2\text{-HBP}} = 2.12\ \mu mol\ g^{-1}\ h^{-1}$) were obtained when strain 1B was desulfurizing DBT, in the presence of fructose as the only carbon source. These results translate into an increase of over 5-fold in the overall 2-HBP production rate and of about 74% in $q_{2\text{-HBP}}$, which clearly demonstrate the strain fructophilic properties.

The metabolic characteristics observed in *G. alkanivorans* strain 1B highlight that there are still to many unknown factors associated to each strain behavior, and thus theoretical models, even if well performed, can only be applied to each strain individually and not extrapolated to an entire species.

Alternative Carbon Sources

The high cost of the carbon source necessary to cultivate the biocatalyst is one of the biggest barriers for the applicability of BDS at the industrial level. Thus, in order to reduce the costs associated with this process, it is important to search for cheaper alternative carbon sources that can contribute to produce high quantities of microbial biomass with the reducing equivalents required for BDS reactions. In the last decade several examples of alternative feedstocks have been explored, many of which based on the use of agroindustrial residues because of their low cost, and high availability. However the use of these complex carbon sources brought upon several additional problems, such as the need to perform prior hydrolysis, and/or the need to remove excess sulfate (Silva et al., 2013; Werther, Saenger, Hartge, Ogada, & Siagi, 2000).

- **Glycerol:** Glycerol is a byproduct of the biodiesel production, so with the increasing production of biodiesel as an alternative fuel, there will be an increase on the availability of this low-cost carbon source. Abo-state, El-Gendy, El-Temtamy, Mahdy, & Nassar (2014) and Tang & Hong, (2014) studied the use of glycerol to produce biocatalysts with desulfurization ability. However, only Tang & Hong (2014) reported that glycerol is the most suitable carbon source for the growth and desulfurization activity of their biocatalyst (strain HT1). They determined that with 5 g l^{-1} glycerol, 102 mg l^{-1} DBT and 2 g l^{-1} NH_4NO_3, at pH 7 and 30°C for four days cultivation time, the maximum desulfurization was obtained by strain HT1.
- **Recycled Paper Sludge:** The first report on the utilization of alternative raw materials as carbon sources in biodesulfurization studies was performed by Alves, Marques, Matos, Tenreiro, & Gírio (2008). They proposed the use of recycled paper sludge (RPS) as carbon source, since RPS is a very abundant type of waste resulting from the pulp and paper industry. The sludge generated by the water treatment facilities is still a major disposal problem which needs to be dealt with (Oral et al., 2005). However, after neutralization, RPS is very rich in cellulose (35%), xylan (10%) and lignin (20%), % dry weight, which can be hydrolyzed into glucose, xylose and cellobiose making RPS an interesting feedstock.

In their work, Alves, Marques, et al. (2008) produced several different hydrolyzates by enzymatic saccharification of RPS and tested them as nutrient source for low-cost DBT desulfurization by *G. alkanivorans* strain 1B at a concentration of 10 g l^{-1} of glucose. Under these conditions strain 1B was able to grow, but it wasn't able to desulfurize. This fact was due to the concentration of sulfate present in the RPS hydrolyzate. So, further work was carried accounting the prior sulfate removal. The sulfate was removed by simple dialysis, and after that strain 1B was able to consume 250 μM DBT in 96 h displaying a maximum $q_{2\text{-HBP}}$ of 1.1 μmol g^{-1} h^{-1}. The maximum specific growth rates, μ_{max}, for growth with non-dialyzed and dialyzed hydrolyzate were 0.051 h^{-1} and 0.035 h^{-1}, respectively. Both these values are above to what is described for glucose $\mu_{max} = 0.025\ h^{-1}$ (Alves & Paixão, 2014b). Further investigation on the formulation led to the development of an ideal medium of RPS hydrolyzate supplemented with phosphates, ammonia, magnesium and zinc. Zinc was found to have a great influence on both growth and BDS activity by *G. alkanivorans* strain 1B (Alves, Matos, Tenreiro, & Gírio, 2008).

Therefore the results obtained by Alves, Marques, et al. (2008) clearly indicate that RPS hydrolyzates can be used as a cheaper alternative carbon source for DBT desulfurization by *G. alkanivorans* strain 1B. Since RPS wastes are harmful to the environment and must be disposed of, their potential as carbon source makes them very interesting for biotechnological processes.

- **Carob Pulp:** The use of byproducts from the carob processing industry as an alternative carbon source is already common for several bioprocesses (Carvalheiro, Moniz, Duarte, Esteves, & Gírio, 2011; Mendes et al., 2007; Sánchez-Segado et al., 2012). Carob industrial wastes are small carob kibbles with a high content of soluble sugars, mainly sucrose, glucose and fructose, which are easily extractable by water producing sugar-rich liquors (Manso, Nunes, Raposo, & Lima-Costa, 2010). However, these liquors are also rich in sulfates and easy access sulfur sources, and so they cannot be directly used for BDS.

In this context, Silva et al. (2013) described an optimized formulation of a culture medium, using carob pulp liquor as an alternative carbon source, for the production of *G. alkanivorans* strain 1B in a BDS process, aiming for a cost reduction associated to the process. In this work, they treated the carob pulp liquor with barium chloride ($BaCl_2$) for prior sulfate removal and demonstrated the potential of this agroindustrial byproduct as a renewable and cheaper alternative carbon source for BDS. Prior to the treatment with $BaCl_2$, no 2-HBP production by strain 1B was observed within 125 hours of the growth on carob pulp liquor, but in the optimized treated liquor strain 1B was able to produce 237 μM of 2-HBP, which is a similar result to what was obtained in the RPS dialyzed hydrolyzate (Alves, Marques, et al., 2008).

- **Sugar Beet Molasses:** Sugar beet molasses (SBM) is a very abundant industrial byproduct very rich in sucrose (~50%, *w/v*). Because of its composition, SBM can be easily hydrolyzed to glucose and fructose by acidic or enzymatic hydrolysis, with the advantage of having a lower price of commercialization ($100–$150 per ton, which is 5 to 6 times less than sucrose).-

Similarly to carob pulp liquor, SBM contains a large concentration of readily available sulfur sources, which can completely inhibit the BDS process. So, before testing the SBM as a potential alternative carbon source it is necessary to perform a prior sulfate removal as described by Silva et al. (2013). Thus, to express the *dsz* operon of the strain 1B, Alves & Paixão (2014a) treated the sugar beet molasses (SBM_t) with 0.25% $BaCl_2$ (*w/v*) to reduce sulfates to residual levels prior to use it as carbon source for DBT desulfurization. With the SBM_t, the strain 1B achieved a μ_{max} of 0.04 h^{-1} and maximum 2-HBP production rate of 2.56 μM h^{-1}, which resulted in a $q_{2\text{-HBP}}$ of 2.20 μmol g^{-1} h^{-1}. The desulfurization results were better than those obtained with commercial sucrose (1.91 μM (2-HBP) h^{-1}; $q_{2\text{-HBP}} = 0.718$ μmol g^{-1} h^{-1} from Alves & Paixão, 2014b), probably due to other nutrients present in a complex feedstock such as SBM that can act as inducers.

Moreover, the DBT desulfurization process by *G. alkanivorans* strain 1B using SBM_t was further enhanced using a simultaneous saccharification and fermentation (SSF) approach with (1% *v/v*) *Z. bailii* strain Talf1 crude extract with invertase activity. The results obtained showed that this approach allowed a faster growth of strain 1B with a μ_{max} of 0.08 h^{-1}, 2-fold higher than in the absence of enzyme extract, and a 2-HBP production rate of 7.78 μM h^{-1} corresponding to a $q_{2\text{-HBP}}$ of 3.12 μmol g^{-1} h^{-1} (Alves & Paixão, 2014a). Comparing this $q_{2\text{-HBP}}$ value to others prior obtained with the same strain grown in pure commercial substrates, such as glucose (1.03 μmol g^{-1} h^{-1} from Alves et al. (2005)) and fructose (2.12 μmol g^{-1} h^{-1} from Alves & Paixão, 2014b), an enhancement of about 203 and 47% was achieved, respectively.

Arez, Alves, & Paixão (2014), also using the SSF approach with commercial sucrose and *Z. bailii* Talf1 enzymatic extract within a DBT desulfurization process by strain 1B, observed a μ_{max} of 0.07 h^{-1} and a 2-HBP productivity of 5.80 μM h^{-1}, corresponding to a $q_{2\text{-HBP}}$ of 2.60 μmol g^{-1} h^{-1}. These desulfurization values, in addition to those obtained by Alves & Paixão (2014a) in the SSF with SBM_t, translate the advantage of the SSF approach towards enhanced BDS when sucrose or sucrose-rich feedstocks are used as carbon source. The higher desulfurization obtained with the SBM_t highlights the potential of this renewable feedstock as a low-cost alternative carbon source to enhance BDS by *G. alkanivorans* strain 1B.

- **Jerusalem Artichoke:** Jerusalem artichoke (JA) is a species of sunflower that has recently gained much attention as a renewable feedstock, especially towards biofuels (bioethanol, biodiesel), because its tubers present high levels of inulin reaching 50–80% of dry matter (Cheng et al., 2009; L. Guo, Zhang, Hu, Dy Ryu, & Bao, 2013; L. Li, Li, Wang, Du, & Qin, 2013; Liang et al., 2012). Inulin is a carbohydrate composed of linear chains of β-2,1-linked D-fructofuranose molecules terminated by a glucose residue through a sucrose-type linkage at the reducing end, which can be easily hydrolyzed into a fructose-rich hydrolyzate either using inulinases or acidic hydrolysis.

The potential of JA juice as an alternative carbon source, rich in fructose, towards BDS by the fructophilic bacterium *G. alkanivorans* strain 1B was exploited by two different approaches, since this bacterium is not able to metabolize pure inulin as carbon source. One approach used was the SSF with *Z. bailii* crude inulinases (Paixão, Teixeira, Silva, Teixeira, & Alves, 2013), in which a maximum 2-HBP production rate of 4.80 $\mu M\ h^{-1}$ was attained from JA juice (~10 $g\ l^{-1}$ of total reducing sugars). In this study, no sulfate removal procedure was used, which interfered with the final desulfurization productivity. In fact, JA, as a complex natural material, contains very high concentrations of sulfates (> 450 mg l^{-1}) that will inhibit the desulfurization and consequently decrease the 2-HBP production. So, the second approach was the application of acidic hydrolysis of the JA juice, combined with $BaCl_2$ precipitation for sulfate removal (Silva, Paixão, Roseiro, & Alves, 2014). In their study, Silva et al. (2014) first optimized the sulfate removal process for JA juice (0.5% (*w*/*v*) $BaCl_2$ at pH 8.73 and 30ºC for 36 h with agitation) and then performed the DBT desulfurization process by *G. alkanivorans* strain 1B using the best treated JA juice (~25 $g\ l^{-1}$ of total reducing sugars). In this process, strain 1B presented a μ_{max} of 0.06 h^{-1} with a total conversion of 400 μM DBT into 2-HBP in less than 90 h, attaining a 2-HBP maximum production rate of 28.2 $\mu M\ h^{-1}$ and a $q_{2\text{-HBP}}$ of 5.06 $\mu mol^{-1}\ g^{-1}\ h^{-1}$, which are 3.6-fold and 1.6-fold higher, respectively, than that observed for SBM_t by Alves & Paixão (2014a). Moreover, this $q_{2\text{-HBP}}$ is similar to that reported by Mohebali et al. (2008) using optimized resting cells of another *G. alkanivorans*, the strain RIPI90A. In both studies the specific production rate was 2-fold higher than the $q_{2\text{-HBP}}$ of 2.54 $\mu mol^{-1}\ g^{-1}\ h^{-1}$ recently predicted by Aggarwal et al. (2013) using *in silico* modelling for a *G. alkanivorans*, assuming an uptake of 20 mg per g (DCW) per h of glucose or fructose.

The results, using JA juice, highlight the efficiency of the treatment applied to JA juice in making this agromaterial a promising low-cost renewable feedstock for improved BDS by the fructophilic strain 1B. Once again, the results obtained using a cheaper alternative carbon source demonstrate the advantages of exploring renewable feedstocks as promoters of the metabolic activity towards a less-expensive biocatalyst production, which is a fundamental step for the application of BDS at the industrial level.

BDS OPERATIONAL CONDITIONS

After the selection of a microorganism with characteristics suitable for the desulfurization process and the determination of the optimal cultivation conditions, the operational settings are of critical importance for BDS scale-up. The industrial application and cost effectiveness of biodesulfurization process is highly dependent on optimization in four main areas: 1) biocatalyst application, 2) bioreactor design and parameters, 3) biomass recovery and water separation on the process downstream, and 4) integration on the refinery operation.

Biocatalyst Application

Process Setup

Biodesulfurization may use as biocatalyst whole cells, free cell extract or pure enzymes, each with its own advantages and disadvantages.

Some consider the use of pure enzymes as good option, since they require much less water than whole cells to play their catalytic role with only a small film being needed, which would be an interesting alternative for the scale-up process (Vazquez-Duhalt et al., 2002). However, enzymes purification is an expensive process. To surpass this problem, other researchers suggest the use of free cell extracts, which do not require the purification and maintain most enzymatic activity. But both to pure enzymes and cell free extracts, there is still a need of supplying NADH and $FMNH_2$ for the biochemical reactions making these alternatives more expensive and less practical. Moreover, the desulfurization activity has been reported to be lower when free cell extract is used (0.01 g (DBT removed) g^{-1} (protein) h^{-1}) than when whole cells are used (0.4 g (DBT removed) g^{-1} (dw biomass) h^{-1}) (Setti, Lanzarini, & Pifferi, 1997).

These setbacks make whole cells biodesulfurization the most consensual approach for the treatment of DBT (Soleimani, Bassi, & Margaritis, 2007). Biodesulfurization based on whole cells can take place either by growing or resting cells.

Growing cells are easily applied in bioreactor, with microbial growth and desulfurization occurring simultaneously. However, these systems present a number of constrains. In general, the process is rather slow, achieving reduced desulfurization yields (Shennan, 1996) and requires the need for complex growth media, which can interfere with the product analysis due to the presence of a complex mixture of metabolites and medium components (J. Konishi, Ishii, Onaka, Okumura, & Suzuki, 1997). Moreover, the desulfurization activity is repressed in the presence of easy access sulfur sources or 2-HBP, the end-product of the 4S pathway that also inhibits cell growth (M. Z. Li et al., 1996; Nekodzuka, Nakajima-Kambe, Nomura, Lu, & Nakahara, 1997; Ohshiro et al., 1996).

Resting cells, non-growing cells that retain most of their enzymatic activity, have shown advantages over growing cells, such as greater resistance to 2-HBP inhibition. Kobayashi et al. (2001) observed that 80% of desulfurization activity of resting cells of *R. erythropolis* KA 2-5-1 remained even in the presence of 2-HBP at 10 mM in a model oil system, reinforcing the benefit of using these cells for a scale-up of biodesulfurization process.

These cells can also be used in much higher concentration than growing cells (Borgne & Quintero, 2003). Many authors have focused in the production of high cell density cultures that can be used for biodesulfurization as resting cells resulting in a reduction of reaction volume (Honda, Sugiyama, Saito, & Kobayashi, 1998; M. Konishi et al., 2005; Wang & Krawiec, 1996). Honda et al. (1998) used a fed-batch reactor assembly to grow *R. erythropolis* IGTS8 in the presence of sulfate and achieved a cell concentration of 33 g l^{-1} in the best conditions, compared to only 1.1 g l^{-1} observed when DBT was used as sulfur source, which could be attributed to the growth inhibition by 2-HBP. Chang et al. (2001), using a different biocatalyst, *Gordonia nitida* CYKS1, achieved a cell concentration of 92.6 g l^{-1}. In both cases desulfurization induction time was around 4 h.

However, high density resting cells production also has some disadvantages since this process may give rise to cross contaminations with C-C attacking microorganisms with higher growth rates. Moreover, economically relevant sized facilities are required to prepare the biocatalyst, with issues related to the maintenance of desulfurization activity and transport to desulfurization site needing to be addressed (Onodera-Yamada, Morimoto, & Tani, 2001).

This problem might be minimized using lyophilized cells. Patel, Killbane, & Webster (1997) tested biodesulfurization in an aqueous-hydrocarbon phase with freeze-dried cells of *R. erythropolis* IGTS8, revived in a minimal amount of water, and despite a loss of 20% of desulfurization activity in the freeze drying process, there was only a 2.8% of activity reduction after 10 weeks at -80^{o}C. This opens the possibility of producing the biocatalyst in a different location of the BDS refinery, since a much smaller biomass volume allows for easier transportation. Furthermore, desulfurization conditions of lyophilized cells are more flexible. Luo et al. (2003) reported that the desulfurization ability of lyophilized cells of *Pseudomonas delafieldii* R-8 was not affected by pH's ranging in 4.6-8.5, unlike growing cells in which the growth was inhibited at pH below 5.

Nano-Upgrading of Biocatalyst

Biocatalyst upgrading is another trend followed for increased efficiency of the process. Functionalization of the microorganism cell surface is a promising trend in bio-nanotechnology (Ansari, Grigoriev, Libor, Tothill, & Ramsden, 2009).

One of the limiting factors for biodesulfurization is the transfer of poly-aromatic sulfur heterocycles such as DBT, from oil to water and from water to cells (Guobin, Huaiying, Weiquan, Jianmin, & Huizhou, 2005). This constrain can be minimized by the use of nanosorbents such as γ-Al_2O_3 or Fe_3O_4 that selectively absorb those compounds from the organic phase at a higher rate than desulfurization, thus removing this limitation on the process. Guobin, Huaiying, Weiquan et al. (2005) reported that assembling γ-Al_2O_3 to microbial cells led to a two fold increase in desulfurization rate of *P. delafieldii* R-8 compared to original cells, making DBT and 2-HBP transfer no longer a limiting factor.

The adsorption of Fe_3O_4 nanoparticles on the surface of *R. erythropolis* IGST8 led to a 56% increase in desulfurization, probably related to an increase in membrane permeability to DBT, and also allowed an easy separation of the microbial biomass given the super magnetic characteristics of these nanoparticles (Ansari et al., 2009).

Nano-shellization of desulfurizing bacteria with bio-hybrids based in amino acids was reported by Jiang, Ying, Liu, Shen, & Hu (2014). These self-encapsulated cells not only gained the ability to be reused, but these shells also served as a platform in which other inorganic compounds could be incorporated to upgrade desulfurization without affecting the cell metabolic activity. The authors reported a 62% increase of the desulfurization rate, when cells were functionalized with TiO_2 nanoparticles, known for increased desulfurization efficiency under UV light. These authors further reported the post-functionalization of cells with magnetic nanoparticles, allowing for an easier mechanism of biomass recovery.

Biocatalyst Immobilization

Another constrain for a large scale BDS is related to the utilization of free cells, which end up being suspended on the oil/water mixture, requiring costly downstream processing for their removal and also a great control to avoid cell contaminations (X.-L. Guo, Deng, Xu, & Wang, 2006). Furthermore free cells are prone to shear stress when applied in a bioreactor, due to the requirements of mixing the oil and water phases.

Given the high demand of water for biological processes, application of free cells to biodesulfurization scale-up would require massive amounts of water and reactors of an unimaginable scale, thus hindering the possibility to make industrial application a reality. So, biocatalyst immobilization emerges as an interesting solution presenting marked advantages such as: ease of recovery and re-use of cells, better stability to different reaction conditions and components, and lower biocatalyst contamination of final product (Zhang, Prabhu, & Lee, 2010).

Many immobilization methods have been successfully used for biocatalysis and biodegradation (Bardania et al., 2013; Dinamarca et al., 2014; Gunam, Sujaya, Aryanta, Tomita, & Asano, 2013; He et al., 2012; F. Li et al., 2005; Y.-G. Li, Gao, Li, Xing, & Liu, 2009; Wu, Lin, & Chan, 1994) and also for biodesulfurization (Nuhu, 2013). Immobilization studies are mainly focused on adsorption or entrapment/ encapsulation. Adsorption uses inorganic supports, such as Al, Si, Ti, Celite or Sepiolite, or inert organic supports such as lignin, with specific area and porosity in which microbial biomass adheres (Chang, Chang, Ryu, & Chang, 2000; Dinamarca et al., 2010; Huaiying, Guobin, Huizhou, & Jianmin, 2007; Mukhopadhyaya, Chowdhury, & Bhattacharya, 2007). Biocatalytic immobilization by adsorption is advantageous in relation to entrapment when considering the better mass transfer and fewer steric problems with large sulfur containing molecules (Guobin, Jianmin, Chen, Huizhou, & Jiayong, 2005). Despite these advantages, adsorption is not a strongly followed strategy as it is a simple physical process and thus cell attachment strength is not enough to avoid a quick detachment from the adsorbent (Dai, Shao, Qi, & Ding, 2014).

Although entrapment and encapsulation refer to different methodologies, with the first referring to the trapping within polymeric structures and the second to the formation of a continuous membrane around encapsulants that wholly coats it, entrapment may be used as a more general term (Willaert & Baron, 1996). Entrapment has obvious advantages for cell immobilization, in relation to adsorption, as a mean to prevent cell lost. Ideally, a carrier for entrapped cells should have a highly porous structure that allows for non-hindered diffusion of solutes and dissolved gas without the loss of cells. Several polymers have been tested in desulfurization, all with advantages and drawbacks. Agar and alginates have found deep application in industrial processes for their biocompatibility, simplicity and low cost (Blandino, Macías, & Cantero, 1999). However, their reduced mechanical strength leads to elevated cell leakage, thus compromising their durability. Naito et al. (2001) tested photo-crosslinked pre-polymers (ENT-4000 and ENTP-4000) and polyurethane (PU-3 and PU-6) in the entrapment of *R. erythropolis* KA 2-5-1 cells, as well as agar and alginates. Polyurethane showed high toxicity to the microorganism, but ENT-4000 showed promising results. Besides being able to retain the biomass, it increased the biocatalyst longevity to 900 h, in contrast with the 192 h of maximum longevity previously reported by Pacheco et al. (1999). Despite the lower desulfurization activity in relation to free cells (attributed to diffusion limitations) and the high cost of this pre-polymer, Naito et al.(2001) reported to have achieved these results with no water addition to the n-tetradecane model oil, which presents as a major breakthrough on the feasibility of biodesulfurization in an industrial scale greatly simplifying separation steps.

Polyvinyl alcohol (PVA) is a nontoxic, biologically compatible, low-cost polymer also being used for cell entrapment. It can be prepared with chemical reagents such as boric acid (Hashimoto & Furukawa,

1987) or with no chemical reagents by the freezing-thawing technique (Lozinsky & Plieva, 1998). Guobin, Jianmin, Chen et al. (2005) used this technique for the preparation of *P. delafieldii* R-8 magnetic beads. These authors report to have been able to reuse PVA-R8 beads for 12 cycles, without significant decrease in desulfurization activity and with a much higher resistance to temperature.

The desulfurization activity of *Sphingomonas subarctica* T7b was studied either in free resting cells or immobilized in different PVA and sodium alginate mixtures by Gunam et al. (2013). They reported a higher stability to pH and temperature variations in immobilized cells when compared to free cells. Furthermore, they also achieved slightly higher desulfurization rates than those obtained for free cells, surpassing one of the limitations of cell entrapment, and the biodesulfurization activity remained stable for 8 cycles with reactivation between cycles. These results indicate PVA as a good candidate for application in large scale biodesulfurization, given its low cost, stability and biocompatibility.

In overall, the integration of the immobilization techniques into BDS allows improved results and increase of process efficiency, besides enhancing separation and biocatalyst reutilization, with great impact in biocatalyst application costs.

Bioreactor System

Mass Transfer

The setup of a fossil fuels BDS process usually occurs in a byphasic system: an aqueous and an oil phase, which in fact can be considered a four phase system, if we consider a gas phase- the oxygen needed for the biocatalytic process; and a solid phase- the microbial biomass (Foght, 2004) One of the biggest challenges for the industrial application of BDS is related to the immiscibility of water (needed for microbial activity) with hydrocarbon feedstocks, which results in a low mass transfer between phases.

In this context, the desulfurizing microorganisms can be distinguished in relation to the character of their membranes, being either hydrophobic of hydrophilic. The hydrophobic membrane microorganisms, such as *Rhodococci* and *Gordoniae*, have better resistance when used in water-oil environments and easier access to sulfur containing substrates dissolved in the organic phase, adhering to the oil-water interface (Abbad-Andaloussi et al., 2003). In contrast, the hydrophilic membrane microorganisms, such as *Pseudomonas*, need the substrates to be dissolved in the aqueous phase (Caro, Boltes, Letón, & García-Calvo, 2007), making the hydrophobic membrane microorganisms a better candidate for large scale biphasic systems (Monticello, 2000).

Oil/water (o/w) volume ratio is amongst the factors that most influence the cost and productivity of large scale BDS (Luo et al., 2003). In one hand, microorganisms require water for their biocatalytic activity and high oil ratios are reported to be toxic to the biocatalyst, with strong impact in BDS (Caro, Boltes, et al., 2007) also hindering oxigen difusion when aqueous phase is below 70% (Guchhait, Biswas, Bhattacharya, & Chowdhury, 2005b). But in the other hand, very low ratios would imply huge costs on a scale-up process, both in reactor scale and separation costs. Furthermore, high water contents decreases the solubility and bioavailability of hydrophobic substrates (Vazquez-Duhalt et al., 2002) and hinders the dissolution of BDS products in the organic phase, thus limiting process productivity (Kobayashi et al., 2001).

Strategies such as encapsulation, as above stated, can drastically increase oil/water ratios, since the water needed for the catalytic activity is immobilized together with the biocatalyst, thus allowing to foresee a future BDS process without the need of biphasic systems.

Bioreactor Design

Knowing the importance of an efficient mass transfer, a good contact surface between phases is needed aiming at getting the BDS system scale-up and has been the focus of several bioreactor design and techniques, which have been optimized to overcome the mass transport limitations.

Most initial bioreactor studies were performed in stirred tank reactors (STR) (Pacheco et al., 1999; Chowdhury & Duttagupta, 2005), and its application has been reported in batch, fed-batch and continuous approach, with the last showing promising results for BDS scale-up (Schilling, Alvarez, Wang, & Cooney, 2002). The optimization of mass transport in this type of reactor is highly dependent on impeller design and speed (Abín-Fuentes, 2013) since a high input of energy and impeller speed is needed in order to remove mass transfer constrains. Monticello (2000) introduced a conceptual design for the continuous desulfurization of fuels. This author emphasized the need of three reactors working in tandem in order to achieve very low sulfur concentration oil. Yang et al., (2007) presented an interesting design of a continuous stirred tank reactor where aqueous and organic phases were kept partitioned, allowing for an actual separation between these phases with the obvious downstream advantages.

The elevated operational costs in power input for mixing and aeration, the high shear stress and poor air-liquid contact of STR's make the utilization of internal loop airlift reactors an interesting alternative (Talvy, Cockx, & Line, 2005) and, despite few oil application studies, a simulation performed by Nandi (2010) reports the applicability towards ultra-low sulfur diesel. Despite the advantages of these reactors, achieving a fine emulsion still requires high power input to surpass mass transfer constrains, and so electrically driven phase contactors could be used to disperse fine droplets between immiscible phases (T. C. Scott & Wham, 1989). This would allow lower power consumption and a reduction of the water demand, as low as only 5% (Kaufman et al., 1997).

All these types of free cells reactors, however, lead to difficulties in separation of the biocatalyst. To avoid this problem many researchers have focused on immobilized cell reactors, which allow for a simpler downstream process and continuous operation. A fluidized bed reactor (FBR) configuration was reported by the Argonne National Laboratory (ANL), where biocatalyst was immobilized in beads and was fluidized by oxygenated gasoline, aerated in a separated unit (McFarland et al., 1998). An alternative reactor design with immobilized cells was also reported by Amin (2011). This author assembled a Vertical Rotating Immobilized Cell Reactor (VRICR) where cells were grown attached to Immobilized Biomass Units (IBUs) in a first stage, and carried out desulfurization in a second one. This design achieved 100% sulfur removal of a model oil continuously for more than 120 h. A very different design was developed by Mukhopadhyaya, Chowdhury, & Bhattacharya (2006): a bio-trickling reactor. In this system, the bacterial cells were immobilized in spheres and then submitted to a stream of oil in a small reactor, with controlled pressure and aeration, successfully achieving a reduction of 99% sulfur content in the tested oil, without the need to separate neither water nor biocatalyst from the final product.

Emulsifiers

Another strategy to improve mass transfer between water and hydrocarbon phases of a BDS system is the addition of surfactants (W. Li & Jiang, 2013). Surfactants are surface-active amphipathic agents with both hydrophobic and hydrophilic components, which act in the interphase of fluids with different polarities such as water-hydrocarbon, reducing surface tension and aiding in the emulsion or solubilization between phases (Rouse, Sabatini, Suflita, & Harwell, 1994). Surfactants have been reported to increase

BDS yield, increase DBT diffusion rate in aqueous phase and avoid end-product accumulation that is related to BDS inhibition (Caro, Letón, García-Calvo, & Setti, 2007). Many of these compounds have been applied to desulfurization. Patel et al. (1997) applied several surfactants to *R. erythropolis* IGTS8 desulfurization of DBT, using hexadecane as hydrocarbon phase and obtained interesting results with oleic diethanolamine and Triton N101, achieving 2-fold higher 2-HBP production.

Improvements were also obtained with Tween-80 on DBT desulfurization in hexadecane by *Corynebacterium* sp. ZD-1, resulting in a 50% increase on 2-HBP production (M. Wang, Li, Shi, Wang, & Feng, 2006). The same agent improved sulfur removal of a previously hydrotreated diesel from 76.8% to 91.2% by the microorganism *R. erythropolis* 1awq (Feng et al., 2006).

Surfactants can also be used to decrease viscosity of heavy oils that are scarcely used due to their high sulfur content, thus increasing BDS efficiency in this type of oils. Biodesulfurization of MFO380 heavy oil with a mixed culture had a sulfur removal increase from 2.88% to 51.7%, when using the surfactant Triton X-100 (W. Li & Jiang, 2013). Kaufman, Borole, Shong, Sides, & Juengst (1999) also reported that surfactants can minimize the stabilization of asphaltene groups in crude oils, when mixed with buffer salts, needed for BDS, which would lead to increased viscosity. Synthetic surfactants, however, have some issues, namely their non-biodegradability and potential toxicity both to the environment and to the desulfurizing microorganism (Banat, Makkar, & Cameotra, 2000; Patel et al., 1997). Different strains of *Pseudomonas aeruginosa*, *Rhodococcus erythropolis*, *Arthrobacter* sp., and *Bacillus subtilis* have been described as natural producers of biological equivalents of chemical surfactants (Batista, Mounteer, Amorim, & Totola, 2006; Cameotra & Singh, 2009; Dehghan-Noudeh, Housaindokht, & Bazzaz, 2005). These biosurfactants are characterized by better physicochemical characteristics and environmental compatibility (Desai & Banat, 1997).

Biodesulfurizing microorganisms have to survive in hydrophobic environments and many can naturally produce biosurfactants such as phospholipids, rhamnolipids and glycolipids (Bandyopadhyay, Chowdhury, Bhattacharjee, & Pan, 2013). Furthermore, 2-HBP can also act as a biosurfactant and its production is related to increased emulsification on water-oil mixtures (Bandyopadhyay et al., 2013). Since biosurfactants are produced during microbial growth, they tend to take time to have a significant effect, and so an external addition of a biosurfactant could be provided to improve BDS efficiency in an industrial scale. Amin, Bazaid, & Abd El-Halim (2013) designed a two-stage bioreactor where BDS of a model oil by *R. erythropolis* ATCC 53968 was coupled with a second bioreactor in which *B. subtilis* strain BDCC-TUSA-3, an efficient producer of surfactin, was generating the biosurfactant that was fed to the BDS bioreactor. Surfactin improved *R. erythropolis* cell growth 33% and the BDS rate 66%, which was better than the results with synthetic surfactants, and the BDS of the model oil decreased sulfur content from 398 to <5 ppm.

Bioemulsifiers, such as exopolysaccharides, are extra-cellular products that are not surface-active as biosurfactants. These are associated with microorganisms that are able to degrade oil substrates, but do not produce biosurfactants (Ta-Chen, Chang, & Young, 2008). These agents, when compared to chemical surfactants, present a higher emulsification of crude oils (Martínez-Checa, Toledo, Vilchez, Quesada, & Calvo, 2002), making them an interesting alternative to solve emulsification problems in BDS.

Separation

The best conditions for good mass transfer in the upstream of BDS, lead to the biggest constrains for the downstream part of the process. The tight emulsion needed for oil-cell-water contact must be broken in order to recover the three components (Monticello, 2000). While desulfurized oil must be clean of microbial contaminants and water to proceed in the refinery, recycling of the microbial biomass is vital for the industrial process, and byproducts separation must also be quick and cost effective.

Bioreactor design, biocatalyst choice and immobilization, and the increase of o/w ratios can greatly improve separation. The two-layer bioreactor design with minimal mixing between water and oil phases (Yang et al., 2007) can significantly reduce the mixture of phases. Designs where biocatalysts are immobilized are also promising for this step of the process, both due to easier recovery of the biocatalyst and increase of o/w ratios (Amin, 2011). The choice of hydrophobic biocatalysts such as *Rhodococci* and the use of emulsifiers, despite the advantages in mass transfer, can create very fine and stable emulsions between the cells and the oil, with cells adherent to oil phases, adding the need of effective and cost-friendly methods for phase separation (Borgne & Quintero, 2003).

Nowadays in industrial processes, centrifugation is one of the most used recovery methods, but its application in three-phase emulsions achieves no relevant separation, which combined with the high energy input needed for this method, turns this into a non-viable separation method, at least as a single step (Choi, Cho, Ryu, & Chang, 2003). An alternative to centrifugation can be the use of hydrocyclones, conical tubes specially designed for phase separation. Fluid is fed to the widest part and the spinning of these hydrocyclones can separate denser (water) from lighter (oil) fractions, as the denser fraction is directed to the outside of the tube and the lighter to the middle. Microbial biomass is associated with the oil-water interface thus, in a water-in-oil emulsion, these cells are associated with the water droplets. This allows a separation of a clean oil fraction in a first phase of de-oiling. Inverting phase emulsion of the overflow, through the addition of fresh oil, can make cells adhere to the oil droplets and thus the running through a second hydrocyclone will lead to a dehydration of the mix with a remaining small fraction of concentrated cells mixed with oil and a clean water phase, which can be recycled back to the bioreactor (Folsom, Meyer, & Yu, 1998). This method appears as an inexpensive and quick alternative to high energy methods such as centrifugation, with great impact on capital and operational costs (Monticello, 2000).

Methods based in filtration can also be an interesting alternative for phase separation (Koltuniewicz, Field, & Arnot, 1995; K. Scott, Jachuck, & Hall, 2001). Chen at al. (1996) patented a method based on a dual filtration system. This system involved the use of wetting agents for the sequenced filters that were: 1) miscible with liquid fossil fuel but not aqueous phase, and 2) miscible with aqueous phase but not with liquid fossil fuel. This filtration sequence allows obtaining a clean fossil fuel filtrate on the first step, followed by the filtration of the retentate to ensure a clean water filtrate, which could then be recycled back to the BDS tank. The final retentate would be mainly comprised of the biocatalyst that could be subjected to purification procedure and reactivation in order to be also recycled back to BDS tank (Chen and Monticello, 1996). A different apparatus proposed by M. Konishi, Kishimoto, Tamesui, et al. (2005), based on the use of a polytetrafluroethylene (PTFE) tubular membrane, was able to separate model oil from a mixture of water in oil (50%, *v*/*v*) containing the biocatalyst in a continuous operation. Filtration methods, although potentially useful, present some constrains for continuous industrial use, namely the need for backwashing in order to avoid flux rate decrease and the high dependence on emulsion viscosity.

Another technique used in industry for phase separations is settling, in which separation is based on density difference between phases. Settling tanks are present in oil refineries, but emulsified mixtures are much harder to separate by settling. Laboratory scale settling of BDS effluent has been applied for a continuous desulfurizing process (Schilling et al., 2002), but large scale application of this technique is unlikely to be effective for emulsified oil-water-biocatalyst effluents.

Destabilization of oil-water emulsions is a crucial step in BDS effluent separation, and different techniques are widely applied, namely in bioremediation and oil spills (Nordvik, Simmons, & Bitting, 1996). Coagulant agents such as aluminum and ferric sulfates have been reported to destabilize this kind of emulsions, allowing for recovery by flocculation (Al-Shamrani, James, & Xiao, 2002). Applied to BDS, however, these pose an obstacle as their toxicity to the biocatalyst can disable its recycling. Demulsifiers such as ethanol, however, present an interesting alternative due to its biocompatibility with the biocatalyst. Despite having little effect in surface tension, its application can reduce the viscosity of the emulsion and thus improve phase separation methods, without affecting BDS ability of the biocatalyst when recycled (Choi et al., 2003). The biodemulsification, *i.e.* the use of microorganisms to brake emulsions, can present itself as a more eco-friendly alternative in the future (Singh, Singh, & Ward, 2012), but no application to BDS has been yet studied, hence the difficulty in evaluating its applicability and cost-effectiveness.

The need to recover the biocatalyst from the BDS effluent for reapplication limits the techniques and chemicals that can be used for phase separation. If the biocatalyst can be successfully removed in advance, oil-water emulsions can be subjected to more effective, harsher separation methods. Immobilization techniques, despite very effective for biocatalyst removal, are usually related with a decrease of desulfurization rates (Naito et al., 2001). The upgrade with magnetic nanoparticles (such as magnetite) of the biocatalyst could emerge as a cost-effective, simple and fast process for biomass recovery (Guobin, Jianmin, Huaiying, & Huizhou, 2005; Haukanes & Kvam, 1993), as it would only require the application of an external magnetic field for the recovery of the biocatalyst. Several authors have applied different techniques and nanoparticles to coat desulfurizing microbial cells with success (Ansari et al., 2009; Guobin, Jianmin, Huaiying, et al., 2005; Y.-G. Li et al., 2009), and in all studies the desulfurizing ability was either unaffected or even improved (Ansari et al., 2009).

The wide array of techniques developed for the BDS downstream or that can be applied to it opens good perspectives for this part of the process towards the industrial application of BDS. These techniques should not be seen as mutually exclusive, but the best setup of integrated techniques should be found as the most effective and better up-scalable, always having in account its cost-effectiveness.

BDS Added-Value

Industrial application of biodesulfurization, amongst other factors, is dependent on its economic viability. The production of added-value products in parallel with BDS can ease the process cost and give economic sense to the changes needed in the refinery process (Bandyopadhyay et al., 2013). One type of byproducts produced in BDS are the biosurfactants, needed for the microorganism to thrive in highly hydrophobic environments (Bandyopadhyay, Chowdhury, & Bhattacharjee, 2014). When compared to chemical surfactants, biosurfactants have important advantages such as biodegradability and effectiveness at extreme temperatures and pH, and moreover a lower toxicity. Besides oil refining enhancement, their application ranges from bioremediation, to healthcare, food processing and cosmetics (Mulligan, 2005; Perfumo, Smyth, Marchant, & Banat, 2010; L. Rodrigues, Banat, Teixeira, & Oliveira, 2006; L. R. Rodrigues & Teixeira, 2010; Urum & Pekdemir, 2004). Biosurfactants cannot yet compete with chemical surfactants due to their high production cost (Cameotra & Makkar, 1998), and here may lie the interest in the BDS technology, as biosurfactants can be produced as a byproduct of fuels desulfurization.

The final product of the 4S pathway (2-HBP) is a hydrotrope that can act as a surfactant (Mohebali et al., 2007). Other hydroxyl and carboxyl compounds, phospholipids, rhamnolipids, and glycolipids, amongst others, also with surfactant and emulsifier characteristics, have been described as extracellular byproducts of BDS process and could be recovered from BDS effluents (Bandyopadhyay et al., 2014).

Energy BioSystems Corporation design for a BDS industrial application included the production of surfactants from low-value oil. This technology implied a modification of the 4S pathway: the removal of *dszB* gene from the desulfurizing microorganism stopped the 4S pathway in the production of hydroxyphenyl benzene sulfonate (HPBS) byproducts, which could then be converted into derivative molecules with application as surfactants (Monticello, 2000). In fact, at an industrial level, the production of high added-value biosurfactants coupled to BDS can greatly improve the overall process economics since their production costs will be included within the sulfur removal bioprocess, performed at mild operational conditions, from a low-value feedstock.

Integration into a Refinery Process

The incorporation of BDS into a refining process arises several issues, even if the constrains focused above are all dealt with. First and foremost, BDS has to operate at same speed and reliability as other refining processes if it is to be integrated, which emerges as a challenge when using microorganisms in a large scale operation, not initially prepared for that purpose (Kilbane & Le Borgne, 2004).

The decision of where to insert and what type of oils BDS should treat in the refinery process is another issue to be dealt with. Ultra low sulfur diesel (ULSD) production is one of the potential goals of BDS, knowing the very strict levels that international regulations have been establishing and the difficulty of HDS in removing the recalcitrant organosulfur compounds.

Some authors refer the application of BDS before HDS as the best option for an integrated process into a refinery towards ultra low sulfur fuels. This upstream approach permits to remove a great portion of the recalcitrant organosulfur compounds prior to HDS, making it more efficient and less energetically costly since will need lower hydrogen input (Stanislaus, Marafi, & Rana, 2010). In an upstream design, there are authors defending that the best application of BDS would be in crude oil, since it has higher water content than diesel or gasoline (Zhou & Zhang, 2004). An integrated process enclosing BDS to upgrade crude oils might reduce their recalcitrance, before being sent to the refinery, improving the effectiveness of the current refinery processes and enabling the utilization of certain low-quality oils that cannot be treated with conventional technology (Kilbane, 2006).

In contrast, other authors defend that BDS has the potential of being developed as a viable technology downstream of classical HDS (Monticello, 2000; Gupta et al., 2005; Mukhopadhyaya et al., 2007; Yang, et al., 2007; Bandyopadhyay et al., 2013, 2014). In this approach, BDS will deal only with the recalcitrant molecules that the HDS is unable to remove.

There are very few reports on BDS process designs and cost analysis (Gupta et al., 2005). Recently, Alves, Paixão, Pacheco, Ferreira, & Silva (2015) reported a study where two BDS process designs were analyzed in terms of energy consumption, greenhouse gas emissions (GHG) and costs. This study pointed out for the application of the BDS downstream HDS as the best cost-effective conceptual design to apply into an oil refinery. Once it is able of desulfurize HDS recalcitrant compounds selectively, BDS integration may led to the accomplishment of the stringent European limit of <10 ppm for S-content on fuels, which otherwise may imply the necessity of more severe conditions within HDS units. Deep desulfurization is a very costly option and is not environmental friendly because implies higher GHG emissions and substantially increase the carbon footprint.

CONCLUSION

Although the new environmental regulations that limit the sulfur levels of diesel and other transportation fuels to very low levels are beneficial from environmental point of view, meeting the required stringent specifications represent a major operational and economic challenge for the petroleum refining industry. The tightening of sulfur specifications of diesel/gasoline fuel to very low levels requires ultra deep desulfurization of diesel/gasoline feed stream. The shift from normal to ultra deep desulfurization is a very complicated technical problem thus demanding to find cost-effective ways for ultra low sulfur fuel production.

BDS has drawn wide attention because of its green processing of fossil fuel. Bioprocesses can potentially provide a solution to the need for improved and expanded fuel upgrading worldwide, because bioprocesses for fuel upgrading do not require hydrogen and produce far less greenhouse gas (GHG) emission than thermochemical processes. In the last decade, many reviews have been written on the topic of biotechnology for fossil fuels and biodesulfurization, but most have centered on the isolation of new microorganisms, the description of the metabolic pathways and the increase of BDS activity through genetic enhancing.

This work aimed to focus the current problems and efforts being made towards the BDS reduction of costs and increase of its efficiency, both required for an industrially feasible process. In this context, different formulations of culture media have been described and optimized for each biocatalyst studied, reducing concentration of inhibitors, increasing desulfurization activity and biocatalyst longevity, and exploring cheaper alternatives for the current commercial reagents. Moreover, the utilization of desulfurizing microorganisms that can grow in low nutrient culture media without vitamins and other growth promoters, like yeast extract, peptone, triptone, etc, is an advantage for BDS upgrade since it may reduce the biocatalyst production costs significantly.

Process-wise, mass transfer, and consequently oil/water ratios, have been identified has two of the greatest problems of the biodesulfurization technology. To surpass them, many approaches have been explored, either by using different types of bioreactors, adding substances such as emulsifiers or biosurfactants to the reaction media, or by looking for better ways to apply the biocatalyst such as encapsulation.

In overall, for BDS to become a reality it is fundamental to achieve a good integration into the oil refinery process. In this field, the biggest setback commonly identified is the separation of the three components characteristic of this process, *i.e.* oil, water and biocatalyst. Different mechanical solutions have been explored, such as filtration, centrifugation and the use of hydrocyclones. However, recently, other approaches have been more in focus including the modification of the biocatalyst through magnetic nanoparticles, or the use of immobilized microorganisms. These techniques may result in a cheaper process to separate and reutilize the biocatalyst.

The use of biotechnology to industrially desulfurize oil is still far from being economically appealing. Even after optimize every drawback, probably, there will be a need to take advantage of the high added-value products resulting from the growth of the biocatalyst. In fact many authors have speculated that the production of biosurfactants, characteristic of most desulfurizing microorganisms, could be the decisive factor to balance the economical scale-up of this process, and even make it more profitable than HDS.

Much work is still required to do. With the increasing pressure being made by the legislators towards the reductions of sulfur levels in fossil fuels, as well as the ever increasing demand for energy, BDS should continue to be explored. It becomes fundamental for the industry to discover new and cheaper ways to process heavier and more contaminated oils. Biodesulfurization coupled with other biological treatments, such as biodenitrification, biological removal of metals and reduction of viscosity, will definitely play a crucial role in the future of sustainable energy from fossil fuels.

ACKNOWLEDGMENT

The present work was financed by FEDER funds through POFC-COMPETE and by national funds through FCT (Fundação para a Ciência e a Tecnologia) in the scope of project Carbon4Desulf - FCOMP-01-0124-FEDER-013932.

REFERENCES

Abbad-Andaloussi, S., Lagnel, C., Warzywoda, M., & Monot, F. (2003). Multi-criteria comparison of resting cell activities of bacterial strains selected for biodesulfurization of petroleum compounds. *Enzyme and Microbial Technology*, *32*(3), 446–454. doi:10.1016/S0141-0229(02)00320-4

Abín-Fuentes, A. (2013). *Mechanistic understanding of microbial desulfurization* (Doctoral dissertation). Massachusetts Institute of Technology.

Abo-state, M. A., El-Gendy, N. S., El-Temtamy, S. A., Mahdy, H. M., & Nassar, H. N. (2014). Modification of basal salts medium for enhancing dibenzothiophene biodesulfurization by *Brevibacillus invocatus* C19 and *Rhodococcus erythropolis* IGTS8. *World Applied Sciences Journal*, *30*(2), 133–140. doi: 10.5829/idosi.wasj.2014.30.02.14023

Aggarwal, S., Karimi, I., & Lee, D. Y. (2011). Reconstruction of a genome-scale metabolic network of *Rhodococcus erythropolis* for desulfurization studies. *Molecular BioSystems*, *7*(11), 3122–3131. doi:10.1039/c1mb05201b PMID:21912787

Aggarwal, S., Karimi, I. A., & Ivan, G. R. (2013). In silico modeling and evaluation of *Gordonia alkanivorans* for biodesulfurization. *Molecular BioSystems*, *9*(10), 2530–2540. doi:10.1039/c3mb70132h PMID:23921469

Aggarwal, S., Karimi, I. A., Kilbane, J. J. II, & Lee, D. Y. (2012). Roles of sulfite oxidoreductase and sulfite reductase in improving desulfurization by *Rhodococcus erythropolis. Molecular BioSystems*, *8*(10), 2724–2732. doi:10.1039/c2mb25127b PMID:22832889

Al-Shamrani, A. A., James, A., & Xiao, H. (2002). Destabilisation of oil–water emulsions and separation by dissolved air flotation. *Water Research*, *36*(6), 1503–1512. doi:10.1016/S0043-1354(01)00347-5 PMID:11996340

Alves, L., Marques, S., Matos, J., Tenreiro, R., & Gírio, F. M. (2008). Dibenzothiophene desulfurization by *Gordonia alkanivorans* strain 1B using recycled paper sludge hydrolyzate. *Chemosphere*, *70*(6), 967–973. doi:10.1016/j.chemosphere.2007.08.016 PMID:17897697

Alves, L., Matos, J., Tenreiro, R., & Gírio, F. M. (2008). Evidence for the role of zinc on the performance of dibenzothiophene desulfurization by *Gordonia alkanivorans* strain 1B. *Journal of Industrial Microbiology & Biotechnology*, *35*(1), 69–73. doi:10.1007/s10295-007-0278-5 PMID:18043954

Alves, L., & Paixão, S. M. (2014a). Enhancement of dibenzothiophene desulfurization by *Gordonia alkanivorans* strain 1B using sugar beet molasses as alternative carbon source. *Applied Biochemistry and Biotechnology*, *172*(6), 3297–3305. doi:10.1007/s12010-014-0763-z PMID:24519629

Alves, L., & Paixão, S. M. (2014b). Fructophilic behaviour of *Gordonia alkanivorans* strain 1B during dibenzothiophene desulfurization process. *New Biotechnology*, *31*(1), 73–79. doi:10.1016/j.nbt.2013.08.007 PMID:24012483

Alves, L., Paixão, S. M., Pacheco, R., Ferreira, A. F., & Silva, C. M. (2015). Biodesulphurization of fossil fuels: Energy, emissions and cost analysis. *RSC Advances*, *5*(43), 34047–34057. doi:10.1039/C4RA14216K

Alves, L., Salgueiro, R., Rodrigues, C., Mesquita, E., Matos, J., & Gírio, F. M. (2005). Desulfurization of dibenzothiophene, benzothiophene, and other thiophene analogs by a newly isolated bacterium, *Gordonia alkanivorans* strain 1B. *Applied Biochemistry and Biotechnology*, *120*(3), 199–208. doi:10.1385/ABAB:120:3:199 PMID:15767694

Amin, G. A. (2011). Integrated two-stage process for biodesulfurization of model oil by vertical rotating immobilized cell reactor with the bacterium *Rhodococcus erythropolis. Journal of Petroleum & Environmental Biotechnology*, *2*(1), 107. doi:10.4172/2157-7463.1000107

Amin, G. A., Bazaid, S. A., & Abd El-Halim, M. (2013). A two-stage immobilized cell bioreactor with *Bacillus subtilis* and *Rhodococcus erythropolis* for the simultaneous production of biosurfactant and biodesulfurization of model oil. *Petroleum Science and Technology*, *31*(21), 2250–2257. doi:10.1080/10916466.2011.565292

Ansari, F., Grigoriev, P., Libor, S., Tothill, I. E., & Ramsden, J. J. (2009). DBT degradation enhancement by decorating *Rhodococcus erythropolis* IGST8 with magnetic Fe_3O_4 nanoparticles. *Biotechnology and Bioengineering*, *102*(5), 1505–1512. doi:10.1002/bit.22161 PMID:19012265

Arez, B. F., Alves, L., & Paixão, S. M. (2014). Production and characterization of a novel yeast extracellular invertase activity towards improved dibenzothiophene biodesulfurization. *Applied Biochemistry and Biotechnology*, *174*(6), 2048–2057. doi:10.1007/s12010-014-1182-x PMID:25163885

Babich, I. V., & Moulijn, J. A. (2003). Science and technology of novel processes for deep desulfurization of oil refinery streams: A review. *Fuel*, *82*(6), 607–631. doi:10.1016/S0016-2361(02)00324-1

Banat, I. M., Makkar, R. S., & Cameotra, S. S. (2000). Potential commercial applications of microbial surfactants. *Applied Microbiology and Biotechnology*, *53*(5), 495–508. doi:10.1007/s002530051648 PMID:10855707

Bandyopadhyay, S., Chowdhury, R., & Bhattacharjee, C. (2014). Production of biosurfactants through biodesulfurization of spent engine oil – an experimental study. *Green Chemistry Letters and Reviews*, *7*(3), 288–295. doi:10.1080/17518253.2014.946972

Bandyopadhyay, S., Chowdhury, R., Bhattacharjee, C., & Pan, S. (2013). Simultaneous production of biosurfactant and ULSD (ultra low sulfur diesel) using *Rhodococcus* sp. in a chemostat. *Fuel*, *113*, 107–112. doi:10.1016/j.fuel.2013.05.036

Bardania, H., Raheb, J., Mohammad-Beigi, H., Rasekh, B., & Arpanaei, A. (2013). Desulfurization activity and reusability of magnetite nanoparticle–coated *Rhodococcus erythropolis* FMF and *R. erythropolis* IGTS8 bacterial cells. *Biotechnology and Applied Biochemistry*, *60*(3), 323–329. doi:10.1002/bab.1090 PMID:23656694

Batista, S. B., Mounteer, A. H., Amorim, F. R., & Totola, M. R. (2006). Isolation and characterization of biosurfactant/bioemulsifier-producing bacteria from petroleum contaminated sites. *Bioresource Technology*, *97*(6), 868–875. doi:10.1016/j.biortech.2005.04.020 PMID:15951168

Bender, J., & Weigel, H.-J. (2011). Changes in atmospheric chemistry and crop health: A review. *Agronomy for Sustainable Development*, *31*(1), 81–89. doi:10.1051/agro/2010013

Bhatia, S., & Sharma, D. K. (2012). Thermophilic desulfurization of dibenzothiophene and different petroleum oils by *Klebsiella* sp. 13T. *Environmental Science and Pollution Research International*, *19*(8), 3491–3497. doi:10.1007/s11356-012-0884-2 PMID:22467237

Blandino, A., Macías, M., & Cantero, D. (1999). Formation of calcium alginate gel capsules: Influence of sodium alginate and $CaCl_2$ concentration on gelation kinetics. *Journal of Bioscience and Bioengineering*, *88*(6), 686–689. doi:10.1016/S1389-1723(00)87103-0 PMID:16232687

Boniek, D., Figueiredo, D., dos Santos, A. F. B., & Stoianoff, M. A. de R. (2014). Biodesulfurization: a mini review about the immediate search for the future technology. *Clean Technologies and Environmental Policy*.

Cameotra, S. S., & Makkar, R. S. (1998). Synthesis of biosurfactants in extreme conditions. *Applied Microbiology and Biotechnology*, *50*(5), 520–529. doi:10.1007/s002530051329 PMID:9866170

Cameotra, S. S., & Singh, P. (2009). Synthesis of rhamnolipid biosurfactant and mode of hexadecane uptake by *Pseudomonas* species. *Microbial Cell Factories*, *8*(1), 16. doi:10.1186/1475-2859-8-16 PMID:19284586

Caro, A., Boltes, K., Letón, P., & García-Calvo, E. (2007). Dibenzothiophene biodesulfurization in resting cell conditions by aerobic bacteria. *Biochemical Engineering Journal*, *35*(2), 191–197. doi:10.1016/j.bej.2007.01.013

Caro, A., Letón, P., García-Calvo, E., & Setti, L. (2007). Enhancement of dibenzothiophene biodesulfurization using β-cyclodextrins in oil-to-water media. *Fuel*, *86*(16), 2632–2636. doi:10.1016/j.fuel.2007.02.033

Carvalheiro, F., Moniz, P., Duarte, L. C., Esteves, M. P., & Gírio, F. M. (2011). Mannitol production by lactic acid bacteria grown in supplemented carob syrup. *Journal of Industrial Microbiology & Biotechnology*, *38*(1), 221–227. doi:10.1007/s10295-010-0823-5 PMID:20820868

Chang, J. H., Chang, Y. K., Ryu, H. W., & Chang, H. N. (2000). Desulfurization of light gas oil in immobilized-cell systems of *Gordona* sp. CYKS1 and *Nocardia* sp. CYKS2. *FEMS Microbiology Letters*, *182*(2), 309–312. doi:10.1111/j.1574-6968.2000.tb08913.x PMID:10620684

Chang, J. H., Kim, Y. J., Lee, B. H., Cho, K., Ryu, H. W., Chang, Y. K., & Chang, H. N. (2001). Production of a desulfurization biocatalyst by two-stage fermentation and its application for the treatment of model and diesel oils. *Biotechnology Progress*, *17*(5), 876–880. doi:10.1021/bp0100676 PMID:11587578

Chen, J. C., & Monticello, D. J. (1996). *U.S. Patent No. 5,525,235*.

Cheng, Y., Zhou, W., Gao, C., Lan, K., Gao, Y., & Wu, Q. (2009). Biodiesel production from Jerusalem artichoke (*Helianthus tuberosus* L.) tuber by heterotrophic microalgae *Chlorella protothecoides*. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *84*(5), 777–781. doi:10.1002/jctb.2111

Choi, O. K., Cho, K. S., Ryu, H. W., & Chang, Y. K. (2003). Enhancement of phase separation by the addition of de-emulsifiers to three-phase (diesel oil / biocatalyst / aqueous phase) emulsion in diesel biodesulfurization. *Biotechnology Letters*, *25*(1), 73–77. doi:10.1023/A:1021750719337 PMID:12882310

Chowdhury, R., & Duttagupta, A. (2005). Mathematical Modeling of the transient behaviour of a chemostat undergoing bio-desulfurization of model organosulfur compounds and diesel using pure and isolated bacterial strains. *International Journal of Chemical Reactor Engineering*, *3*(1), 1–12. doi:10.2202/1542-6580.1239

Dai, Y., Shao, R., Qi, G., & Ding, B.-B. (2014). Enhanced dibenzothiophene biodesulfurization by immobilized cells of *Brevibacterium lutescens* in n-octane-water biphasic system. *Applied Biochemistry and Biotechnology*, *174*(6), 2236–2244. doi:10.1007/s12010-014-1184-8 PMID:25173674

Dehghan-Noudeh, G., Housaindokht, M., & Bazzaz, B. S. F. (2005). Isolation, characterization, and investigation of surface and hemolytic activities of a lipopeptide biosurfactant produced by *Bacillus subtilis* ATCC 6633. *Journal of Microbiology-Seoul*, *43*(3), 272. PMID:15995646

Del Olmo, C. H., Santos, V. E., Alcon, A., & Garcia-Ochoa, F. (2005). Production of a *Rhodococcus erythropolis* IGTS8 biocatalyst for DBT biodesulfurization: Influence of operational conditions. *Biochemical Engineering Journal*, *22*(3), 229–237. doi:10.1016/j.bej.2004.09.015

Denis, P. A. (2010). On the enthalpy of formation of thiophene. *Theoretical Chemistry Accounts*, *127*(5-6), 621–626. doi:10.1007/s00214-010-0759-x

Derikvand, P., Etemadifar, Z., & Biria, D. (2014). Taguchi optimization of dibenzothiophene biodesulfurization by *Rhodococcus erythropolis* R1 immobilized cells in a biphasic system. *International Biodeterioration & Biodegradation*, *86*, 343–348. doi:10.1016/j.ibiod.2013.10.006

Desai, J. D., & Banat, I. M. (1997). Microbial production of surfactants and their commercial potential. *Microbiology and Molecular Biology Reviews*, *61*(1), 47–64. PMID:9106364

Dinamarca, M. A., Ibacache-Quiroga, C., Baeza, P., Galvez, S., Villarroel, M., Olivero, P., & Ojeda, J. (2010). Biodesulfurization of gas oil using inorganic supports biomodified with metabolically active cells immobilized by adsorption. *Bioresource Technology*, *101*(7), 2375–2378. doi:10.1016/j.biortech.2009.11.086 PMID:20034786

Dinamarca, M. A., Rojas, A., Baeza, P., Espinoza, G., Ibacache-Quiroga, C., & Ojeda, J. (2014). Optimizing the biodesulfurization of gas oil by adding surfactants to immobilized cell systems. *Fuel*, *116*, 237–241. doi:10.1016/j.fuel.2013.07.108

Feng, J., Zeng, Y., Ma, C., Cai, X., Zhang, Q., & Tong, M. et al. (2006). The surfactant tween 80 enhances biodesulfurization. *Applied and Environmental Microbiology*, *72*(11), 7390–7393. doi:10.1128/AEM.01474-06 PMID:16980422

Foght, J. M. (2004). Whole-cell bio-processing of aromatic compounds in crude oil and fuels. In R. Vazquez-Duhalt & R. Quintero-Ramirez (Eds.), Petroleum biotechnology: Developments and perspectives (Amsterdam., pp. 145–176). Amsterdam: Elsevier. doi:10.1016/S0167-2991(04)80146-0

Folsom, B. R., Meyer, T. A., & Yu, L. Q. (1998). *U.S. Patent No. 5,772,901*. Washington, DC: U.S. Patent and Trademark Office.

Gray, K., Mrachko, G., & Squires, C. (2003). Biodesulfurization of fossil fuels. *Current Opinion in Microbiology*, *6*(3), 229–235. doi:10.1016/S1369-5274(03)00065-1 PMID:12831898

Guchhait, S., Biswas, D., Bhattacharya, P., & Chowdhury, R. (2005a). Bio-desulfurization of model organo-sulfur compounds and hydrotreated diesel - Experiments and modelling. *Chemical Engineering Journal*, *112*(1-3), 145–151. doi:10.1016/j.cej.2005.05.006

Guchhait, S., Biswas, D., Bhattacharya, P., & Chowdhury, R. (2005b). Bi-phasic bio-conversion of sulfur present in model organo-sulfur compounds and hydro-treated diesel. *Catalysis Today*, *106*(1-4), 233–237. doi:10.1016/j.cattod.2005.07.137

Gunam, I. B. W., Sujaya, I. N., Aryanta, W. R., Tomita, F., & Asano, K. (2013). Biodesulfurization of dibenzothiophene and its derivatives using resting and immobilized cells of *Sphingomonas subarctica* T7b. *Journal of Microbiology and Biotechnology*, *23*(4), 473–482. doi:10.4014/jmb.1207.07070 PMID:23568201

Guo, L., Zhang, J., Hu, F., Dy Ryu, D., & Bao, J. (2013). Consolidated bioprocessing of highly concentrated Jerusalem artichoke tubers for simultaneous saccharification and ethanol fermentation. *Biotechnology and Bioengineering*, *110*(10), 2606–2615. doi:10.1002/bit.24929 PMID:23568827

Guo, X.-L., Deng, G., Xu, J., & Wang, M.-X. (2006). Immobilization of *Rhodococcus* sp. AJ270 in alginate capsules and its application in enantioselective biotransformation of trans-2-methyl-3-phenyl-oxiranecarbonitrile and amide. *Enzyme and Microbial Technology*, *39*(1), 1–5. doi:10.1016/j.enzmictec.2005.01.044

Guobin, S., Huaiying, Z., Jianmin, X., Guo, C., Wangliang, L., & Huizhou, L. (2006). Biodesulfurization of hydrodesulfurized diesel oil with *Pseudomonas delafieldii* R-8 from high density culture. *Biochemical Engineering Journal*, *27*(3), 305–309. doi:10.1016/j.bej.2005.07.003

Guobin, S., Huaiying, Z., Weiquan, C., Jianmin, X., & Huizhou, L. (2005). Improvement of biodesulfurization rate by assembling nanosorbents on the surfaces of microbial cells. *Biophysical Journal*, *89*(6), L58–L60. doi:10.1529/biophysj.105.073718 PMID:16258046

Guobin, S., Jianmin, X., Chen, G., Huizhou, L., & Jiayong, C. (2005). Biodesulfurization using *Pseudomonas delafieldii* in magnetic polyvinyl alcohol beads. *Letters in Applied Microbiology*, *40*(1), 30–36. doi:10.1111/j.1472-765X.2004.01617.x PMID:15612999

Guobin, S., Jianmin, X., Huaiying, Z., & Huizhou, L. (2005). Deep desulfurization of hydrodesulfurized diesel oil by *Pseudomonas delafieldii* R-8. *Journal of Chemical Technology & Biotechnology, 80*(4), 420–424. doi:10.1002/jctb.1197

Gupta, N., Roychoudhury, P. K., & Deb, J. K. (2005). Biotechnology of desulfurization of diesel: Prospects and challenges. *Applied Microbiology and Biotechnology*, *66*(4), 356–366. doi:10.1007/s00253-004-1755-7 PMID:15538557

Hashimoto, S., & Furukawa, K. (1987). Immobilization of activated sludge by PVA–boric acid method. *Biotechnology and Bioengineering*, *30*(1), 52–59. doi:10.1002/bit.260300108 PMID:18576582

Haukanes, B.-I., & Kvam, C. (1993). Application of magnetic beads in bioassays. *Nature Biotechnology*, *11*(1), 60–63. doi:10.1038/nbt0193-60 PMID:7763485

He, Y.-C., Zhou, Q., Ma, C.-L., Cai, Z.-Q., Wang, L.-Q., & Zhao, X.-Y. et al. (2012). Biosynthesis of benzoylformic acid from benzoyl cyanide by a newly isolated *Rhodococcus* sp. CCZU10-1 in toluene–water biphasic system. *Bioresource Technology*, *115*, 88–95. doi:10.1016/j.biortech.2011.09.084 PMID:22033370

Hirasawa, K., Ishii, Y., Kobayashi, M., Koizumi, K., & Maruhashi, K. (2001). Improvement of desulfurization activity in *Rhodococcus erythropolis* KA2-5-1 by genetic engineering. *Bioscience, Biotechnology, and Biochemistry*, *65*(2), 239–246. doi:10.1271/bbb.65.239 PMID:11302154

Ho, K. F., & Lee, S. C. (2002). Identification of atmospheric volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and carbonyl compounds in Hong Kong. *The Science of the Total Environment*, *289*(1-3), 145–158. doi:10.1016/S0048-9697(01)01031-2 PMID:12049391

Honda, H., Sugiyama, H., Saito, I., & Kobayashi, T. (1998). High cell density culture of *Rhodococcus rhodochrous* by pH-stat feeding and dibenzothiophene degradation. *Journal of Fermentation and Bioengineering*, *85*(3), 334–338. doi:10.1016/S0922-338X(97)85685-1

Huaiying, Z., Guobin, S., & Huizhou, L., & JianMin, X. (2007). Surface modification of γ-Al_2O_3 nanoparticles with gum arabic and its applications in adsorption and biodesulfurization. *Surface and Coatings Technology*, *201*(16), 6917–6921.

Jiang, N., Ying, G. L., Liu, S. Y., Shen, L., Hu, J., & Dai, L. J. et al. (2014). Amino acid-based biohybrids for nano-shellization of individual desulfurizing bacteria. *Chemical Communications (Cambridge)*, *50*(97), 15407–15410. doi:10.1039/C4CC06323F PMID:25350878

Kaufman, E. N., Borole, A. P., Shong, R., Sides, J. L., & Juengst, C. (1999). Sulfur specificity in the bench-scale biological desulfurization of crude oil by *Rhodococcus. Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *74*(10), 1000–1004. doi:10.1002/(SICI)1097-4660(199910)74:10<1000::AID-JCTB134>3.0.CO;2-0

Kaufman, E. N., Harkins, J. B., & Borole, A. P. (1998). Comparison of Batch-Stirred and Electro-Spray Reactors for Biodesulfurization of dibenzothiophene in Crude Oil and Hydrocarbon Feedstocks. *Applied Biochemistry and Biotechnology*, *73*(2-3), 127–144. doi:10.1007/BF02785650

Kaufman, E. N., Harkins, J. B., Rodriguez, M. Jr, Tsouris, C., Selvaraj, P. T., & Murphy, S. E. (1997). Development of an electro-spray bioreactor for crude oil processing. *Fuel Processing Technology*, *52*(1), 127–144. doi:10.1016/S0378-3820(97)00022-2

Khedkar, S., & Shanker, R. (2014). Isolation and classification of a soil actinomycete capable of sulphur-specific biotransformation of dibenzothiophene, benzothiophene and thianthrene. *Journal of Applied Microbiology*. PMID:25319398

Kilbane, J. J. II. (2006). Microbial biocatalyst developments to upgrade fossil fuels. *Current Opinion in Biotechnology*, *17*(3), 305–314. doi:10.1016/j.copbio.2006.04.005 PMID:16678400

Kilbane, J. J. II, & Le Borgne, S. (2004). Petroleum biorefining: The selective removal of sulfur, nitrogen, and metals. *Studies in Surface Science and Catalysis*, *151*, 29–65. doi:10.1016/S0167-2991(04)80143-5

Kirimura, K., Harada, K., Iwasawa, H., Tanaka, T., Iwasaki, Y., & Furuya, T. et al. (2004). Identification and functional analysis of the genes encoding dibenzothiophene-desulfurizing enzymes from thermophilic bacteria. *Applied Microbiology and Biotechnology*, *65*(6), 703–713. doi:10.1007/s00253-004-1652-0 PMID:15221222

Kobayashi, M., Horiuchi, K., Yoshikawa, O., Hirasawa, K., Ishii, Y., & Fujino, K. et al. (2001). Kinetic analysis of microbial desulfurization of model and light gas oils containing multiple alkyl dibenzothiophenes. *Bioscience, Biotechnology, and Biochemistry*, *65*(2), 298–304. doi:10.1271/bbb.65.298 PMID:11302162

Kobayashi, M., Onaka, T., Ishii, Y., Konishi, J., Takaki, M., & Okada, H. et al. (2000). Desulfurization of alkylated forms of both dibenzothiophene and benzothiophene by a single bacterial strain. *FEMS Microbiology Letters*, *187*(2), 123–126. doi:10.1111/j.1574-6968.2000.tb09147.x PMID:10856644

Koltuniewicz, A. B., Field, R. W., & Arnot, T. C. (1995). Cross-flow and dead-end microfiltration of oily-water emulsion. Part I: Experimental study and analysis of flux decline. *Journal of Membrane Science*, *102*, 193–207. doi:10.1016/0376-7388(94)00320-X

Konishi, J., Ishii, Y., Onaka, T., Okumura, K., & Suzuki, M. (1997). Thermophilic carbon-sulfur-bond-targeted biodesulfurization. *Applied and Environmental Microbiology*, *63*(8), 3164–3169. PMID:16535672

Konishi, M., Kishimoto, M., Omasa, T., Katakura, Y., Shioya, S., & Ohtake, H. (2005). Effect of sulfur sources on specific desulfurization activity of *Rhodococcus erythropolis* KA2-5-1 in exponential fed-batch culture. *Journal of Bioscience and Bioengineering*, *99*(3), 259–263. doi:10.1263/jbb.99.259 PMID:16233786

Konishi, M., Kishimoto, M., Tamesui, N., Omasa, T., Shioya, S., & Ohtake, H. (2005). The separation of oil from an oil–water–bacteria mixture using a hydrophobic tubular membrane. *Biochemical Engineering Journal*, *24*(1), 49–54. doi:10.1016/j.bej.2004.11.012

Le Borgne, S., & Quintero, R. (2003). Biotechnological processes for the refining of petroleum. *Fuel Processing Technology*, *81*(2), 155–169. doi:10.1016/S0378-3820(03)00007-9

Lee, M. K., Senius, J. D., & Grossman, M. J. (1995). Sulfur-specific microbial desulfurization of sterically hindered analogs of dibenzothiophene. *Applied and Environmental Microbiology*, *61*(12), 4362–4366. PMID:16535189

Li, F., Xu, P., Feng, J., Meng, L., Zheng, Y., Luo, L., & Ma, C. (2005). Microbial desulfurization of gasoline in a *Mycobacterium goodii* X7B immobilized-cell system. *Applied and Environmental Microbiology*, *71*(1), 276–281. doi:10.1128/AEM.71.1.276-281.2005 PMID:15640198

Li, L., Li, L., Wang, Y., Du, Y., & Qin, S. (2013). Biorefinery products from the inulin-containing crop Jerusalem artichoke. *Biotechnology Letters*, *35*(4), 471–477. doi:10.1007/s10529-012-1104-3 PMID:23242496

Li, M. Z., Squires, C. H., Monticello, D. J., & Childs, J. D. (1996). Genetic analysis of the dsz promoter and associated regulatory regions of *Rhodococcus erythropolis* IGTS8. *Journal of Bacteriology*, *178*(22), 6409–6418. PMID:8932295

Li, W., & Jiang, X. (2013). Enhancement of bunker oil biodesulfurization by adding surfactant. *World Journal of Microbiology & Biotechnology*, *29*(1), 103–108. doi:10.1007/s11274-012-1162-7 PMID:22940903

Li, Y.-G., Gao, H.-S., Li, W.-L., Xing, J.-M., & Liu, H.-Z. (2009). *In situ* magnetic separation and immobilization of dibenzothiophene-desulfurizing bacteria. *Bioresource Technology*, *100*(21), 5092–50966. doi:10.1016/j.biortech.2009.05.064 PMID:19541480

Liang, Z.-X., Li, L., Li, S., Cai, Y.-H., Yang, S.-T., & Wang, J.-F. (2012). Enhanced propionic acid production from Jerusalem artichoke hydrolysate by immobilized *Propionibacterium acidipropionici* in a fibrous-bed bioreactor. *Bioprocess and Biosystems Engineering*, *35*(6), 915–921. doi:10.1007/s00449-011-0676-y PMID:22228298

Linguist, L., & Pacheco, M. (1999). Enzyme-based diesel desulfurization process offers energy, CO_2 advantages. *Oil & Gas Journal*, *97*(8), 45–50.

Lozinsky, V. I., & Plieva, F. M. (1998). Poly (vinyl alcohol) cryogels employed as matrices for cell immobilization. 3. Overview of recent research and developments. *Enzyme and Microbial Technology*, *23*(3), 227–242. doi:10.1016/S0141-0229(98)00036-2

Luo, M. F., Xing, J. M., Gou, Z. X., Li, S., Liu, H. Z., & Chen, J. Y. (2003). Desulfurization of dibenzothiophene by lyophilized cells of *Pseudomonas delafieldii* R-8 in the presence of dodecane. *Biochemical Engineering Journal*, *13*(1), 1–6. doi:10.1016/S1369-703X(02)00078-5

Ma, C., Feng, J., Zeng, Y., Cai, X., Sun, B., & Zhang, Z. et al. (2006). Methods for the preparation of a biodesulfurization biocatalyst using *Rhodococcus* sp. *Chemosphere*, *65*(1), 165–169. doi:10.1016/j.chemosphere.2006.03.010 PMID:16624377

Manso, T., Nunes, C., Raposo, S., & Lima-Costa, M. E. (2010). Carob pulp as raw material for production of the biocontrol agent *P. agglomerans* PBC-1. *Journal of Industrial Microbiology & Biotechnology*, *37*(11), 1145–1155. doi:10.1007/s10295-010-0762-1 PMID:20593299

Maricq, M. M., Chase, R. E., Xu, N., & Laing, P. M. (2002). The effects of the catalytic converter and fuel sulfur level on motor vehicle particulate matter emissions: Light duty diesel vehicles. *Environmental Science & Technology*, *36*(2), 283–289. doi:10.1021/es010962l PMID:11827064

Martin, A. B., Alcon, A., Santos, V. E., & Garcia-ochoa, F. (2004). Production of a biocatalyst of *Pseudomonas putida* CECT5279 for dibenzothiophene (DBT) biodesulfurization for different media compositions. *Energy & Fuels*, *18*(3), 851–857. doi:10.1021/ef030174c

Martinez, I., Santos, V. E., Alcon, A., & Garcia-Ochoa, F. (2015). Enhancement of the biodesulfurization capacity of *Pseudomonas putida* CECT5279 by co-substrate addition. *Process Biochemistry*, *50*(1), 119–124. doi:10.1016/j.procbio.2014.11.001

Martínez-Checa, F., Toledo, F., Vilchez, R., Quesada, E., & Calvo, C. (2002). Yield production, chemical composition, and functional properties of emulsifier H28 synthesized by *Halomonas eurihalina* strain H-28 in media containing various hydrocarbons. *Applied Microbiology and Biotechnology*, *58*(3), 358–363. doi:10.1007/s00253-001-0903-6 PMID:11935188

Mcfarland, B. L. (1999). Biodesulfurization. *Current Opinion in Microbiology*, *2*(3), 257–264. doi:10.1016/S1369-5274(99)80045-9 PMID:10383871

McFarland, B. L., Boron, D. J., Deever, W., Meyer, J. A., Johnson, A. R., & Atlas, R. M. (1998). Biocatalytic sulfur removal from fuels: Applicability for producing low sulfur gasoline. *Critical Reviews in Microbiology*, *24*(2), 99–147. doi:10.1080/10408419891294208 PMID:9675512

Mendes, A., Guerra, P., Madeira, V., Ruano, F., da Silva, T. L., & Reis, A. (2007). Study of docosahexaenoic acid production by the heterotrophic microalga *Crypthecodinium cohnii* CCMP 316 using carob pulp as a promising carbon source. *World Journal of Microbiology & Biotechnology*, *23*(9), 1209–1215. doi:10.1007/s11274-007-9349-z

Mohebali, G., Ball, A., Kaytash, A., & Rasekh, B. (2007). Stabilization of water/gas oil emulsions by desulfurizing cells of *Gordonia alkanivorans* RIPI90A. *Microbiology*, *153*(Pt 5), 1573–1581. doi:10.1099/mic.0.2006/002543-0 PMID:17464072

Mohebali, G., & Ball, A. S. (2008). Biocatalytic desulfurization (BDS) of petrodiesel fuels. *Microbiology*, *154*(Pt 8), 2169–2183. doi:10.1099/mic.0.2008/017608-0 PMID:18667551

Mohebali, G., Ball, A. S., Kaytash, A., & Rasekh, B. (2008). Dimethyl sulfoxide (DMSO) as the sulfur source for the production of desulfurizing resting cells of *Gordonia alkanivorans* RIPI90A. *Microbiology*, *154*(3), 878–885. doi:10.1099/mic.0.2007/013011-0 PMID:18310033

Monticello, D. J. (2000). Biodesulfurization and the upgrading of petroleum distillates. *Current Opinion in Biotechnology*, *11*(6), 540–546. doi:10.1016/S0958-1669(00)00154-3 PMID:11102787

Monticello, D. J., & Finnerty, W. R. (1985). Microbial desulfurization of fossil fuels. *Annual Review of Microbiology*, *39*(1), 371–389. doi:10.1146/annurev.mi.39.100185.002103 PMID:3904605

Mukhopadhyaya, M., Chowdhury, R., & Bhattacharya, P. (2005). Two phase mathematical model for a bio-trickling reactor for the production of Ultra low sulfur diesel (ULSD) from deeply hydrodesulfurized diesel. *Catalysis Today*, *106*(1-4), 180–185. doi:10.1016/j.cattod.2005.07.128

Mukhopadhyaya, M., Chowdhury, R., & Bhattacharya, P. (2006). Biodesulfurization of hydrodesulfurized diesel in a trickle bed reactor - Experiments and modeling. *Journal of Scientific and Industrial Research*, *65*(5), 432–436.

Mukhopadhyaya, M., Chowdhury, R., & Bhattacharya, P. (2007). Trickle bed biodesulfurizer of diesel with backwash and recycle. *AIChE Journal. American Institute of Chemical Engineers*, *53*(8), 2188–2197. doi:10.1002/aic.11240

Mulligan, C. N. (2005). Environmental applications for biosurfactants. *Environmental Pollution*, *133*(2), 183–198. doi:10.1016/j.envpol.2004.06.009 PMID:15519450

Murphy, S. E., Amin, S., Coletta, K., & Hoffman, D. (1992). Rat liver metabolism of benzo[b]naphtho[2,1-d]thiophene. *Chemical Research in Toxicology*, *5*(4), 491–495. doi:10.1021/tx00028a006 PMID:1382648

Naito, M., Kawamoto, T., Fujino, K., Kobayashi, M., Maruhashi, K., & Tanaka, A. (2001). Long-term repeated biodesulfurization by immobilized *Rhodococcus erythropolis* KA 2-5-1 cells. *Applied Microbiology and Biotechnology*, *55*(3), 374–378. doi:10.1007/s002530000527 PMID:11341322

Nandi, S. (2010). Biodesulfurization of hydro-desulfurized diesel in airlift reactor. *Journal of Scientific and Industrial Research*, *69*(7), 543–547.

Nekodzuka, S., Nakajima-Kambe, T., Nomura, N., Lu, J., & Nakahara, T. (1997). Specific desulfurization of dibenzothiophene by *Mycobacterium sp*. strain G3. *Biocatalysis and Biotransformation*, *15*(1), 17–27. doi:10.3109/10242429709003607

Nordvik, A. B., Simmons, J. L., Bitting, K. R., Lewis, A., & Strøm-Kristiansen, T. (1996). Oil and water separation in marine oil spill clean-up operations. *Spill Science & Technology Bulletin*, *3*(3), 107–122. doi:10.1016/S1353-2561(96)00021-7

Nuhu, A. A. (2013). Bio-catalytic desulfurization of fossil fuels: A mini review. *Reviews in Environmental Science and Biotechnology*, *12*(1), 9–23. doi:10.1007/s11157-012-9267-x

Ohshiro, T., & Izumi, Y. (1999). Microbial desulfurization of organic sulfur compounds in petroleum. *Bioscience, Biotechnology, and Biochemistry*, *63*(1), 1–9. doi:10.1271/bbb.63.1 PMID:10052116

Ohshiro, T., Suzuki, K., & Izumi, Y. (1996). Regulation of dibenzothiophene degrading enzyme activity of *Rhodococcus erythropolis* D-1. *Journal of Fermentation and Bioengineering*, *81*(2), 121–124. doi:10.1016/0922-338X(96)87588-X

Okada, H., Nomura, N., Nakahara, T., Saitoh, K., Uchiyama, H., & Maruhashi, K. (2003). Analyses of microbial desulfurization reaction of alkylated dibenzothiophenes dissolved in oil phase. *Biotechnology and Bioengineering*, *83*(4), 489–497. doi:10.1002/bit.10694 PMID:12800143

Oldfield, C., Pogrebinsky, O., Simmonds, J., Olson, E. S., & Kulpa, C. F. (1997). Elucidation of the metabolic pathway for dibenzothiophene desulphurization by *Rhodococcus* sp. strain IGTS8 (ATCC 53968). *Microbiology*, *143*(9), 2961–2973. doi:10.1099/00221287-143-9-2961 PMID:9308179

Onodera-Yamada, K., Morimoto, M., & Tani, Y. (2001). Degradation of dibenzothiophene by sulfate-reducing bacteria cultured in the presence of only nitrogen gas. *Journal of Bioscience and Bioengineering*, *91*(1), 91–93. doi:10.1016/S1389-1723(01)80119-5 PMID:16232954

Oral, J., Sikula, J., Puchyr, R., Hajny, Z., Stehlik, P., & Bebar, L. (2005). Processing of waste from pulp and paper plant. *Journal of Cleaner Production*, *13*(5), 509–515. doi:10.1016/j.jclepro.2003.09.005

Pacheco, M. A., Lange, E. A., Pienkos, P. T., Yu, L.-Q., Rouse, M. P., Lin, Q., & Linguist, L. K. (1999). *Recent advances in biodesulfurization of diesel fuel*. National Petrochemical And Refiners Association-Publications-All Series.

Paixão, S. M., Teixeira, P. D., Silva, T. P., Teixeira, A. V., & Alves, L. (2013). Screening of novel yeast inulinases and further application to bioprocesses. *New Biotechnology*, *30*(6), 598–606. doi:10.1016/j.nbt.2013.02.002 PMID:23419675

Patel, S. B., Killbane, J. J., & Webster, D. A. (1997). Biodesulphurisation of dibenzothiophene in hydrophobic media by *Rhodococcus* sp. strain IGTS8. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *69*(1), 100–106. doi:10.1002/(SICI)1097-4660(199705)69:1<100::AID-JCTB675>3.0.CO;2-9

Perfumo, A., Smyth, T. J. P., Marchant, R., & Banat, I. M. (2010). Production and roles of biosurfactants and bioemulsifiers in accessing hydrophobic substrates. In *Handbook of hydrocarbon and lipid microbiology* (pp. 1501–1512). Springer. doi:10.1007/978-3-540-77587-4_103

Pope, C. A. III, Burnett, R. T., Thun, M. J., Calle, E. E., Krewski, D., Ito, K., & Thurston, G. D. (2002). Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *Journal of the American Medical Association*, *287*(9), 1132–1141. doi:10.1001/jama.287.9.1132 PMID:11879110

Reichmuth, D. S., Hittle, J. L., Blanch, H. W., & Keasling, J. D. (2000). Biodesulfurization of dibenzothiophene in *Escherichia coli* is enhanced by expression of a *Vibrio harveyi* oxidoreductase gene. *Biotechnology and Bioengineering*, *67*(1), 72–79. doi:10.1002/(SICI)1097-0290(20000105)67:1<72::AID-BIT8>3.0.CO;2-C PMID:10581437

Rivera, J. L., Navarro-Santos, P., Guerra-Gonzalez, R., & Lima, E. (2014). Interaction of refractory dibenzothiophenes and polymerizable structures. *International Journal of Polymer Science*, *2014*, 1–11. doi:10.1155/2014/103945

Rodrigues, L., Banat, I. M., Teixeira, J., & Oliveira, R. (2006). Biosurfactants: Potential applications in medicine. *The Journal of Antimicrobial Chemotherapy*, *57*(4), 609–618. doi:10.1093/jac/dkl024 PMID:16469849

Rodrigues, L. R., & Teixeira, J. A. (2010). *Biomedical and therapeutic applications of biosurfactants* (pp. 75–87). New York: Springer.

Rouse, J. D., Sabatini, D. A., Suflita, J. M., & Harwell, J. H. (1994). Influence of surfactants on microbial degradation of organic compounds. *Critical Reviews in Environmental Science and Technology*, *24*(4), 325–370. doi:10.1080/10643389409388471

Sánchez-Segado, S., Lozano, L. J., de Los Ríos, A. P., Hernández-Fernández, F. J., Godínez, C., & Juan, D. (2012). Process design and economic analysis of a hypothetical bioethanol production plant using carob pod as feedstock. *Bioresource Technology*, *104*, 324–328. doi:10.1016/j.biortech.2011.10.046 PMID:22100234

Schilling, B. M., Alvarez, L. M., Wang, D. I. C., & Cooney, C. L. (2002). Continuous desulfurization of dibenzothiophene with *Rhodococcus rhodochrous* IGTS8 (ATCC 53968). *Biotechnology Progress*, *18*(6), 1207–1213. doi:10.1021/bp0200144 PMID:12467453

Scott, K., Jachuck, R. J., & Hall, D. (2001). Crossflow microfiltration of water-in-oil emulsions using corrugated membranes. *Separation and Purification Technology*, *22*(1-2), 431–441. doi:10.1016/S1383-5866(00)00180-5

Scott, T. C., & Wham, R. M. (1989). An electrically driven multistage countercurrent solvent extraction device: The emulsion-phase contactor. *Industrial & Engineering Chemistry Research*, *28*(1), 94–97. doi:10.1021/ie00085a016

Setti, L., Lanzarini, G., & Pifferi, P. G. (1997). Whole cell biocatalysis for an oil desulfurization process. *Fuel Processing Technology*, *52*(1-3), 145–153. doi:10.1016/S0378-3820(97)00023-4

Shennan, J. L. (1996). Microbial attack on sulphur-containing hydrocarbons: Implications for the biodesulphurisation of oils and coals. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *67*(2), 109–123. doi:10.1002/(SICI)1097-4660(199610)67:2<109::AID-JCTB532>3.0.CO;2-Y

Silva, C. R., Silva, M. L. C., Kamida, H. M., Goes-Neto, A., & Koblitz, M. G. B. (2014). Lytic enzyme production optimization using low-cost substrates and its application in the clarification of xanthan gum culture broth. *Food Science & Nutrition*, *2*(4), 299–307. doi:10.1002/fsn3.87 PMID:25473487

Silva, T. P., Paixão, S. M., Roseiro, J. C., & Alves, L. (2015). Jerusalem artichoke as low-cost fructose-rich feedstock for fossil fuels desulfurization by a fructophilic bacterium. *Journal of Applied Microbiology*, 118(3), 609–618. doi: 10.1111/jam.12721

Silva, T. P., Paixão, S. M., Teixeira, A. V., Roseiro, J. C., & Alves, L. (2013). Optimization of low sulfur carob pulp liquor as carbon source for fossil fuels biodesulfurization. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *88*(5), 919–923. doi:10.1002/jctb.3921

Singh, A., Singh, B., & Ward, O. (2012). Potential applications of bioprocess technology in petroleum industry. *Biodegradation*, *23*(6), 865–880. doi:10.1007/s10532-012-9577-2 PMID:22829348

Soleimani, M., Bassi, A., & Margaritis, A. (2007). Biodesulfurization of refractory organic sulfur compounds in fossil fuels. *Biotechnology Advances*, *25*(6), 570–596. doi:10.1016/j.biotechadv.2007.07.003 PMID:17716849

Srivastava, V. C. (2012). An evaluation of desulfurization technologies for sulfur removal from liquid fuels. *RSC Advances*, *2*(3), 759–783. doi:10.1039/C1RA00309G

Stanislaus, A., Marafi, A., & Rana, M. S. (2010). Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production. *Catalysis Today*, *153*(1-2), 1–68. doi:10.1016/j.cattod.2010.05.011

Stoner, D. L., Wey, J. E., Barrett, K. B., Jolley, J. G., Wright, R. B., & Dugan, P. R. (1990). Modification of water-soluble coal-derived products by dibenzothiophene-degrading microorganisms. *Applied and Environmental Microbiology*, *56*(9), 2667–2676. PMID:16348275

Ta-Chen, L., Chang, J.-S., & Young, C.-C. (2008). Exopolysaccharides produced by *Gordonia alkanivorans* enhance bacterial degradation activity for diesel. *Biotechnology Letters*, *30*(7), 1201–1206. doi:10.1007/s10529-008-9667-8 PMID:18286235

Takada, M., Nomura, N., Okada, H., Nakajima-Kambe, T., Nakahara, T., & Uchiyama, H. (2005). De-repression and comparison of oil-water separation activity of the dibenzothiophene desulfurizing bacterium, *Mycobacterium* sp. G3. *Biotechnology Letters*, *27*(12), 871–874. doi:10.1007/s10529-005-6721-7 PMID:16086250

Talvy, S., Cockx, A., & Line, A. (2005). Global modelling of a gas–liquid–solid airlift reactor. *Chemical Engineering Science*, *60*(22), 5991–6003. doi:10.1016/j.ces.2005.04.067

Tanaka, Y., Yoshikawa, O., Maruhashi, K., & Kurane, R. (2002). The cbs mutant strain of *Rhodococcus erythropolis* KA2-5-1 expresses high levels of Dsz enzymes in the presence of sulfate. *Archives of Microbiology*, *178*(5), 351–357. doi:10.1007/s00203-002-0466-7 PMID:12375103

Tang, K., & Hong, X. (2014). A characterization of bacterium for fcc diesel oil desulfurization. *Petroleum Science and Technology*, *32*(13), 1545–1552. doi:10.1080/10916466.2012.689795

Tuli, D., & Kumar, A. (2008). Non-conventional technologies for fuel desulphurization. Proceedings of the *19th World Petroleum Congress*.

Urum, K., & Pekdemir, T. (2004). Evaluation of biosurfactants for crude oil contaminated soil washing. *Chemosphere*, *57*(9), 1139–1150. doi:10.1016/j.chemosphere.2004.07.048 PMID:15504473

Vazquez-Duhalt, R., Torres, E., Valderrama, B., & Le Borgne, S. (2002). Will biochemical catalysis impact the petroleum refining industry? *Energy & Fuels*, *16*(5), 1239–1250. doi:10.1021/ef020038s

Wang, M., Li, W., Shi, Y., Wang, D., & Feng, H. (2006). Effects of surfactant on biodesulfurization by *Corynebacterium* sp. ZD-1 in the presence of organic phase. *Journal of Zhejiang University SCIENCE A*, *7*(S2), 371–375. doi:10.1631/jzus.2006.AS0371

Wang, P., & Krawiec, S. (1996). Kinetic analyses of desulfurization of dibenzothiophene by *Rhodococcus erythropolis* in batch and fed-batch cultures. *Applied and Environmental Microbiology*, *62*(5), 1670–1675. PMID:16535315

Wang, Z., Wang, D., Li, Q., Li, W., Tang, H., & Xing, J. (2011). Enhanced biodesulfurization by expression of dibenzothiophene uptake genes in *Rhodococcus erythropolis. World Journal of Microbiology & Biotechnology*, *27*(9), 1965–1970. doi:10.1007/s11274-011-0656-z

Werther, J., Saenger, M., Hartge, E.-U., Ogada, T., & Siagi, Z. (2000). Combustion of agricultural residues. *Progress in Energy and Combustion Science*, *26*(1), 1–27. doi:10.1016/S0360-1285(99)00005-2

Willaert, R. G., & Baron, G. V. (1996). Gel entrapment and micro-encapsulation: Methods, applications and engineering principles. *Reviews in Chemical Engineering*, *12*(1), 1–205. doi:10.1515/REVCE.1996.12.1-2.1

Wu, S., Lin, J., & Chan, S. I. (1994). Oxidation of dibenzothiophene catalyzed by heme-containing enzymes encapsulated in sol-gel glass. *Applied Biochemistry and Biotechnology*, *47*(1), 11–20. doi:10.1007/BF02788671 PMID:8203869

Yang, J., Hu, Y., Zhao, D., Wang, S., Lau, P. C. K., & Marison, I. W. (2007). Two-layer continuous-process design for the biodesulfurization of diesel oils under bacterial growth conditions. *Biochemical Engineering Journal*, *37*(2), 212–218. doi:10.1016/j.bej.2007.04.012

Yoshikawa, O., Ishii, Y., Koizumi, K.-I., Ohshiro, T., Izumi, Y., & Maruhashi, K. (2002). Enhancement and stabilization of desulfurization activity of *Rhodococcus erythropolis* KA2-5-1 by feeding ethanol and sulfur components. *Journal of Bioscience and Bioengineering*, *94*(5), 447–452. doi:10.1016/S1389-1723(02)80223-7 PMID:16233332

Zhang, Y.-W., Prabhu, P., & Lee, J.-K. (2010). Alginate immobilization of recombinant *Escherichia coli* whole cells harboring L-arabinose isomerase for L-ribulose production. *Bioprocess and Biosystems Engineering*, *33*(6), 741–748. doi:10.1007/s00449-009-0397-7 PMID:19946709

Zhou, Z., & Zhang, K. (2004). Development situation and prospect of oil fields in China. *Petroleum Exploration and Development*, *31*(1), 84–87.

Compilation of References

Rang, H., Kann, J., & Oja, V. (2006). Advances in desulfurization Research of Liquid Fuel *Oil Shale, 23*(2), 164-176.

Sipma, J., Svitelskaya, A., van der Mark, B., Hulshoff Pol, L. W., Lettinga, G., Buisman, C. J. N., & Janssen, A. J. H. (2004). Potentials of biological oxidation processes for the treatment of spent sulfidic caustics containing thiols. *Water Research*, *38*(20), 4331–4340. doi:10.1016/j.watres.2004.08.022 PMID:15556208

(2001). Quality requirements for liquid fuels[in Estonian]. *State Announcer. App.*, *66*, 2765–2775.

A history of flue gas desulfurization systems since 1850. Research, development and demonstration. (1977). *Journal of Air Pollution Control Association*, *27*, 948–61.

Abbad-Andaloussi, S., Lagnel, C., Warzywoda, M., & Monot, F. (2003). Multi-criteria comparison of resting cell activities of bacterial strains selected for biodesulfurization of petroleum compounds. *Enzyme and Microbial Technology*, *32*(3), 446–454. doi:10.1016/S0141-0229(02)00320-4

Abdullah, W. N. W., Bakar, W. A. W. A., & Rusmidah, A. (2015). Catalytic oxidative desulfurization of diesel fuel utilizing a polymolybdate alumina supported catalyst: Characterization, catalytic activity and mechanistic study. *Reaction Kinetics, Mechanisms and Catalysis*, *114*(2), 547–560. doi:10.1007/s11144-014-0801-4

Abdullah, W., Nazwanie, W., Bakar, W. A., Azelee, W., Rusmidah, A., & Zaidi, E. (2015). Oxidative desulfurization of commercial diesel catalyzed by *tert*-butyl hydroperoxide polymolybdate on alumina: Optimization by Box-Behnken design. *Clean Technologies and Environmental Policy*, *17*(2), 433–441. doi:10.1007/s10098-014-0797-5

Abín-Fuentes, A. (2013). *Mechanistic understanding of microbial desulfurization* (Doctoral dissertation). Massachusetts Institute of Technology.

Abo-state, M. A., El-Gendy, N. S., El-Temtamy, S. A., Mahdy, H. M., & Nassar, H. N. (2014). Modification of basal salts medium for enhancing dibenzothiophene biodesulfurization by *Brevibacillus invocatus* C19 and *Rhodococcus erythropolis* IGTS8. *World Applied Sciences Journal*, *30*(2), 133–140. doi: 10.5829/idosi.wasj.2014.30.02.14023

Absi Halabi, M., Stanislaus, A., Qamra, A., & Chopra, S. (1996). Effect of presulfiding on the activity and deactivation of hydrotreating catalysts in processing Kuwait vacuum residue. In J. B. M. Absi-Halabi & A. Stanislaus (Eds.), Studies in Surface Science and Catalysis (Vol. 100, pp. 243-251). Elsevier. doi:10.1016/S0167-2991(96)80025-5

Aburto, J., & Le Borgne, S. (2004). Selective Adsorption of Dibenzothiophene Sulfone by an Imprinted and Stimuli-Responsive Chitosan Hydrogel. *Macromolecules*, *37*(8), 2938–2943. doi:10.1021/ma049961e

Adams, R. D., Kwon, O.-S., & Smith, M. D. (2002). Disulfides of Manganese Carbonyl. Synthesis of $Mn_2(CO)_7(\mu\text{-}S_2)$ and Its Reactions with Tertiary Phosphines and Arsines. *Inorganic Chemistry*, *41*(24), 6281–6290. doi:10.1021/ic0203670 PMID:12444771

Adams, R. D., Kwon, O.-S., & Smith, M. D. (2002). Insertion of Cyclopentadienylmetal Groups into the S−S Bond of $Mn_2(CO)_7(\mu\text{-}S_2)$. *Organometallics*, *21*(9), 1960–1965. doi:10.1021/om020028e

Adams, R. D., Pompeo, M. P., Wu, W., & Yamamoto, J. H. (1993). Formation of butenethiolate by ring opening of tetrahydrothiphene by a triosmium cluster complex. *Journal of the American Chemical Society*, *115*(18), 8207–8213. doi:10.1021/ja00071a033

Adewuyi, Y. G., He, X., Shaw, H., & Lolertpihop, W. (1999). Simultaneous absorption and oxidation of NO and SO_2 by aqueous solutions of sodium chlorite. *Chemical Engineering Communications*, *174*(1), 21–51. doi:10.1080/00986449908912788

Afferden, van M., Schacht, S., Klein, J., & Truper, H. G. (1990). Degradation of dibenzothiophene by Brevibacterium s.p. DO. *Archives of Microbiology, 153*, 324-328.

Afferden, M., Schacht, S., Klein, J., & Trüper, H. (1990). Degradation of dibenzothiophene by Brevibacterium sp.DO. *Archives of Microbiology*, *153*(4), 324–328. doi:10.1007/BF00249000

Afferden, M., Tappe, D., Beyer, M., Trüper, H. G., & Klein, J. (1993). Biochemical mechanisms for the desulfurization of coal-relevant organic sulfur compounds. *Fuel*, *72*(12), 1635–1643. doi:10.1016/0016-2361(93)90348-6

Agarwal, P., & Sharma, D. K. (2009). Comparative Studies on the Bio-desulfurization of Crude Oil with Other Desulfurization Techniques and Deep Desulfurization through Integrated Processes. *Energy & Fuels*, *24*(1), 518–524. doi:10.1021/ef900876j

Aggarwal, S., Karimi, I. A., & Ivan, G. R. (2013). In silico modeling and evaluation of *Gordonia alkanivorans* for biodesulfurization. *Molecular BioSystems*, *9*(10), 2530–2540. doi:10.1039/c3mb70132h PMID:23921469

Aggarwal, S., Karimi, I. A., Kilbane, J. J. II, & Lee, D. Y. (2012). Roles of sulfite oxidoreductase and sulfite reductase in improving desulfurization by *Rhodococcus erythropolis. Molecular BioSystems*, *8*(10), 2724–2732. doi:10.1039/c2mb25127b PMID:22832889

Aggarwal, S., Karimi, I., & Lee, D. Y. (2011). Reconstruction of a genome-scale metabolic network of *Rhodococcus erythropolis* for desulfurization studies. *Molecular BioSystems*, *7*(11), 3122–3131. doi:10.1039/c1mb05201b PMID:21912787

Aguiar, A., Ferraz, A., Contreras, D., & Rodriguez, J. (2007). Mechanism and applications of the Fenton reaction assisted by iron-reducing phenolic compounds. *Quimica Nova*, *30*, 623–628. doi:10.1590/S0100-40422007000300023

Ahlbeck, J., Engman, T., Fältén, S., & Vihma, M. (1995). Measuring the reactivity of limestone for wet flue-gas desulfurization. *Chemical Engineering Science*, *50*(7), 1081–1089. doi:10.1016/0009-2509(94)00482-7

Ahmad, W. (2013). *Study on cost effective methodes for desulfurization of kerosene, diesel and furnace oil (PhD)*. Peshawar: University of Peshawar.

Aida, T., & Yamamoto, D. (1994). Annual book of ASTM standards, 2005. Standard test method for determination of sulfur compounds in natural gas and gaseous fuels by gas chromatography and chemiluminescence. *Preprints of Papers-American Chemical Society. Division of Fuel Chemistry*, *39*(5), 623.

Aida, T., Yamamoto, D., Iwata, M., & Sakata, K. (2000). Development of oxidative desulfurization process for diesel. *Review on Heteroatom Chemistry*, *22*, 241–256.

Aida, T., Yamamoto, D., & Sakata, K. (2000). Development of Oxidative desulfurization process for diesel fuel. *Reviews on Heteroatom Chemistry*, *22*, 241–256.

Aijun, D., Peng, Z., Liang, Z., Jingjing, J., & Zhen, Z. (2014, August 22-24). Computational simulation application in the research of desulfurization mechanism. Proceedings of the 9th International conference on computer science & education (ICCSE 2014), Vancouver, Canada.

Akbarzadeh, K., Ahmed Hammami, A., Abdel Kharrat, A., Dan Zhang, D., Stephan Allenson, S., & Jefferson, C., Creek, S.K., Jamaluddin, A., Marshall, A., Rodgers, R., Mullins, O.C., Solbakken, T. (2007). Asphaltenes-Problematic but Rich in Potential. *Oilfield Review*, *19*(2), 22–43.

Al Zubaidy, I. A. H., Tarsh, F. B., Darwish, N. N., Majeed, B. S. S. A., Al Sharafi, A., & Abu Chacra, L. (2013).. . *Adsorption Process of Sulfur Removal from Diesel Oil Using Sorbent Materials*, *1*(1), 66–68.

Alcántara, S., Velasco, A., Muñoz, A., Cid, J., Revah, S., & Razo-Flores, E. (2004). Hydrogen sulfide oxidation by a microbial consortium in a recirculation reactor system: Sulfur formation under oxygen limitation and removal of phenols. *Environmental Science & Technology*, *38*(3), 918–923. doi:10.1021/es034527y PMID:14968883

Al-Enezi, G., Ettouney, H., El-Dessouky, H., & Fawzi, N. (2001). Solubility of sulfur dioxide in seawater. *Industrial & Engineering Chemistry Research*, *40*(5), 1434–1441. doi:10.1021/ie9905963

Alexander, T. et al. (2011). Shale Gas Revolution. *Oilfield Review 23*, 40-55.

Alfonso, D. R. (2008). First-principles studies of H_2S adsorption and dissociation on metal surfaces. *Surface Science*, *602*(16), 2758–2768. doi:10.1016/j.susc.2008.07.001

Ali, M. F., Al-Malki, A., El-Ali, B., Martinie, G., & Siddiqui, M. N. (2006). Deep desulphurization of gasoline and diesel fuels using non-hydrogen consuming techniques. *Fuel*, *85*(10–11), 1354–1363. doi:10.1016/j.fuel.2005.12.006

Allen, B. L., Kichambare, P. D., & Star, A. (2008). Synthesis, characterization, and manipulation of nitrogen-doped carbon nanotube cups. *ACS Nano*, *2*(9), 1914–1920. doi:10.1021/nn800355v PMID:19206432

Allen, B. L., Shade, C. M., Yingling, A. M., Petoud, S., & Star, A. (2009). Graphitic nanocapsules. *Advanced Materials*, *21*, 4692–4695.

Alonso, G., & Chianelli, R. R. (2004). WS_2 catalysts from tetraalkyl thiotungstate precursors and their concurrent in situ activation during HDS of DBT. *Journal of Catalysis*, *221*(2), 657–661. doi:10.1016/j.jcat.2003.10.003

Alonso, G., Del Valle, M., Cruz-Reyes, J., Licea-Claverie, A., Petranovskii, V., & Fuentes, S. (1998). Preparation of MoS_2 catalysts by in situ decomposition of tetraalkylammonium thiomolybdates. *Catalysis Today*, *43*(1-2), 117–122. doi:10.1016/S0920-5861(98)00140-0

Al-Shahrani, F., Xiao, T., Llewellyn, S. A., Barri, S., Jiang, Z., & Shi, H. et al. (2007). Desulfurization of diesel via the H_2O_2 oxidation of aromatic sulfides to sulfones using a tungstate catalyst. *Applied Catalysis B: Environmental*, *73*(3-4), 311–316. doi:10.1016/j.apcatb.2006.12.016

Al-Shamrani, A. A., James, A., & Xiao, H. (2002). Destabilisation of oil–water emulsions and separation by dissolved air flotation. *Water Research*, *36*(6), 1503–1512. doi:10.1016/S0043-1354(01)00347-5 PMID:11996340

Alstrup, I., Chorkendoff, I., Candia, R., Clausen, B. S., & Topsse, H. (1982). A combined X-Ray photoelectron and Mössbauer emission spectroscopy study of the state of cobalt in sulfided, supported, and unsupported Co-Mo catalysts. *Journal of Catalysis*, *77*(2), 397–409. doi:10.1016/0021-9517(82)90181-6

Álvarez-Ayuso, E., Querol, X., & Tomás, A. (2006). Environmental impact of a coal combustion-desulphurisation plant: Abatement capacity of desulphurisation process and environmental characterisation of combustion by-products. *Chemosphere*, *65*(11), 2009–2017. doi:10.1016/j.chemosphere.2006.06.070 PMID:16890268

Alvarez, L. H., & Cervantes, F. J. (2011). (Bio)nanotechnologies to enhance environmental quality and energy production. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *86*(11), 1354–1363. doi:10.1002/jctb.2697

Alvarez, L., Berhault, G., & Alonso, G. (2008). Unsupported NiMo sulfide catalysts obtained from nickel/ammonium and nickel/tetraalkylammonium thiomolybdates: Synthesis and application in the hydrodesulfurization of dibenzothiophene. *Catalysis Letters*, *125*(1-2), 35–45. doi:10.1007/s10562-008-9541-2

Alvarez, L., Espino, J., Ornelas, C., Rico, J. L., Cortez, M. T., Berhault, G., & Alonso, G. (2004). Comparative study of MoS_2 and Co/MoS_2 catalysts prepared by ex situ/in situ activation of ammonium and tetraalkylammonium thiomolybdates. *Journal of Molecular Catalysis A Chemical*, *210*(1-2), 105–117. doi:10.1016/j.molcata.2003.09.002

Alves, L., Marques, S., Matos, J., Tenreiro, R., & Gírio, F. M. (2008). Dibenzothiophene desulfurization by *Gordonia alkanivorans* strain 1B using recycled paper sludge hydrolyzate. *Chemosphere*, *70*(6), 967–973. doi:10.1016/j.chemosphere.2007.08.016 PMID:17897697

Alves, L., Matos, J., Tenreiro, R., & Gírio, F. M. (2008). Evidence for the role of zinc on the performance of dibenzothiophene desulfurization by *Gordonia alkanivorans* strain 1B. *Journal of Industrial Microbiology & Biotechnology*, *35*(1), 69–73. doi:10.1007/s10295-007-0278-5 PMID:18043954

Alves, L., & Paixão, S. M. (2014a). Enhancement of dibenzothiophene desulfurization by *Gordonia alkanivorans* strain 1B using sugar beet molasses as alternative carbon source. *Applied Biochemistry and Biotechnology*, *172*(6), 3297–3305. doi:10.1007/s12010-014-0763-z PMID:24519629

Alves, L., & Paixão, S. M. (2014b). Fructophilic behaviour of *Gordonia alkanivorans* strain 1B during dibenzothiophene desulfurization process. *New Biotechnology*, *31*(1), 73–79. doi:10.1016/j.nbt.2013.08.007 PMID:24012483

Alves, L., Paixão, S. M., Pacheco, R., Ferreira, A. F., & Silva, C. M. (2015). Biodesulphurization of fossil fuels: Energy, emissions and cost analysis. *RSC Advances*, *5*(43), 34047–34057. doi:10.1039/C4RA14216K

Alves, L., Salgueiro, R., Rodrigues, C., Mesquita, E., Matos, J., & Gírio, F. M. (2005). Desulfurization of dibenzothiophene, benzothiophene, and other thiophene analogs by a newly isolated bacterium, *Gordonia alkanivorans* strain 1B. *Applied Biochemistry and Biotechnology*, *120*(3), 199–208. doi:10.1385/ABAB:120:3:199 PMID:15767694

Amarasekera, J., Rauchfuss, T. B., & Wilson, S. R. (1988). Synthesis and structure of $[CpRu(PPh_3)_2(SC_2H_4)]OSO_2CF_3$. A transition-metal analog of an episulfonium salt. *Journal of the American Chemical Society*, *110*(7), 2332–2334. doi:10.1021/ja00215a071

Amaya, S. L., Alonso-Núñez, G., Cruz-Reyes, J., Fuentes, S., & Echavarría, A. (2015). Influence of the sulfidation temperature in a NiMoW catalyst derived from layered structure $(NH_4)Ni_2OH(H_2O)(MoO_4)_2$. *Fuel*, *139*, 575–583. doi:10.1016/j.fuel.2014.09.046

Amaya, S. L., Alonso-Núñez, G., Zepeda, T. A., Fuentes, S., & Echavarría, A. (2014). Effect of the divalent metal and the activation temperature of NiMoW and CoMoW on the dibenzothiophene hydrodesulfurization reaction. *Applied Catalysis B: Environmental*, *149*, 221–230. doi:10.1016/j.apcatb.2013.10.057

Amin, G. A. (2011). Integrated two-stage process for biodesulfurization of model oil by vertical rotating immobilized cell reactor with the bacterium *Rhodococcus erythropolis*. *Journal of Petroleum & Environmental Biotechnology*, *2*(1), 107. doi:10.4172/2157-7463.1000107

Amin, G. A., Bazaid, S. A., & Abd El-Halim, M. (2013). A two-stage immobilized cell bioreactor with *Bacillus subtilis* and *Rhodococcus erythropolis* for the simultaneous production of biosurfactant and biodesulfurization of model oil. *Petroleum Science and Technology*, *31*(21), 2250–2257. doi:10.1080/10916466.2011.565292

Anbia, M., & Parvin, Z. (2011). Desulfurization of fuels by means of a nanoporous carbon adsorbent. *Chemical Engineering Research & Design*, *89*(66A), 641–647. doi:10.1016/j.cherd.2010.09.014

Andersson, J. T., Panda, S. K., & Schrader, W. (2007). Analysis of large sulfur aromatic compounds in fossil fuels by FT-ICR MS. In O. R. Koseoglu & S. Kasztelan (Eds.), *Hydrotreating/Hydrocracking Processing*. Washington, D.C.: American Chemical Society.

Andersson, J. T., & Schade, T. (2006). Speciation of alkylated dibenzothiophenes in a deeply desulfurized diesel fuel. *Energy & Fuels*, *20*(4), 1614–1620. doi:10.1021/ef0502507

Angelici, R. J. (1990). Structural aspects of Thiophene coordination in transition metal complexes. *Coordination Chemistry Reviews*, *105*(1), 61–76. doi:10.1016/0010-8545(90)80018-O

Angelici, R. J. (1997). An overview of modeling studies in HDS, HDN and HDO catalysis. *Polyhedron*, *16*(18), 3073–3088. doi:10.1016/S0277-5387(96)00581-5

Angelici, R. J. (2001). Thiophenes in Organotransition Metal Chemistry: Patterns of Reactivity. *Organometallics*, *20*(7), 1259–1275. doi:10.1021/om010040r

Ania, C. O., & Bandosz, T. J. (2006a). Metal-loaded polystyrene-based activated carbons as dibenzothiophene removal media via reactive adsorption. *Carbon*, *44*(12), 2404–2412. doi:10.1016/j.carbon.2006.05.016

Ania, C. O., & Bandosz, T. J. (2006b). Sodium on the surface of activated carbons as a factor enhancing reactive adsorption of dibenzothiophene. *Energy & Fuels*, *20*(3), 1076–1080. doi:10.1021/ef050425c

Ania, C. O., Parra, J. B., Arenillas, A., Rubiera, F., Bandosz, T. J., & Pis, J. J. (2007). On the mechanism of reactive adsorption of dibenzothiophene on organic waste derived carbons. *Applied Surface Science*, *253*(13), 5899–5903. doi:10.1016/j.apsusc.2006.12.065

Anisimov, A. V., Fedorova, E. V., Lesnugin, A. Z., Senyavin, V. M., Aslanov, L. A., Rybakov, V. B., & Tarakanova, A. V. (2003). Vanadium peroxocomplexes as oxidation catalysts of sulfur organic compounds by hydrogen peroxide in biphase systems. *Catalysis Today*, *78*(1-4), 319–325. doi:10.1016/S0920-5861(02)00311-5

An, K. H., Kim, W. S., Park, Y. S., Moon, J.-M., Bae, D. J., & Lim, S. C. et al. (2001). Electrochemical Properties of High-Power Supercapacitors Using Single-Walled Carbon Nanotube Electrodes. *Journal of Advanced Functional. Materials (Basel)*, *11*, 387–392.

Anne Rodrigues, K. O., Ramos, J. E. T., Cavalcante, C. L., Rodriguez-Castellon, E., & Azevedo, D. C. S. (2014). Pd-loaded mesoporous silica as a robust adsorbent in adsorption/desorption desulfurization cycles. *Fuel*, *126*, 96–103. doi:10.1016/j.fuel.2014.02.019

Ansari, F., Grigoriev, P., Libor, S., Tothill, I. E., & Ramsden, J. J. (2009). DBT Degradation Enhancement by Decorating Rhodococcus erythropolis IGST8 with Magnetic Fe_3O_4 Nanoparticles. *Biotechnology and Bioengineering*, *102*(5), 1505–1512. doi:10.1002/bit.22161 PMID:19012265

Antcliff, K. L., Murphy, D. M., Griffiths, E., & Giamello, E. (2003). The interaction of H2O2 with exchanged titanium oxide systems (TS-1, TiO2, Ti–APO-5, Ti–ZSM-5). *Physical Chemistry Chemical Physics*, *5*(19), 4306–4316. doi:10.1039/b306398b

Anton, N. S., Mehdi, M. Y., Romaneh, J., Ouseph, P. J., Cohn, R. W., & Sumanasekera, G. U. (2007). Electrostatic deposition of graphene. *Nanotechnology*, *18*, 13530–13534. PMID:21730375

Arez, B. F., Alves, L., & Paixão, S. M. (2014). Production and characterization of a novel yeast extracellular invertase activity towards improved dibenzothiophene biodesulfurization. *Applied Biochemistry and Biotechnology*, *174*(6), 2048–2057. doi:10.1007/s12010-014-1182-x PMID:25163885

Armstrong, S. M., Samkey, B. M., & Voordan, G. (1995). Conversion of dibenzothiophene to biophenyl by sulfate reducing bacteria isolated from oil field production facilities. *Biotechnology Letters*, *17*(10), 1133–1136. doi:10.1007/BF00143117

Aryal, S., Kim, C. K., Kim, K. W., Khil, M. S., & Kim, H. Y. (2008). Multi-walled carbon nanotubes/TiO2 composite nanofiber by electrospinning. *Materials Science and Engineering C*, *28*(1), 75–79. doi:10.1016/j.msec.2007.10.002

Atanasova, P., Vladov, Ch., Halachev, T., Fierro, J. L. G., & López, A. A. (1995). Influence on the phosphorus concentration and the method of preparation on the hydrodesulfurization activity of P-Ni-W/alumina catalysts. *Bulletin des Sociétés Chimiques Belges*, *104*(4), 219–223.

Austin, G. T. (1984). *Shreve's Chemical Process Industries*. New York: McGraw-Hill.

Avouris, P. (2002). Molecular electronics with carbon nanotubes. *Accounts of Chemical Research*, *35*(12), 1026–1034. doi:10.1021/ar010152e PMID:12484790

Babich, I. V., & Moulijn, J. A. (2003). Science and technology of novel processes for deep desulfurization of oil refinery streams: A review. *Fuel*, *82*(6), 607–631. doi:10.1016/S0016-2361(02)00324-1

Baboian, R. (1986). Materials Degradation Caused by Acid Rain. Proceedings of the *American Chemical Society Symposium Series*, 318. doi:10.1021/bk-1986-0318

Bae, Y. S., Lee, C. Y., Kim, K. C., Farha, O. K., Nickias, P., & Hupp, J. T. … Goddard, W. A. (2007). Improved Designs of Metal–Organic Frameworks for Hydrogen Storag. Angewandte Chemie International Edition, 46, 6289-6292.

Baeza p, G. Aguila, F. Gracia, P. Araya (2008): Desulfurization by adsorption with copper supported on zirconia. *Catalysis Communications,* 9, 751-755.

Bagiyan, G. A., Koroleva, I. K., Soroka, N. V., & Ufimtsev, A. V. (2004). Kinetics of the catalytic oxidation reactions of thiol compounds in aqueous solutions in the presence of copper ions. *Kinetics and Catalysis*, *45*(3), 372–380. doi:10.1023/B:KICA.0000032171.81652.91

Bailey, N. J. L., Krouse, H. R., Evans C. R., and Rogers, M. A. (1973). *Alteration of crude oil by waters and bacteria-evidence from geochemical and isotope studies*. Am. Assoc. Petrol. Geologists Bull., 57.

Bai, S., & Shen, X. (2012). Graphene-inorganic nanocomposites. *Royal Society of Chemistry Advances*, *2*, 64–98.

Baker, R. T. K. (1995). A review of in-situ electron microscopy studies of metal/metal oxide graphite interactions. *Journal of Adhesion and Adhensives*, *52*(1-4), 13–40.

Baker, R. T. K., & Chludzinski, J. J. Jr. (1981). Catalytic gasification of graphite by chromium and copper in oxygen, steam and hydrogen. *Carbon*, *19*(2), 75–82. doi:10.1016/0008-6223(81)90110-X

Balula, S. S., Cunha-Silva, L., Santos, I. C. M. S., Estrada, A. C., Fernandes, A. C., & Cavaleiro, A. M. V. et al. (2013). Mono-substituted silicotungstates as active catalysts for sustainable oxidations: Homo- and heterogeneous performance. *New Journal of Chemistry*, *37*(8), 2341–2350. doi:10.1039/c3nj00243h

Balzani, V., Credi, A., & Venture, M. (2008). Photochemical conversion of solar energy. *ChemSusChem*, *1*(1-2), 26–58. doi:10.1002/cssc.200700087 PMID:18605661

Banat, I. M., Makkar, R. S., & Cameotra, S. S. (2000). Potential commercial applications of microbial surfactants. *Applied Microbiology and Biotechnology*, *53*(5), 495–508. doi:10.1007/s002530051648 PMID:10855707

Bandyopadhyay, A., & Biswas, M. N. (2006). Prediction of the removal efficiency of a novel two-stage hybrid scrubber for flue gas desulfurization. *Chemical Engineering & Technology*, *29*(1), 130–145. doi:10.1002/ceat.200500160

Bandyopadhyay, S., Chowdhury, R., & Bhattacharjee, C. (2014). Production of biosurfactants through biodesulfurization of spent engine oil – an experimental study. *Green Chemistry Letters and Reviews*, *7*(3), 288–295. doi:10.1080/17518253.2014.946972

Bandyopadhyay, S., Chowdhury, R., Bhattacharjee, C., & Pan, S. (2013). Simultaneous production of biosurfactant and ULSD (ultra low sulfur diesel) using *Rhodococcus* sp. in a chemostat. *Fuel*, *113*, 107–112. doi:10.1016/j.fuel.2013.05.036

Bansel, R. C., & Goyal, M. (2005). *Activated Carbon Adsorption*. USA: Taylor and Francis Group. doi:10.1201/9781420028812

Bardania, H., Raheb, J., Mohammad-Beigi, H., Rasekh, B., & Arpanaei, A. (2013). Desulfurization activity and reusability of magnetite nanoparticle-coated Rhodococcus erythropolis FMF and R. erythropolis IGTS8 bacterial cells. *Biotechnology and Applied Biochemistry*, *60*(May), 323–329. doi:10.1002/bab.1090 PMID:23656694

Bataille, F., Lemberton, J., Michaud, P., Pérot, G., Vrinat, M., & Lemaire, M. et al. (2000). Alkyldibenzothiophenes Hydrodesulfurization-Promoter Effect, Reactivity, and Reaction Mechanism. *Journal of Catalysis*, *191*(2), 409–422. doi:10.1006/jcat.1999.2790

Batista, S. B., Mounteer, A. H., Amorim, F. R., & Totola, M. R. (2006). Isolation and characterization of biosurfactant/bioemulsifier-producing bacteria from petroleum contaminated sites. *Bioresource Technology*, *97*(6), 868–875. doi:10.1016/j.biortech.2005.04.020 PMID:15951168

Baughman, R. H., Zakhidov, A. A., & de Heer, W. A. (2002). Carbon nanotubes--the route towards applications. *Science*, *297*(5582), 787–792. doi:10.1126/science.1060928 PMID:12161643

Bavykin, D. V., Friedrich, J. M., & Walsh, F. C. (2006). Protonated titanates and TiO2 nanostructured materials: Synthesis, properties, and applications. *Advanced Materials*, *18*(21), 2807–2824. doi:10.1002/adma.200502696

Bavykin, D. V., Lapkin, A. A., Plucinski, P. K., Torrente-Murciano, L., Friedrich, J. M., & Walsh, F. C. (2006). Deposition of Pt, Pd, Ru and Au on the surfaces of titanate nanotubes. *Topics in Catalysis*, *39*(3-4), 151–160. doi:10.1007/s11244-006-0051-4

Baxendale, J. H., Evans, M. G., & Park, G. S. (1946). The mechanism and kinetics of the initiation of polymerisation by systems containing hydrogen peroxide. *Transactions of the Faraday Society*, *42*, 155–169. doi:10.1039/tf9464200155

Begin, D., Ulrich, G., Amadou, J., Su, D. S., Pham-Huu, C., & Ziessel, R. (2009). Oxidative dehydrogenation of 9, 10-dihydroanthracene using multi-walled carbon nanotubes. *Journal of Molecular Catalysis A Chemical*, *302*(1-2), 119–123. doi:10.1016/j.molcata.2008.12.006

Bej Shyamal, K. (n. d.). Revamping of diesel hydro-desulfurizers: Options available and future research needs. *Fuel Process. Technol,* 85(13), 1503–1517.

Bej, S. K. (2004). Revamping of diesel hydrodesulfurizers: Options available and future research needs. *Fuel Processing Technology*, *85*(13), 1503–1517. doi:10.1016/j.fuproc.2003.07.002

Bej, S. K., Maity, S. K., & Turaga, U. T. (2004). Search for an efficient 4,6-DMDBT hydrodesulphurization catalyst: A review of recent studies. *Energy & Fuels*, *18*(5), 1227–1237. doi:10.1021/ef030179+

Bekassy-Molnar, E., Marki, E., & Majeed, J. G. (2005). Sulphur dioxide absorption in air-lift-tube absorbers by sodium citrate buffer solution. *Chemical Engineering and Processing: Process Intensification*, *44*(9), 1039–1046. doi:10.1016/j.cep.2005.02.001

Bellas, A. S. (1998). Empirical evidence of advances in scrubber technology. *Resource and Energy Economics*, *20*(4), 327–343. doi:10.1016/S0928-7655(97)00039-0

Ben Li, W. L., Wu, H., Yu, S., Cao, R., & Jiang, Z. (2012). Desulfurization of model gasoline by bioinspired oleophilic nanocomposite membranes. *Journal of Membrane Science*, *415–416*, 278–287.

Bender, J., & Weigel, H.-J. (2011). Changes in atmospheric chemistry and crop health: A review. *Agronomy for Sustainable Development*, *31*(1), 81–89. doi:10.1051/agro/2010013

Benyamna, A., Bennouna, C., Leglise, J., van Gestel, J., Duyme, M., & Duchet, J.-C. et al. (1998). Effect of the association of Co and Ni on the Catalytic Properties of Sulfided CoNiMo/Al_2O_3. *Am. Chem. Soc. Div. Petrol. Prep.*, *43*, 39–42.

Berhault, G., Dela Rosa, M. P., Mehta, A., Yacaman, M. J., & Chanelli, R. R. (2008). The single-layered morphology of supported MoS_2-based catalysts—The role of the cobalt promoter and its effects in the hydrodesulfurization of dibenzothiophene. *Applied Catalysis A, General*, *345*(1), 80–88. doi:10.1016/j.apcata.2008.04.034

Berk, Z. (2013). Food Process Engineering and Technology (Ch. 12) (2nd ed.). Food science and technology.

Berman, Y., Tanklevsky, A., Oren, Y., & Tamir, A. (2000). Modeling and experimental studies of SO_2 absorption in coaxial cylinders with impinging streams: Part I. *Chemical Engineering Science*, *55*(5), 1009–1021. doi:10.1016/S0009-2509(99)00380-2

Berman, Y., Tanklevsky, A., Oren, Y., & Tamir, A. (2000b). Modeling and experimental studies of SO_2 absorption in coaxial cylinders with impinging streams: Part II. *Chemical Engineering Science*, *55*(5), 1023–1028. doi:10.1016/S0009-2509(99)00381-4

Bernier, P., & Ajayan, P. M. (1994). Application of Carbon Nanotubes as Supports in Heterogeneous Catalysis. *Journal of the American Chemical Society*, *116*(17), 7935–7936. doi:10.1021/ja00096a076

Bettelheim, J., Kyte, W.S. and Littler, A. (1981). Fifty years experience of flue gas desulphurisation at power stations in the United Kingdom. *The Chemical Engineer*, 275-277(284).

Bezeverkhyy, I., Ryzhikov, A., Gadacz, G., & Bellat, J. P. (2008). Kinetics of thiophene reactive adsorption on Ni/SiO_2 and Ni/ZnO. *Catalysis Today*, *130*(1), 199–205. doi:10.1016/j.cattod.2007.06.038

Bezverkhyy, I., Safonova, O. V., Afanasiev, P., & Bellat, J. P. (2009). Reaction between thiophene and Ni nanoparticles supported on SiO_2 or ZnO: In situ synchrotron X-ray diffraction study. *The Journal of Physical Chemistry C*, *113*(39), 17064–17069. doi:10.1021/jp903488p

Bhandari, V.M., Hyun Ko, C., Geun Park, J., Han, S.-S., Cho, S.-H., Kim, J.-N. (2006). Desulfurization of diesel using ion-exchanged zeolites. *Chemical Engineering Science*, *61*, 2599–2608.

Bhandari, V. M., Ko, C. H., Park, J. G., Han, S., Cho, S., & Kim, J. (2006). Desulfurization of diesel using ion-exchanged zeolites. *Chemical Engineering Science*, *61*(8), 2599–2608. doi:10.1016/j.ces.2005.11.015

Bhasarkar, J. B., Chakma, S., & Moholkar, V. S. (2013). Mechanistic features of oxidative desulfurization using sono-fenton-peracetic acid (ultrasound/Fe^{2+}-CH_3COOH-H_2O_2) system. *Industrial & Engineering Chemistry Research*, *52*(26), 9038–9047. doi:10.1021/ie400879j

Bhatia, S., & Sharma, D. K. (2006). Emerging role of bio-refining of heavier crude oils and integration of bio-refining with petroleum refineries in the future. *Petroleum Science and Technology*, *24*(10), 1125–1159. doi:10.1080/10916460600817447

Bhatia, S., & Sharma, D. K. (2012). Thermophilic desulfurization of dibenzothiophene and different petroleum oils by *Klebsiella* sp. 13T. *Environmental Science and Pollution Research International*, *19*(8), 3491–3497. doi:10.1007/s11356-012-0884-2 PMID:22467237

Biondo, S. J., & Marten, J. C. (1977). A History Of Flue Gas Desulfurization Systems Since 1850. *Journal of the Air Pollution Control Association*, *27*(10), 948–961. doi:10.1080/00022470.1977.10470518

Birch, S. F., & Norris, W. S. G. P. (1925). CXXVI.-The chemistry of petroleum. Part I. The occurrence of compounds of sulphur in the light distillate from the crude oil of maidan-i-naftun. *Journal of the Chemical Society Transactions*, *127*(0), 898–907. doi:10.1039/ct9252700898

Biswas, R., Devotta, S., Chakrabarti, T., & Pandey, R. A. (2005). Flue Gas Desulfurization: Physicochemical and Biotechnological Approaches. *Critical Reviews in Environmental Science and Technology*, *35*(6), 571–622. doi:10.1080/10643380500326374

Blanco-Brieva, G., Campos-Martin, J. M., Al-Zahrani, S. M., & Fierro, J. L. G. (2011). Effectiveness of metal–organic frameworks for removal of refractory organo-sulfur compound present in liquid fuels. *Fuel*, *90*(1), 190–197. doi:10.1016/j.fuel.2010.08.008

Blanco-Brieva, G., Campos-Martin, J. M., Al-Zahrani, S. M., & Fierro, J. L. G. (2013). Thermal regeneration of the metal organic frameworks used in the adsorption of refractory organosulfur compounds from liquid fuels. *Fuel*, *105*, 459–465. doi:10.1016/j.fuel.2012.08.003

Blanco-López, M. C., Gutiérrez-Fernández, C., Lobo-Castañón, M. J., Miranda-Ordieres, A. J., Tuñón-Blanco, P. (2004). Electrochemical sensing with electrodes modified with molecularly imprinted polymer films. *Analytical and Bioanalytical Chemistry*, 378(8), 1922 –1928.

Blandino, A., Macías, M., & Cantero, D. (1999). Formation of calcium alginate gel capsules: Influence of sodium alginate and $CaCl_2$ concentration on gelation kinetics. *Journal of Bioscience and Bioengineering*, *88*(6), 686–689. doi:10.1016/S1389-1723(00)87103-0 PMID:16232687

Bocarando, J., Alonso-Núñez, G., Bensch, W., Huirache-Acuña, R., Del Valle, M., & Cruz-Reyes, J. (2009). (a)). Comparative study of *in situ/ex situ* activated trimetallic NiMoW sulfide catalysts prepared from ammonium thiomolybdotungstates. *Catalysis Letters*, *130*(3-4), 301–307. doi:10.1007/s10562-009-9913-2

Bocarando, J., Huirache-Acuña, R., Bensch, W., Huang, Z.-D., Petranovskii, V., Fuentes, S., & Alonso-Núñez, G. (2009). (b)). Unsupported Ni-Mo-W sulphide HDS catalysts with the varying nickel concentration. *Applied Catalysis A, General*, *363*(1-2), 45–51. doi:10.1016/j.apcata.2009.04.031

Boikov, E. V., Vakhrushim, P. A., & Vishnetskaya, M. V. (2008). Oxidative desulfurization of hydrocarbon feedstock. *Chemistry and Technology of Fuels and Oils*, *44*(4), 271–274. doi:10.1007/s10553-008-0054-x

Bolla, M. K., Choudhury, H. A., & Moholkar, V. S. (2012). Mechanistic features of ultrasound-assisted oxidative desulfurization of liquids fuels. *Industrial & Engineering Chemistry Research*, *51*(29), 9705–9712. doi:10.1021/ie300807a

Boniek, D., Figueiredo, D., dos Santos, A. F. B., & Stoianoff, M. A. de R. (2014). Biodesulfurization: a mini review about the immediate search for the future technology. *Clean Technologies and Environmental Policy*.

Booth, B., Buglass, J. G., & Unsworth, J. F. (2001). Tailoring fuels for the new millennium. *Topics in Catalysis*, *16-17*(1/4), 39–46. doi:10.1023/A:1016670528451

Bordwell, F. G., & Andersen, H. M., Pitt, & B. M. (. (1954). The Reaction of Grignard Reagents with 4-Hydroxy- and 4-Ethoxycoumarin. *Journal of the American Chemical Society*, *7*, 1082–1085. doi:10.1021/ja01633a045

Bösmann, A., Datsevich, L., Jess, A., Lauter, A., Schmitz, C., & Wasserscheid, P. (2001). Deep desulfurization of diesel fuel by extraction with ionic liquids. *Chemical Communications (Cambridge)*, *23*(23), 2494–2495. doi:10.1039/b108411a PMID:12240031

Box, G. E. P., & Behnken, D. W. (1960). Some new three level designs for the study of quantitative variables. *Technometrics*, *2*(4), 455–475. doi:10.1080/00401706.1960.10489912

Braid, C., & Cann, M. (2005). Environmental chemistry. (3rd ed.). New York: W.H Freeman and company.

Brandon, N. P., Skinner, S., & Steele, B. C. (2003). Recent advances in materials for fuel cells. *Annual Review of Materials Research*, *33*(1), 183–213. doi:10.1146/annurev.matsci.33.022802.094122

Brasseur, G. P., Orlando, J. J., & Tyndall, G. S. (Eds.). (1999). *Atmospheric Chemistry and Global Change*. New York: Oxford University Press.

Brauer, H. (1984). Air Pollution Control Equipment. In O. Hutzinger (Ed.), The handbook of environmental chemistry (Volume 4, part B, pp. 188–252).

Bravo, V., R., F. Camacho, R., M. Moya, V., & A. I. García, L. (. (2002). Desulphurization of SO_2–N_2 mixtures by limestone slurries. *Chemical Engineering Science*, *57*(11), 2047–2058. doi:10.1016/S0009-2509(02)00095-7

Brevoord, E., & Gerritsen, L. A., & L., P. F. (2000, November 13–15). Paper presented at The European Refinery Technology Conference, Rome, Italy.

Brien, W. X. S. O., Chen, J. W., Nayak, R. V., & Carr, G. S. (1986). Catalytic hydrodesulfurization of dibenzothiophene and a coal-derived liquid. *Industrial & Engineering Chemistry Process Design and Development*, *25*(1), 221–229. doi:10.1021/i200032a036

Brieva, GB, Campos-Martin, J M, & Al-Zahrani, S M, & G, F. J. L. (2010). Removal of refractory organic sulphur compounds in fossil fuels using MOF sorbents. *Global NEST Journal*, *12*, 296–304.

Brogren, C., & Karlsson, H. T. (1997). Modeling the absorption of SO_2 in a spray scrubber using the penetration theory. *Chemical Engineering Science*, *52*(18), 3085–3099. doi:10.1016/S0009-2509(97)00126-7

Bromley, L. A. (1972). Use of sea water to scrub sulfur dioxide from stack gases. *Int. J. Sulfur Chem. Part B*, *7*(1), 77–84.

Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gasses in multimolecular layer. *Journal of the American Chemical Society*, *60*(2), 309–319. doi:10.1021/ja01269a023

Brunet, S., Mey, D., Pérot, G., Bouchy, C., & Diehl, F. (2005). On the Hydrodesulfurization of FCC Gasoline: A Review, *Applied Catalysis, A, 278*, 143.

Brunet, S., Mey, D., Pe'rot, G., Bouchy, C., & Diehl, F. (2005). On the hydrodesulfurization of FCC gasoline: A review. *Applied Catalysis A*, *278*(2), 143–172. doi:10.1016/j.apcata.2004.10.012

Bunger, J. W., & Li, N. C. (Eds.). (1981). *Chemistry of Asphaltenes*. Washington, DC: American Chemical Society.

Burney, J., & Ramanathan, V. (2014). Recent climate and air pollution impacts on Indian Agriculture. *Proceedings of the National Academy of Sciences of the United States of America*, *111*(46), 16319–16324. doi:10.1073/pnas.1317275111 PMID:25368149

Byskov, L. S., Hammer, B., Nørskov, J. K., Clausen, B. S., & Topsoe, H. (1997). Sulfur bonding in MoS_2 and Co-Mo-S structures. *Catalysis Letters*, *47*(3/4), 177–182. doi:10.1023/A:1019009105792

Cáceres, C., Fierro, J. L. G., López Agudo, A., Severino, F., & Laine, L. (1986). Relationship between hydrodesulfurization activity and the state of promoters in precursor calcined Ni-Co-Mo/Al_2O_3 catalysts. *Journal of Catalysis*, *97*(1), 219–227. doi:10.1016/0021-9517(86)90052-7

Caiazzo, G., Di Nardo, A., Langella, G., & Scala, F. (2012). Seawater scrubbing desulfurization: A model for SO_2 absorption in fall-down droplets. *Environmental Progress and Sustainable Energy*, *31*(2), 277–287. doi:10.1002/ep.10541

Calkins, W. H. (1994). Fuel, *The Chemical Forms of Sulfur in Coal*. *RE:view*, *73*(4), 475–484.

Calkins, W. H. (1994). The chemical forms of sulfur in coal: A review. *Fuel*, *73*(4), 475–484. doi:10.1016/0016-2361(94)90028-0

Cameotra, S. S., & Makkar, R. S. (1998). Synthesis of biosurfactants in extreme conditions. *Applied Microbiology and Biotechnology*, *50*(5), 520–529. doi:10.1007/s002530051329 PMID:9866170

Cameotra, S. S., & Singh, P. (2009). Synthesis of rhamnolipid biosurfactant and mode of hexadecane uptake by *Pseudomonas* species. *Microbial Cell Factories*, *8*(1), 16. doi:10.1186/1475-2859-8-16 PMID:19284586

Campelo, J. M., Luna, D., Luque, R., Marinas, J. M., & Romero, A. A. (2009). Sustainable preparation of supported metal nanoparticles and their applications in catalysis. *ChemSusChem*, *2*(1), 18–45. doi:10.1002/cssc.200800227 PMID:19142903

Campestrini, S., Conte, V., Di Furia, F., Modena, G., & Bortolini, O. (1988). Metal catalysis in oxidation by peroxides. 30. Electrophilic oxygen transfer from anionic, coordinatively saturated molybdenum peroxo complexes. *The Journal of Organic Chemistry*, *53*(24), 5721–5724. doi:10.1021/jo00259a021

Campos-Martin, J. M., Capel-Sanchez, M. C., Perez-Presas, P., & Fierro, J. L. G. (2010). Oxidative processes of desulfurization of liquid fuels. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *85*(7), 879–890. doi:10.1002/jctb.2371

Cao, G. (2004). *Nanostructures and Nanomaterials: Synthesis, properties and applications*. United Kingdom: Imperial College. doi:10.1142/p305

Capel-Sanchez, M. C., Campos-Martin, J. M., Fierro, J. L. G., de Frutos, M. P., & Padilla Polo, A. (2000). Effective alkene epoxidation with dilute hydrogen peroxide on amorphous silica-supported titanium catalysts. *Chemical Communications (Cambridge)*, *10*(10), 855–856. doi:10.1039/b000929f

Carati, A., Flego, C., Previde Massara, E., Millini, R., Carluccio, L., Parker, W. O. Jr, & Bellussi, G. (1999). Stability of Ti in MFI and Beta structures: A comparative study. *Microporous and Mesoporous Materials*, *30*(1), 137–144. doi:10.1016/S1387-1811(99)00018-9

Carleson, T. E., & Berg, J. C. (1983). The effect of electric fields on the absorption of pure sulfur dioxide by water drops. *Chemical Engineering Science*, *38*(6), 871–876. doi:10.1016/0009-2509(83)80008-6

Carletti, C., Bjondahl, F., De Blasio, C., Ahlbeck, J., Järvinen, L., & Westerlund, T. (2013). Modeling limestone reactivity and sizing the dissolution tank in wet flue gas desulfurization scrubbers. *Environmental Progress and Sustainable Energy*, *32*(3), 663–672. doi:10.1002/ep.11683

Caro, A., Baltes, K., Leton, P., & Garcia-Calvo, E. (2007). Dibenzothiophene biodesulfurization in resting cell conditions by aerobic bacteria. *Biochemical Engineering Journal*, *35*(2), 191–197. doi:10.1016/j.bej.2007.01.013

Caro, A., Letón, P., García-Calvo, E., & Setti, L. (2007). Enhancement of dibenzothiophene biodesulfurization using β-cyclodextrins in oil-to-water media. *Fuel*, *86*(16), 2632–2636. doi:10.1016/j.fuel.2007.02.033

Carvalheiro, F., Moniz, P., Duarte, L. C., Esteves, M. P., & Gírio, F. M. (2011). Mannitol production by lactic acid bacteria grown in supplemented carob syrup. *Journal of Industrial Microbiology & Biotechnology*, *38*(1), 221–227. doi:10.1007/s10295-010-0823-5 PMID:20820868

Castro, B., Whitcombe, M. J., Vulfson, E. N., Vazquez-Duhalt, R., & Barzana, E. (2001). Molecular imprinting for the selective adsorption of organosulfur compounds present in fuels. *Analytica Chimica Acta*, *435*(1), 83–90. doi:10.1016/S0003-2670(01)00799-1

Cedeño-Caero, L., Ramos-Luna, M., Méndez-Cruz, M., & Ramírez-Solís, J. (2011). Oxidative desulfurization of dibenzothiophene compounds with titania based catalysts. *Catalysis Today*, *172*(1), 189–194. doi:10.1016/j.cattod.2011.01.048

Cervantes-Gaxiola, M. E., Arroyo-Albiter, M., Maya-Yescas, R., Rico-Cerda, J. L., Guevara-Lara, A., & Espino-Valencia, J. (2012). Synthesis, characterization and catalytic activity during hydrodesulphurization of dibenzothiophene of NiMoW catalysts supported on Al-Ti mixed oxides modified with MgO. *Fuel*, *100*, 57–65. doi:10.1016/j.fuel.2011.12.040

Chandrasekhar, V., Kingsley, S., Vij, A., Lam, K. C., & Rheingold, A. L. (2000). Formation of a Tetranuclear Copper (II) Cluster Assembled by Metal-Assisted Hydrolysis and Desulfurization of Bis(3,5-dimethylpyrazolyl)methylphosphine Sulfide, MeP(S)(3,5-$Me_2Pz)_2$. *Inorganic Chemistry*, *39*(15), 3238–3242. doi:10.1021/ic991255k PMID:11196859

Chang, G., Song, C., & Wang, L. (2011). A modeling and experimental study of flue gas desulfurization in a dense phase tower. *Journal of Hazardous Materials*, *189*(1-2), 134–140. doi:10.1016/j.jhazmat.2011.02.009 PMID:21377795

Chang, J. H., Chang, Y. K., Cho, K. S., & Chang, H. N. (2000). Desulfurization of model and diesel oils by resting cells of Gordona sp. *Biotechnology Letters*, *22*(3), 193–196. doi:10.1023/A:1005637013879

Chang, J. H., Chang, Y. K., Ryu, H. W., & Chang, H. N. (2000). Desulfurization of light gas oil in immobilized-cell systems of *Gordona* sp. CYKS1 and *Nocardia* sp. CYKS2. *FEMS Microbiology Letters*, *182*(2), 309–312. doi:10.1111/j.1574-6968.2000.tb08913.x PMID:10620684

Chang, J. H., Kim, Y. J., Lee, B. H., Cho, K., Ryu, H. W., Chang, Y. K., & Chang, H. N. (2001). Production of a desulfurization biocatalyst by two-stage fermentation and its application for the treatment of model and diesel oils. *Biotechnology Progress*, *17*(5), 876–880. doi:10.1021/bp0100676 PMID:11587578

Chang, J. H., Rhee, S. K., Chang, Y. K., & Chang, H. N. (1998). Desulfurization of diesel oils by a newly isolated dibenzothiophene-degrading Norcadia sp. strain CYKS2. *Biotechnology Progress*, *14*(6), 851–855. doi:10.1021/bp9800788 PMID:9841646

Chang, J., Wang, A., Liu, J., Li, X., & Hu, Y. (2010). Oxidation of dibenzothiophene with cumene hydroperoxide on MoO3/SiO2 modified with alkaline earth metals. *Catalysis Today*, *149*(1–2), 122–126. doi:10.1016/j.cattod.2009.04.026

Charlier, J. C. (2002). Defects in carbon nano tubes. *Accounts of Chemical Research*, *35*(12), 1063–1069. doi:10.1021/ar010166k PMID:12484794

Chaturvedi, J., Bhattacharya, S., & Nethaji, M. (2008). A new reaction of dithiocarbamates: CS_2 elimination and two C–C bond formations leading to formation of cyclic ammonium salts. *Inorganic Chemistry Communications*, *11*(7), 720–722. doi:10.1016/j.inoche.2008.03.021

Chen, J. C., & Monticello, D. J. (1996). *U.S. Patent No. 5,525,235.*

Chen, C. T. (1987). Concept and Design Procedure for Cylindrical Element Monochromators for Synchrotron Radiation. *Nucl. Instrum. Methods Phys. Sec. A*, *256*(3), 595–604. doi:10.1016/0168-9002(87)90307-X

Cheng, G., & Guo, T. (2002). Surface segregation in Ni/Co bimetallic nanoparticles produced in single-walled carbon nanotube synthesis. *The Journal of Physical Chemistry B*, *106*(23), 5833–5839. doi:10.1021/jp025530r

Cheng, J.-K., Chen, Y.-B., Wu, L., Zhang, J., Wen, Y.-H., Li, Z.-J., & Yao, Y.-G. (2005). A 3-D Noninterpenetrating Diamondoid Network of a Decanuclear Copper(I) Complex. *Inorganic Chemistry*, *44*(10), 3386–3388. doi:10.1021/ic050301f PMID:15877417

Cheng, P., Zhang, S., Wang, P., Huang, S., & Tian, H. (2013). First-principles investigation of thiophene adsorption on Ni13 and Zn@Ni12 nanoclusters. *Computational and Theoretical Chemistry*, *1020*, 136–142. doi:10.1016/j.comptc.2013.07.044

Cheng, Y., Zhou, W., Gao, C., Lan, K., Gao, Y., & Wu, Q. (2009). Biodiesel production from Jerusalem artichoke (*Helianthus tuberosus* L.) tuber by heterotrophic microalgae *Chlorella protothecoides. Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *84*(5), 777–781. doi:10.1002/jctb.2111

Chen, H., Ge, H., Dou, B., Pan, W., & Zhou, G. (2009). Thermogravimetric Kinetics of $MgSO_3 \cdot 6H_2O$ Byproduct from Magnesia Wet Flue Gas Desulfurization. *Energy & Fuels*, *23*(5), 2552–2556. doi:10.1021/ef900083f

Chen, H., & Hsieh, Y. L. (2004). Ultrafine hydrogel fibers with dual temperature- and pH-responsive swelling behaviors. *Journal of Polymer Science. Part A, Polymer Chemistry*, *42*(24), 6331–6339. doi:10.1002/pola.20461

Chen, J., Daniels, L. M., & Angelici, R. J. (1996). Unexpected Reactions of 2,5-Dimethylthiophene (2,5-Me_2T) in $Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)^{2+}$, $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$, and $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$ with Cobaltocene. *Organometallics*, *15*(4), 1223–1229. doi:10.1021/om9505625

Chen, L., Guo, S., & Zhao, D.CHEN. (2006). Oxidation of thiophenes over silica gel in hydrogen peroxide/formic acid system. *Chinese Journal of Chemical Engineering*, *14*(6), 835–838. doi:10.1016/S1004-9541(07)60022-6

Chen, M. L., Zhang, F. J., & Oh, W. C. (2009). Synthesis, characterization, and photocatalytic analysis of CNT/TiO2 composites derived from MWCNTs and titanium sources. *New Carbon Materials*, *24*(2), 159–166. doi:10.1016/S1872-5805(08)60045-1

Chen, W., Maugé, F., Van Gestel, J., Nie, H., Li, D., & Long, X. (2013). Effect of modification of the alumina acidity on the properties of supported Mo and CoMo sulfide catalysts. *Journal of Catalysis*, *304*, 47–62. doi:10.1016/j.jcat.2013.03.004

Chen, Y., Zhang, F., Fang, Y., Zhu, X., Zhen, W., Wang, R., & Ma, J. (2013). Phosphotungstic acid containing ionic liquid immobilized on magnetic mesoporous silica rod catalyst for the oxidation of dibenzothiophene with H2O2. *Catalysis Communications*, *38*, 54–58. doi:10.1016/j.catcom.2013.04.005

Chen, Y., Zhao, S., & Song, Y. F. (2013). An efficient heterogeneous catalyst based on highly dispersed Na2H2Law10O36·32 H2O nanoparticles on mesoporous silica for deep desulfurization. *Applied Catalysis A, General*, *466*, 307–314. doi:10.1016/j.apcata.2013.06.030

Chen, Z., Yates, D., Neathery, J. K., & Liu, K. (2012). The effect of fly ash on fluid dynamics of CO_2 scrubber in coal-fired power plant. *Chemical Engineering Research & Design*, *90*(3), 328–335. doi:10.1016/j.cherd.2011.07.024

Cheruku, S. K., & Banerjee, T. (2012). Liquid–liquid equilibrium data for 1-ethyl-3-methylimidazolium acetate–thiophene–diesel compound: Experiments and correlations. *Journal of Solution Chemistry*, *41*(5), 898–913. doi:10.1007/s10953-012-9840-5

Chianelli, R. R., & Pecoraro, T. A. (1985). Carbon-containing molybdenum and tungsten sulphide catalysts. *U.S. Patent* 4,508,847.

Chianelli, R. R., & Berhault, G. (1999). Symmetrical synergism and the role of carbon in transition metal sulfide catalytic materials. *Catalysis Today*, *53*(3), 357–366. doi:10.1016/S0920-5861(99)00130-3

Chianelli, R. R., Berhault, G., Raybaud, P., Kasztelan, S., Hafner, J., & Toulhoat, H. (2002). Periodic trends in hydrodesulfurization: In support of the Sabatier principle. *Applied Catalysis A, General*, *227*(1-2), 83–96. doi:10.1016/S0926-860X(01)00924-3

Chica, A., Corma, A., & Dómine, M. E. (2006). Catalytic oxidative desulfurization (ODS) of diesel fuel on a continuous fixed-bed reactor. *Journal of Catalysis*, *242*(2), 299–308. doi:10.1016/j.jcat.2006.06.013

Chica, A., Gatti, G., Moden, B., Marchese, L., & Iglesia, E. (2006). Selective Catalytic Oxidation of Organosulfur Compounds with tert-Butyl Hydroperoxide. *Chemistry (Weinheim an der Bergstrasse, Germany)*, *12*(7), 1960–1967. doi:10.1002/chem.200500858 PMID:16385590

Chica, A., Strohmaier, K. G., & Iglesia, E. (2005). Effects of zeolite structure and aluminum content on thiophene adsorption, desorption, and surface reactions. *Applied Catalysis B: Environmental*, *60*(3-4), 223–232. doi:10.1016/j.apcatb.2005.02.031

Chien, T.-W., & Chu, H. (2000). Removal of SO_2 and NO from flue gas by wet scrubbing using an aqueous $NaClO_2$ solution. *Journal of Hazardous Materials*, *80*(1-3), 43–57. doi:10.1016/S0304-3894(00)00274-0 PMID:11080568

Chilingarian, G. V., & Yen, T. F. (Eds.). (1978). *Bitumens, Asphalts, and Tar Sands*. Amsterdam: Elsevier Pub. Co.

Chitnis, G. K., Novak, W. J., Ortelli, D. E., & Lewis, E. (2005). *Debottlenecking hydrocrackers with NEBULATM catalyst*. Presented at the 103rd NPRA Annual Meeting, San Francisco, CA.

Choi, O. K., Cho, K. S., Ryu, H. W., & Chang, Y. K. (2003). Enhancement of phase separation by the addition of de-emulsifiers to three-phase (diesel oil / biocatalyst / aqueous phase) emulsion in diesel biodesulfurization. *Biotechnology Letters*, *25*(1), 73–77. doi:10.1023/A:1021750719337 PMID:12882310

Choi, W.-J., Seo, J.-B., Cho, S.-W., Park, S.-W., & Oh, K.-J. (2009). Simultaneous absorption of CO_2 and SO_2 into aqueous AMP/NH_3 solutions in binary composite absorption system. *Korean Journal of Chemical Engineering*, *26*(3), 705–710. doi:10.1007/s11814-009-0118-6

Cho, J., Schaab, S., Roether, J., & Boccaccini, A. R. (2008). Nanostructured carbon nanotube/TiO2 composite coatings using electrophoretic deposition (EPD). *Journal of Nanoparticle Research*, *10*(1), 99–105. doi:10.1007/s11051-007-9230-x

Chong, E. J., Phan, T. T., Lim, I. J., Zhang, Y. Z., Bay, B. H., Ramakrishna, S., & Lim, C. T. (2007). Evaluation of electrospun PCL/gelatin nanofibrous scaffold for wound healing and layered dermal reconstitution. *Acta Biomaterialia*, *3*(3), 321–330. doi:10.1016/j.actbio.2007.01.002 PMID:17321811

Chowdhury, R., & Duttagupta, A. (2005). Mathematical Modeling of the transient behaviour of a chemostat undergoing bio-desulfurization of model organosulfur compounds and diesel using pure and isolated bacterial strains. *International Journal of Chemical Reactor Engineering*, *3*(1), 1–12. doi:10.2202/1542-6580.1239

Chu, H., Chien, T. W., & Li, S. Y. (2001). Simultaneous absorption of SO_2 and NO from flue gas with $KMnO_4$/NaOH solutions. *The Science of the Total Environment*, *275*(1–3), 127–135. doi:10.1016/S0048-9697(00)00860-3 PMID:11482398

Chung, L. L., Erathodiyil, N., & Ying, J. Y. (2013). Nanostructured Catalysts for Organic Transformations. *Accounts of Chemical Research*, *46*(8), 1825–1837. doi:10.1021/ar300197s PMID:23350747

Ciclosi, M., Dinoi, C. C., Gonsalvi, L., Peruzzini, M., Monoury, E., & Poli, R. (2008). Oxidation of Thiophene Derivatives with H2O2 in Acetonitrile Catalyzed by [Cp*2M2O5] (M = Mo, W): A Kinetic Study. *Organometallics*, *27*(10), 2281–2286. doi:10.1021/om800035f

Clark, R. B., Ritchey, K. D., & Baligar, V. C. (2001). Benefits and constraints for use of FGD products on agricultural land. *Fuel*, *80*(6), 821–828. doi:10.1016/S0016-2361(00)00162-9

Clean Air Act Tier 2. (1999). EPA (US).

Colle, S., Thomas, D., & Vanderschuren, J. (2005). Process simulations of sulphur dioxide abatement with hydrogen peroxide solutions in a packed column. *Chemical Engineering Research and Design*, 83(1 A), 81–87.

Colle, S., Vanderschuren, J., & Thomas, D. (2004). Pilot-scale validation of the kinetics of SO2 absorption into sulphuric acid solutions containing hydrogen peroxide. *Chemical Engineering and Processing: Process Intensification*, *43*(11), 1397–1402. doi:10.1016/j.cep.2004.04.005

Colle, S., Vanderschuren, J., & Thomas, D. (2005). Simulation of SO2 absorption into sulfuric acid solutions containing hydrogen peroxide in the fast and moderately fast kinetic regimes. *Chemical Engineering Science*, *60*(22), 6472–6479. doi:10.1016/j.ces.2005.04.076

Colle, S., Vanderschuren, J., & Thomas, D. (2008). Effect of temperature on SO2 absorption into sulphuric acid solutions containing hydrogen peroxide. *Chemical Engineering and Processing: Process Intensification*, *47*(9-10), 1603–1608. doi:10.1016/j.cep.2007.08.014

Collins, F. M., Lucy, A. R., & Sharp, C. (1997). Oxidative desulphurisation of oils via hydrogen peroxide and heteropoly-anion catalysis. *Journal of Molecular Catalysis A Chemical*, *117*(1–3), 397–403. doi:10.1016/S1381-1169(96)00251-8

Comission of the European Communities. (2006). *Green Paper – A European Strategy for Sustainable*. Brussels: Competitive and Secure Energy.

Corrias, M., Caussat, B., Ayral, A., Durand, J., Kihn, Y., Kalck, P., & Serp, P. (2003). Carbon nanotubes produced by fluidized bed catalytic CVD: First approach of the process. *Chemical Engineering Science*, *58*(19), 4475–4482. doi:10.1016/S0009-2509(03)00265-3

Corro, G. (2002). Sulfur impact on diesel emission control—a review. *Reaction Kinetics and Catalysis Letters*, *75*, 89–106. doi:10.1023/A:1014853602908

Cortes-Jácome, M. A., Morales, M., Angeles Chavez, C., Ramírez-Verduzco, L. F., López-Salinas, E., & Toledo-Antonio, J. A. (2007). WOx/TiO2 Catalysts via Titania Nanotubes for the Oxidation of Dibenzothiophene. *Chemistry of Materials*, *19*(26), 6605–6614. doi:10.1021/cm702010k

Costa, R. C. C., Moura, F. C. C., Ardisson, J. D., Fabris, J. D., & Lago, R. M. (2008). Highly active heterogeneous Fenton-like systems based on Fe0/Fe3O4 composites prepared by controlled reduction of iron oxides. *Applied Catalysis B: Environmental*, *83*(1-2), 131–139. doi:10.1016/j.apcatb.2008.01.039

Cramer, S. P., Tench, O., Yocum, M., Kraner, H., Rogers, L., & Radeka, V. (1991). X-ray absorption fine structure. In S. S. Hassian (Ed.), *Proc. of 6th Intl. XAFS Conf* (p. 640).

Crawford, D. L., & Gupta, R. K. (1990). Oxidation of dibenzothiophene by Cunnighamella elegans. *Current Microbiology*, *21*(4), 229–231. doi:10.1007/BF02092161

Crnkovic, P. M., Milioli, F. E., & Pagliuso, J. D. (2006). Kinetics study of the SO_2 sorption by Brazilian dolomite using thermogravimetry. *Thermochimica Acta*, *447*(2), 161–166. doi:10.1016/j.tca.2006.05.023

Crude oil reserves and spatial distribution. (n. d.). Retrieved from http://web2.mendelu.cz/af_291_projekty2/vseo/stranka.php?kod=312

Cui, R. L., Zhang, Y., Wang, J. Y., Zhou, W. W., & Li, Y. (2010). Comparison between copper and iron as catalyst for chemical vapor deposition of horizontally aligned ultralong single-walled carbon nanotubes on silicon substrates. *Journal of Physical Chemistry*, *114*(37), 15547–15552.

Cui, X., Yao, D., Li, H., Yang, J., & Hu, D. (2012). Nano-magnetic particles as multifunctional microreactor for deep desulfurization. *Journal of Hazardous Materials*, *205*, 17–23. doi:10.1016/j.jhazmat.2011.11.063 PMID:22244972

Curtis, M. D. (1996). Electron-Deficient Molybdenum/Cobalt/Sulfido Clusters: Chemistry Related to Hydrodesulfurization. *Journal of Cluster Science*, *7*(3), 247–262. doi:10.1007/BF01171183

Curtis, M. D., & Druker, S. H. (1997). Homolytic C–S Bond Scission in the Desulfurization of Aromatic and Aliphatic Thiols Mediated by a Mo/Co/S Cluster: Mechanistic Aspects Relevant to HDS Catalysis. *Journal of the American Chemical Society*, *119*(5), 1027–1036. doi:10.1021/ja9621096

Daage, M., & Chianelli, R. R. (1994). Structure-Function Relations in Molybdenum Sulfide Catalysts: The "Rim-Edge" Model. *Journal of Catalysis*, *149*(2), 414–427. doi:10.1006/jcat.1994.1308

Daenen, M., De Fouw, R., Hamers, B., Janssen, P., Schouteden, K., & Veld, M. (2003). The Wondrous World of Carbon Nanotubes. A Review of Current Carbon Nanotube Technologies. Eindhoven University of Technology, 89.

Dagaonkar, V., M., A.C.M. Beenackers, A., & G. Pangarkar, V. (. (2001). Absorption of sulfur dioxide into aqueous reactive slurries of calcium and magnesium hydroxide in a stirre cell. *Chemical Engineering Science*, *56*(3), 1095–1101. doi:10.1016/S0009-2509(00)00326-2

Dai, H. (2002). Carbon nanotubes: Opportunities and challenges. *Surface Science*, *500*(1-3), 218–241. doi:10.1016/S0039-6028(01)01558-8

Daimler–Chrysler AG. (2000). Method for desulfurization engine fuel on board a motor vehicle // W.O 2000/20531.

Dai, Y., Shao, R., Qi, G., & Ding, B.-B. (2014). Enhanced dibenzothiophene biodesulfurization by immobilized cells of *Brevibacterium lutescens* in n-octane-water biphasic system. *Applied Biochemistry and Biotechnology*, *174*(6), 2236–2244. doi:10.1007/s12010-014-1184-8 PMID:25173674

Darian, S. T., & Arabshshi, S. H. (1988). Process for upgrading diesel oils. US Patent 4746420.

Dasgupta, S., Gupta, P., Aarti, A. N., Goswami, A. N., Garg, M. O., & Tangstad, E. et al. (2013). Adsorptive desulfurization of diesel by regenerable nickel based adsorbents. *Fuel*, *108*, 184–189. doi:10.1016/j.fuel.2012.12.060

Davis, F. J. (2004). Polymer chemistry-A practical approach. Oxford University Press, Great Clarendon Street, Oxford OX2 6DP. pp 19-21

Davis, D. L., Bell, M. L., & Fletcher, T. (2002). A Look Back at the London Smog of 1952 and the Half Century Since. *Environmental Health Perspectives*, *110*(12), A734–A735. doi:10.1289/ehp.110-a734 PMID:12501843

Davis, J. B. (1967). *Petroleum Microbiology*. Elsevier Pub. Cr.

Davis, R. E. (1958). Cyclic Sulfides. III. The Reaction of Some Ethylene Sulfides with Triphenylphosphine and with Triethyl Phosphite. *The Journal of Organic Chemistry*, *23*(11), 1767–1768. doi:10.1021/jo01105a052

Davoodi-Dehaghani, F., Vosoughi, M., & Ziaee, A. A. (2010). Biodesulfurization of dibenzothiophene by a newly isolated Rhodococcus erythropolis strain. *Bioresource Technology*, *101*(3), 1102–1105. doi:10.1016/j.biortech.2009.08.058 PMID:19819129

de Angelis, A., Pollesel, P., Molinari, D., O'Neal Parker Jr, W., Frattini, A., Cavani, F., Martins, S., & Perego, C. (2007). Heteropolyacids as effective catalysts to obtain zero sulfur diesel. *Pure and Applied Chemistry*, *79*(11), 1887–1894.

De Filippis, P., & Scarsella, M. (2008). Functionalized hexagonal mesoporous silica as an oxidizing agent for the oxidative desulfurization of organosulfur compounds. *Industrial & Engineering Chemistry Research*, *47*(3), 973–975. doi:10.1021/ie071057y

De Filippis, P., Scarsella, M., & Verdone, N. (2010). Oxidative Desulfurization I: Peroxyformic Acid Oxidation of Benzothiophene and Dibenzothiophene. *Industrial & Engineering Chemistry Research*, *49*(10), 4594–4600. doi:10.1021/ie9017622

de Souza, W. F., Guimarães, I. R., Guerreiro, M. C., & Oliveira, L. C. A. (2009). Catalytic oxidation of sulfur and nitrogen compounds from diesel fuel. *Applied Catalysis A, General*, *360*(2), 205–209. doi:10.1016/j.apcata.2009.03.023

De Volder, M. F. L., Tawfick, S. H., Baughman, R. H., & Hart, A. J. (2013). Carbon nanotubes: Present and future commercial applications. *Science*, *339*(6119), 535–539. doi:10.1126/science.1222453 PMID:23372006

Dean, R. A., & Whitehead, E. V. (1967). Proceedings of the 7th World Petroleum Congress, *Panel Discussion 23*, paper 7.

Deck, C. P., & Vecchio, K. (2006). Prediction of carbon nanotube growth success by the analysis of carbon-catalyst binary phase diagrams. *Carbon*, *44*(2), 267–275. doi:10.1016/j.carbon.2005.07.023

Dehghan-Noudeh, G., Housaindokht, M., & Bazzaz, B. S. F. (2005). Isolation, characterization, and investigation of surface and hemolytic activities of a lipopeptide biosurfactant produced by *Bacillus subtilis* ATCC 6633. *Journal of Microbiology-Seoul*, *43*(3), 272. PMID:15995646

Dehkordi, A. M., Sobati, M. A., & Nazem, M. A. (2009). Oxidative Desulfurization of Non-hydrotreated Kerosene Using Hydrogen Peroxide and Acetic Acid. *Chinese Journal of Chemical Engineering*, *17*(5), 869–874. doi:10.1016/S1004-9541(08)60289-X

Dekker, M., Yocum, R.H., & Nyquist, E.B. (1973). Functional monomers; their preparation, polymerization, and application. Michigan, USA. ISBN-0824718100, 9780824718107.

Del Olmo, C. H., Santos, V. E., Alcon, A., & Garcia-Ochoa, F. (2005). Production of a *Rhodococcus erythropolis* IGTS8 biocatalyst for DBT biodesulfurization: Influence of operational conditions. *Biochemical Engineering Journal*, *22*(3), 229–237. doi:10.1016/j.bej.2004.09.015

Del Valle-Zermeño, R., Formosa, J., Aparicio, J. A., & Chimenos, J. M. (2014). Reutilization of low-grade magnesium oxides for flue gas desulfurization during calcination of natural magnesite: A closed-loop process. *Chemical Engineering Journal*, *254*, 63–72. doi:10.1016/j.cej.2014.05.089

Del Valle-Zermeño, R., Niubó, M., Formosa, J., Guembe, M., Aparicio, J. A., & Chimenos, J. M. (2015). Synergistic effect of the parameters affecting wet flue gas desulfurization using magnesium oxides by-products. *Chemical Engineering Journal*, *262*, 268–277. doi:10.1016/j.cej.2014.09.085

Delgado, J. L., Herranz, M. A., & Martin, N. (2008). The nano-forms of carbon. *Journal of Materials Chemistry*, *18*(13), 1417–1426. doi:10.1039/b717218d

Delitala, C., Cadoni, E., Delpiano, D., Meloni, D., Melis, S., & Ferino, I. (2008). Liquid-phase thiophene adsorption on MCM-22 zeolite and activated carbon. *Microporous and Mesoporous Materials*, *110*(2-3), 197–215. doi:10.1016/j.micromeso.2007.06.018

Dembicki, H. Jr. (2009). Three common source rock evaluation errors made by geologists during prospect or play appraisals. *AAPG Bulletin*, *93*(3), 341–356. doi:10.1306/10230808076

Demir, M. M., Yilgor, I., Yilgor, E., & Erman, B. (2002). Electrospinning of polyurethane fibers. *Polymer*, *43*(11), 3303–3309. doi:10.1016/S0032-3861(02)00136-2

Deneuve, A., Wang, K., Janowska, I., Chizari, K., Edouard, D., & Ersen, O. et al. (2011). Bucky paper with improved mechanical stability made from vertically aligned carbon nanotubes for desulfurization process. *Applied Catalysis A, General*, *400*(1), 230–237. doi:10.1016/j.apcata.2011.04.042

Denis, P. A. (2010). On the enthalpy of formation of thiophene. *Theoretical Chemistry Accounts*, *127*(5-6), 621–626. doi:10.1007/s00214-010-0759-x

Denome, S. A., Oldfield, C., Nash, L. J., & Young, K. D. (1994). Characterization of the desulfurization genes from Rhodococcus sp. strain IGTS8. *Journal of Bacteriology*, *176*(21), 6707–6716. PMID:7961424

Denome, S. A., Stanley, D. C., Olson, E. S., & Young, K. D. (1993). Metabolism of dibenzothiophene and naphthalene in Pseudomonas strains: Complete DNA sequence of an upper naphthalene catabolic pathway. *Journal of Bacteriology*, *175*(21), 6890–6901. PMID:8226631

Depauw, G. A., & Froment, G. F. (1997). Molecular analysis of the sulphur components in a light cycle oil of a catalytic cracking unit by gas chromatography with mass spectrometric and atomic emission detection. *Journal of Chromatography. A*, *761*(1-2), 231–247. doi:10.1016/S0021-9673(96)00819-9

Derikvand, P., & Etemadifar, Z. (2014). Improvement of biodesulfurization rate of alginate immobilized *Rhodococcus erythropolis* R1. *Jundishapur Journal of Microbiology*, *7*(3), 1–7. doi:10.5812/jjm.9123 PMID:25147685

Derikvand, P., Etemadifar, Z., & Biria, D. (2014). Taguchi optimization of dibenzothiophene biodesulfurization by *Rhodococcus erythropolis* R1 immobilized cells in a biphasic system. *International Biodeterioration & Biodegradation*, *86*, 343–348. doi:10.1016/j.ibiod.2013.10.006

Desai, J. D., & Banat, I. M. (1997). Microbial production of surfactants and their commercial potential. *Microbiology and Molecular Biology Reviews*, *61*(1), 47–64. PMID:9106364

Deshpande, A., Bassi, A., & Prakash, A. (2004). Ultrasound-Assisted, Base-Catalyzed Oxidation of 4,6-Dimethyldibenzothiophene in a Biphasic Diesel−Acetonitrile System. *Energy & Fuels*, *19*(1), 28–34. doi:10.1021/ef0340965

Di Giuseppe, A., Crucianelli, M., De Angelis, F., Crestini, C., & Saladino, R. (2009). Efficient oxidation of thiophene derivatives with homogeneous and heterogeneous MTO/H2O2 systems: A novel approach for oxidative desulfurization (ODS) of diesel fuel. *Applied Catalysis B: Environmental*, *89*(1-2), 239–245. doi:10.1016/j.apcatb.2009.02.009

Díaz de León, J. N., Picquart, M., Massin, L., Vrinat, M., & de los Reyes, J. A. (2012). Hydrodesulfurization of sulfur refractory compounds: Effect of gallium as an additive in NiWS/-Al_2O_3 catalysts. *Journal of Molecular Catalysis A Chemical*, *363–364*, 311–321. doi:10.1016/j.molcata.2012.07.006

Dinamarca, A. M., Orellana, L., Aguirre, J., Baeza, P., Espinoza, G., Canales, C., & Ojeda, J. (2014). Biodesulfurization of dibenzothiophene and gas oil using a bioreactor containing a catalytic bed with Rhodococcus rhodochrous immobilized on silica. *Biotechnology Letters*, *36*(8), 1649–1652. doi:10.1007/s10529-014-1529-y PMID:24748430

Dinamarca, M. A., Ibacache-Quiroga, C., Baeza, P., Galvez, S., Villarroel, M., Olivero, P., & Ojeda, J. (2010). Biodesulfurization of gas oil using inorganic supports biomodified with metabolically active cells immobilized by adsorption. *Bioresource Technology*, *101*(7), 2375–2378. doi:10.1016/j.biortech.2009.11.086 PMID:20034786

Dinamarca, M. A., Rojas, A., Baeza, P., Espinoza, G., Ibacache-Quiroga, C., & Ojeda, J. (2014). Optimizing the biodesulfurization of gas oil by adding surfactants to immobilized cell systems. *Fuel*, *116*, 237–241. doi:10.1016/j.fuel.2013.07.108

Ding, B., Kim, H. Y., Lee, S. C., Shao, C. L., Lee, D. R., Park, S. J., & Choi, K. J. et al. (2002). Preparation and characterization of a nanoscale poly(vinyl alcohol) fiber aggregate produced by an electrospinning method. *Journal of Polymer Science. Part B, Polymer Physics*, *40*(13), 1261–1268. doi:10.1002/polb.10191

Ding, B., Kimura, E., Sato, T., Fujita, S., & Shiratori, S. (2004). Fabrication of blend biodegradable nanofibrous nonwoven mats via multi-jet electrospinning. *Polymer*, *45*(6), 1895–1902. doi:10.1016/j.polymer.2004.01.026

Ding, F., Larsson, P., Larsson, J. A., Ahuja, R., Duan, H. M., Rosen, A., & Bolton, K. (2008). The importance of strong carbon-metal adhesion for catalytic nucleation of single-walled carbon nanotubes. *Nano Letters*, *8*(2), 63–68. doi:10.1021/nl072431m PMID:18162001

Ding, M., Tang, Y., & Star, A. (2012). Understanding Interfaces in Metal–Graphitic Hybrid Nanostructures. *The Journal of Physical Chemistry Letters*, *4*(1), 147–160. doi:10.1021/jz301711a

Djangkung, S., Murti, S., Yang, H., Choi, K., Kora, Y., & Mochida, I. (2003). Influences of nitrogen species on the hydrodesulfurization reactivity of a gas oil over sulfide catalysts of variable activity. *Applied Catalysis A, General*, *252*(2), 331–346. doi:10.1016/S0926-860X(03)00468-X

Dolan, M. D., Ilyushechkin, A. Y., Mclennan, K. G., & Sharma, S. D. (2012). Sulfur removal from coal-derived syngas : Thermodynamic considerations and review. *Asia-Pacific Journal of Chemical Engineering*, *7*(1), 1–13. doi:10.1002/apj.528

Dolbear, G. E., & Skov, E. R. (2000). Selective Oxidation as a route to petroleum desulfurization. *American Chemical Society Division of Petroleum Chemistry*, *45*, 375–378.

Dong, L., Duckett, S. B., Ohman, K. F., & Jones, W. D. (1992). A Model for Homogeneous Hydrodesulfurization: The importance of η2-Coordination and Sulfur Coordination in C-H and C-S bond Cleavage Reactions of Thiophene. *Journal of the American Chemical Society*, *114*, 151–160.

Doshi, J., & Reneker, D. H. (1995). Electrospinning process and applications of electrospun fibers. *Journal of Electrostatics*, *35*(2-3), 151–160. doi:10.1016/0304-3886(95)00041-8

Douabul, A., & Riley, J. (1979). Solubility of Sulfur Dioxide in distilled water and decarbonated sea water. *Journal of Chemical & Engineering Data*, *24*(4), 274–276. doi:10.1021/je60083a014

Dou, B., Byun, Y.-C., & Hwang, J. (2008). Flue gas desulfurization with an electrostatic spraying absorber. *Energy & Fuels*, *22*(2), 1041–1045. doi:10.1021/ef700646c

Dou, B., Pan, W., Jin, Q., Wang, W., & Li, Y. (2009). Prediction of SO_2 removal efficiency for wet Flue Gas Desulfurization. *Energy Conversion and Management*, *50*(10), 2547–2553. doi:10.1016/j.enconman.2009.06.012

Dragan, S., & Ozunu, A. (2012). Characterization of calcium carbonates used in wet flue gas desulphurization processes. *Central European Journal of Chemistry*, *10*(5), 1556–1564. doi:10.2478/s11532-012-0068-4

Dreizler, R. M., & Gross, E. K. U. (1990). *Density functional theory*. Berlin: Springer. doi:10.1007/978-3-642-86105-5

Dribinskii, A. V., Tarasevich, M. R., & Kazarinov, V. E. (1989). Electrocatalysis on carbon materials. *Materials Chemistry and Physics*, *22*(3-4), 377–400. doi:10.1016/0254-0584(89)90006-0

Druker, S. H., & Curtis, M. D. (1995). Activation of C-S Bond Homolysis by Coordination to a Mo/Co/S-Conatining Cluster. *Journal of the American Chemical Society*, *117*(23), 6366–6367. doi:10.1021/ja00128a030

Drushel, H. V. (1970). Sulfur compounds in petroleum - known and unknown. *ACS Div. of Petroleum Chemistry Preprints*, *15*(2), C12–C42.

Duan, B., Dong, C. H., Yuan, X. Y., & Yao, K. D. (2004). Electrospinning of chitosan solutions in acetic acid with poly(ethylene oxide). *Journal of Biomaterials Science. Polymer Edition*, *15*(6), 797–811. doi:10.1163/156856204774196171 PMID:15255527

Duan, L., Sun, H., Zhao, C., Zhou, W., & Chen, X. (2014). Coal combustion characteristics on an oxy-fuel circulating fluidized bed combustor with warm flue gas recycle. *Fuel*, *127*, 47–51. doi:10.1016/j.fuel.2013.06.016

Dube, G., Osifo, P., & Rutto, H. (2013). *Preparation of bagasse ash/CaO/ammonium acetate sorbent and modelling their desulphurization reaction*. Clean Techn Environ Policy; doi:10.1007/s10098-013-0681-8

Du, Q., Zhao, H., Ming, L., Gao, J., Zhao, G., & Wu, S. (2011). Experimental Investigation on the Kinetics of NO Complex Absorption through Fe II EDTA Solvent in a Double-Stirred Reactor. *Industrial & Engineering Chemistry Research*, *50*(8), 4425–4431. doi:10.1021/ie102501h

Dutta Majumdar, R., Gerken, M., Mikula, R., & Hazendonk, P. (2013). Validation of the Yen–Mullins Model of Athabasca Oil-Sands Asphaltenes using Solution-State1H NMR Relaxation and 2D HSQC Spectroscopy. *Energy & Fuels*, *27*(11), 6528–6537. doi:10.1021/ef401412w

Dzenis, Y. (2004). Spinning continuous fibers for nanotechnology. *Science*, 304, 1917-1919. EPA sulfur distribution. Retrieved January 28, 2013, from http://www.eia.gov/todayinenergy/detail.cfm?id=7110

Ebbesen, T. W., & Ajayan, P. M. (1992). Large scale synthesis of carbon nanotubes. *Nature*, *358*(6383), 220–222. doi:10.1038/358220a0

Ebbesen, T. W., Hiura, H., Bisher, M. E., Treacy, M. M. J., Shreeve-Keyer, J. L., & Haushalter, R. C. (1996). Decoration of carbon nano tubes. *Advanced Materials*, *8*(2), 155–157. doi:10.1002/adma.19960080212

Ebrahimi, S., Picioreanu, C., Kleerebezem, R., Heijnen, J. J., & van Loosdrecht, M. C. M. (2003). Rate-based modelling of SO_2 absorption into aqueous $NaHCO_3/Na_2CO_3$ solutions accompanied by the desorption of CO_2. *Chemical Engineering Science*, *58*(16), 3589–3600. doi:10.1016/S0009-2509(03)00231-8

Eden, D., & Luckas, M. (1998). A heat and mass transfer model for the simulation of the wet limestone flue gas scrubbing process. *Chemical Engineering & Technology*, *21*(1), 56–60. doi:10.1002/(SICI)1521-4125(199801)21:1<56::AID-CEAT56>3.0.CO;2-9

Edwards, R. S., & Coleman, K. S. (2013). Graphene film growth on polycrystalline metals. *Accounts of Chemical Research*, *46*(1), 23–30. doi:10.1021/ar3001266 PMID:22891883

Eglington, T. I., Irvine, J. E., Vairavamurthy, A., Zhou, W., & Manowitz, B. (1994). Formation and diagenesis of macromolecular organic sulfur in Peru margin sediments. *Organic Geochemistry*, *22*(3-5), 781–799. doi:10.1016/0146-6380(94)90139-2

Egorova, M., & Prins, R. (2004). Hydrodesulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene over sulfided NiMo/γ-Al_2O_3, CoMo/γ-Al_2O_3, and Mo/γ-Al_2O_3 catalysts. *Journal of Catalysis*, *225*(2), 417–427. doi:10.1016/j.jcat.2004.05.002

Ehhalt, D. H. (1999). Photooxidation of trace gases in the troposphere Plenary Lecture. *Physical Chemistry Chemical Physics*, *1*(24), 5401–5408. doi:10.1039/a905097c

Electric Power Research Institute (EPRI). (2001). *Alternative By-Products from Flue Gas Desulfurization Systems: Utilization of Clean Coal By-Products from SO_2 Control Process*. Retrieved from www.epri.com/abstracts/Pages/ProductAbstract.aspx?ProductId=000000000001004611

Electric Power Research Institute (EPRI). (2006). *Flue Gas Desulfurization (FGD) Wastewater Characterization: Screening Study*. Retrieved from http://www.epri.com/abstracts/Pages/ProductAbstract.aspx?ProductId=000000000001010162

Electric Power Research Institute (EPRI). (2006). *SO_3 Mitigation: Current Utility Operating Experience*. Retrieved from http://www.epri.com/abstracts/Pages/ProductAbstract.aspx?ProductId=000000000001010754

Electric Power Research Institute (EPRI)EPRI. (2007). *Use of Flue Gas Desulfurization Products in Agricultural Applicatio*ns. Retrieved from http://www.epri.com/abstracts/Pages/ProductAbstract.aspx?ProductId=000000000001012698

Elmolla, E. S., Chaudhure, M., & Eltoukhy, M. M. (2010). The use of artificial neural network (ANN) for modeling of COD removal from antibiotic aqueous solution by fenton process. *Journal of Hazardous Materials*, *179*(1-3), 127–134. doi:10.1016/j.jhazmat.2010.02.068 PMID:20307930

El-Newehy, M.H., Al, D.S.S., Kenawy, E.R., & Abdel, M.A. (2011) Nanospider technology for the production of nylon 6-nanofibers for biomedical applications. *Journal of Nanomaterial* 1-8.

Emtsev, K. V., Bostwick, A., Horn, K., Jobst, J., Kellogg, G. L., & Ley, L. et al. (2009). Towards wafersize graphene layers by atmospheric pressure graphitization ofsilicon carbide. *Nature Materials*, *8*(3), 203–207. doi:10.1038/nmat2382 PMID:19202545

EORC. (2000, June 29-30). Paper presented at the European Oil Refining Conference Exhibition, Berlin, Germany.

Erga, O. (1980). SO_2 Recovery by a sodium citrate solution scrubbing. *Chemical Engineering Science*, *35*(1-2), 162–169. doi:10.1016/0009-2509(80)80083-2

Espinoza-Armenta, Y., Cruz-Reyes, J., Paraguay-Delgado, F., Del Valle, M., Alonso, G., Fuentes, S., & Romero-Rivera, R. (2014). CoMoW sulfide nanocatalysts for the HDS of DBT from novel ammonium and alkyltrimethylammonium-thiomolybdate-thiotungstate-cobaltate (II) precursors. *Applied Catalysis A, General*, *486*, 62–68. doi:10.1016/j.apcata.2014.08.017

European Environment Agency. (2014). *Air Quality in Europe*, Retrieved from http://www.eea.europa.eu/publications/air-quality-in-europe-2013

Eustis, S., & El-Sayed, M. A. (2006). Why gold nanoparticles are more precious than pretty gold: Noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes. *Chemical Society Reviews*, *35*(3), 209–217. doi:10.1039/B514191E PMID:16505915

Eyssautier, J., Levitz, P., Espinat, D., Jestin, J., Gummel, J., Grillo, I., & Barre, L. (2011). Insight into asphaltene nanoaggregate structure inferred by small angle neutron and X-ray scattering. *The Journal of Physical Chemistry B*, *115*(21), 6827–6837. doi:10.1021/jp111468d PMID:21553910

Faghihian, H., & Naeemi, S. (2013). Application of a Novel Nanocomposite for Desulfurization of a Typical Organo Sulfur Compound. *Iran. J. Chem. Chem. Eng.,* 32(3).

Fang, Y., & Hu, H. (2007). Mesoporous TS-1: Nano casting synthesis with CMK-3 as template and its performance in catalytic oxidation of aromatic thiophene. *Catalysis Communications*, *8*(5), 817–820. doi:10.1016/j.catcom.2006.09.018

Fan, J., Wang, G., Sun, Y., Xu, C., Zhou, H., Zhou, G., & Gao, J. (2010). Research on reactive adsorption desulfurization over $Ni/ZnO\text{-}SiO_2\text{-}Al_2O_3$ adsorbent in a fixed-fluidized bed reactor. *Industrial & Engineering Chemistry Research*, *49*(18), 8450–8460. doi:10.1021/ie100923v

Farag, H., Whitehurst, D. D., Skanishi, K., & Mochida, I. (1999). Carbon versus alumina as a support for Co–Mo catalysts reactivity towards HDS of dibenzothiophenes and diesel fuel. *Catalysis Today*, *50*(1), 9–17. doi:10.1016/S0920-5861(98)00476-3

Fariba, G., Vasheghani-Farahani, S., & Vasheghani-Farahani, E. (2010). Theoretical description of hydrogel swelling: A review. *Iranian Polymer Journal*, *19*, 375–398.

Fazaeli, R., Aliyan, H., Moghadam, M., & Masoudinia, M. (2013). Nano-rod catalysts: Building MOF bottles (MIL-101 family as heterogeneous single-site catalysts) around vanadium oxide ships. *Journal of Molecular Catalysis A Chemical*, *374*, 46–52. doi:10.1016/j.molcata.2013.03.020

Feng, J., Zeng, Y., Ma, C., Cai, X., Zhang, Q., & Tong, M. et al. (2006). The surfactant tween 80 enhances biodesulfurization. *Applied and Environmental Microbiology*, *72*(11), 7390–7393. doi:10.1128/AEM.01474-06 PMID:16980422

Feng, Q., Krautscheid, H., Rauchfuss, T. B., Skaugset, A. E., & Venturelli, A. (1995). Thermal Fragmentation of Acyl Thiolato Complexes to Reactive Metal Sulfido Intermediates. Structure of Ru (η^6-SC_3Me_3COMe) $(PPh_3)_2$. *Organometallics*, *14*(1), 297–304. doi:10.1021/om00001a043

Feux, A. N. (1977). The use of stable carbon isotopes in hydrocarbon exploration. *J. Geochem. Res.*, *7*, 155–188. doi:10.1016/0375-6742(77)90080-2

Figueras, F., Palomeque, J., Loridant, S., Feche, C., Essayem, N., & Gelbard, G. (2004). Influence of the coordination on the catalytic properties of supported W catalysts. *Journal of Catalysis*, *226*(1), 25–31. doi:10.1016/j.jcat.2004.05.006

Foght, J. M. (2004). Whole-cell bio-processing of aromatic compounds in crude oil and fuels. In R. Vazquez-Duhalt & R. Quintero-Ramirez (Eds.), Petroleum biotechnology: Developments and perspectives (Amsterdam., pp. 145–176). Amsterdam: Elsevier. doi:10.1016/S0167-2991(04)80146-0

Folsom, B. R., Meyer, T. A., & Yu, L. Q. (1998). *U.S. Patent No. 5,772,901*. Washington, DC: U.S. Patent and Trademark Office.

Fong, H., Chun, I., & Reneker, D. H. (1999). Beaded nanofibers formed during electrospinning. *Polymer*, *40*(16), 4585–4592. doi:10.1016/S0032-3861(99)00068-3

Ford, J. F., Rayne, T. A., & Adlington, D. G. (1967). Desulfurization of hydrocarbons using oxidative and hydrotreatments. *US Patent*, 3341448.

Forte, P. (1996). Process for the Removal of Sulfur from Petroleum Fractions. *US Patent*, 5582714.

Forte, P. (1996). US Patents 5582714.

Frandsen, J. B. W., Kiil, S., & Johnsson, J. E. (2001). Optimisation of a wet FGD pilot plant using fine limestone and organic acids. *Chemical Engineering Science*, *56*(10), 3275–3287. doi:10.1016/S0009-2509(01)00010-0

Freese, E. (1920). Absorption of sulfur dioxide by water. *Wochbl. Papierfabr.*, 51(861).

Freundlich, H. M. F. (1906). Over the adsorption in solution. *Journal of Physical Chemistry*, *57*, 385–471.

Froment, G. F., & Delmon, B. (1987). *Catalyst Deactivation 1987*. Elsevier Science.

Fuchs, W. (1931). *Die Chemie der Kohle*. Berlin: Springer. doi:10.1007/978-3-642-91582-6

Fukunaga, T., Katsuno, H., Matsumoto, H., Takahashi, O., & Akai, Y. (2003). Development of kerosene fuel processing system for PEFC. *Catalysis Today*, *84*(3-4), 197–200. doi:10.1016/S0920-5861(03)00274-8

Funakashi, I., & Aida, T. (2002). EP 711 819 B1.

Funakoshi, I. & Aida, T. (1998). US Patents 5753102. U. Patents.

Funakoshi, I., & Aida, T. (1998). Process for recovering organic sulfur compounds from fuel oil. *US Patent,* 5753102.

Furimsky, E. (1996). Spent refinery catalysts: Environment, safety and utilization. *Catalysis Today*, *30*(4), 223–286. doi:10.1016/0920-5861(96)00094-6

Gabay, J., Dietz, S., Bernatis, P., & DuBois, M. R. (1993). Dinuclear cyclopentadienylmolybdenum complexes containing thioether ligands. Ligand substitution and desulfurization reactions. *Organometallics*, *12*(9), 3630–3635. doi:10.1021/om00033a040

Gal'pern, G. D. (1971). Organic sulfides in petroleum. *Intl. J. Sulfur Chem.*, *6*, 115.

Gallagher, J. R., Olson, E. S., & Stanley, D. C. (1993). Microbial desulfurization of dibenzothiophene: A sulfur-specific pathway. *FEMS Microbiology Letters*, *107*(1), 31–35. doi:10.1111/j.1574-6968.1993.tb05999.x PMID:8467997

Gao, H., Li, C., Zeng, G., Zhang, W., Shi, L., & Fan, X. et al. (2011). Experimental study of wet flue gas desulphurization with a novel type PCF device. *Chemical Engineering and Processing: Process Intensification*, *50*(2), 189–195. doi:10.1016/j.cep.2010.12.011

Gao, H., Luo, M., Xing, J., Wu, Y., Li, Y., & Li, W. et al. (2008). Desulfurization of Fuel by Extraction with Pyridinium-Based Ionic Liquids. *Industrial & Engineering Chemistry Research*, *47*(21), 8384–8388. doi:10.1021/ie800739w

Gao, J., Wang, S., Jiang, Z., Lu, H., Yang, Y., Jing, F., & Li, C. (2006). Deep desulfurization from fuel oil via selective oxidation using an amphiphilic peroxotungsten catalyst assembled in emulsion droplets. *Journal of Molecular Catalysis A Chemical*, *258*(1–2), 261–266. doi:10.1016/j.molcata.2006.05.058

Garcia, C. L., Becchi, M., Grenier-Loustalot, O., & Szymanski, R. (2002). Analysis of aromatic sulfur compounds in gas oils using GC with sulfur chemiluminescence detection and high-resolution MS. *Analytical Chemistry*, *74*(15), 3849–3857. doi:10.1021/ac011190e PMID:12175175

García-Gutiérrez, J. L., Fuentes, G. A., Hernández-Terán, M. E., Murrieta, F., Navarrete, J., & Jiménez-Cruz, F. (2006). Ultra-deep oxidative desulfurization of diesel fuel with H_2O_2 catalyzed under mild conditions by polymolybdates supported on Al_2O_3. *Applied Catalysis A*, *305*(1), 15–20. doi:10.1016/j.apcata.2006.01.027

Gatan, R., Barger, P., Gembicki, V., Cavanna, A., & Molinari, D. (2004). Oxidative desulfurization: A new technology for U LSD. *American Chemical Society Fuel Chemistry*, *49*, 577–579.

Gates, B. C., Katzer, J. R., & Schuit, G. C. A. (1979). *Chemistry of catalytic processes*. McGraw-Hill.

Gates, B. C., Katzer, J. R., & Schuit, G. C. A. (1979). *Chemistry of Catalytic Processes*. New York: McGraw-Hill.

Gates, B. C., & Topsøe, H. (1997). Reactivities in deep catalytic hydrodesulfurization: Challenges, opportunities, and the importance of 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene. *Polyhedron*, *16*(18), 3213–3217. doi:10.1016/S0277-5387(97)00074-0

Geim, A. K. (2009). Graphene: Status and prospects. *Science*, *324*(5934), 1530–1534. doi:10.1126/science.1158877 PMID:19541989

Geim, A. K., & Novoselov, K. S. (2007). The rise of graphene. *Nature Materials*, *6*(3), 183–191. doi:10.1038/nmat1849 PMID:17330084

Geng, X. Y., Kwon, O. H., & Jang, J. H. (2005). Electrospinning of chitosan dissolved in concentrated acetic acid solution. *Biomaterials*, *26*(27), 5427–5432. doi:10.1016/j.biomaterials.2005.01.066 PMID:15860199

George, G. N., & Gorbaty, M. L. (1989). Sulfur K-edge absorption spectroscopy of petroleum asphaltenes and model compounds. *Journal of the American Chemical Society*, *111*(9), 3182–3186. doi:10.1021/ja00191a012

Ghenciu, A. F. (2002). Review of fuel processing catalysts for hydrogen production in PEM fuel cell systems. *Current Opinion in Solid State and Materials Science*, *6*(5), 389–399. doi:10.1016/S1359-0286(02)00108-0

Girgis, M. J., & Gates, B. C. (1991). Reactivities, reaction networks, and kinetics in high-pressure catalytic hydroprocessing. *Industrial & Engineering Chemistry Research*, *30*(9), 2021–2058. doi:10.1021/ie00057a001

Giroto, G. A., Guardani, R., Teixeira, A. C. S. C., & Nascimento, C. A. O. (2006). Study on the photophenton degradation of polyvininyl alcohol in aqueous solution. *Chemical Engineering and Processing*, *45*(7), 523–532. doi:10.1016/j.cep.2005.12.001

Glasson, C., Geantet, C., Lacroix, M., Labruyere, M., & Dufresne, P. (2002). Beneficial Effect of Carbon on Hydrotreating Catalysts. *Journal of Catalysis*, *212*(1), 76–85. doi:10.1006/jcat.2002.3781

Gochi, Y., Ornelas, C., Paraguay, F., Fuentes, S., Alvarez, L., Rico, J. L., & Alonso-Núñez, G. (2005). Effect of sulfidation on Mo-W-Ni trimetallic catalysts in the HDS of DBT. *Catalysis Today*, *107-108*, 531–536. doi:10.1016/j.cattod.2005.07.068

Goh, L. Y., Weng, Z., Leong, W. K., & Leung, P. H. (2001). C−S Bond Cleavage and C−C Coupling in Cyclopentadienylchromium Complexes To Give the First Dithiooxamide-Bridged and Doubly Dithiocarbamate-Bridged Double Cubanes: $[\mathrm{Cp_6Cr_8S_8\{(C(S)NEt_2)_2\}}]$ and $[\mathrm{Cp_6Cr_8S_8(S_2CNEt_2)_2}]$). *Angewandte Chemie International Edition*, *40*(17), 3236–3239. doi:10.1002/1521-3773(20010903)40:17<3236::AID-ANIE3236>3.0.CO;2-#

Gokel, G. W., Gerdes, H. M., & Dishong, D. M. (1980). Sulfur Heterocycles. 3. Heterogeneous, Phase Transfer and Acid Catalyzed Potassium Permanganate Oxidation of Sulfides to Sulfones and a Survey of their C-13 NMR Spectra. *The Journal of Organic Chemistry*, *45*, 3634–3639. doi:10.1021/jo01306a019

Gómez, A., Fueyo, N., & Tomás, A. (2007). Detailed modelling of a flue-gas desulfurisation plant. *Computers & Chemical Engineering*, *31*(11), 1419–1431. doi:10.1016/j.compchemeng.2006.12.004

Gongshin, Q. (2006). Ph.D. Dissertation, University of Michigan.

González-Cortés, S. L., Rugmini, S., Xiao, T., Green, M. L. H., Rodulfo-Baechler, S. M., & Imbert, F. E. (2014). Deep hydrotreating of different feedstocks over a highly active Al_2O_3-supported NiMoW sulfide catalyst. *Applied Catalysis A, General*, *475*, 270–281. doi:10.1016/j.apcata.2014.01.045

Gonzalez-Sanchez, A., & Revah, S. (2006). Product recovery from H_2S containing gases. In P. N. L. Lens, C. Kennes, P. LeCloirec, & M. Deshusses (Eds.), *Waste gas treatment for resource recovery* (pp. 399–406). London, UK: IWA Publishing.

Goots, T. R., De Pero, M. J., & Nolan, P. S. (1992). *Demonstration Project Extension and Coolside Demonstration*. Retrieved from http://netl.doe.gov/File%20Library/Research/Coal/major%20demonstrations/cctdp/Round1/000000A7.pdf

Goubin, S., Huaiying, Z., Weiquan, C., Jianmin, X., & Huizhou, L. (2005). Improvement of biodesulfurization rate by assembling nanosorbents on the surfaces of microbial cells. *Biophysical Journal*, *89*(6), L58–L60. doi:10.1529/biophysj.105.073718 PMID:16258046

Gransch, J. A., & Posthuma, J. (1974). *On the oriqin of sulfur in crudes*, Adv. In B. Tissot & F. Bienner (Eds.), *Org. Geochemistry* (Vol. 727). Paris: Editions Technip.

Gray, K. A., Mrachko, G. T., & Squires, C. H. (2003). Biodesulfurization of fossil fuels. *Current Opinion in Microbiology*, *6*(3), 229–235. doi:10.1016/S1369-5274(03)00065-1 PMID:12831898

Gray, M. R., Ayasse, A. R., Chan, E. W., & Veljkovic, M. (1995). Kinetics of Hydrodesulfurization of Thiophenic and Sulfide Sulfur in Athabasca Bitumen. *Energy & Fuels*, *9*(3), 500–506. doi:10.1021/ef00051a015

Groenzin, H., & Mullins, O. C. (1999). Asphaltene molecular size and structure. *The Journal of Physical Chemistry A*, *103*(50), 11237–11245. doi:10.1021/jp992609w

Groenzin, H., & Mullins, O. C. (2000). Molecular sizes of asphaltenes from different origin. *Energy & Fuels*, *14*, 677. doi:10.1021/ef990225z

Grossman, M. J., Siskin, M., Ferrughelli, D. T., Lee, M. K., & Senius, J. D. (1999). *US Patent No. 5910440.*

Gruse, W. A., & Stevens, D. R. (1960). Chemical technology of petroleum. (3rd ed.). New York: Mc. Graw Hill.

Guchhait, S., Biswas, D., Bhattacharya, P., & Chowdhury, R. (2005a). Bio-desulfurization of model organo-sulfur compounds and hydrotreated diesel - Experiments and modelling. *Chemical Engineering Journal*, *112*(1-3), 145–151. doi:10.1016/j.cej.2005.05.006

Guchhait, S., Biswas, D., Bhattacharya, P., & Chowdhury, R. (2005b). Bi-phasic bio-conversion of sulfur present in model organo-sulfur compounds and hydro-treated diesel. *Catalysis Today*, *106*(1-4), 233–237. doi:10.1016/j.cattod.2005.07.137

Gui, X., Wei, J., Wang, K., Cao, A., Zhu, H., & Jia, Y. et al. (2010). Carbon Nanotube Sponges. *Advanced Materials*, *22*(5), 617–621. doi:10.1002/adma.200902986 PMID:20217760

Gunam, I. B. W., Sujaya, I. N., Aryanta, W. R., Tomita, F., & Asano, K. (2013). Biodesulfurization of dibenzothiophene and its derivatives using resting and immobilized cells of *Sphingomonas subarctica* T7b. *Journal of Microbiology and Biotechnology*, *23*(4), 473–482. doi:10.4014/jmb.1207.07070 PMID:23568201

Guobin, S., Jianmin, X., Huaiying, Z., & Huizhou, L. (2005). Deep desulfurization of hydrodesulfurized diesel oil by *Pseudomonas delafieldii* R-8. *Journal of Chemical Technology & Biotechnology, 80*(4), 420–424. doi:10.1002/jctb.1197

Guobin, S., Huaiying, Z., Jianmin, X., Guo, C., Wangliang, L., & Huizhou, L. (2006). Biodesulfurization of hydrodesulfurized diesel oil with *Pseudomonas delafieldii* R-8 from high density culture. *Biochemical Engineering Journal*, *27*(3), 305–309. doi:10.1016/j.bej.2005.07.003

Guobin, S., Jianmin, X., Chen, G., Huizhou, L., & Jiayong, C. (2005). Biodesulfurization using *Pseudomonas delafieldii* in magnetic polyvinyl alcohol beads. *Letters in Applied Microbiology*, *40*(1), 30–36. doi:10.1111/j.1472-765X.2004.01617.x PMID:15612999

Guo, L., Zhang, J., Hu, F., Dy Ryu, D., & Bao, J. (2013). Consolidated bioprocessing of highly concentrated Jerusalem artichoke tubers for simultaneous saccharification and ethanol fermentation. *Biotechnology and Bioengineering*, *110*(10), 2606–2615. doi:10.1002/bit.24929 PMID:23568827

Guo, R.-T., Pan, W.-G., Zhang, X.-B., Xu, H.-J., & Ren, J.-X. (2011). Dissolution rate of magnesium hydrate for wet flue gas desulfurization. *Fuel*, *90*(1), 7–10. doi:10.1016/j.fuel.2010.08.016

Guo, W., Wang, C., Lin, P., & Lu, X. (2011). Oxidative desulfurization of diesel with TBHP/isobutyl aldehyde/air oxidation system. *Applied Energy*, *88*(1), 175–179. doi:10.1016/j.apenergy.2010.08.003

Guo, X.-L., Deng, G., Xu, J., & Wang, M.-X. (2006). Immobilization of *Rhodococcus* sp. AJ270 in alginate capsules and its application in enantioselective biotransformation of trans-2-methyl-3-phenyl-oxiranecarbonitrile and amide. *Enzyme and Microbial Technology*, *39*(1), 1–5. doi:10.1016/j.enzmictec.2005.01.044

Gupta, N., Roychoudhury, P. K., & Deb, J. K. (2005). Biotechnology of desulfurization of diesel: Prospects and challenges. *Applied Microbiology and Biotechnology*, *66*(4), 356–366. doi:10.1007/s00253-004-1755-7 PMID:15538557

Gupta, P., Elkins, C., Long, T. E., & Wilkes, G. L. (2005). Electrospinning of linear homopolymers of poly(methyl methacrylate): Exploring relationships between fiber formation, viscosity, molecular weight and concentration in a good solvent. *Polymer*, *46*(13), 4799–4810. doi:10.1016/j.polymer.2005.04.021

Gutiérrez Ortiz, F. J., & Ollero, P. (2001). A pilot plant technical assessment of an advanced in-duct desulphurisation process. *Journal of Hazardous Materials*, *83*(3), 197–218. doi:10.1016/S0304-3894(00)00364-2 PMID:11348732

Gutiérrez Ortiz, F. J., & Ollero, P. (2003). Flue-Gas Desulfurization in an Advanced in-Duct Desulfurization Process: An Empirical Model from an Experimental Pilot-Plant Study. *Industrial & Engineering Chemistry Research*, *42*(25), 6625–6637. doi:10.1021/ie030185t

Gutiérrez Ortiz, F. J., Vidal, F., Ollero, P., Salvador, L., Cortés, V., & Giménez, A. (2006). Pilot-plant technical assessment of wet flue gas desulfurization using limestone. *Industrial & Engineering Chemistry Research*, *45*(4), 1466–1477. doi:10.1021/ie051316o

Guzmán, M. A., Huirache-Acuña, R., Loricera, C. V., Hernández, J. R., Díaz de León, J. N., de los Reyes, J. A., & Pawelec, B. (2013). Removal of refractory S-containing compounds from liquid fuels over P-loaded NiMoW/SBA-16 sulfide catalysts. *Fuel*, *103*, 321–333. doi:10.1016/j.fuel.2012.07.005

Gyanesh, K. (2001). Sorbent composition, process for producing and use in desulfurization. *PCT Int. App1.* WO 0114051.

Gyanesh, P. Khare, R., D., Engelbert, & Cass, B. W. (2000). US Patents 6056871. U. Patents.

Hallensleben, M. L. (2000). *Polyvinyl compounds*, others. In *Ullmann's encyclopedia of industrial chemistry*. Weinheim: Wiley-VCH; doi:10.1002/14356007.a21_743

Han Y.-Z., & Leyshon D. W. (2005). U.S Patent No 2005109677.

Hanks, W. V., & McAdams, W. H. (1929). Studies in absorption. I-Very soluble gases. *Industrial & Engineering Chemistry*, *21*(1034).

Hansen, B. B., Fogh, F., Knudsen, N. O., & Kiil, S. (2011). Performance of a wet flue gas desulfurization pilot plant under oxy-fuel conditions. *Industrial & Engineering Chemistry Research*, *50*(8), 4238–4244. doi:10.1021/ie1022173

Hansen, B. B., & Kiil, S. (2012). Investigation of Parameters affecting Gypsum Dewatering Properties in a Wet Flue Gas Desulphurization Pilot Plant. *Industrial & Engineering Chemistry Research*, *51*(30), 10100–10107. doi:10.1021/ie3005435

Hansen, B. B., Kiil, S., Johnsson, J. E., & Sonder, K. B. (2008). Foaming in wet flue gas desulfurization plants: The influence of particles, electrolytes, and buffers. *Industrial & Engineering Chemistry Research*, *47*(9), 3239–3246. doi:10.1021/ie071660g

Hao, L., Benxian, S., & Zhou, X. (2005). An Improved Desulfurization Process Based on H2O2/Formic Acid Oxidation System Followed by Liquid-Liquid Extraction. Part 1. Coker Gas Oil Feedstocks. *Petroleum Science and Technology*, *23*(7-8), 991–999. doi:10.1081/LFT-200034498

Harb, F., Gérand, B., Nowogrocki, G., & Figlarz, M. (1989). Structural filiation between a new hydrate $MoO_{3.}$ ⅓H_2O and a new monoclinic form of MoO_3 obtained by dehydration. *Solid State Ionics*, *32-33*(Part 1), 84–90.

Harrison, R. M. (2007). *Principles of Environmental Chemistry*. RSC Publishing. doi:10.1039/9781847557780

Harris, S., & Chianelli, R. R. (1984). Catalysis by transition metal sulfides: The relation between calculated electronic trends and HDS activity. *Journal of Catalysis*, *86*(2), 400–412. doi:10.1016/0021-9517(84)90385-3

Harris, S., & Chianelli, R. R. (1986). Catalysis by transition metal sulfides: A theoretical and experimental study of the relation between the synergic systems and the binary transition metal sulfides. *Journal of Catalysis*, *98*(1), 17–31. doi:10.1016/0021-9517(86)90292-7

Hart, A. J., & Slocum, A. H. (2006). Rapid growth and flow-mediated nucleation of millimeter-scale aligned carbon nanotube structures from a thin-film catalyst. *The Journal of Physical Chemistry B*, *110*(16), 8250–8257. doi:10.1021/jp055498b PMID:16623503

Hartdegen, F. J., Coburn, J. M., & Roberts, R. L. (1984). Microbial desulfurization of petroleum. *Chemical Engineering Progress*, *80*, 63–67.

Hasan, Z., Jeon, J., Hwa Jhung, S. (2012). Oxidative desulfurization of benzothiophene and thiophene with WOx/ZrO2 catalysts: Effect of calcination temperature of catalysts. *Journal of Hazardous Materials,* 205–206, 216–221.

Hashimoto, S., & Furukawa, K. (1987). Immobilization of activated sludge by PVA–boric acid method. *Biotechnology and Bioengineering*, *30*(1), 52–59. doi:10.1002/bit.260300108 PMID:18576582

Haukanes, B.-I., & Kvam, C. (1993). Application of magnetic beads in bioassays. *Nature Biotechnology*, *11*(1), 60–63. doi:10.1038/nbt0193-60 PMID:7763485

Haupt, K. (2003). Molecularly imprinted polymers: The next generation. *Analytical Chemistry*, *75*(17), 376A–383A. doi:10.1021/ac031385h PMID:14632031

Heinrich G, & S, K. (2001). Hydrotreating. In Leprince, P., (Ed), *Petroleum Refining Conversion Processes,* (Vol. 3). Paris: Technip.

He, L., Li, H., Zhu, W., Guo, J., Jiang, X., Lu, J., & Yan, Y. (2008). Deep Oxidative Desulfurization of Fuels Using Peroxophosphomolybdate Catalysts in Ionic Liquids. *Industrial & Engineering Chemistry Research*, *47*(18), 6890–6895. doi:10.1021/ie800857a

Helveg, S., Lauritsen, J. V., Laegsgaard, E., Stensgaard, I., Nørskov, J., & Clausen, B. S. et al. (2000). Atomic-Scale Structure of Single-Layer MoS_2 Nanoclusters. *Physical Review Letters*, *84*(5), 951–954. doi:10.1103/PhysRevLett.84.951 PMID:11017413

Hensen, E. J. M., Brans, H. J. A., Lardinois, G. M. H. J., de Beer, V. H. J., Van Veen, J. A. R., & Van Santen, R. A. (2000). Periodic Trends in Hydrotreating Catalysis: Thiophene Hydrodesulfurization over Carbon-Supported 4*d* Transition Metal Sulfides. *Journal of Catalysis*, *192*(1), 98–107. doi:10.1006/jcat.2000.2824

Herm, Z. R., Wiers, B. M., Mason, J. A., van Baten, J. M., Hudson, M. R., & Zajdel, P. et al. (2013). Separation of hexane isomers in a metal-organic framework with triangular channels. *Science*, *24*(6135), 960–964. doi:10.1126/science.1234071 PMID:23704568

Herna'ndez-Maldonado, A. J., & Yang, R. T. (2004). New Sorbents for Desulfurization of Diesel Fuels via π-Complexation. *AIChE Journal. American Institute of Chemical Engineers*, *50*(4).

Hernandez-Maldonado, A. J., Qi, G., & Yang, R. T. (2005). Desulfurization of commercial fuels by p-complexation monolayer CuCl/g-Al_2O_3. *Applied Catalysis B: Environmental*, *61*(3-4), 212–218. doi:10.1016/j.apcatb.2005.05.003

Hernandez-Maldonado, A. J., Stamatis, S. D., Yang, R. T., He, A. Z., & Cannella, W. (2004). New sorbents for desulfurization of diesel fuels via pi-complexation: Layered beds and regeneration. *Industrial & Engineering Chemistry Research*, *43*(3), 769–776. doi:10.1021/ie034108+

Hernández-Maldonado, A. J., Yang, F. H., Qi, G., & Yang, R. T. (2005). Desulfurization of transportation fuels by π-complexation sorbents: Cu(I)-, Ni(II)-, and Zn(II)-zeolites. *Applied Catalysis B: Environmental*, *56*(1–2), 111–126. doi:10.1016/j.apcatb.2004.06.023

Hernández-Maldonado, A. J., & Yang, R. T. (2002). Desulfurization of Liquid Fuels by Adsorption via π Complexation with Cu(I)−Y and Ag−Y Zeolites. *Industrial & Engineering Chemistry Research*, *42*(1), 123–129. doi:10.1021/ie020728j

Hernandez-Maldonado, A. J., & Yang, R. T. (2003). Desulfurization of commercial liquid fuels by selective adsorption via pi-complexation with Cu(I)-Y zeolite. *Industrial & Engineering Chemistry Research*, 423103–423110.

Hernández-Maldonado, A. J., & Yang, R. T. (2004a). Denitrogenation of Transportation Fuels by Zeolites at Ambient Temperature and Pressure. *Angewandte Chemie International Edition*, *43*(8), 1004–1006. doi:10.1002/anie.200353162 PMID:14966892

Hernandez-Maldonado, A. J., & Yang, R. T. (2004a). Desulfurization of diesel fuels by adsorption via pi-complexation with vapor phase exchanged (VPIE) Cu(I)-Y zeolites. *Journal of the American Chemical Society*, *126*(4), 992–993. doi:10.1021/ja039304m PMID:14746446

Hernandez-Maldonado, A. J., & Yang, R. T. (2004b). Desulfurization of diesel fuels via pi-complexation with nickel(JI)-exchanged X- and Y-zeolites. *Industrial & Engineering Chemistry Research*, *43*(4), 1081–1089. doi:10.1021/ie034206v

Hernández-Maldonado, A. J., & Yang, R. T. (2004b). New sorbents for desulfurization of diesel fuels via π-complexation. *AIChE Journal. American Institute of Chemical Engineers*, *50*(4), 791–801. doi:10.1002/aic.10074

Hernandez, S. P., Fino, D., & Russo, N. (2010). High performance sorbents for diesel oil desulfurization. *Chemical Engineering Science*, *65*(1), 603–609. doi:10.1016/j.ces.2009.06.050

Hernandez, Y., Nicolosi, V., Lotya, M., Blighe, F. M., Sun, Z., & De, S. et al. (2008). High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature Nanotechnology*, *3*(9), 563–568. doi:10.1038/nnano.2008.215 PMID:18772919

Heunis, T. D. J., Botes, M., & Dicks, L. M. T. (2010). Encapsulation of *Lactobacillus plantarum* 423 and its bacteriocin in nanofibers. *Probiotics and Antimicrobial Proteins*, *2*(1), 46–51. doi:10.1007/s12602-009-9024-9

Heunis, T. D. J., & Dicks, L. M. T. (2010). Nanofibers offer alternative ways to the treatment of skin infections. *Journal of Biomedicine & Biotechnology*, *2010*, 1–10. doi:10.1155/2010/510682 PMID:20798871

Heunis, T., Bshena, O., Klumperman, B., & Dicks, L. (2011). Release of bacteriocins from nanofibers prepared with combinations of poly(D,L-lactide) (PDLLA) and poly(ethylene oxide) (PEO). *International Journal of Molecular Sciences*, *12*(12), 2158–2173. doi:10.3390/ijms12042158 PMID:21731433

He, Y.-C., Zhou, Q., Ma, C.-L., Cai, Z.-Q., Wang, L.-Q., & Zhao, X.-Y. et al. (2012). Biosynthesis of benzoylformic acid from benzoyl cyanide by a newly isolated *Rhodococcus* sp. CCZU10-1 in toluene–water biphasic system. *Bioresource Technology*, *115*, 88–95. doi:10.1016/j.biortech.2011.09.084 PMID:22033370

Higbie, R. (1935). The rate of absorption of a pure gas into a still liquid during short periods of exposure. *Transactions of American Institute of Chemical Engineers*, *31*, 365–389.

Hikita, H., Asai, S., & Takatsuka, T. (1972). Gas absorption with a two-step instantaneous chemical reaction. *The Chemical Engineering Journal*, *4*(1), 31–40. doi:10.1016/0300-9467(72)80050-9

Hirai, T., Ogawa, K., & Komasawa, I. (1996). *Desulfurization process for dibenzothiophenes from light oil by photochemical reaction and liquid-liquid extraction. Journal Name: Industrial and Engineering Chemistry Research; Journal Volume: 35; Journal Issue: 2; Other Information: PBD: Feb 1996, Medium: X* (pp. 586–589). Size.

Hirai, T., Shiraishi, Y., Ogawa, K., & Komasawa, I. (1997). Effect of Photosensitizer and Hydrogen Peroxide on Desulfurization of Light Oil by Photochemical Reaction and Liquid−Liquid Extraction. *Industrial & Engineering Chemistry Research*, *36*(3), 530–533. doi:10.1021/ie960576q

Hirasawa, K., Ishii, Y., Kobayashi, M., Koizumi, K., & Maruhashi, K. (2001). Improvement of desulfurization activity in *Rhodococcus erythropolis* KA2-5-1 by genetic engineering. *Bioscience, Biotechnology, and Biochemistry*, *65*(2), 239–246. doi:10.1271/bbb.65.239 PMID:11302154

Hizaddin, H. F., Hashim, M. A., & Anantharaj, R. (2013). Evaluation of molecular interaction in binary mixture of ionic liquids+ heterocyclic nitrogen compounds: Ab Initio method and COSMORS model. *Industrial & Engineering Chemistry Research*, *52*(50), 18043–18058. doi:10.1021/ie403032t

Hjuler, K., & Dam-Johansen, K. (1994). Wet oxidation of residual product from spray absorption of sulphur dioxide. *Chemical Engineering Science*, *49*(2424 PART A), 4515–4521. doi:10.1016/S0009-2509(05)80037-5

Hlincik, T., & Buryan, P. (2013). Desulfurization of boiler flue gas by means of activated calcium oxide. *Fuel Processing Technology*, *111*(0), 62–67. doi:10.1016/j.fuproc.2013.01.018

Hlincik, T., & Buryan, P. (2013). Evaluation of limestones for the purposes of desulphurisation during the fluid combustion of brown coal. *Fuel*, *104*(0), 208–215. doi:10.1016/j.fuel.2012.09.074

Hobson, G. D., & Petroleum, I. o. (1984). *Modern petroleum technology*. Wiley.

Ho, K. F., & Lee, S. C. (2002). Identification of atmospheric volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and carbonyl compounds in Hong Kong. *The Science of the Total Environment*, *289*(1-3), 145–158. doi:10.1016/S0048-9697(01)01031-2 PMID:12049391

Holbrey, J. D., López-Martín, I., Rothenberg, G., Seddon, K. R., Silveiro, G., & Zheng, X. (2008). Desulfurisation of oils using ionic liquids: Selection of cationic and anionic components to enhance extraction efficiency. *Green Chemistry*, *10*(1), 87–92. doi:10.1039/B710651C

Holmes, A. B., & Stephenson, G. R. (1994). Molecular imprinting. *Chemistry & Industry*, *18*, 304.

Homma, T., Echard, M., & Leglise, J. (2005). Investigation of CoNiMo/Al_2O_3 catalysts: Relationship between H_2S adsorption and HDS activity. *Catalysis Today*, *106*(1-4), 238–242. doi:10.1016/j.cattod.2005.07.187

Homs, N., Llorca, J., & de la Piscina, P. R. (2006). Low-temperature steam-reforming of ethanol over ZnO-supported Ni and Cu catalysts: The effect of nickel and copper addition to ZnO-supported cobalt-based catalysts. *Catalysis Today*, *116*(3), 361–366. doi:10.1016/j.cattod.2006.05.081

Honda, H., Sugiyama, H., Saito, I., & Kobayashi, T. (1998). High cell density culture of *Rhodococcus rhodochrous* by pH-stat feeding and dibenzothiophene degradation. *Journal of Fermentation and Bioengineering*, *85*(3), 334–338. doi:10.1016/S0922-338X(97)85685-1

Horii, Y., Onuki, H., Doi, S., Mori, T., Takatori, T., Sato, H., & Ookuro, T. & Sugawara., T. (1996). US Patents 5494572. U. Patents.

Horii, Y., Onuki, H., Doi, S., Mori, T., Takatori, T., Sato, H., et al. (1996). Desulfurization and denitration of light oil by extraction. *US Patent*, 5494572.

Ho, T. C. (2004). Deep HDS of diesel fuel: Chemistry and catalysis. *Catalysis Today*, *98*(1-2), 3–18. doi:10.1016/j.cattod.2004.07.048

Ho, T. C. (2008). Hydroprocessing catalysis on metal sulfides prepared from molecular complexes. *Catalysis Today*, *130*(1), 206–220. doi:10.1016/j.cattod.2007.06.076

Ho, T. C., Pan, W. H., Jacobson, A. J., & Chianelli, R. R. (2012). Hydroprocessing on chromium-containing metal sulfide catalysts. *Applied Catalysis A, General*, *421–422*, 38–47. doi:10.1016/j.apcata.2012.01.031

Houalla, M., Broderick, D. H., Sapre, A. V., Nag, N. K., de Beer, V. H. J., Gates, B. C., & Kwart, H. (1980). Hydrodesulfurization of methyl-substituted dibenzothiophenes catalyzed by sulfided Co-Mo/ γ-Al_2O_3. *Journal of Catalysis*, *61*(2), 523–527. doi:10.1016/0021-9517(80)90400-5

Houalla, M., Nag, N. K., Sapre, A. V., Borderick, D. H., & Gates, B. C. (1978). Hydrodesulfurization of dibenzothiophene catalyzed by sulfided CoO-$MoO_3\gamma$-Al_2O_3: The reaction network. *AIChE Journal. American Institute of Chemical Engineers*, *24*(6), 1015–1021. doi:10.1002/aic.690240611

Hou, X., & Zhuang, J. (Eds.). (2013). *Technology handbook of S-Zorb unit for desorption desulfurization of FCC gasoline*. Beijing, China: China Petrochemical Press.

Hrastel, I., Gerbec, M., & Stergaršek, A. (2007). Technology Optimization of Wet Flue Gas Desulfurization Process. *Chemical Engineering & Technology*, *30*(2), 220–233. doi:10.1002/ceat.200600314

Hsu, W. K.; Terrones, M.; Hare, J. P.; Terrones, H.; Kroto, H. W.; Walton, D. R. M. Electrochemical formation of carbon nanostructures. *Chemical Physics Lettters,* 262, 161-166.

Huaiying, Z., Guobin, S., & Huizhou, L., & JianMin, X. (2007). Surface modification of γ-Al_2O_3 nano-particles with gum arabic and its applications in adsorption and biodesulfurization. *Surface and Coatings Technology*, *201*(16), 6917–6921.

Huang, D., Wang, Y. J., Cui, Y. C., & Luo, G. S. (2008). Direct synthesis of mesoporous TiO2 and its catalytic performance in DBT oxidative desulfurization. *Microporous and Mesoporous Materials*, *116*(1-3), 378–385. doi:10.1016/j.micromeso.2008.04.031

Huang, D., Wang, Y. J., Yang, L. M., & Luo, G. S. (2006). Chemical Oxidation of Dibenzothiophene with a Directly Combined Amphiphilic Catalyst for Deep Desulfurization. *Industrial & Engineering Chemistry Research*, *45*(6), 1880–1885. doi:10.1021/ie0513346

Huang, D., Wang, Y. J., Yang, L. M., & Luo, G. S. (2006). Direct synthesis of mesoporous TiO2 modified with phosphotungstic acid under template free condition. *Microporous and Mesoporous Materials*, *96*(1-3), 301–306. doi:10.1016/j.micromeso.2006.06.040

Huang, L., Nagapudi, K., Apkarian, R. P., & Chaikof, E. L. (2001). Engineered collagen-PEO nanofibers and fabrics. *Journal of Biomaterials Science. Polymer Edition*, *12*, 979–993. doi:10.1163/156856201753252516 PMID:11787524

Huang, L., Qin, Z., Wang, G., Du, M., Ge, H., & Li, X. et al. (2010a). A detailed study on the negative effect of residual sodium on the performance of Ni/ZnO adsorbent for diesel fuel desulfurization. *Industrial & Engineering Chemistry Research*, *49*(10), 4670–4675. doi:10.1021/ie100293h

Huang, L., Wang, G., Qin, Z., Dong, M., Du, M., & Ge, H. et al. (2011). In situ XAS study on the mechanism of reactive adsorption desulfurization of oil product over Ni/ZnO. *Applied Catalysis B: Environmental*, *106*(1-2), 26–38.

Huang, L., Wang, G., Qin, Z., Dong, M., Du, M., & Ge, H. et al. (2011). In situ XAS study on the mechanism of reactive adsorption desulfurization of oil product over Ni/ZnO. *Applied Catalysis B: Environmental*, *106*, 26–38.

Huang, L., Wang, G., Qin, Z., Du, M., Dong, M., & Ge, H. et al. (2010b). A sulfur K-edge XANES study on the transfer of sulfur species in the reactive adsorption desulfurization of diesel oil over Ni/ZnO. *Catalysis Communications*, *11*(7), 592–596. doi:10.1016/j.catcom.2010.01.001

Huang, X., Qi, X., Boey, F., & Zhang, H. (2012). Graphene-based composites. *Chemical Society Reviews*, *41*(2), 666–686. doi:10.1039/C1CS15078B PMID:21796314

Huang, Z. M., Zhang, Y. Z., Kotaki, M., & Ramakrishna, S. (2003). A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Composites Science and Technology*, *63*(15), 2223–2253. doi:10.1016/S0266-3538(03)00178-7

Hua, R., Li, Y., Liu, W., Zheng, J., Wei, H., & Wang, J. et al. (2003). Determination of sulfur-containing compounds in diesel oils by comprehensive two-dimensional gas chromatography with a sulfur chemiluminescence detector. *Journal of Chromatography. A*, *1019*(1–2), 101–109. doi:10.1016/j.chroma.2003.08.048 PMID:14650608

Hudlicky, M. (1990). *Oxidations in Organic Chemistry. ACS monograph 186* (pp. 252–259). Washington, DC: ACS.

Huffman, G. P., Mitra, S., Huggins, F. E., Shah, N., Vaidya, F., & Lu, F. (1991). Quantitative analysis of all major forms of sulfur in coal by x-ray absorption fine structure spectroscopy. *Energy & Fuels*, *5*(4), 574–581. doi:10.1021/ef00028a008

Hughes, W. B., Holba, A. G., & Dzou, L. (1989). A method for determining the depositional. Soc. environment and lithology of crude oil and source rocks. Proceedings of the 1989 ACS *Meeting*, Honolulu, Hawaii.

Hughey, C. A., Rodgers, R. P., & Marshall, A. G. (2002). Resolution of 11,000 compositionally distinct components in a single electrospray ionization FT-ICR mass spectrum of crude oil. *Analytical Chemistry*, *74*, 4145–4149. doi:10.1021/ac020146b PMID:12199586

Huirache-Acuña, R., Albiter, M. A., Espino, J., Ornelas, C., Alonso-Núñez, G., & Paraguay-Delgado, F. et al. (2006). (a)). Synthesis of Ni–Mo–W sulphide catalysts by ex situ decomposition of trimetallic precursors. *Applied Catalysis A, General*, *304*, 124–130. doi:10.1016/j.apcata.2006.02.032

Huirache-Acuña, R., Albiter, M. A., Ornelas, C., Paraguay-Delgado, F., Martínez-Sánchez, R., & Alonso-Núñez, G. (2006). (b)). Ni(Co)-Mo-W sulphide unsupported HDS catalysts by ex situ decomposition of alkylthiomolybdotungstates. *Applied Catalysis A, General*, *308*, 134–142. doi:10.1016/j.apcata.2006.04.015

Huirache-Acuña, R., Alonso-Núñez, G., Paraguay-Delgado, F., Lara-Romero, J., Berhault, G., & Rivera-Muñoz, E. M. (2015). Unsupported trimetallic CoMoW sulfide HDS catalysts prepared by *in situ* decomposition of sulfur-containing precursors. *Catalysis Today*, *250*, 28–37. doi:10.1016/j.cattod.2014.06.044

Huirache-Acuña, R., Pawelec, B., Loricera, C. V., Rivera-Muñoz, E. M., Nava, R., Torres, B., & Fierro, J. L. G. (2012). Comparison of the morphology and HDS activity of ternary Ni(Co)-Mo-W catalysts supported on Al-HMS and Al-SBA-16 substrates. *Applied Catalysis B: Environmental*, *125*, 473–485. doi:10.1016/j.apcatb.2012.05.034

Huirache-Acuña, R., Pawelec, B., Rivera-Muñoz, E., Nava, R., Espino, J., & Fierro, J. L. G. (2009). Comparison of the morphology and HDS activity of ternary Co-Mo-W catalysts supported on P-modified SBA-15 and SBA-16 substrates. *Applied Catalysis B: Environmental*, *92*(1-2), 168–184. doi:10.1016/j.apcatb.2009.07.012

Huirache-Acuña, R., Rivera-Muñoz, E. M., Pawelec, B., Ostrooumov, M., Maya-Yescas, R., & Rico, J. L. (2014). The use of a natural Mexican zeolite as support of NiMoW sulphide hydrotreating catalysts. *Catalysis Today*, *220-222*, 301–309. doi:10.1016/j.cattod.2013.07.019

Huirache-Acuña, R., Sánchez-Bautista, M. G., Lemus-Ruiz, J., Ornelas, C., Paraguay-Delgado, F., & Rivera-Muñoz, E. M. (2010). Synthesis and characterization of partially sulfided CoMoW oxides nanostructures and their application in the HDS of DBT DBT. *Revista Mexicana de Ingeniería Química*, *9*(2), 209–218.

Hu, J., Wang, Y., Vander Wiel, D., Chin, C., Palo, D., & Rozmiarek, R. et al. (2003). Fuel processing for portable power applications. *Chemical Engineering Journal*, *93*(1), 55–60. doi:10.1016/S1385-8947(02)00108-0

Hulea, V., & Dimitriu, E. (2004). Styrene oxidation with H2O2 over Ti-containing molecular sieves with MFI, BEA and MCM-41 topologies. *Applied Catalysis A, General*, *277*(1-2), 99–106. doi:10.1016/j.apcata.2004.09.001

Hulea, V., Fajula, F., & Bousquet, J. (2001). Mild Oxidation with H2O2 over Ti-Containing Molecular Sieves - A very Efficient Method for Removing Aromatic Sulfur Compounds from Fuels. *Journal of Catalysis*, *198*(2), 179–186. doi:10.1006/jcat.2000.3149

Hunt, J. M. (1979). *Petroleum Geochemistry and Geology*, W. H. *The Freeman*, 617.

Hussain, F., Hojjati, M., Okamoto, M., & Gorga, R. (2006). Polymer-matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview. *Journal of Composites Material*, *40*(17), 1511–1575. doi:10.1177/0021998306067321

Hwang, K.-S., Kim, D.-W., Park, S.-W., Park, D.-W., Oh, K.-J., & Kim, S.-S. (2009). Simultaneous absorption of carbon dioxide and sulfur dioxide into aqueous 1,8-diamino-p-menthane. *Separation Science and Technology*, *44*(16), 3888–3910. doi:10.1080/01496390903338444

Hwang, T., Bryan, R., Goldsmith, B. R., Peters, B., & Scott, S. L. (2013). Water-Catalyzed Activation of H2O2 by Methyltrioxorhenium: A Combined Computational–Experimental Study. *Inorganic Chemistry*, *52*(24), 13904–13917. doi:10.1021/ic401343m PMID:24261486

Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature*, *354*(6348), 56–58. doi:10.1038/354056a0

Imamura, S., Sasaki, H., Shono, M., & Kanai, H. (1998). Structure of molybdenum supported on α-, γ-, and x-aluminas in Relation to Its Epoxidation Activity. *Journal of Catalysis*, *177*(1), 72–81. doi:10.1006/jcat.1998.2088

International Energy Agency. (2014). *World Energy Investment Outlook*. Retrieved from http://www.iea.org/publications/freepublications/publication/world-energy-investment-outlook---special-report---.html

Irvine, R. L. (1998). Process for desulfurizing gasoline and hydrocarbon feedstocks. *US Patent*, 5730860.

Irvine, R. L., & Benson, B. A., & M, V. D. (1999, 21–23 March 1999). *IRVAD™ Process—low cost breakthrough for low sulphur gasoline - paper AM-99-42* Paper presented at the NPRA 1999 Annual Meeting, San Antonio, Texas.

Irvine, R. L., Benson, B. A., Varraveto, D. M., & Frye, R. A. NPRA (1999, March 21-23). Proceedings of the *Annual Meeting*, *AM-99-42*, San Antonio, Texas.

Irvine, R. L., Varraveto, D. M. (1999). Adsorption process for nitrogen and sulfur. *Petroleum Technology Quarter Summer* 3, 37- 40.

Isarankura-Na-Ayudhya, C., Nantasenamat, C., Buraparuangsang, P., Piacham, T., Ye, L., Bülow, L., & Prachayasittikul, V. (2008). Computational insights on sulfonamide imprinted polymers. *Molecules (Basel, Switzerland)*, *13*(12), 3077–3091. doi:10.3390/molecules13123077 PMID:19078850

Ishihara, A., Wang, D., Dumeignil, F., Amano, H., Qian, E. W., & Kabe, T. (2005). Oxidative desulfurization and denitrogenation of a light gas oil using an oxidation/adsorption continuous flow process. *Applied Catalysis A, General*, *279*(1–2), 279–287. doi:10.1016/j.apcata.2004.10.037

Ismagilov, Z., Yashnik, S., Kerzhentsev, M., Parman, V., Bourane, A., Al-Shahrani, A. A., & Koseoglu, O. R. (2011). Oxidative desulfurization of hydrocarbon fuels. *Catalysis Reviews. Science and Engineering*, *53*(3), 199–255. doi:10.1080/01614940.2011.596426

Isoda, T., Nagao, S., Ma, X. L., Korai, Y., & Mochida, I. (1996). Hydrodesulfurization of Refractory Sulfur Species. 1. Selective Hydrodesulfurization of 4,6-Dimethyldibenzothiophene in the Major Presence of Naphthalene over CoMo/Al_2O_3 and Ru/Al_2O_3 Blend Catalysts. *Energy & Fuels*, *10*(2), 482–486. doi:10.1021/ef950144c

Ito, E., & Rob van Veen, J. A. (2006). On novel processes for removing sulphur from refinery streams. *Catalysis Today*, *116*(4), 446–460. doi:10.1016/j.cattod.2006.06.040

Ivanov, V., Fonseca, A., Nagy, J. B., Lucas, A., Lambin, P., Bernaerts, D., & Zhang, X. B. (1995). Catalytic production and purification of nanotubulles having fullerene-scale diameters. *Carbon*, *33*(12), 1727–1738. doi:10.1016/0008-6223(95)00132-1

Iwamoto, R., & Grimblot, J. (1997). Acidity and hydrogenation properties of Mo-P-alumina catalysts prepared by a sol-gel method. *Journal of Catalysis*, *172*(1), 252–255. doi:10.1006/jcat.1997.1855

Iwamoto, R., & Grimblot, J. (2000). Influence of Phosphorus on the Properties of Alumina-Based Hydrotreating Catalysts. *Advances in Catalysis*, *44*, 417–503. doi:10.1016/S0360-0564(08)60516-7

Iwata, Y., Sato, K., Yoneda, T., Miki, Y., Sugimoto, Y., Nishijima, A., & Shimada, H. (1998). Present State of the Art and Future Challenges in the Hydrodesulfurization of Polyaromatic Sulfur Compounds. *Catalysis Today*, *45*, 353–359. doi:10.1016/S0920-5861(98)00262-4

Jacobs, C. B., Peairs, M. J., & Venton, B. J. (2010). Carbon nanotubes electrochemical sensors for biomolecules. *Analytica Chimica Acta*, *662*(2), 105–127. doi:10.1016/j.aca.2010.01.009 PMID:20171310

Janak, K. E., Tanski, J. M., Churchill, D. G., & Parkin, G. (2002). Thiophene and Butadiene−Thiolate Complexes of Molybdenum: Observations Relevant to the Mechanism of Hydrodesulfurization. *Journal of the American Chemical Society*, *124*(16), 4182–4183. doi:10.1021/ja012771o PMID:11960426

Janssen, A., Sleyster, R., van der Kaa, C., Jochemsen, A., Bontsema, J., & Lettinga, G. (1995). Biological sulphide oxidation in a fed-batch reactor. *Biotechnology and Bioengineering*, *47*(3), 327–333. doi:10.1002/bit.260470307 PMID:18623408

Jarusuwannapoom, T., Hongroijanawiwat, W., Jitjaicham, S., Wannatong, L., Nithitanakul, M., Pattamaprom, C., & Supaphol, P. et al. (2005). Effect of solvents on electro-spinnability of polystyrene solutions and morphological appearance of resulting electrospun polystyrene fibers. *European Polymer Journal*, *41*(3), 409–421. doi:10.1016/j.eurpolymj.2004.10.010

Javadli, R., & Klerk, A. (2012). Desulfurization of heavy oil. *Applied Petrochemical Research*, *1*(1-4), 3–19. doi:10.1007/s13203-012-0006-6

Jeevanandam, P., Klabunde, K. J., & Tetzler, S. H. (2005). Adsorption of thiophenes out of hydrocarbons using metal impregnated nanocrystalline aluminum oxide. *Microporous and Mesoporous Materials*, *79*(1-3), 101–110. doi:10.1016/j.micromeso.2004.10.029

Jeon, H., Ko, C. H., Kim, S. H., & Kim, J. (2009). Removal of refractory sulphur compounds in diesel using activated carbon with controlled porosity. *Energy & Fuels*, *23*(5), 2537–2543. doi:10.1021/ef801050k

Jia, G. (2014). Domestic FCAS of catalyst used to achieve long period (in Chinese). Retrieved from http://www.sinopecnews.com.cn/news/content/2014-02/17/content_1377530.shtml

Jiang, H. L., Fang, D. F., Hsiao, B. S., Chu, B., & Chen, W. L. (2004). Optimization and characterization of dextran membranes prepared by electrospinning. *Biomacromolecules*, *5*(2), 326–333. doi:10.1021/bm034345w PMID:15002991

Jiang, N., Ying, G. L., Liu, S. Y., Shen, L., Hu, J., & Dai, L. J. et al. (2014). Amino acid-based biohybrids for nanoshellization of individual desulfurizing bacteria. *Chemical Communications (Cambridge)*, *50*(97), 15407–15410. doi:10.1039/C4CC06323F PMID:25350878

Jiang, X., Li, H., Zhu, W., He, L., Shu, H., & Lu, J. (2009). Deep desulfurization of fuels catalyzed by surfactant-type decatungstates using H2O2 as oxidant. *Fuel*, *88*(3), 431–436. doi:10.1016/j.fuel.2008.11.010

Jiang, Z., Liu, Y., Sun, X., Tian, F., Sun, F., & Liang, C. et al. (2003). Activated carbons chemically modified by concentrated H_2SO_4 for the adsorption of the pollutants from wastewater and the dibenzothiophene from fuel oils. *Langmuir*, *19*(3), 731–736. doi:10.1021/la020670d

Jiang, Z., Lü, H., Zhang, Y., & Li, C. (2011). Oxidative Desulfurization of Fuel Oils. *Chinese Journal of Catalysis*, *32*(5), 707–715. doi:10.1016/S1872-2067(10)60246-X

Jian-long, WANG, & Di-shun, ZHAO, & ZHOU-Er-peng. (2008). Application of Bronsted acidic ionic liquid in extraction and oxidation of dibenzothiophene.[Petroleum Processing Section]. *Acta Petrolei Sinica*, *24*(2), 227–231.

Jin, D.-S., Deshwal, B.-R., Park, Y.-S., & Lee, H.-K. (2006). Simultaneous removal of SO2 and NO by wet scrubbing using aqueous chlorine dioxide solution. *Journal of Hazardous Materials*, *135*(1-3), 412–417. doi:10.1016/j.jhazmat.2005.12.001 PMID:16442222

Jitianu, T. C. A., Berger, M., Benoit, R., Béguin, F., & Bonnamy, S. (2004). New carbon multiwall nanotubes–TiO2 nanocomposites obtained by the sol–gel method. *Journal of Non-Crystalline Solids*, *345*, 596–600. doi:10.1016/j.jnoncrysol.2004.08.104

Johnson, B. G., Slater, P., & Kidd, D. (2001). Application of Phillips's Zorb process to distillates-meeting the challenge. Proceedings of AM-01-14. New Orleans.

Johnson, R. W., Gordon, G. E., Calkins, W., & Elzerman, A. Z. (Eds.). (1987). *The Chemistry of Acid Rain: Sources and Atmospheric Processes*. Washington, D.C.: American Chemical Society. doi:10.1021/bk-1987-0349

Johnstone, H. F. (1931). Metallic ions as catalysts for the Removal of Sulfur Dioxide from Boiler Furnace Gases. *Industrial & Engineering Chemistry*, *23*(5), 559–561. doi:10.1021/ie50257a022

Johnstone, H. F., & Leppla, P. W. (1934). The solubility of sulfur dioxide at low partial pressures. The ionization constant and heat of ionization of sulfurous acid. *Journal of the American Chemical Society*, *56*(11), 2233–2238. doi:10.1021/ja01326a009

Johnstone, H. F., & Singh, A. D. (1940). Recovery of Sulfur Dioxide from Waste Gases. Regeneration of the Absorbent by Treatment with Zinc Oxide. *Industrial & Engineering Chemistry*, *32*(8), 1037–1048. doi:10.1021/ie50368a007

Jones, W. D., & Dong, L. (1991). Insertion of rhodium into the carbon-sulfur bond of thiophene. Mechanism of a model for the hydrodesulfurization reaction. *Journal of the American Chemical Society*, *113*(2), 559–564. doi:10.1021/ja00002a025

Jordana, J., Jacobb, K. I., Tannenbaumc, R., Sharafb, M. A., & Jasiukd, I. (2005). Experimental trends in polymer nanocomposite: A review. *Materials Science and Engineering A*, *393*(1-2), 1–11. doi:10.1016/j.msea.2004.09.044

Joseph, G., & Beachler, D. (1998). *Scrubber Systems Operation Review. Flue Gas Desulfurization (Acid Gas Removal) Systems*. Retrieved from http://yosemite.epa.gov/oaqps/eogtrain.nsf/b81bacb527b016d785256e4a004c0393/d4ec501f07c0e03a85256b6c006caf64/$FILE/si412c_lesson9.pdf

Jourdain, V., & Bichara, C. (2013). Current understanding of the growth of carbon nanotubes in catalytic chemical vapour deposition. *Carbon*, *58*, 2–39. doi:10.1016/j.carbon.2013.02.046

Journet, C., Bernier, P. (n. d.). Production of carbon nanotubes. *Journal of Applied Physics A,* 67, 1-9.

Journet, C., Maser, W. K., Bernier, P., Loiseau, A., de la Chapelle, M. L., & Lefrant, S. et al. (1997). Large-scale production of single-walled carbon nanotubes by the electric-arc technique. *Nature*, *388*(6644), 756–758. doi:10.1038/41972

Jun, S., Joo, S. H., Ryoo, R., Kruk, M., Jaroniec, M., & Liu, Z. et al. (2000). Synthesis of New, Nanoporous Carbon with Hexagonally Ordered Mesostructure. *Journal of the American Chemical Society*, *122*(43), 10712–10713. doi:10.1021/ja002261e

Kabe, T., Ishihara, A., & Tajima, H. (1992). Hydrodesulfurization of sulfur-containing polyaromatic compounds in light oil. *Industrial & Engineering Chemistry Process Design and Development*, *31*, 1577–1580.

Kabe, T., Ishihara, A., & Zhang, Q. (1993). Deep desulfurization of light oil. Part 2: Hydrodesulfurization of dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene. *Applied Catalysis A*, *97*(1), L1–L9. doi:10.1016/0926-860X(93)80059-Y

Kakaraniya, S., Kari, C., Verma, R., & Mehra, A. (2007). Gas absorption in slurries of fine particles: SO_2-$Mg(OH)_2$-$MgSO_3$ system. *Industrial & Engineering Chemistry Research*, *46*(7), 1904–1913. doi:10.1021/ie061461h

Kallinikos, L. E., Farsari, E. I., Spartinos, D. N., & Papayannakos, N. G. (2010). Simulation of the operation of an industrial wet flue gas desulfurization system. *Fuel Processing Technology*, *91*(12), 1794–1802. doi:10.1016/j.fuproc.2010.07.020

Kaluzˇa, L., Gulkova´, D., Vı't, Z., & Zdrazˇil, M. (2007). Effect of support type on the magnitude of synergism and promotion in CoMo sulphide hydrodesulphurisation catalyst. *Applied Catalysis A, General*, *324*, 30–35. doi:10.1016/j.apcata.2007.02.050

Kaminski, J. (2003). Technologies and costs of SO_2-emissions reduction for the energy sector. *Applied Energy*, *75*(3-4), 165–172. doi:10.1016/S0306-2619(03)00029-1

Kane, R. D., and Cayard, M. S. (2002). *A Comprehensive Study on Naphthenic Acid Corrosion.* NACE Intl., paper 02555.

Kappe, C. (2012). Controlled Microwave Heating in Modern Organic Synthesis. *Angewandte Chemie International Edition*, *43*, 6250–6284.

Karas, L. J., Grey, R. A., & Lynch, M. W. (2008). *Desulfurization process*. US Patent 2008047875.

Karas, L. J., Han, Y. Z., & Leyshon, D. W. (2004). *Organosulfur oxidation process*. US Patent 2004178122.

Karas, L. J., Han, Y.-Z., & Leyshon, D. W. (2004). United States Patent No.

Karas, L., Grey, R. & Lynch, M. (2008). US Patent 2008047875.

Karlsson, H. T., Klingspor, J., Linne, M., & Bjerle, I. (1983). Activated wet-dry scrubbing of SO_2. *Journal of the Air Pollution Control Association*, *33*(1), 23–28. doi:10.1080/00022470.1983.10465543

Karlsson, H. T., & Rosenberg, H. S. (1980). Technical aspects of lime/limestone scrubbers for coal-fired power plants. I. Process chemistry and scrubber systems. *Journal of the Air Pollution Control Association*, *30*(6), 710–714. doi:10.1080/00022470.1980.10465999

Kasrai, M., Bancroft, G. M., Brunner, R. W., Jonasson, R. G., Brown, J. R., Tan, K. H., & Feng, X. (1994). Sulfur speciation in bitumens and asphaltenes by x-ray absorption fine structure spectroscopy. *Geochimica et Cosmochimica Acta*, *58*(13), 2865–2872. doi:10.1016/0016-7037(94)90120-1

Kasuga, T., Hiramatsu, M., Hoson, A., Sekino, T., & Niihara, K. (1998). Formation of Titanium Oxide Nanotube. *Langmuir*, *14*(12), 3160–3163. doi:10.1021/la9713816

Katz, H. E. (2004). Chemically Sensitive Field-Effect Transistors and Chemiresistors: New Materials and Device. Structures. *Journal of Electroanalytical Chemistry*, *16*(22), 1837–1842. doi:10.1002/elan.200403071

Kauffman, D. R., & Star, A. (2008). Carbon Nanotube Gas and Vapor Sensors. Angewandte Chemmie International Edition, 47(35), 6550-6570.

Kauffman, D. R., Shade, C. M., Uh, H., Petoud, S., & Star, A. (2009). Decorated carbon nanotubes with unique oxygen sensitivity. *Nature Chemistry*, *1*(6), 500–506. doi:10.1038/nchem.323 PMID:21378918

Kauffman, D. R., Tang, Y., Kichambare, P. D., Jackovitz, J. F., & Star, A. (2010). Long-Term Performance of Pt-Decorated Carbon Nanotube Cathodes in Phosphoric Acid Fuel Cells. *Energy & Fuels*, *24*(3), 1877–1881. doi:10.1021/ef100013v

Kaufman, E. N., Borole, A. P., Shong, R., Sides, J. L., & Juengst, C. (1999). Sulfur specificity in the bench-scale biological desulfurization of crude oil by *Rhodococcus. Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *74*(10), 1000–1004. doi:10.1002/(SICI)1097-4660(199910)74:10<1000::AID-JCTB134>3.0.CO;2-0

Kaufman, E. N., Harkins, J. B., Rodriguez, M. Jr, Tsouris, C., Selvaraj, P. T., & Murphy, S. E. (1997). Development of an electro-spray bioreactor for crude oil processing. *Fuel Processing Technology*, *52*(1), 127–144. doi:10.1016/S0378-3820(97)00022-2

Kaufman, E., Harkins, J., & Borole, A. (1998). Comparison of batchstirred and electrospray reactors for biodesulfurization of dibenzothiophene in crude oil and hydrocarbon feedstocks. *Applied Biochemistry and Biotechnology*, *73*(2-3), 127–144. doi:10.1007/BF02785650

Kent, J. A. (2010). *Kent and Riegel's Handbook of Industrial Chemistry and Biotechnology* (Vol. 1). Springer.

Kerby, M., Degnan, T. Jr, Marler, D., & Beck, J. (2005). Advanced catalyst technology and applications for high quality fuels and lubricants. *Catalysis Today*, *104*(1), 55–63. doi:10.1016/j.cattod.2005.03.028

Khan, A. (2004). The theory of adsorption equilibria analysis based on general equilibrium constant expression. *Turkish Journal of Chemistry*, *36*, 219–231.

Khare, G. P. (1999). *Sorbent compositions* (p. 5958830). US: US Pat Appl.

Khedkar, S., & Shanker, R. (2014). Isolation and classification of a soil actinomycete capable of sulphur-specific biotransformation of dibenzothiophene, benzothiophene and thianthrene. *Journal of Applied Microbiology*. PMID:25319398

Kiatkittipong, K., Scott, J., & Amal, R. (2011). Hydrothermally synthesized titanate nanostructures: Impact of heat treatment on particle characteristics and photocatalytic properties. *ACS Applied Materials & Interfaces*, *3*(10), 3988–3996. doi:10.1021/am2008568 PMID:21939232

Ki, C. S., Baek, D. H., Gang, K. D., Lee, K. H., Um, I. C., & Park, Y. H. (2005). Characterization of gelatin nanofiber prepared from gelatin-formic acid solution. *Polymer*, *46*(14), 5094–5102. doi:10.1016/j.polymer.2005.04.040

Kidoaki, S., Kwon, I. K., & Matsuda, T. (2005). Mesoscopic spatial designs of nano- and micron-fiber meshes for tissue-engineering matrix and scaffold based on newly devised multilayering and mixing electrospinning techniques. *Biomaterials*, *26*(1), 37–46. doi:10.1016/j.biomaterials.2004.01.063 PMID:15193879

Kiil, S., Michelsen, M. L., & Dam-johansen, K. (1998). Experimental Investigation and Modeling of a Wet Flue Gas Desulfurization Pilot Plant. *Industrial & Engineering Chemistry Research*, *37*(7), 2792–2806. doi:10.1021/ie9709446

Kikkawa, H., Nakamoto, T., Morishita, M., & Yamada, K. (2002). New wet FGD process using granular limestone. *Industrial & Engineering Chemistry Research*, *41*(12), 3028–3036. doi:10.1021/ie0109760

Kilanowski, D. R., Teeuwen, H., Gates, B. C., Beer, V. H. J. D., Schuit, G. C. A., & Kwart, H. (1978). Hydrodesulfurization of thiophene, benzothiophene, dibenzothiophene, and related compounds catalyzed by sulfided CoO-MoO$_3$/g-Al$_2$O$_3$: Low-pressure reactivity studies. *Journal of Catalysis*, *55*(2), 129–137. doi:10.1016/0021-9517(78)90199-9

Kilbane, J. J., II. (1996). Enzyme from Rhodococcus rhodochrous ATCC 53968, Bacillus sphaericus ATCC 53969 or a mutant thereof for cleavage of organic C-S bonds. US patent number 5, 516, 677.

Kilbane, J. J. (1989). Desulfurization of coal: The microbial solution. *Trends in Biotechnology*, *7*(4), 97–101. doi:10.1016/0167-7799(89)90007-3

Kilbane, J. J. II. (2006). Microbial biocatalyst developments to upgrade fossil fuels. *Current Opinion in Biotechnology*, *17*(3), 305–314. doi:10.1016/j.copbio.2006.04.005 PMID:16678400

Kilbane, J. J. II, & Jackowski, K. (1992). Biodesulfurization of water soluble coal-derived material by Rhodococcus rhodochrous IGTS8. *Biotechnology and Bioengineering*, *40*(9), 1107–1114. doi:10.1002/bit.260400915 PMID:18601220

Kilbane, J. J. II, & Le Borgne, S. (2004). Petroleum biorefining: The selective removal of sulfur, nitrogen, and metals. *Studies in Surface Science and Catalysis*, *151*, 29–65. doi:10.1016/S0167-2991(04)80143-5

Killops, S. D., & Killops, V. J. (1993). *An Introduction to Organic Geochemistry* (2nd ed.). Longma Scientific and Technical.

Kim, B. H., Kim, H. Y., Kim, T. S., & Park, D. H. (1995). Selectivity of desulfurization activity of Desulfovibrio desulfuricans M6 on different petroleum products. *Fuel Processing Technology*, *43*(1), 87–94. doi:10.1016/0378-3820(95)00010-5

Kim, B., Park, H., Lee, S. H., & Sigmund, W. M. (2005). Poly(acrylic acid) nanofibers by electrospinning. *Materials Letters*, *59*(7), 829–832. doi:10.1016/j.matlet.2004.11.032

Kim, H. S., Kim, K., Jin, H. J., & Chin, I. J. (2005). Morphological characterization of electrospun nano-fibrous membranes of biodegradable poly(L-lactide) and poly(lactideco-glycolide). *Macromolecular Symposia*, *224*(1), 145–154. doi:10.1002/masy.200550613

Kim, J. H., Ma, X., Song, C., Lee, Y., & Oyama, S. T. (2005). Kinetics of Two Pathways for 4,6-Dimethyldibenzothiophene Hydrodesulfurization over NiMo, CoMo Sulfide, and Nickel Phosphide Catalysts. *Energy & Fuels*, *19*(2), 353–364. doi:10.1021/ef049804g

Kim, J. H., Ma, X., Zhou, A., & Song, C. (2006). Ultra-deep desulfurization and denitrogenation of diesel fuel by selective adsorption over three different adsorbents: A study on adsorptive selectivity and mechanism. *Catalysis Today*, *111*(1-2), 74–83. doi:10.1016/j.cattod.2005.10.017

Kim, J., Lee, J. E., Yu, J. H., Kim, B. C., An, K., & Hwang, Y. et al. (2006). Magnetic fluorescent delivery vehicle using uniform mesoporous silica spheres embedded with mono disperse magnetic and semiconductor nanocrystals. *Journal of the American Chemical Society*, *128*(3), 688–689. doi:10.1021/ja0565875 PMID:16417336

Kim, J., McNamara, N. D., Her, T. H., & Hicks, J. C. (2013). Carbothermal reduction of Ti-modified IRMOF-3: An adaptable synthetic method to support catalytic nanoparticles on carbon. *ACS Applied Materials & Interfaces*, *5*(21), 11479–11487. doi:10.1021/am404089v PMID:24111792

Kim, T. W., Kim, M. J., Kleitz, F., Nair, M. M., Guillet-Nicolas, R., & Jeong, K. E. et al. (2012). Tailormade mesoporous Ti-SBA-15 catalysts for oxidative desulfurization of refractory aromatic sulfur compounds in transport fuel. *ChemCatChem*, *4*(5), 687–697. doi:10.1002/cctc.201100417

Kim, Y., Yeong, H., Kim, T. S., & Kim, B. H. (1990). Degradation of ogranic sulfur compounds and the reduction of dibenzothiophene to biphenyl and hydrogen sulfide by Desulfovibrio desulfuricans M6. *Biotechnology Letters*, *12*(10), 761–764. doi:10.1007/BF01024736

King, D. L., & Li, L. (2006). Removal of sulfur components from low sulfur gasoline using copper exchanged zeolite Y at ambient temperature. *Catalysis Today*, *116*(4), 526–529. doi:10.1016/j.cattod.2006.06.026

Kinoshita, K., & Bett, J. A. S. (1973). Potentiodynamic analysis of surface oxides on carbon blacks. *Carbon*, *11*(4), 403–411. doi:10.1016/0008-6223(73)90080-8

Kirimura, K., Furuya, T., Sato, R., Ishii, Y., Kino, K., & Usami, S. (2002). Biodesulfurization of naphthothiophene and benzothiophene through selective cleavage of carbon-sulfur bonds by Rhodococcus sp. strain WU-K2R. *Applied and Environmental Microbiology*, *68*(8), 3867–3872. doi:10.1128/AEM.68.8.3867-3872.2002 PMID:12147483

Kirimura, K., Harada, K., Iwasawa, H., Tanaka, T., Iwasaki, Y., & Furuya, T. et al. (2004). Identification and functional analysis of the genes encoding dibenzothiophene-desulfurizing enzymes from thermophilic bacteria. *Applied Microbiology and Biotechnology*, *65*(6), 703–713. doi:10.1007/s00253-004-1652-0 PMID:15221222

Kiselev, N. A., Sloan, J., Zakharov, D. N., Kukovitskii, E. F., Hutchison, J. L., Hammer, J., & Kotosonov, A. S. (1998). Carbon nanotubes from polyethylene precursors: Structure and structural changes as revealed by HREM. *Carbon*, *36*, 1149–1157. doi:10.1016/S0008-6223(98)00092-X

Kitano, M., Nakajima, K., Kondo, J. N., Hayashi, S., & Hara, M. (2010). Protonated titanate nanotubes as solid acid catalyst. *Journal of the American Chemical Society*, *132*(19), 6622–6623. doi:10.1021/ja100435w PMID:20426412

Klicpera, T., & Zdrazil, M. (1999). High surface area MoO_3 /MgO: Preparation by the new slurry impregnation method and activity in sulphided state in hydrodesulphurization of benzothiophene. *Catalysis Letters*, *58*(1), 47–51. doi:10.1023/A:1019036724583

Klimont, Z., Smith, S. J., & Cofala, J. (2013).The last decade of global anthropogenic sulfur dioxide: 2000–2011 emissions. EPA-Environmental Protection Agency *Environmental Research Letters, 8*, 014003. Retrieved from http:// www.epa.gov/air/urbanair; http://www.epa.gov/airquality/sulfurdioxide/implement.html#jan14

Klimova, T., Mendoza Vara, P., & Puente Lee, I. (2010). Development of new NiMo/g-alumina catalysts doped with noble metals for deep HDS. *Catalysis Today*, *150*(3-4), 171–178. doi:10.1016/j.cattod.2009.08.003

Klobes, P., Meyer, K., & Munro, R. G. (2006). Porosity and specific surface area measurements for solid materials. *National Institute of Standards and Technology Special Publication*, *89*, 960–917.

Kluge, R., Schulz, M., & Liebsch, S. (1996). Sulfonic peracids – III. Heeteroatom oxidation and chemoselectivity. *Tetrahedron*, *52*(16), 5773–5782. doi:10.1016/0040-4020(96)00202-5

Knudsen, K. G., Cooper, B. H., & Topsoe, H. (1999). Catalyst and process technologies for ultra low sulfur diesel. *Applied Catalysis A, General*, *189*(2), 205–215. doi:10.1016/S0926-860X(99)00277-X

Kobayashi, M., Horiuchi, K., Yoshikawa, O., Hirasawa, K., Ishii, Y., & Fujino, K. et al. (2001). Kinetic analysis of microbial desulfurization of model and light gas oils containing multiple alkyl dibenzothiophenes. *Bioscience, Biotechnology, and Biochemistry*, *65*(2), 298–304. doi:10.1271/bbb.65.298 PMID:11302162

Kobayashi, M., Onaka, T., Ishii, Y., Konishi, J., Takaki, M., & Okada, H. et al. (2000). Desulfurization of alkylated forms of both dibenzothiophene and benzothiophene by a single bacterial strain. *FEMS Microbiology Letters*, *187*(2), 123–126. doi:10.1111/j.1574-6968.2000.tb09147.x PMID:10856644

Kocal, J. A. (2001). US Patent 6277271.

Kocal, J. A., & Branvold, T. A. (2002). *Removal of sulfur-containing compounds from liquid hydrocarbon streams*. US Patent 6368495.

Kocal, J. A., & Branvold, T. A. (2002). US Patent 6368495.

Kodama, K., Umehara, K., Shimizu, K., Nakatani, S., Minoda, Y., & Yamada, K. (1973). Identification of microbial products from dibenzothiophene and its proposed oxidation pathway. *Agricultural and Biological Chemistry*, *37*(1), 45–50. doi:10.1271/bbb1961.37.45

Koltuniewicz, A. B., Field, R. W., & Arnot, T. C. (1995). Cross-flow and dead-end microfiltration of oily-water emulsion. Part I: Experimental study and analysis of flux decline. *Journal of Membrane Science*, *102*, 193–207. doi:10.1016/0376-7388(94)00320-X

Komintarachat, C., & Trakarnpruk, W. (2006). Oxidative Desulfurization Using Polyoxometalates. *Industrial & Engineering Chemistry Research*, *45*(6), 1853–1856. doi:10.1021/ie051199x

Kongkanand, A., Martínez Domínguez, R., & Kamat, P. V. (2007). Single wall carbon nanotube scaffolds for photoelectrochemical solar cells. capture and transport of photogenerated electrons. *Nano Letters*, *7*(3), 676–680. doi:10.1021/nl0627238 PMID:17309316

Kong, L. Y., Li, G., & Wang, X. S. (2004). Mild oxidation of thiophene over TS-1/H2O2. *Catalysis Today*, *93*, 341–345. doi:10.1016/j.cattod.2004.06.016

Kong, L. Y., Li, G., Wang, X. S., & Wu, B. (2006). Oxidative desulfurization of organic sulfur in gasoline over Ag/TS-1. *Energy & Fuels*, *20*(3), 896–902. doi:10.1021/ef050252r

Konishi, I., Yoshitaka, I., Kouichi, O., & Suzuki, M. (1999) *US Patent No. 5925560.*

Konishi, J., Ishii, Y., Onaka, T., Okumura, K., & Suzuki, M. (1997). Thermophilic carbon-sulfur-bond-targeted biodesulfurization. *Applied and Environmental Microbiology*, *63*(8), 3164–3169. PMID:16535672

Konishi, M., Kishimoto, M., Omasa, T., Katakura, Y., Shioya, S., & Ohtake, H. (2005). Effect of sulfur sources on specific desulfurization activity of *Rhodococcus erythropolis* KA2-5-1 in exponential fed-batch culture. *Journal of Bioscience and Bioengineering*, *99*(3), 259–263. doi:10.1263/jbb.99.259 PMID:16233786

Konishi, M., Kishimoto, M., Tamesui, N., Omasa, T., Shioya, S., & Ohtake, H. (2005). The separation of oil from an oil–water–bacteria mixture using a hydrophobic tubular membrane. *Biochemical Engineering Journal*, *24*(1), 49–54. doi:10.1016/j.bej.2004.11.012

Koriakin, A., Kim, Y.-H., & Lee, C.-H. (2012). Adsorptive Desulfurization of Natural Gas Using Lithium-Modified Mesoporous Silica. *Industrial & Engineering Chemistry Research*, *51*(44), 14489–14495. doi:10.1021/ie301066n

Koski, A., Yim, K., & Shivkumar, S. (2004). Effect of molecular weight on fibrous PVA produced by electrospinning. *Materials Letters*, *58*(3-4), 493–497. doi:10.1016/S0167-577X(03)00532-9

Kosynkin, D. V., Higginbotham, A. L., Sinitskii, A., Lomeda, J. R., Dimiev, A., Price, B. K., & Tour, J. M. (2009). Mechanically Assisted Exfoliation and Functionalization of Thermally Converted Graphene Sheets. *Nature*, *458*, 872–876. doi:10.1038/nature07872 PMID:19370030

Kozhevnikov, I. V. (Ed.). (2002). *Catalysts for Fine Chemical Synthesis, Catalysis by Polyoxometalates* (Vol. 2). Chichester: John Wiley & Sons.

Krammer, G., Brunner, C., Khinast, J., & Staudinger, G. (1997). Reaction of $Ca(OH)_2$ with SO_2 at Low Temperature. *Industrial & Engineering Chemistry Research*, *36*(5), 1410–1418. doi:10.1021/ie960628b

Krishna, R., Colyar, J. J., Kressmann, S., Boyer, C., Schweitzer, J. M., & Viguie, J. C. (2000). Improvements of Ebullated-Bed Technology for Upgrading Heavy Oils. *Oil & Gas Science and Technology - Rev. IFP*, *55*(4), 397–406.

Kropp, K. G., Anderson, J. K., & Fedorak, P. M. (1997). Biotrasformations of three dimethyl dibenzothiophenes by pure and mixed bacterial cultures. *Environmental Science & Technology*, *31*(5), 1547–1554. doi:10.1021/es960869a

Krouse, H. R. (1977). Sulfur isotope studies and their role in petroleum exploration. *Journal of Geochemical Exploration*, *7*, 189–211. doi:10.1016/0375-6742(77)90081-4

Kruger, M., Buitelaar, M. R., Nussbaumer, T., Schonenberger, C., & Forro, L. (2001). Electrochemical carbon nanotube field-effect transistor. *Applied Physics Letters*, *78*(9), 1291–1293. doi:10.1063/1.1350427

Kruusma, J., Mould, N., Jurkschat, K., Crossley, A., & Banks, C. E. (2007). Single walled carbon nanotubes contain residual iron oxide impurities which can dominate their electrochemical activity. *Electrochemistry Communications*, *9*(9), 2330–2333. doi:10.1016/j.elecom.2007.06.024

Kubata, Y., Koyama, Y., Yamada, T., Imagaki, S., & Tatsumi, T. (2008). Synthesis and catalytic performance of Ti-MCM-68 for effective oxidation reactions. *Chemical Communications (Cambridge)*, *46*(46), 6224–6226. doi:10.1039/b814286f PMID:19082127

Kubota, A., & Takeuchi, H. (2004). An Unexpected Incident with m-CPBA. *Organic Process Research & Development*, *8*(6), 1076–1078. doi:10.1021/op049825+

Kulkarni, P.S., & Afonso, C.A.M. (2010). Deep desulfurization of diesel fuel using ionic liquids: current status and future challenges. *Green Chem.*, 12, 1139-1149.

Kumar, A. (2010). *Nanofibers*. Vukovar: Intech. doi:10.5772/45660

Kumar, S., Kumar, R., & Bandopadhyay, A. (2006). Innovative methodologies for the utilisation of wastes from metallurgical and allied industries. *Resources, Conservation and Recycling*, *48*(4), 301–314. doi:10.1016/j.resconrec.2006.03.003

Kumar, S., Srivastava, V. C., & Badoni, R. P. (2011). Studies on adsorptive desulfurization by zirconia based adsorbents. *Fuel*, *90*(11), 3209–3216. doi:10.1016/j.fuel.2011.06.029

Kumar, S., Srivastava, V. C., & Badoni, R. P. (2012). Oxidative desulfurization by chromium promoted sulfated zirconia. *Fuel Processing Technology*, *93*(1), 18–25. doi:10.1016/j.fuproc.2011.08.017

Kundu, S., Wang, Y., Xia, W., & Muhler, M. (2008). Thermal Stability and Reducibility of Oxygen-Containing Functional Groups on Multiwalled Carbon Nanotube Surfaces: A Quantitative High-Resolution XPS and TPD/TPR Study. *The Journal of Physical Chemistry C*, *112*(43), 16869–16878. doi:10.1021/jp804413a

Kuznetsova, L., Detusheva, L., Kuznetsov, N., Duplyakin, V., & Likholobov, V. (2008). Liquid-phase oxidation of benzothiophene and dibenzothiophene by cumyl-hydroperoxide in the presence of catalysts based on supported metal oxides. *Kinetics and Catalysis*, *49*(5), 644–652. doi:10.1134/S002315840805008X

Kwart, H., Schuit, G. C. A., & Gates, B. C. (1980). Hydrodesulfurization of thiophenic compounds: The reaction mechanism. *Journal of Catalysis*, *61*(1), 128–134. doi:10.1016/0021-9517(80)90347-4

Kwon, J.-M., Moon, J.-H., Bae, Y.-S., Lee, D.-G., Sohn, H.-C., & Lee, C.-H. (2008). Adsorptive desulfurization and denitrogenation of refinery fuels using mesopourous silica adsorbents. *ChemSusChem*, *1*(4), 307–309. doi:10.1002/cssc.200700011 PMID:18605095

Kymakis, E., & Amaratunga, G. (2007). Single-wall carbon nanotube/conjugated polymer photovoltaic devices. *Applied Physics Letters*, *80*(1), 112–114. doi:10.1063/1.1428416

Lam, E., & Luong, J. H. T. (2014). Carbon Materials as Catalyst Supports and Catalysts in the Transformation of Biomass to Fuels and Chemicals. *ACS Catalysis*, *4*(10), 3393–3410. doi:10.1021/cs5008393

Lamoreaux, W. F. (1916, May 16). *Recovering elemental sulfur from sulfurous gases*. U. S. Patent 1,182,915. CA 10:1918.

Lam, V., Li, G., Song, C., Chen, J., Fairbridge, C., Hui, R., & Zhang, J. (2012). A review of electrochemicaldesulfurization technologies for fossil fuels. *Fuel Processing Technology*, *98*, 30–38. doi:10.1016/j.fuproc.2012.01.022

Lancia, A., Musmarra, D., & Pepe, F. (1997). Modeling of SO_2 Absorption into Limestone Suspensions. *Industrial & Engineering Chemistry Research*, *36*(1), 197–203. doi:10.1021/ie9602365

Lancia, A., Musmarra, D., Pepe, F., & Volpicelli, G. (1994). Characteristic times for limestone particle dissolution in the production of gypsum from the wet flue gas desulfurization process. *Environmental Science & Technology*, *28*(6), 1031–1036. doi:10.1021/es00055a011 PMID:22176227

Landau, M. V., Berger, D., & Herskowitz, M. (1996). Hydrodesulfurization of Methyl-Substituted Dibenzothiophenes: Fundamental Study of Routes to Deep Desulfurization. *Journal of Catalysis*, *159*(1), 236–245. doi:10.1006/jcat.1996.0083

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, *40*(9), 1361–1403. doi:10.1021/ja02242a004

Lanju, C. H. E. N. (2007). Oxidative desulfurization of simulated gasoline over metal oxide-loaded molecular sieve. *Chinese Journal of Chemical Engineering*, *15*(4), 520–523. doi:10.1016/S1004-9541(07)60118-9

Lan, L., Ge, S., Liu, K., Hou, Y., & Bao, X. (2011). Synthesis of Ni_2P promoted trimetallic NiMoW/γ-Al_2O_3 catalysts for diesel oil hydrotreatment. *Journal of Natural Gas Chemistry*, *20*(2), 117–122. doi:10.1016/S1003-9953(10)60173-9

Laplaze, D., Bernier, P., Maser, W. K., Flamant, G., Guillard, T., & Loiseau, A. (1998, January). Carbon nanotubes: The solar approach. *Carbon*, *36*(5-6), 685–688. doi:10.1016/S0008-6223(98)00025-6

Largeteau, D., Ross, J., Laborde, M., & Wisdom Axens, L. (2012). Challenges and opportunities of 10 ppm sulphur gasoline: Part 2. *Petroleum Technology Quarterly*, *17*(5), 25.

Larrubia, M. A., A`ıda, G.-A., Ram`ırez, J., & Busca, G. (2002). A FT-IR study of the adsorption of indole, carbazole, benzothiophene, dibenzothiophene and 4,6-dibenzothiophene over solid adsorbents and catalysts. *Applied Catalysis A, General*, *224*(1-2), 167–178. doi:10.1016/S0926-860X(01)00769-4

Lauritsen, J. V., Bollinger, M. V., Lægsgaard, E., Jacobsen, K. W., Nørskov, J. K., & Clausen, B. S. et al. (2004 a). Atomic-scale insight into structure and morphology changes of MoS_2 nanoclusters in hydrotreating catalysts. *Journal of Catalysis*, *221*(2), 510–522. doi:10.1016/j.jcat.2003.09.015

Lauritsen, J. V., Helveg, S., Lægsgaard, E., Stensgaard, I., Clausen, B. S., Topsøe, H., & Besenbacher, F. (2001). Atomic-Scale Structure of Co–Mo–S Nanoclusters in Hydrotreating Catalysts. *Journal of Catalysis*, *197*(1), 1–5. doi:10.1006/jcat.2000.3088

Lauritsen, J. V., Nyberg, M., Nørskov, J. K., Clausen, B. S., Topsøe, H., Lægsgaard, E., & Besenbacher, F. (2004 b). Hydrodesulfurization reaction pathways on MoS_2 nanoclusters revealed by scanning tunneling microscopy. *Journal of Catalysis*, *224*(1), 94–106. doi:10.1016/j.jcat.2004.02.009

Le Borgne, S., & Quintero, R. (2003). Biotechnological processes for the refining of petroleum. *Fuel Processing Technology*, *81*(2), 155–169. doi:10.1016/S0378-3820(03)00007-9

Ledoux, M. J., Michaux, O., Agostini, G., & Panissod, P. J. (1986). The influence of sulfide structures on the hydrodesulfurization activity of carbon-supported catalysts. *Journal of Catalysis*, *102*(2), 275–288. doi:10.1016/0021-9517(86)90164-8

Lee, C. C., & Huffman, G. L. (2007). Wet and Dry Scrubbers for Emission Control. In C. C. Lee & S. Dar Lin (Eds.), *Handbook of Environmental Engineering Calculations* (pp. 3103–3140). New York: McGraw-Hill.

Lee, C. C., Huffman, G. L., & Chang, J. C. S. (2007). Air Emission Control. In C. C. Lee & S. Dar Lin (Eds.), *Handbook of Environmental Engineering Calculations*. New York: McGraw-Hill.

Lee, C., Wei, X., Kysar, J. W., & Hone, J. (2008). Measurement of the elastic properties and intrinsic Strength of monolayer graphene. *Science*, *321*(5887), 385–388. doi:10.1126/science.1157996 PMID:18635798

Lee, J. S., Choi, K. H., Do Ghim, H., Kim, S. S., Chun, D. H., Kim, H. Y., & Lyoo, W. S. (2004). Role of molecular weight of a tactic poly(vinyl alcohol) (PVA) in the structure and properties of PVA nanofabric prepared by electrospinning. *Journal of Applied Polymer Science*, *94*(4), 1638–1646. doi:10.1002/app.20602

Lee, M. K., Senius, J. D., & Grossman, M. J. (1995). Sulfur-specific microbial desulfurization of sterically hindered analogs of dibenzothiophene. *Applied and Environmental Microbiology*, *61*(12), 4362–4366. PMID:16535189

Lefohn, A. S., Husar, J. D., & Husar, R. B. (1999). Estimating historical anthropogenic global sulfur emission patterns for the period 1850-1990. *Atmospheric Environment*, *33*(21), 3435–3444. doi:10.1016/S1352-2310(99)00112-0

Lepsoe, R. (1938). Chemistry of Sulfur Dioxide Reduction. Thermodynamics. *Industrial & Engineering Chemistry*, *30*(1), 92–100. doi:10.1021/ie50337a019

Lepsoe, R. (1940). Chemistry of Sulfur Dioxide Reduction. *Industrial & Engineering Chemistry*, *32*(7), 910–918. doi:10.1021/ie50367a011

Lesch, D. A., Richardson, J. W., Jacobson, R. A., & Angelici, R. J. (1984). Reactions of the π-thiophene ligand in (η-$C_4H_4S)Mn(CO)_3{}^+$]. Mechanistic possibilities for catalytic hydrodesulfurization. *Journal of the American Chemical Society*, *106*, 2901–2906. doi:10.1021/ja00322a027

Lewan, M. D. (1998). Sulfur-radical control on petroleum formation rates. *Nature*, *391*(6663), 164–166. doi:10.1038/34391

Lewan, M. D., Spiro, B., Illich, H., Raiswell, R., Mackenzie, A. S., & Durand, B. et al. (1985). Evaluation of petroleum generation by hydrous pyrolysis experimentation. *Philos. Trans. R. Soc. London, A*, *315*(1531), 123–134. doi:10.1098/rsta.1985.0033

Lewis, W. K., & Chang, K. C. (1928). Distillation III. The mechanism of rectification. Trans. *AlChE.*, *21*, 127.

Liang, Z.-X., Li, L., Li, S., Cai, Y.-H., Yang, S.-T., & Wang, J.-F. (2012). Enhanced propionic acid production from Jerusalem artichoke hydrolysate by immobilized *Propionibacterium acidipropionici* in a fibrous-bed bioreactor. *Bioprocess and Biosystems Engineering*, *35*(6), 915–921. doi:10.1007/s00449-011-0676-y PMID:22228298

Li, B., Xu, D., Jiang, Z., Zhang, X., Liu, W., & Dong, X. (2008). Pervaporation performance of PDMS-Ni^{2+}Y zeolite hybrid membranes in the desulfurization of gasoline. *Journal of Membrane Science*, *322*(2), 293–301. doi:10.1016/j.memsci.2008.06.015

Li, C., Gao, J., Jiang, Z., Wang, S., Lu, H., Yang, Y., & Jing, F. (2005). Selective Oxidations on Recoverable Catalysts Assembled in Emulsions. *Topics in Catalysis*, *35*(1-2), 169–175. doi:10.1007/s11244-005-3821-5

Li, C., Jiang, Z., Gao, J., Yang, Y., Wang, S., & Tian, F. et al. (2004). Ultra-Deep Desulfurization of Diesel: Oxidation with a Recoverable Catalyst Assembled in Emulsion. *Chemistry (Weinheim an der Bergstrasse, Germany)*, *10*(9), 2277–2280. doi:10.1002/chem.200305679 PMID:15112217

Li, D.-C., Dai, L., Huang, S., Mau, A. W. H., & Wang, Z. L. (2000). Structure and growth of aligned carbon nanotube films by pyrolysis. *Chemical Physics Letters*, *316*(5-6), 349–355. doi:10.1016/S0009-2614(99)01334-2

Li, F. T., Liu, R. H., Jin Hhua, W., Zhao, D. S., Sun, Z. M., & Liu, Y. (2009). Desulfurization of dibenzothiophene by chemical oxidation and solvent extraction with $Me_3NCH_2C_6H_5Cl.2ZnCl_2$ ionic liquid. *Green Chemistry*, *11*(6), 883–888. doi:10.1039/b815575e

Li, F. T., Liu, Y., Sun, Z. M., Chen, L. J., Zhao, D. S., Liu, R. H., & Kou, C. G. (2010). Deep Extractive Desulfurization of Gasoline with xEt3NHCl·FeCl3 Ionic Liquids. *Energy & Fuels*, *24*(8), 4285–4289. doi:10.1021/ef100408h

Li, F. T., Liu, Y., Sun, Z. M., Zhao, Y., Liu, R. H., Chen, L. J., & Zhao, D. S. (2012). Photocatalytic oxidative desulfurization of dibenzothiophene under simulated sunlight irradiation with mixed-phase Fe2O3 prepared by solution combustion. *Catalysis Science and Technology*, *2*(7), 1455–1462. doi:10.1039/c2cy00485b

Li, F., Xu, P., Feng, J., Meng, L., Zheng, Y., Luo, L., & Ma, C. (2005). Microbial desulfurization of gasoline in a *Mycobacterium goodii* X7B immobilized-cell system. *Applied and Environmental Microbiology*, *71*(1), 276–281. doi:10.1128/AEM.71.1.276-281.2005 PMID:15640198

Li, F., Zhang, Z., Feng, J., Cai, X., & Ping, X. (2007). Biodesulfurization of DBT in tetradecane and crude oil by a facultative thermophilic bacterium Mycobacterium goodii X7B. *Journal of Biotechnology*, *127*(2), 222–228. doi:10.1016/j.jbiotec.2006.07.002 PMID:16905217

Li, H., Carpenter, G. B., & Sweigart, D. A. (2000). Models for Homogeneous Deep Hydrodesulfurization. Intramolecular CO Substitution by the Sulfur in [(η^6-2-methylbenzothiophene)Mn$(CO)_3$]$^+$ and [(η^6-dibenzothiophene)Mn$(CO)_3$]$^+$ after Regiospecific Insertion of Platinum into a C-S Bond. *Organometallics*, *19*(10), 1823–1825. doi:10.1021/om000100d

Li, H., Eddaoudi, M., O'Keeffe, M., & Yaghi, O. M. (1999). Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature*, *402*(6759), 276–279. doi:10.1038/46248

Li, H., He, L., Lu, J., Zhu, W., Jiang, X., Wang, Y., & Yan, Y. (2009). Deep Oxidative Desulfurization of Fuels Catalyzed by Phosphotungstic Acid in Ionic Liquids at Room Temperature. *Energy & Fuels*, *23*(3), 1354–1357. doi:10.1021/ef800797n

Li, H., Jiang, X., Zhu, W., Lu, J., Shu, H., & Yan, Y. (2009). Deep Oxidative Desulfurization of Fuel Oils Catalyzed by Decatungstates in the Ionic Liquid of [Bmim] PF6. *Industrial & Engineering Chemistry Research*, *48*(19), 9034–9039. doi:10.1021/ie900754f

Li, H., Li, M., Chu, Y., Liu, F., & Nie, H. (2014). Effect of different preparation methods of MoO_3/Al_2O_3 catalysts on the existing states of Mo species and hydrodesulfurization activity. *Fuel*, *116*, 168–174. doi:10.1016/j.fuel.2013.07.127

Li, H., Zhu, W., Wang, Y., Zhang, J., Lu, J., & Yan, Y. (2009). Deep oxidative desulfurization of fuels in redox ionic liquids based on iron chloride. *Green Chemistry*, *11*(6), 810–815. doi:10.1039/b901127g

Li, J. (2009). In P. Serp & J. L. Figueiredo (Eds.), *Carbon Materials for Catalysis* (pp. 507–533).

Li, L., Li, L., Wang, Y., Du, Y., & Qin, S. (2013). Biorefinery products from the inulin-containing crop Jerusalem artichoke. *Biotechnology Letters*, *35*(4), 471–477. doi:10.1007/s10529-012-1104-3 PMID:23242496

Li, M. Z., Squires, C. H., Monticello, D. J., & Childs, J. D. (1996). Genetic analysis of the dsz promoter and associated regulatory regions of Rhodococcus erythropolis IGTS8. *Journal of Bacteriology*, *178*(22), 6409–6418. PMID:8932295

Lin, F., Wang, D. E., Jiang, Z. H., Ma, Y., Li, J., Li, R. G., & Li, C. (2012). Photocatalytic oxidation of thiophene on Bi VO4 with dual co-catalysts Pt and RuO2 under visible light irradiation using molecular oxygen as oxidant. *Energy Environmental Science*, *5*(4), 6400–6406. doi:10.1039/C1EE02880D

Ling, L., Zhang, R., Han, P., & Wang, B. (2013). DFT study on the sulfurization mechanism during the desulfurization of H_2S on the ZnO desulfurizer. *Fuel Processing Technology*, *106*, 222–230. doi:10.1016/j.fuproc.2012.08.001

Linguist,, L.K., & Pacheco, M. (1999). Enzyme-based diesel desulfurization process offers energy, CO_2 advantages. *Oil & Gas Journal*, *97*(8), 45–48.

Lin, L., Kong, Y., Wang, G., Qu, H., Yang, J., & Shi, D. (2006). Selection and crosslinking modification of membrane material for FCC gasoline desulfurization. *Journal of Membrane Science*, *285*(1–2), 144–151. doi:10.1016/j.memsci.2006.08.016

Lin, L., Kong, Y., Xie, K., Lu, F., Liu, R., & Guo, L. et al. (2008). Polyethylene glycol/polyurethane blend membranes for gasoline desulphurization by pervaporation technique. *Separation and Purification Technology*, *61*(3), 293–300. doi:10.1016/j.seppur.2007.10.020

Lin, L., Zhang, Y., & Kong, Y. (2009). Recent advances in sulfur removal from gasoline by pervaporation. *Fuel*, *88*(10), 1799–1809. doi:10.1016/j.fuel.2009.03.031

Lin, R. Z., & Wang, P. R. (1991). PAH in fossil fuels and their geochemical significance. Journal of Southeast Asian Earth Sciences. *Journal of Southeast Asian Earth Sciences*, *5*(1-4), 257–262. doi:10.1016/0743-9547(91)90034-U

Lin, S. D., & Song, C. (1996). Noble metal catalysts for low-temperature naphthalene hydrogenation in the presence of benzothiophene. *Catalysis Today*, *31*(1-2), 93–104. doi:10.1016/0920-5861(96)00038-7

Lin, T., Wang, H. X., Wang, H. M., & Wang, X. G. (2004). The charge effect of cationic surfactants on the elimination of fibre microspheres in the electrospinning of polystyrene. *Nanotechnology*, *15*(9), 1375–1381. doi:10.1088/0957-4484/15/9/044

Lipfert, F. W. (1984). Mortality and Air Pollution. In O. Hutzinger (Ed.), The Handbook of Environmental Chemistry. Volume 4, part B: Air Pollution. Berlin, Springer-Verlag.

Lippmann, M. (2009). Sulfur Oxides-SO_2, H_2SO_4, NH_4HSO_4, and $(NH_4)2SO_4$. In M. Lippmann (Ed.), *Environmental Toxicants: Human Exposures and Their Health Effects*. United States: Wiley. doi:10.1002/9780470442890.ch25

Lipsch, J. M. J. G., & Schuit, G. C. A. (1969). The CoO-MoO_3-Al_2O_3 catalyst: III. Catalytic properties. *Journal of Catalysis*, *15*(2), 179–189. doi:10.1016/0021-9517(69)90022-0

Li, Q., Li, G., & Sun, H. (2014). Synthesis of hierarchical TS-1 with convenient separation and the application for the oxidative desulfurization of bulky and small reactants. *Fuel*, *130*, 70–75. doi:10.1016/j.fuel.2014.04.042

Li, Q., Wang, G., Qiu, J., Wang, N., Zhang, Q., & Lei, Q. et al. (2012). Catalytic Oxidative Desulfurization of Model Fuel using $[HPMo][HTAC]_2/SiO_2$ as a Amphiphilic Catalyst. *Adv. Mater. Res.*, *82*, 396–398.

Liu, B. S., Xu, D. F., Chu, J. X., Liu, W., & Au, C. T. (2007). Deep desulfurization by the adsorption process of fluidized catalytic cracking (FCC) diesel over mesoporous Al-MCM- 41 materials. *Energy & Fuels*, *21*(1), 250–255. doi:10.1021/ef060249n

Liu, D., Liu, L., Li, G., & Liu, C. (2010). Synthesis, characterization and hydrodesulfurization activity of silica-dispersed NiMoW trimetallic catalysts. *Journal of Natural Gas Chemistry*, *19*(5), 530–533. doi:10.1016/S1003-9953(09)60108-0

Liu, G., Rodriguez, J. A., Chang, Z., Hrbek, J., & Gonzalez, L. J. (2002). Chemistry of sulfur-containing molecules on Au(1 1 1): Thiophene, sulfur dioxide, and methanethiol adsorption. *Surface Science*, *505*(1-3), 295–307. doi:10.1016/S0039-6028(02)01377-8

Liu, J., & Kumar, S. (2005). Microscopic polymer cups by electrospinning. *Polymer*, *46*(10), 3211–3214. doi:10.1016/j.polymer.2004.11.116

Liu, N., Luo, F., Wu, H., Liu, Y., Zhang, C., & Chen, J. (2008). One-step ionic-liquid-assisted electrochemical synthesis of ionic-liquid-functionalized graphene sheets directly from graphite. *Advanced Functional Materials*, *18*(10), 1518–1525. doi:10.1002/adfm.200700797

Liu, S.-Y., & Xiao, W.-D. (2006). Modeling and simulation of a bubbling SO_2 absorber with granular limestone slurry and an organic acid additive. *Chemical Engineering & Technology*, *29*(10), 1167–1173. doi:10.1002/ceat.200600101

Liu, X., Su, D. S., & Schlögl, R. (2008). Oxidative dehydrogenation of 1-butene to butadiene over carbon nanotube catalysts. *Carbon*, *46*(3), 547–549. doi:10.1016/j.carbon.2007.12.014

Liu, Y., Bisson, T. M., Yang, H., & Xu, Z. (2010). Recent developments in novel sorbents for flue gas clean up. *Fuel Processing Technology*, *91*(10), 1175–1197. doi:10.1016/j.fuproc.2010.04.015

Li, W. Z., Xie, S. S., Qian, L. X., Chang, B. H., Zou, B. S., & Zhou, W. Y. et al. (1996). Large scale synthesis of aligned carbon nanotubes. *Science*, *274*(5293), 1701–1703. doi:10.1126/science.274.5293.1701 PMID:8939858

Li, W., & Jiang, X. (2013). Enhancement of bunker oil biodesulfurization by adding surfactant. *World Journal of Microbiology & Biotechnology*, *29*(1), 103–108. doi:10.1007/s11274-012-1162-7 PMID:22940903

Li, W., Xing, J., Xiong, X., Huang, J., & Liu, H. (2006). Feasibility study on the integration of adsorption/bioregeneration of π-complexation adsorbent for desulfurization. *Industrial & Engineering Chemistry Research*, *45*(8), 2845–2849. doi:10.1021/ie051125l

Li, W., Zhang, Y., Wang, M. D., & Shi, Y. (2005). Biodesulfurization of dibenzothiophene and other organic sulfur compounds by a newly isolated microbacterium strain 2D-M2. *FEMS Microbiology Letters*, *247*(1), 45–50. doi:10.1016/j.femsle.2005.04.025 PMID:15927746

Li, X., Cai, W., An, J., Kim, S., Nah, J., & Yang, D. et al. (2009). Large-area synthesis of high-quality anduniform graphene films on copper foils. *Science*, *324*(5932), 1312–1314. doi:10.1126/science.1171245 PMID:19423775

Li, X., Qin, Y., Picraux, S. T., & Guo, Z.-X. (2011). Noncovalent assembly of carbon nanotube-inorganic hybrids. *Journal of Materials Chemistry*, *21*(21), 7527–7547. doi:10.1039/c1jm10516g

Li, X., Wang, A., Egorova, M., & Prins, R. (2007). Kinetics of the HDS of 4,6-dimethyldibenzothiophene and its hydrogenated intermediates over sulfided Mo and NiMo on γ -Al_2O_3. *Journal of Catalysis*, *250*(2), 283–293. doi:10.1016/j.jcat.2007.06.005

Li, X., Zhu, C., & Ma, Y. (2013). Removal of SO_2 using ammonium bicarbonate aqueous solution as absorbent in a bubble column reactor. *Frontiers of Chemical Science and Engineering*, *7*(2), 185–191. doi:10.1007/s11705-013-1326-5

Li, Y., Cui, R. L., Ding, L., Liu, Y., Zhou, W. W., & Zhang, Y. et al. (2010). How catalysts affect the growth of single-walled carbon nanotubes on substrates. *Advanced Materials*, *22*(13), 1508–1515. doi:10.1002/adma.200904366 PMID:20437500

Li, Y.-G., Gao, H.-S., Li, W.-L., Xing, J.-M., & Liu, H.-Z. (2009). In situ magnetic separation and immobilization of dibenzothiophene-desulfurizing bacteria. *Bioresource Technology*, *100*(21), 5092–5096. doi:10.1016/j.biortech.2009.05.064 PMID:19541480

Lizama, H., Wilkins, L., & Scott, T. (1995). Dibenzothiophene sulfur can serve as the sole electron acceptor during growth by sulfate-reducing bacteria. *Biotechnology Letters*, *17*(1), 113–116. doi:10.1007/BF00134206

Lomeda, J. R., Doyle, C. D., Kosynkin, D. V., Hwang, W. F., & Tour, J. M. (2008). Diazonium functionalization of surfactant-wrapped chemically converted graphene sheets. *Journal of the American Chemical Society*, *130*(48), 16201–16206. doi:10.1021/ja806499w PMID:18998637

Long, D. L., Burkholder, E., & Cronin, L. (2007). Polyoxometalate clusters, nanostructures and materials: From self assembly to designer materials and devices. *Chemical Society Reviews*, *36*(1), 105–121. doi:10.1039/B502666K PMID:17173149

Loo, A. H., Bonanni, A., & Pumera, M. (2013). Biorecognition on graphene: Physical, covalent, and affinity immobilization methods exhibiting dramatic differences. *Asian Journal of Chemistry*, *8*(1), 198–203. doi:10.1002/asia.201200756 PMID:23090869

Lorençon, E., Alves, D. C. B., Krambrock, K., Ávila, E. S., Resende, R. R., Ferlauto, A. S., & Lago, R. M. (2014). Oxidative desulfurization of dibenzothiophene over titanate nanotubes. *Fuel*, *132*, 53–61. doi:10.1016/j.fuel.2014.04.020

Loucks, R. G., Reed, R. M., Ruppel, S. C., & Jarvie, D. M. (2009). Morphology, Genesis, and Distribution of Nanometer-scale Pores in Siliceous Mudstones of the Mississippian Barnett Shale. *Journal of Sedimentary Research*, *79*(12), 848–861. doi:10.2110/jsr.2009.092

Lo, W. H., Yang, H. Y., & Wei, G.-T. (2003). One-pot desulfurization of light oils by chemical oxidation and solvent extraction with room temperature ionic liquids. *Green Chemistry*, *5*(5), 639–642. doi:10.1039/b305993f

Lozinsky, V. I., & Plieva, F. M. (1998). Poly (vinyl alcohol) cryogels employed as matrices for cell immobilization. 3. Overview of recent research and developments. *Enzyme and Microbial Technology*, *23*(3), 227–242. doi:10.1016/S0141-0229(98)00036-2

Lu, Y., Wang, Y., Gao, L., Chen, J., Mao, J., Xue, Q., Liu, Y., Wu, H., Gao, G., & He, M. (2008). Aerobic oxidative desulfurization: a promising approach for sulfur removal from fuels. *Chem Sus Chem., 1*(4), 302-306. doi: 3.10.1002/cssc.200700144

Lü, H., Gao, J., Jiang, Z., Jing, F., Yang, Y., Wang, G., & Li, C. (2006). Ultra-deep desulfurization of diesel by selective oxidation with $[C_{18}H_{37}N(CH_3)_3]4[H_2NaPW_{10}O_{36}]$ catalyst assembled in emulsion droplets. *Journal of Catalysis*, *239*(2), 369–375. doi:10.1016/j.jcat.2006.01.025

Lu, H., Gao, J., Jiang, Z., Yang, Y., Song, B., & Li, C. (2007). Oxidative desulfurization of dibenzothiophene with molecular oxygen using emulsion catalysis. *Chemical Communications*, *0*(2), 150–152. doi:10.1039/B610504A PMID:17180229

Lu, H., Zhang, Y., Jiang, Z., & Li, C. (2010). Aerobic oxidative desulfurization of benzothiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene using an Anderson-type catalyst $[(C_{18}H_{37})_2N(CH_3)_2]5[IMo6O24]$. *Green Chemistry*, *12*(11), 1954–1958. doi:10.1039/c0gc00271b

Lu, L., Cheng, S., Gao, J., Gao, G., & He, M.-y. (2006). Deep Oxidative Desulfurization of Fuels Catalyzed by Ionic Liquid in the Presence of H_2O_2. *Energy & Fuels*, *21*(1), 383–384. doi:10.1021/ef060345o

Lumbreras, J. A., Huirache-Acuña, R., Rivera-Muñoz, E. M., Berhault, G., & Alonso-Núñez, G. (2010). Unsupported Ni/Mo(W)S2 catalysts from hexamethylenediammonium thiometallates precursors: In situ activation during the HDS of DBT. *Catalysis Letters*, *134*(1-2), 138–146. doi:10.1007/s10562-009-0209-3

Luo, M. F., Xing, J. M., Gou, Z. X., Li, S., Liu, H. Z., & Chen, J. Y. (2003). Desulfurization of dibenzothiophene by lyophilized cells of *Pseudomonas delafieldii* R-8 in the presence of dodecane. *Biochemical Engineering Journal*, *13*(1), 1–6. doi:10.1016/S1369-703X(02)00078-5

Ma, X . & Velu, V.& Sun, L.& Song, C., "Adsorptive desulfurization of diesel fuel over a metal sulfide-based adsorbent", Prepr. Pap.-Am. Chem. Soc., Div. Pet. Chem., vol. 48, 2, (2003), p.522-523

Ma, C., Feng, J., Zeng, Y., Cai, X., Sun, B., & Zhang, Z. et al. (2006). Methods for the preparation of a biodesulfurization biocatalyst using *Rhodococcus* sp. *Chemosphere*, *65*(1), 165–169. doi:10.1016/j.chemosphere.2006.03.010 PMID:16624377

Mackenzie, L. D., & Cornwell, D. A. (1998). *Introduction to Environmental Engineering*. McGraw-Hill.

Magyar, S., Hancsók, J., & Kalló, D. (2005). Hydrodesulfurization and hydroconversion of heavy FCC gasoline on PtPd/H-USY zeolite. *Fuel Processing Technology*, *86*(11), 1151–1164. doi:10.1016/j.fuproc.2004.11.012

Maity, U., Basu, J. K., & Sengupta, S. (2013). A neural network prediction of conversion of benzothiopene oxidation catalyzed by nano-Ti-beta catalyst. *Fuel*, *113*, 180–186. doi:10.1016/j.fuel.2013.05.079

Malaga-Starzec, K., Panas, I., & Lindqvist, O. (2004). Model study of initial adsorption of SO_2 on calcite and dolomite. *Applied Surface Science*, *222*(1-4), 82–88. doi:10.1016/j.apsusc.2003.08.019

Manahan, S. E. (2010). *Environmental Chemistry* (7th ed.). Taylor & Francis.

Manias, E., Touny, A., Wu, L., Strawhecker, K., Lu, B., & Chung, T. C. (2001). Polypropylene/Montmorillonite Nanocomposites. Review of the Synthetic Routes and Materials. *Properties Chemical Materials*, *13*(10), 3516–3523. doi:10.1021/cm0110627

Manning and Thompson. (1991). *Oilfield Processing of Petroleum*. PennWell books.

Mansfeld, F., Haagenrud, S., Kucera, V., Haynie, F., & Sinclair, J. (1986). *Proceedings of the Symposia on Corrosion Effects of Acid Deposition and Corrosion of Electronic Materials*. *The Electrochemical Society*, 86(6), 108–154.

Manso, T., Nunes, C., Raposo, S., & Lima-Costa, M. E. (2010). Carob pulp as raw material for production of the biocontrol agent *P. agglomerans* PBC-1. *Journal of Industrial Microbiology & Biotechnology*, *37*(11), 1145–1155. doi:10.1007/s10295-010-0762-1 PMID:20593299

Mansouri, A., Khodadadi, A. A., & Mortazavi, Y. (2014). Ultra-deep adsorptive desulfurization of a model diesel fuel on regenerable Ni–Cu/-Al2O3 at low temperatures in absence of hydrogen. *Journal of Hazardous Materials*, *271*, 120–130. doi:10.1016/j.jhazmat.2014.02.006 PMID:24632365

Marécot, P., Paraiso, E., Dumas, J. M., & Barbier, J. (1992). Deactivation of nickel catalysts by sulphur compounds: I. Benzene hydrogenation. *Applied Catalysis A*, *80*(1-2), 79–88. doi:10.1016/0926-860X(92)85109-O

Maricq, M. M., Chase, R. E., Xu, N., & Laing, P. M. (2002). The effects of the catalytic converter and fuel sulfur level on motor vehicle particulate matter emissions: Light duty diesel vehicles. *Environmental Science & Technology*, *36*(2), 283–289. doi:10.1021/es010962l PMID:11827064

Marín-Rosas, C., Ramírez-Verduzco, L. F., Murrieta-Guevara, F. R., Hernández-Tapia, G., & Rodrı'guez-Otal, L. M. (2010). Desulfurization of Low Sulfur Diesel by Adsorption Using Activated Carbon: Adsorption Isotherms. *Industrial & Engineering Chemistry Research*, *49*(9), 4372–4376. doi:10.1021/ie901756b

Markusson, N. (2012). *Scaling up and deployment of FGD in the US (1960s-2009).* Retrieved from www.geos.ed.ac.uk/homes/nmarkuss/CaseScaling.pdf

Marocco, L. (2010). Modeling of the fluid dynamics and SO_2 absorption in a gas-liquid reactor. *Chemical Engineering Journal*, *162*(1), 217–226. doi:10.1016/j.cej.2010.05.033

Marshall, A. G., & Rodgers, R. P. (2003). Petroleomics: The next grand challenge for chemical analysis. *Accounts of Chemical Research*, *37*(1), 53–59. doi:10.1021/ar020177t PMID:14730994

Marshall, A. G., & Rodgers, R. P. (2008). Petroleomics: Chemistry of the underworld. *Proceedings of the National Academy of Sciences of the United States of America*, *105*(47), 18090–18095. doi:10.1073/pnas.0805069105 PMID:18836082

Martin, A. B., Alcon, A., Santos, V. E., & Garcia-ochoa, F. (2004). Production of a biocatalyst of *Pseudomonas putida* CECT5279 for dibenzothiophene (DBT) biodesulfurization for different media compositions. *Energy & Fuels*, *18*(3), 851–857. doi:10.1021/ef030174c

Martínez-Checa, F., Toledo, F., Vilchez, R., Quesada, E., & Calvo, C. (2002). Yield production, chemical composition, and functional properties of emulsifier H28 synthesized by *Halomonas eurihalina* strain H-28 in media containing various hydrocarbons. *Applied Microbiology and Biotechnology*, *58*(3), 358–363. doi:10.1007/s00253-001-0903-6 PMID:11935188

Martinez, I., Santos, V. E., Alcon, A., & Garcia-Ochoa, F. (2015). Enhancement of the biodesulfurization capacity of *Pseudomonas putida* CECT5279 by co-substrate addition. *Process Biochemistry*, *50*(1), 119–124. doi:10.1016/j.procbio.2014.11.001

Martin, R. L., & Grant, J. A. (1965). Determination of Sulfur-Compound Distributions in Petroleum Samples by Gas Chromatography with a Coulometric Detector. *Analytical Chemistry*, *37*(6), 644–649. doi:10.1021/ac60225a005

Martin, R. L., & Grant, J. A. (1965). Determination of Thiophenic Compounds by Types in Petroleum Samples. *Analytical Chemistry*, *37*(6), 649–657. doi:10.1021/ac60225a006

Mathieu, Y., Tzanis, L., Soulard, M., Patarin, J., Vierling, M., & Molière, M. (2013). Adsorption of SOx by oxide materials: A review. *Fuel Processing Technology*, *114*(0), 81–100. doi:10.1016/j.fuproc.2013.03.019

Matsui, M., Horiba, T., Yamamoto, O., Takeda, Y., Seki, N., & Imanishi, N. (2013). Carbon paper substrate for silicon-carbon composite anodes in lithium-ion batteries. *Journal of Power Sources*, *241*, 744–750. doi:10.1016/j.jpowsour.2013.05.090

Matsushima, N., Li, Y., Nishioka, M., Sadakata, M., Qi, H., & Xu, X. (2004). Novel dry-desulfurization process using $Ca(OH)_2$/fly ash sorbent in a circulating fluidized bed. *Environmental Science & Technology*, *38*(24), 6867–6874. doi:10.1021/es035373p PMID:15669351

Mattevi, C., Kim, H., & Chhowalla, M. (2011). A review of chemical vapour deposition of grapheme on copper. *Journal of Materials Chemistry*, *21*(10), 3324–3334. doi:10.1039/C0JM02126A

Ma, X., Kim, J. H., & Song, C. (2003). Effect of Methyl Groups at 4- and 6-Positions on Adsorption of Dibenzothiophenes over CoMo and NiMo Sulfide Catalysts. *Fuel Chemistry Division Preprints*, *48*, 135–137.

Ma, X., Lu, S., Yin, Z., & Song, C. (2001). New approaches to deep desulfurization of diesel fuel, jet fuel, and gasoline by adsorption for ultra-clean fuels and for fuel cell applications. *American Chemical Society. Division of Fuel Chemistry*, *46*(2), 648–649.

Ma, X., Sakanishi, K., Isoda, T., & Mochida, I. (1995). Hydrodesulfurization Reactivities of Narrow-Cut Fractions in a Gas Oil. *Industrial & Engineering Chemistry Research*, *34*(3), 748–754. doi:10.1021/ie00042a006

Ma, X., Sakanishi, K., Isoda, T., & Mochida, I. (1995). Quantum chemical calculation on the desulfurization reactivities of heterocyclic sulfur compounds. *Energy & Fuels*, *9*(1), 33–37. doi:10.1021/ef00049a005

Ma, X., Sakanishi, K., & Mochida, I. (1994). Hydrodesulfurization reactivities of various sulfur compounds in diesel fuel. *Industrial & Engineering Chemistry Research*, *33*(2), 218–222. doi:10.1021/ie00026a007

Ma, X., Sakanishi, K., & Mochida, I. (1996). Hydrodesulfurization reactivities of various sulfur compounds in vacuum gas oil. *Industrial & Engineering Chemistry Research*, *35*(8), 2487–2494. doi:10.1021/ie960137r

Ma, X., & Schobert, H. H. (2000). Molecular simulation on hydrodesulfurization of Thiophenic compounds over MoS_2 using ZINDO. *Journal of Molecular Catalysis A Chemical*, *160*(2), 409–427. doi:10.1016/S1381-1169(00)00278-8

Ma, X., Sun, L., & Song, C. (2002). A new approach to deep desulfurization of gasoline, diesel fuel and jet fuel by selective adsorption for ultra-clean fuels and for fuel cell applications. *Catalysis Today*, *77*(1-2), 107–116. doi:10.1016/S0920-5861(02)00237-7

Ma, X., Velu, S., Kim, J. H., & Song, C. (2005). Deep desulfurization of gasoline by selective adsorption over solid adsorbents and impact of analytical methods on ppm-level sulfur quantification for fuel cell applications. *Applied Catalysis B: Environmental*, *56*(1–2), 137–147. doi:10.1016/j.apcatb.2004.08.013

Ma, X., Zhou, A., & Song, C. (2007). A novel method for oxidative desulfurization of liquid hydrocarbon fuels based on catalytic oxidation using molecular oxygen coupled with selective adsorption. *Catalysis Today*, *123*(1–4), 276–284. doi:10.1016/j.cattod.2007.02.036

Mayo S, Plantenga F, Leliveld B, & A., M. Y. (2001, March 18–20). Paper presented at the National Petrochemical & Refiners Association (NPRA) annual meeting, AM-01-09, New Orleans.

Mazov, I., Kuznetsov, V. L., Simonova, I. A., Stadnichenko, A. I., Ishchenko, A. V., & Romanenko, A. I. et al. (2012). Oxidation behavior of multiwall carbon nanotubes with different diameters and morphology. *Applied Surface Science*, *258*(17), 6272–6280. doi:10.1016/j.apsusc.2012.03.021

Mc Allister, M. J., Li, J.-L., Adamson, D. H., Schniepp, H. C., Abdala, A. A., & Liu, J. et al. (2007). Single sheet functionalized graphene by oxidation and thermal expansion of graphite. *Chemistry of Materials*, *19*(18), 4396–4404. doi:10.1021/cm0630800

McEuen, P. L., Fuhrer, M. S., & Park, H. K. (2002). Single-walled carbon nanotube electronics. *IEEE Transactions on Nanotechnology*, *1*(1), 78–85. doi:10.1109/TNANO.2002.1005429

McFarland, B. L. (1999). Biodesulf urization. *Current Opinion in Microbiology*, *2*(3), 257–264. doi:10.1016/S1369-5274(99)80045-9 PMID:10383871

McFarland, B. L., Boron, D. J., Deever, W., Meyer, J. A., Johnson, A. R., & Atlas, R. M. (1998). Biocatalytic Sulfur Removal from Fuels: Applicability for Producing Low Sulfur Gasoline. *Critical Reviews in Microbiology*, *24*(2), 99–147. doi:10.1080/10408419891294208 PMID:9675512

McKetta, J. J. (1992). *Petroleum processing hand book*. Taylor & Francis Inc.

McKinley, S. G., & Angelici, R. J. (2003). Deep desulfurization by selective adsorption of dibenzothiophenes on Ag^+/SBA-15 and Ag^+/SiO_2. *Chemical Communications*, (20): 2620–2621. doi:10.1039/b309249f PMID:14594310

McLafferty, F. W. (2008). Mass spectrometry across the sciences. *Proceedings of the National Academy of Sciences of the United States of America*, *105*(47), 18088–18089. doi:10.1073/pnas.0800784105 PMID:18922771

Mehmet, Y. (1971). Alberta Sulfur Research Quart. *Bull*, *6*, 1–17.

Mehra, A. (1996). Gas absorption in reactive slurries: Particle dissolution near gas-liquid interface. *Chemical Engineering Science*, *51*(3), 461–477. doi:10.1016/0009-2509(95)00259-6

Mei, H., Mei, B. W., & Yen, T. F. (2003). A new method for obtaining ultra-low sulfur diesel fuel via ultrasound assisted oxidative desulfurization☆. *Fuel*, *82*(4), 405–414. doi:10.1016/S0016-2361(02)00318-6

Meikap, B. C., Kundu, G., & Biswas, M. N. (2002). A novel modified multi-stage bubble column scrubber for SO2 removal from industrial off gases. *Separation Science and Technology*, *37*(15), 3421–3442. doi:10.1081/SS-120014435

Meikap, B. C., Kundu, G., & Biswas, M. N. (2002). Modeling of a novel multi-stage bubble column scrubber for flue gas desulfurization. *Chemical Engineering Journal*, *86*(3), 331–342. doi:10.1016/S1385-8947(01)00226-1

Meikap, B. C., Kundu, G., & Biswas, M. N. (2002c). Scrubbing of fly-ash laden SO_2 in modified multistage bubble column scrubber. *AIChE Journal. American Institute of Chemical Engineers*, *48*(9), 2074–2083. doi:10.1002/aic.690480920

Meille, V., Schulz, E., Vrinat, M., & Lemaire, M. (1998). A new route towards deep desulfurization: Selective charge transfer complex formation. *Chemical Communications*, *0*(3), 305–306. doi:10.1039/a706877h

Meille, V., Shulz, E., Vrinat, M., & Lemaire, M. (1997). Hydrodesulfurization of alkyldibenzothiophenes over a NiMo/Al_2O_3 catalyst: Kinetics and mechanism. *Journal of Catalysis*, *170*(1), 29–36. doi:10.1006/jcat.1997.1732

Meman, N. M., Pourkhalil, M., Rashidi, A., & Zarenezhad, B. (2014). Synthesis, characterization and operation of a functionalized multi-walled CNT supported MnOx nanocatalyst for deep oxidative desulfurization of sour petroleum fractions. *Journal of Industrial and Engineering Chemistry*, *20*(6), 4054–4058. doi:10.1016/j.jiec.2014.01.004

Meman, N. M., Zarenezhad, B., Rashidi, A., Hajjar, Z., & Esmaeili, E. (in press). Application of palladium supported on functionalized MWNTs for oxidative desulfurization of naphtha. *Journal of Industrial and Engineering Chemistry*.

Mendes, A., Guerra, P., Madeira, V., Ruano, F., da Silva, T. L., & Reis, A. (2007). Study of docosahexaenoic acid production by the heterotrophic microalga *Crypthecodinium cohnii* CCMP 316 using carob pulp as a promising carbon source. *World Journal of Microbiology & Biotechnology*, *23*(9), 1209–1215. doi:10.1007/s11274-007-9349-z

Mendoza-Nieto, J. A., Vera-Vallejo, O., Escobar-Alarcón, L., Solís-Casados, D., & Klimova, T. (2013). Development of new trimetallic NiMoW catalysts supported on SBA-15 for deep hydrodesulfurization. *Fuel*, *110*, 268–277. doi:10.1016/j.fuel.2012.07.057

Meng, X. M., De Jong, W., & Verkooijen, A. H. M. (2009). Thermodynamic Analysis and Kinetics Model of H 2 S Sorption Using Different Sorbents. *Environmental Progress and Sustainable Energy*, *28*(3), 360–371. doi:10.1002/ep.10386

Meng, X., Huang, H., & Shi, L. (2013). Reactive Mechanism and Regeneration Performance of NiZnO/Al_2O_3-Diatomite Adsorbent by Reactive Adsorption Desulfurization. *Industrial & Engineering Chemistry Research*, *52*(18), 6092–6100. doi:10.1021/ie303514y

Mestl, G., Maksimova, N. I., Keller, N., Roddatis, V. V., & Schlögl, R. (2001). Carbon Nanofilaments in Heterogeneous Catalysis: An Industrial Application for New Carbon Materials? *Angewandte Chemie International Edition*, *40*(11), 2066–2068. doi:10.1002/1521-3773(20010601)40:11<2066::AID-ANIE2066>3.0.CO;2-I PMID:11433444

Meyer, K., Klobes, P., & Röhl-Kuhn, B. (1997). Certification of reference material with special emphasis on porous solids. *Crystal Research and Technology*, *32*(1), 173–183. doi:10.1002/crat.2170320118

Michalski, J. (1999). The influence of aerodynamic characteristics on mass exchange efficiency in FGD scrubbers. *Chemical Engineering & Technology*, *22*(4), 343–351. doi:10.1002/(SICI)1521-4125(199904)22:4<343::AID-CEAT343>3.0.CO;2-T

Michalski, J. A. (1997). Aerodynamic characteristics of FGD spray towers. *Chemical Engineering & Technology*, *20*(2), 108–117. doi:10.1002/ceat.270200208

Michalski, J. A. (1998). The influence of spraying angle on aerodynamic characteristics of FGD spray towers. *Chemical Engineering Communications*, *165*(1), 17–40. doi:10.1080/00986449808912368

Mikhail, S., Zaki, T., & Khalil, L. (2002). Desulfurization by an economically adsorption technique. *Applied Catalysis A, General*, *227*(1–2), 265–278. doi:10.1016/S0926-860X(01)00937-1

Miknis, F. P., & Turner, T. F. (1995). The Bitumen Intermediate in Isothermal and Nonisothermal Decomposition of Oil Shales. In C. Snape (Ed.), *Composition, Geochemistry, and Conversion of Oil Shales* (pp. 295–311). The Netherlands: Kluwer Academic Publishers. doi:10.1007/978-94-011-0317-6_18

Milenkovic, A., Schulz, E., Meille, V., Loffreda, D., Forissier, M., & Vrinat, M. et al. (1999). Selective Elimination of Alkyldibenzothiophenes from Gas Oil by Formation of Insoluble Charge-Transfer Complexes. *Energy & Fuels*, *13*(4), 881–887. doi:10.1021/ef980262a

Milenkovic, A., Shulz, E., Meille, V., Lofferda, D., Forissier, M., Vrinat, M., & Sautet, P. (2004). Charge transfer complexes between tetranitrofluorenone and polyaromatic compounds from gasoil: A combined DFT and experimental study. *Physical Chemistry*, *6*, 1169–1180.

Milkins, F. P., Turner, T. F., Berdan, G. L., & Conn, P. J. (1987). Formation of soluble products from thermal decomposition of Colorado and Kentucky oil shales. *Energy & Fuels*, *1*(6), 477–483. doi:10.1021/ef00006a004

Miller, J. T., Marshall, C. L., & Kropf, A. J. (2001). (Co)MoS_2/Alumina Hydrotreating Catalysts: An EXAFS Study of the Chemisorption and Partial Oxidation with O_2**.** *Journal of Catalysis*, *202*(1), 89–99. doi:10.1006/jcat.2001.3273

Minhas, B. S., & Chuba, M. R. & Saxton., R. J. (2004). Patent US 0026321 A1.

Minhas, B. S., & Saxton, R. J. (2002). Patent WO 02/064529 A1.

Mitra-Kirtley, S., & Mullins, O. C. (2007). *Sulfur Chemical Moieties in Carbonaceous Materials, Asphaltenes, Heavy Oils, and Petroleomics* (O. C. Mullins, E. Sheu, A. Hammami, & A. Marshall, Eds.). Springer.

Mitra-Kirtley, S., Mullins, O. C., Branthaver, J. F., & Cramer, S. P. (1993). Nitrogen chemistry of kerogens from XANES spectroscopy. *Energy & Fuels*, *7*(6), 1128. doi:10.1021/ef00042a062

Mitra-Kirtley, S., Mullins, O. C., Ralston, C. Y., Sellis, D., & Pareis, C. (1998). *Determination of sulfur species in asphaltene, resin, and oil fractions of crude oils,* Appl. *Spec.*, *52*(12), 1522.

Mitra-Kirtley, S., Mullins, O. C., van Elp, J., George, S. J., Chen, J., & Cramer, S. P. (1993). Determination of the Nitrogen Chemical Structures in Petroleum Asphaltenes Using XANES Spectroscopy. *Journal of the American Chemical Society*, *115*(1), 252–258. doi:10.1021/ja00054a036

Mit-Uppatham, C., Nithitanakul, M., & Supaphol, P. (2004). Ultrafine electrospun polyamide-6 fibers: Effect of solution conditions on morphology and average fiber diameter. *Macromolecular Chemistry and Physics*, *205*(17), 2327–2338. doi:10.1002/macp.200400225

Miyazaki, T., Takeda, Y., Akane, S., Itou, T., Hoshiko, A., & En, K. (2010). Role of boric acid for a poly (vinyl alcohol) film as a cross-linking agent: Melting behaviors of the films with boric acid. *Polymer*, *51*(23), 5539–5549. doi:10.1016/j.polymer.2010.09.048

Mochizuki, Y., & Sugawara, K. (2008). Removal of organic sulfur from hydrocarbon resources using ionic liquids. *Energy & Fuels*, *22*(5), 3303–3307. doi:10.1021/ef800400k

Moezzi, A., McDonagh, A. M., & Cortie, M. B. (2012). Zinc oxide particles: Synthesis, properties and applications. *Chemical Engineering Journal*, *185-186*, 1–22. doi:10.1016/j.cej.2012.01.076

Mohan, B. R., Biswas, S., & Meikap, B. C. (2008). Performance characteristics of the particulates scrubbing in a countercurrent spray-column. *Separation and Purification Technology*, *61*(1), 96–102. doi:10.1016/j.seppur.2007.09.018

Mohebali, G., & Ball, A. S. (2008). Biocatalytic desulfurization (BDS) of petrodiesel fuels. *Microbiology*, *154*(8), 2169–2183. doi:10.1099/mic.0.2008/017608-0 PMID:18667551

Mohebali, G., Ball, A. S., Kaytash, A., & Rasekh, B. (2008). Dimethyl sulfoxide (DMSO) as the sulfur source for the production of desulfurizing resting cells of *Gordonia alkanivorans* RIPI90A. *Microbiology*, *154*(3), 878–885. doi:10.1099/mic.0.2007/013011-0 PMID:18310033

Mohebali, G., Ball, A., Kaytash, A., & Rasekh, B. (2007). Stabilization of water/gas oil emulsions by desulfurizing cells of *Gordonia alkanivorans* RIPI90A. *Microbiology*, *153*(Pt 5), 1573–1581. doi:10.1099/mic.0.2006/002543-0 PMID:17464072

Mokhtar, W. N. A. W., Bakar, W. A. W. A., Ali, R., & Abdul-Kadir, A. A. (2014). Deep desulfurization of model diesel by extraction with *N,N*-dimethylformamide: Optimization by Box–Behnken design. *Journal of the Taiwan Institute of Chemical Engineers*, *45*(4), 1542–1548. doi:10.1016/j.jtice.2014.03.017

Molina-Ontoria, A., Chaur, M. N., Plonska-Brzezinska, M. E., & Echegoyen, L. (2013a). Preparation and characterization of soluble carbon nano-onions by covalent functionalization, employing a Na-K alloy. *Chemical Communications (Cambridge)*, *49*(24), 2406–2408. doi:10.1039/c3cc39077b PMID:23411670

Mondal, M. K., Chelluboyana, V. R., & Rao, J. S. (2013). Solubility of SO2 in aqueous blend of sodium citrate and sodium hydroxide. *Fluid Phase Equilibria*, *349*, 56–60. doi:10.1016/j.fluid.2013.03.025

Monteiro, O. A. C. Jr, & Airoldi, C. (1999). Some studies of crosslinking chitosan–glutaraldehyde interaction in a homogeneous system. *International Journal of Biological Macromolecules*, *26*(2-3), 119–128. doi:10.1016/S0141-8130(99)00068-9 PMID:10517518

Monticello, D. J. (2000). Biodesulfurization and the upgrading of petroleum distillates. *Current Opinion in Biotechnology*, *11*(6), 540–546. doi:10.1016/S0958-1669(00)00154-3 PMID:11102787

Monticello, D. J., Bakker, D., & Finnerty, W. R. (1985). Plasmid-mediated degradation of dibenzothiophene by Pseudomonas species. *Applied and Environmental Microbiology*, *49*, 756–760. PMID:4004209

Monticello, D. J., & Finnerty, W. R. (1985). Microbial desulfurization of fossil fuels. *Annual Review of Microbiology*, *39*(1), 371–389. doi:10.1146/annurev.mi.39.100185.002103 PMID:3904605

Moreau, P., Hulea, V., Gomez, S., Brunel, D., & Di Renzo, F. (1997). Oxidation of sulfoxides to sulfones by hydrogen peroxide over Ti-containing zeolites. *Applied Catalysis A, General*, *155*(2), 253–263. doi:10.1016/S0926-860X(96)00400-0

Morris, R. (1989). *Acid Toxicity and Aquatic Animals*. Cambridge University Press. doi:10.1017/CBO9780511983344

Mosbach, K. (1994). Molecular imprinting. *Trends in Biochemical Sciences*, *19*(1), 9–14. doi:10.1016/0968-0004(94)90166-X PMID:8140624

Moura, F. C. C., Araujo, M. H., Costa, R. C. C., Fabrisa, J. D., Ardisson, J. D., Macedo, W. A. A., & Lago, R. M. (2005). Efficient use of Fe metal as an electron transfer agent in a heterogeneous Fenton system basedon Fe0/Fe3O4 composites. *Chemosphere*, *60*(8), 1118–1123. doi:10.1016/j.chemosphere.2004.12.076 PMID:15993160

Mueller, H., Andersson, J. T., & Schrader, W. (2005). Selective characterization of high-molecular weight sulfur containing aromatics in vacuum residues using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Analytical Chemistry*, *77*(8), 2536–2543. doi:10.1021/ac0483522 PMID:15828790

Muginstein, A., Fichman, M., & Gutfinger, C. (2001). Gas absorption in a moving drop containing suspended solids. *International Journal of Multiphase Flow*, *27*(6), 1079–1094. doi:10.1016/S0301-9322(00)00063-X

Mukhopadhyaya, M., Chowdhury, R., & Bhattacharya, P. (2005). Two phase mathematical model for a bio-trickling reactor for the production of Ultra low sulfur diesel (ULSD) from deeply hydrodesulfurized diesel. *Catalysis Today*, *106*(1-4), 180–185. doi:10.1016/j.cattod.2005.07.128

Mukhopadhyaya, M., Chowdhury, R., & Bhattacharya, P. (2006). Biodesulfurization of hydrodesulfurized diesel in a trickle bed reactor - Experiments and modeling. *Journal of Scientific and Industrial Research*, *65*(5), 432–436.

Mukhopadhyaya, M., Chowdhury, R., & Bhattacharya, P. (2007). Trickle bed biodesulfurizer of diesel with backwash and recycle. *AIChE Journal. American Institute of Chemical Engineers*, *53*(8), 2188–2197. doi:10.1002/aic.11240

Mulligan, C. N. (2005). Environmental applications for biosurfactants. *Environmental Pollution*, *133*(2), 183–198. doi:10.1016/j.envpol.2004.06.009 PMID:15519450

Mullins, O. C.; Pomerantz, A. E.; Zuo, J. Y.; Dong, C. (2014). Downhole fluid analysis and asphaltene science for petroleum reservoir evaluation. *Annual review of chemical and biomolecular engineering*, 5, 325-45.

Mullins, O. C. (2010). The Modified Yen Model. *Energy & Fuels*, *24*(4), 2179–2207. doi:10.1021/ef900975e

Mullins, O. C., Mitra-Kirtley, S., van Elp, J., & Cramer, S. P. (1993). Molecular structure of nitrogen in coal from XANES spectroscopy. *Appl*, *47*(Spec.), 1268.

Mullins, O. C., Sabbah, H., Eyssautier, J., Pomerantz, A. E., Barré, L., & Andrews, A. B. et al. (2012). Advances in asphaltene science and the Yen–Mullins model. *Energy & Fuels*, *26*(7), 3986–4003. doi:10.1021/ef300185p

Mullins, O. C., Seifert, D. J., Zuo, J. Y., & Zeybek, M. (2013). Clusters of Asphaltene Nanoaggregates Observed in Oilfield Reservoirs. *Energy & Fuels*, *27*(4), 1752–1761. doi:10.1021/ef301338q

Muramatsu, K., Shimizu, T., Shinoda, N., & Tatani, A. (1984). Development of Mitsubishi wet flue gas desulfurization system. *Chem. Econ. Eng. Rev*, *16*(11), 15–22.

Murata, S., Murata, K., Kidena, K., & Nomura, M. (2003). A Novel Oxidative Desulfurization System for Diesel Fuels with Molecular Oxygen in the Presence of Cobalt Catalysts and Aldehydes. *Energy & Fuels*, *18*(1), 116–121. doi:10.1021/ef034001z

Murphy, S. E., Amin, S., Coletta, K., & Hoffman, D. (1992). Rat liver metabolism of benzo[b]naphtho[2,1-d]thiophene. *Chemical Research in Toxicology*, *5*(4), 491–495. doi:10.1021/tx00028a006 PMID:1382648

Muzic, M., Sertic-Bionda, K., & Adzamic, T. (2012). Evaluation of Commercial adsorbents and their application for desulfurization of model fuel. *Clean Techn Environ Policy*, *14*(2), 283–290. doi:10.1007/s10098-011-0399-4

Nagai, M., Goto, Y., Ishii, H., & Omi, S. (2000). XPS and TPSR study of nitrided molybdena-alumina catalyst for the hydrodesulfurization of dibenzothiophene. *Applied Catalysis A, General*, *192*(2), 189–199. doi:10.1016/S0926-860X(99)00341-5

Nagaveni, K., Hegde, M. S., Ravishan-Kar, N., Subbanna, G. N., & Madras, G. (2004). Synthesis and structure of nanocrystalline TiO2 with lower band gap showing high photocatalytic activity. *Langmuir*, *20*(7), 2900–2907. doi:10.1021/la035777v PMID:15835170

Nag, N. K., Sapre, A. V., Broderick, D. H., & Gates, B. C. (1979). Hydrodesulfurization of polycyclic aromatics catalyzed by sulfided CoO-MoO3γ-Al2O3: The relative reactivities. *Journal of Catalysis*, *57*(3), 509–512. doi:10.1016/0021-9517(79)90016-2

Naidich, J. V. (1981). The wettability of solids by liquid metals. *Progress in Surface Membrane Science*, *14*, 353–484. doi:10.1016/B978-0-12-571814-1.50011-7

Naito, M., Kawamoto, T., Fujino, K., Kobayashi, M., Maruhashi, K., & Tanaka, A. (2001). Long-term repeated biodesulfurization by immobilized *Rhodococcus erythropolis* KA 2-5-1 cells. *Applied Microbiology and Biotechnology*, *55*(3), 374–378. doi:10.1007/s002530000527 PMID:11341322

Nandi, S. (2010). Biodesulfurization of hydro-desulfurized diesel in airlift reactor. *Journal of Scientific and Industrial Research*, *69*(7), 543–547.

Nantasenamat, C., Isarankura-Na-Ayudhya, C., Naenna, T., & Prachayasittikul, V. (2007). Quantitative structure-imprinting factor relationship of molecularly imprinted polymers. *Biosensors & Bioelectronics*, *22*(12), 3309–3317. doi:10.1016/j.bios.2007.01.017 PMID:17317143

Nantasenamat, C., Naenna, T., Isarankura Na Ayudhya, C., & Prachayasittikul, V. (2005). Quantitative prediction of imprinting factor of molecularly imprinted polymers by artificial neural network. *Journal of Computer-Aided Molecular Design*, *19*(7), 509–524. doi:10.1007/s10822-005-9004-4 PMID:16244792

Nantasenamat, C., Tantimongcolwat, T., Naenna, T., Isarankura-Na-Ayudhya, C., & Prachayasittikul, V. (2006). Prediction of selectivity index of pentachlorophenol-imprinted polymers. *EXCLI Journal*, *5*, 150–163.

Napanang, T., & Sooknoi, T. (2009). Oxidative extraction of thiophene from n-dodecane over TS-1 in continuous process: A model for non-severe sulfur removal from liquid fuels. *Catalysis Communications*, *11*(1), 1–6. doi:10.1016/j.catcom.2009.07.022

Naumann, A. W., & Behan, A. S. (1981). Molybdenum disulfide catalyst and the preparation thereof. U.S. Patent 4,243,554.

Nava, H., Espino, J., Berhault, G., & Alonso-Nuñez, G. (2006). Effect of phosphorus addition on unsupported Ni–Mo–W sulfide catalysts prepared by the in situ activation of nickel/tetramethylammonium thiomolybdotungstate. *Applied Catalysis A, General*, *302*(2), 177–184. doi:10.1016/j.apcata.2005.12.025

Nava, H., Pedraza, F., & Alonso, G. (2005). Nickel-Molybdenum-Tungsten sulfide catalysts prepared by *in situ* activation of tri-metallic (Ni-Mo-W) alkylthiomolybdotungstates. *Catalysis Letters*, *99*(1-2), 65–71. doi:10.1007/s10562-004-0777-1

Nehlsen, J. P., Benziger, J. B., & Kevrekidis, I. G. (2003). Removal of Alkanethiols from a Hydrocarbon Mixture by a Heterogeneous Reaction with Metal Oxides. *Industrial & Engineering Chemistry Research*, *42*(26), 6919–6923. doi:10.1021/ie030665k

Nehlsen, J. P., Benziger, J. B., & Kevrekidis, I. G. (2004). A Process for the Removal of Thiols from a Hydrocarbon Stream by a Heterogeneous Reaction with Lead Oxide. *Energy & Fuels*, *18*(3), 721–726. doi:10.1021/ef034064h

Nekodzuka, S., Nakajima-Kambe, T., Nomura, N., Lu, J., & Nakahara, T. (1997). Specific desulfurization of dibenzothiophene by *Mycobacterium sp.* strain G3. *Biocatalysis and Biotransformation*, *15*(1), 17–27. doi:10.3109/10242429709003607

Nelli, C. H., & Rochelle, G. T. (1998). Simultaneous sulfur dioxide and nitrogen dioxide removal by calcium hydroxide and calcium silicate solids. *Journal of the Air & Waste Management Association*, *48*(9), 819–828. doi:10.1080/10473289.1998.10463728 PMID:9775761

Neves, C. S., Granadeiro, C. M., Cunha-Silva, L., Ananias, D., Gago, S., Feio, G., & Pereira, E. (2013). Europium polyoxometalates encapsulated in silica nanoparticles-characterization and photoluminescence studies. *European Journal of Inorganic Chemistry*, *16*(16), 2877–2886. doi:10.1002/ejic.201201482

Ngah, W. S. W., & Liang, K. H. (1999). Adsorption of gold(III) ions onto chitosan and *N*-carboxymethyl chitosan: Equilibrium studies. *Industrial & Engineering Chemistry Research*, *38*(4), 1411–1414. doi:10.1021/ie9803164

Ngamcharussrivichai, C., Chatratananon, C., Nuntang, S., & Prasassarakich, P. (2008). Adsorptive removal of thiophene and benzothiophene over zeolites from Mae Moh coal fly ash. *Fuel*, *87*(10-11), 2347–2351. doi:10.1016/j.fuel.2007.10.003

Nicholls, I. A., Adbo, K., Andersson, H. S., Andersson, P. O., Ankarloo, J., Hedin-Dahlström, J., & Wikman, S. et al. (2001). Can we rationally design molecularly imprinted polymers? *Analytica Chimica Acta*, *435*(1), 9–18. doi:10.1016/S0003-2670(01)00932-1

Nie, Y., Li, C.-X., & Wang, Z.-H. (2007). Extractive Desulfurization of Fuel Oil Using Alkylimidazole and Its Mixture with Dialkylphosphate Ionic Liquids. *Industrial & Engineering Chemistry Research*, *46*(15), 5108–5112. doi:10.1021/ie070385v

Nikolaev, P., Smalley, R. E., Bronikowski, M. J., Bradley, R. K., Rohmund, F., Colbert, D. T., & Smith, K. A. (1999). Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide. *Chemical Physics Letters*, *313*(1-2), 91–97. doi:10.1016/S0009-2614(99)01029-5

Nikolas, I. K., Stergiade, M., Papadopoulou, M. P., & Karatzas, G. P. (2008). Artificial neural networks as an alternative approach to groundwater modeling and environmental design. *Hydrological Processes*, *22*(17), 3337–3348. doi:10.1002/hyp.6916

Nogueira, R. F. P., Trovò, A. G., da Silva, M. R. A., Villa, R. D., & de Oliveira, M. C. (2007). Fundaments and environmental application of fenton and photofenon processes. *Quimica Nova*, *30*, 400–408. doi:10.1590/S0100-40422007000200030

Noguera, L. S., Ribeiro, S., Granadeiro, C. M., Pereira, E., Feio, G., Cunha-Silva, L., & Balula, S. S. (2014). Novel polyoxometalate silica nano-sized sphere: Efficient catalysts for olefin oxidation and the deep desulfurization process. *Dalton Troins*, *43*(25), 9518–9528. doi:10.1039/c3dt53444h

Noh, J., Jang, S., Lee, D., Shin, S., Ko, Y. J., Ito, E., & Joo, S. W. (2007). Abnormal adsorption behavior of dimethyl disulfide on gold surfaces. *Current Applied Physics*, *7*(6), 605–610. doi:10.1016/j.cap.2006.12.007

Noijiri, H., Habe, H., & Omori, T. (2001). Bacterial degradation of aromatic compounds via angular dioxygenation. *The Journal of General and Applied Microbiology*, *47*(6), 279–305. doi:10.2323/jgam.47.279 PMID:12483604

Nolan, P. S. (2000). *Flue Gas Desulfurization Technologies for Coal-Fired Power Plants*. Retrieved from http://www.babcock.com/library/Documents/br-1709.pdf

Nolan, P. S., Becker, T. W., Rodemeyer, P. O., & Prodesky, E. J. (1992). *Demonstration of Sorbent Injection Technology on a Wall-Fired Utility Boiler (Edgewater LIMB Demonstration).* Retrieved from http://nepis.epa.gov/

Nolte, T., Posch, T. N., Huhn, C., & Andersson, J. T. (2013). Desulfurized fuels from Athabasca bitumen and their polycyclic aromatic sulfur heterocycles. Analysis based on capillary electrophoresis coupled with TOF MS. *Energy & Fuels*, *27*(1), 97–107. doi:10.1021/ef301424d

Nordvik, A. B., Simmons, J. L., Bitting, K. R., Lewis, A., & Strøm-Kristiansen, T. (1996). Oil and water separation in marine oil spill clean-up operations. *Spill Science & Technology Bulletin*, *3*(3), 107–122. doi:10.1016/S1353-2561(96)00021-7

Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., & Dubonos, S. V. (2004). Electric field effect in atomically thin carbon films. *Science*, *306*(5696), 666–669. doi:10.1126/science.1102896 PMID:15499015

Nuhu, A. A. (2013). Bio-catalytic desulfurization of fossil fuels: A mini review. *Reviews in Environmental Science and Biotechnology*, *12*(1), 9–23. doi:10.1007/s11157-012-9267-x

Nygaard, H. G., Kiil, S., Johnsson, J. E., Jensen, J. N., Hansen, J., Fogh, F., & Dam-Johansen, K. (2004). Full-scale measurements of SO_2 gas phase concentrations and slurry compositions in a wet flue gas desulphurisation spray absorber. *Fuel*, *83*(9), 1151–1164. doi:10.1016/j.fuel.2003.12.007

Nylén, U., Delgado, J. F., Järås, S., & Boutonnet, M. (2004). Characterization of alkylated aromatic sulphur compounds in light cycle oil from hydrotreated vacuum gas oil using GC-SCD. *Fuel Processing Technology*, *86*(2), 223–234. doi:10.1016/j.fuproc.2004.03.001

Nyman, G. B. G. (1991). Seawater scrubbing removes SO_2 from refinery flue gases. *Oil & Gas Journal*, *89*(26), 51–55.

Ochoa González, R., Díaz-Somoano, M., López Antón, M. A., & Martínez-Tarazona, M. R. (2012). Effect of adding aluminum salts to wet FGD systems upon the stabilization of mercury. *Fuel*, *96*(0), 568–571. doi:10.1016/j.fuel.2012.01.054

Ogilvy, A. E., Draganjac, M., Rauchfuss, T. B., & Wilson, S. R. (1988). Activation and desulfurization of thiophene and benzothiophene by iron carbonyls. *Organometallics*, *7*(5), 1171–1177. doi:10.1021/om00095a024

Ogilvy, A. E., Skaugset, A. E., & Rauchfuss, T. B. (1989). Electron-transfer activation of coordinated thiophene: Preparation and desulfurization of (η^5-C_5Me_5)Rh(η^4-C_4Me_4S). *Organometallics*, *8*(11), 2739–2741. doi:10.1021/om00113a037

Ogunlaja, A. S., Coombes, M. J., Torto, N., & Tshentu, Z. R. (2014). The adsorptive extraction of oxidized sulfur-containing compounds from fuels by using molecularly imprinted chitosan materials. *Reactive & Functional Polymers*, *81*, 61–76. doi:10.1016/j.reactfunctpolym.2014.04.006

Ogunlaja, A. S., du Sautoy, C., Torto, N., & Tshentu, Z. R. (2014). Design, fabrication and evaluation of intelligent sulfone-selective polybenzimidazole nanofibers. *Talanta*, *126*, 61–72. doi:10.1016/j.talanta.2014.03.035 PMID:24881535

Ogunlaja, A. S., Khene, S., Antunes, E., Nyokong, T., Torto, N., & Tshentu, Z. R. (2013). The development of catalytic oxovanadium(IV)-containing microspheres for the oxidation of various organosulfur compounds. *Applied Catalysis A, General*, *462-463*, 157–167. doi:10.1016/j.apcata.2013.05.004

Ogunlaja, A. S., Walmsley, R. S., du Sautoy, C., Torto, N., Zenixole, R., & Tshentu, Z. R. (2013). Development of a Continuous Flow System for the Oxidative Desulfurization of Refractory Organosulfur Compounds in Hydrotreated Diesel. *Energy & Fuels*, *27*(12), 7714–7723. doi:10.1021/ef401708f

Ohshiro, T., Hirata, T., Hashimoto, I., & Izumi, Y. (1996). Characterization of dibenzothiophene desulfurization reaction by whole cell of Rhodococcus erythropolis H-2 in the presence of hydrocarbons. *Journal of Fermentation and Bioengineering*, *82*(6), 610–612. doi:10.1016/S0922-338X(97)81264-0

Ohshiro, T., Hirata, T., & Izumi, Y. (1996). Desulfurization of dibenzothiophene derivatives by whole cells of Rhodococcus erythropolis H-2. *FEMS Microbiology Letters*, *142*(1), 65–70. doi:10.1111/j.1574-6968.1996.tb08409.x

Ohshiro, T., & Izumi, Y. (1999). Microbial desulfurization of organic sulfur compounds in petroleum. *Bioscience, Biotechnology, and Biochemistry*, *63*(1), 1–9. doi:10.1271/bbb.63.1 PMID:10052116

Ohshiro, T., Suzuki, K., & Izumi, Y. (1996). Regulation of dibenzothiophene degrading enzyme activity of *Rhodococcus erythropolis* D-1. *Journal of Fermentation and Bioengineering*, *81*(2), 121–124. doi:10.1016/0922-338X(96)87588-X

Oikawa, K., Yongsiri, C., Takeda, K., & Harimoto, T. (2003). Seawater flue gas desulfurization: Its technical implications and performance results. *Environment and Progress*, *22*(1), 67–73. doi:10.1002/ep.670220118

Okada, H., Nomura, N., Nakahara, T., Saitoh, K., Uchiyama, H., & Maruhashi, K. (2003). Analyses of microbial desulfurization reaction of alkylated dibenzothiophenes dissolved in oil phase. *Biotechnology and Bioengineering*, *83*(4), 489–497. doi:10.1002/bit.10694 PMID:12800143

Okamoto, Y. (1997). Preparation and characterization of zeolite-supported molybdenum and cobalt-molybdenum sulfide catalysts. *Catalysis Today*, *39*(1-2), 45–49. doi:10.1016/S0920-5861(97)00087-4

Olausson, S., Wallin, M., & Bjerle, I. (1993). A model for the absorption of sulphur dioxide into a limestone slurry. *Chemical Engineering Journal*, *51*(2), 99–108. doi:10.1016/0300-9467(93)80016-H

Oldfield, C., Pogrebinsky, O., Simmonds, J., Olson, E. S., & Kulpa, C. F. (1997). Elucidation of the metabolic pathway for dibenzothiophene desulphurization by Rhodococcus sp. strain IGTS8 (ATCC 53968). *Microbiology*, *143*(9), 2961–2973. doi:10.1099/00221287-143-9-2961 PMID:9308179

Olguin, E., & Vrinat, M., Ceden˜o, L., Ramirez, J., Borque, M., & López-Agudo, A. (. (1997). The use of TiO_2-Al_2O_3 binary oxides as supports for Mo-based catalysts in hydrodesulfurization of thiophene and dibenzothiophene. *Applied Catalysis A, General*, *165*(1–2), 1–13. doi:10.1016/S0926-860X(97)00184-1

Olivas, A., Galván, D. H., Alonso, G., & Fuentes, S. (2009). Trimetallic NiMoW unsupported catalysts for HDS. *Applied Catalysis A, General*, *352*(1-2), 10–16. doi:10.1016/j.apcata.2008.09.022

Oliveira, A. A., Teixeira, I. F., Leandro, P., Ribeiro, E. L., Lorencon, E., Ardisson, J. D., & Moura, C. C. (2013). Magnetic amphiphilic nanocomposites produced via chemical vapor deposition of CH4 on Fe-Mo/nano-Al2O3. *Applied Catalysis A, General*, *456*, 126–134. doi:10.1016/j.apcata.2013.02.027

Ollero, P., Gutiérrez Ortiz, F. J., Cabanillas, A., & Otero, J. (2001). Flue-gas desulfurization in circulating fluidized beds: An empirical model from an experimental pilot-plant study. *Industrial & Engineering Chemistry Research*, *40*(23), 5640–5648. doi:10.1021/ie010152i

Ollero, P., Salvador, L., & Cañadas, L. (1997). An experimental study of flue gas desulfurization in a pilot spray dryer. *Environment and Progress*, *16*(1), 20–28. doi:10.1002/ep.3300160116

Olmos, A., Olguin, P., Fajardo, C., Razo, E., & Monroy, O. (2004). Physicochemical characterization of spent caustic from the OXIMER process and sour waters from Mexican oil refineries. *Energy & Fuels*, *18*(2), 302–304. doi:10.1021/ef030053c

Oral, J., Sikula, J., Puchyr, R., Hajny, Z., Stehlik, P., & Bebar, L. (2005). Processing of waste from pulp and paper plant. *Journal of Cleaner Production*, *13*(5), 509–515. doi:10.1016/j.jclepro.2003.09.005

Orita, H., Uchida, K., & Itoh, N. (2004). A volcano-type relationship between the adsorption energy of thiophene on promoted MoS2 cluster-model catalysts and the experimental HDS activity: Ab initio density functional study. *Applied Catalysis A, General*, *258*(1), 115–120. doi:10.1016/j.apcata.2003.08.016

Orr, W. L. & White, C.M. (Eds.) (1990). Geochemistry of Sulfur in Fossil Fuels. ACS Books, Washington. doi:10.1021/bk-1990-0429

Orr, W. L. (1975). Sulfur in petroleum and related fossil organic materials. *ACS Div Petr. Chem. Preprints*, *21*, 417–421.

Orr, W. L. (1978). In O. P. Strausz & E. M. Lown (Eds.), *Oil Sand and Oil Shale Chemistry* (pp. 223–243). Verlag Chemie.

Oshiro, T., Kanbayashi, Y., Hine, Y., & Izumi, Y. (1995). Involvment of flavin coenzyme in dibenzothiophene degrading enzyme system from Rhodococcus erythropolis D-1. *Bioscience, Biotechnology, and Biochemistry*, *59*(7), 1349–1351. doi:10.1271/bbb.59.1349

Otsuki, S., Nonaka, T., Qian, W., Ishihara, A., & Kabe, T. (1999). Oxidative desulfurization of middle distillate using ozone. *Journal of the Japan Petroleum Institute*, *42*(5), 315–320. doi:10.1627/jpi1958.42.315

Otsuki, S., Nonaka, T., Qian, W., Ishihara, A., & Kabe, T. (2001). Oxidative desulfurization of middle distillate-oxidation of dibenzothiophene using t-butyl hypochlorite. *Journal of the Japan Petroleum Institute*, *44*(1), 18–24. doi:10.1627/jpi1958.44.18

Otsuki, S., Nonaka, T., Takashima, N., Qian, W., Ishihara, A., Imai, T., & Kabe, T. (2000). Oxidative desulfurization of light gas oil and vacuum gas oil by oxidation and solvent extraction. *Energy & Fuels*, *14*(6), 1232–1239. doi:10.1021/ef000096i

Pacheco, M. A., Lange, E. A., Pienkos, P. T., & Yu, L. Q., R. M., Lin Q, & LK, L. (1999). *Recent advances in biodesulfurization of diesel fuel.* Paper presented at the National Petrochemical and Refiners Association Annual Meeting NPRA AM-99-27, San Antonio, Texas.

Pacheco, M. A., Lange, E. A., Pienkos, P. T., Yu, L.-Q., Rouse, M. P., Lin, Q., & Linguist, L. K. (1999). *Recent advances in biodesulfurization of diesel fuel*. National Petrochemical And Refiners Association-Publications-All Series.

Paixão, S. M., Teixeira, P. D., Silva, T. P., Teixeira, A. V., & Alves, L. (2013). Screening of novel yeast inulinases and further application to bioprocesses. *New Biotechnology*, *30*(6), 598–606. doi:10.1016/j.nbt.2013.02.002 PMID:23419675

Palomeque, J., Clacens, J. M., & Figueras, F. (2002). Oxidation of dibenzothiophene by hydrogen peroxide catalysed by solid bases. *Journal of Catalysis*, *211*(1), 103–108. doi:10.1016/S0021-9517(02)93721-8

Palomino, J. M., Tran, D. T., Hausser, J. L., Dong, H., & Oliver, S. R. J. (2014). Mesopourous Silica nanoparticles for high Capacity adsorptive desulfurization. *J. Matter. Chem A*, *2*(36), 14890. doi:10.1039/C4TA02570A

Pandey, R. A., & Malhotra, S. (1999). Desulfurization of gaseous fuels with recovery of elemental sulfur: An overview. *Critical Reviews in Environmental Science and Technology*, *29*(3), 229–268. doi:10.1080/10643389991259236

Paraguay-Delgado, F., Huirache-Acuña, R., Jose-Yacaman, M., & Alonso-Nuñez, G. (2008). Synthesis and structural characterization of Mo-Ni-W oxide nanostructures. *Journal of Nanoscience and Nanotechnology*, *8*(6), 2983–2989. doi:10.1166/jnn.2008.117 PMID:18681035

Park, J. G., Ko, C. H., Yi, K. B., Park, J. H., Han, S. S., Cho, S. H., & Kim, J. N. (2008). Reactive adsorption of sulfur compounds in diesel on nickel supported on mesoporous silica. *Applied Catalysis B: Environmental*, *81*(3-4), 244–250. doi:10.1016/j.apcatb.2007.12.014

Park, S., & Ruoff, R. S. (2009). Chemical methods for the production of graphenes. *Nature Nanotechnology*, *4*(4), 217–224. doi:10.1038/nnano.2009.58 PMID:19350030

Parr, R. G., & Yang, W. (1989). *Density functional theory of atoms and molecules*. Oxford: Oxford University Press.

Pasquali, L., Terzi, F., Montecchi, M., Doyle, B. P., Lukkari, J., & Zanfrognini, B. et al. (2009). Adsorption of 3, 4-ethylenedioxytiophene (EDOT) on noble metal surfaces: A photoemission and X-ray absorption study. *Journal of Electron Spectroscopy and Related Phenomena*, *172*(1-3), 114–119. doi:10.1016/j.elspec.2009.03.014

Patel, S. B., Killbane, J. J., & Webster, D. A. (1997). Biodesulphurisation of dibenzothiophene in hydrophobic media by *Rhodococcus* sp. strain IGTS8. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *69*(1), 100–106. doi:10.1002/(SICI)1097-4660(199705)69:1<100::AID-JCTB675>3.0.CO;2-9

Pawelec, B., Mariscal, R., Fierro, J. L. G., Greenwood, A., & Vasudevan, P. T. (2001). Carbon-supported tungsten and nickel catalysts for hydrodesulfurization and hydrogenation reactions. *Applied Catalysis A, General*, *206*(2), 295–307. doi:10.1016/S0926-860X(00)00605-0

Pawelec, B., Navarro, R. M., Campos-Martin, J. M., & Fierro, J. L. G. (2010). Towards near zero-sulfur liquid fuels: A perspective review. *Catalysis Science & Technology*, *1*(1), 23–42. doi:10.1039/c0cy00049c

Paybarah, A., Bone, R. L., & Corcoran, W. H. (1982). Selective oxidation of dibenzothiophene by peroxybenzoic acid formed in situ. *Industrial & Engineering Chemistry Process Design and Development*, *21*(3), 426–431. doi:10.1021/i200018a014

Pearson, R. G. (1986). Absolute electronegativity and hardness correlated with molecular orbital theory. *Proceedings of the National Academy of Sciences of the United States of America*, *83*(22), 8440–8441. doi:10.1073/pnas.83.22.8440 PMID:16578791

Pecoraro, T. A., & Chianelli, R. R. (1981). Hydrodesulfurization catalysis by transition metal sulphides. *Journal of Catalysis*, *67*(2), 430–445. doi:10.1016/0021-9517(81)90303-1

Peng, Y., Meng, Z., Zhong, C., Lu, J., Yu, W., Yang, Z., & Qian, Y. (2001). Hydrothermal Synthesis of MoS2 and Its Pressure-Related Crystallization. *Journal of Solid State Chemistry*, *159*(1), 170–173. doi:10.1006/jssc.2001.9146

Perathoner, S., Gangeri, M., Lanzafame, P., & Centi, G. (2007). Nanostructured electrocatalytic Pt-carbon materials for fuel cells and CO_2conversion. *Kinetics and Catalysis*, *48*(6), 877–883. doi:10.1134/S0023158407060171

Perfumo, A., Smyth, T. J. P., Marchant, R., & Banat, I. M. (2010). Production and roles of biosurfactants and bioemulsifiers in accessing hydrophobic substrates. In *Handbook of hydrocarbon and lipid microbiology* (pp. 1501–1512). Springer. doi:10.1007/978-3-540-77587-4_103

Persano, L., Camposeo, A., Tekmen, C., & Pisignano, D. (2013). Industrial upscaling of electrospinning and applications of polymer nanofibers: A review. *Macromolecular Materials and Engineering*, *298*(5), 504–520. doi:10.1002/mame.201200290

Petit, C., Peterson, G. W., Mahle, J., & Bandosz, T. J. (2010). The effects of oxidation on the surface chemistry of sulfur-containing carbons and their arsine adsorption capacity. *Carbon*, *48*(6), 1779–1787. doi:10.1016/j.carbon.2010.01.024

Pfeiffer, J. P. (1950). *The Properties of Asphaltic Bitumen*. Amsterdam: Elsevier.

Pfüller, O., & Walstra, F. P. (2003). Patent No. DE 102 17 469 C1.

Pham, Q. P., Sharma, U., & Mikos, A. G. (2006). Electrospinning of polymeric nanofibers for tissue engineering applications: A review. *Tissue Engineering*, *12*(5), 1197–1211. doi:10.1089/ten.2006.12.1197 PMID:16771634

Phillips, J. A., Canagaratna, M., Goodfriend, H., & Leopold, K. R. (1995). Microwave Detection of A Key Intermediate in the Formation of Atmospheric Sulfuric Acid: The Structure of H20-SO3. *Journal of Physical Chemistry*, *99*(2), 501–504. doi:10.1021/j100002a008

Piddington, C. S., Kovacevich, B. R., & Rambosek, J. (1995). Sequence and molecular characterization of a DNA region encoding the dibenzothiophene desulfurization operon of Rhodococcus sp. strain IGTS8. *Applied and Environmental Microbiology*, *61*(2), 468–475. PMID:7574582

Piehl, R. L. (1987). Paper 196, *Naphthenic Acid Corrosion in Crude Distillation Units*. *Corrosion*, 87.

Pintado-Sierra, M., Rosero-Almansa, A. M., Corma, A., Iglesias, M., & Sanchez, F. (2013). Bifunctional iridium-(2-aminoterephthalate)–Zr-MOF chemoselective catalyst for the synthesis of secondary amines by one-pot three-step cascade reaction. *Journal of Catalysis*, *299*, 147–145. doi:10.1016/j.jcat.2012.12.004

Planeta, J., Karasek, P., & Roth, M. (2006). Distribution of sulfur-containing aromatics between [hmim][Tf_2N] and supercritical CO_2: A case study for deep desulfurization of oil refinery streams by extraction with ionic liquids. *Green Chemistry*, *8*(1), 70–77. doi:10.1039/B511778J

Plantenga, F. L., & Leliveld, R. G. (2003). Sulfur in fuels: More stringent sulfur specifications for fuels are driving innovation. *Applied Catalysis A, General*, *248*(1-2), 1–7. doi:10.1016/S0926-860X(03)00133-9

Plummer, M. A., & Bonelli, J. R. F. (2002). Patent US 0139713 A1.

Poisot, M., Bensch, W., Fuentes, S., Ornelas, C., & Alonso, G. (2007). High activity Ni/MoS_2 catalysts obtained from alkylthiometalate mixtures for the hydrodesulfurization of dibenzothiophene. *Catalysis Letters*, *117*(1-2), 43–52. doi:10.1007/s10562-007-9143-4

Poladi, R. H., & Landry, C. C. (2002). Oxidation of octane and ciclohexane using a new porous substrate, Ti-MMM1. *Microporous and Mesoporous Materials*, *52*(1), 11–18. doi:10.1016/S1387-1811(02)00272-X

Polshettiwar, V., & Varma, R. S. (2010). Green Chemistry by Nano-catalysis. *Green Chemistry*, *12*(5), 743–754. doi:10.1039/b921171c

Pomerantz, A. E., Bake, K. D., Craddock, P. R., Kurzenhauser, K., Kodalen, B. G., Mitra-Kirtley, S., & Bolin, T. (2014). Sulfur speciation in kerogen and bitumen from gas and oil shales. *Organic Geochemistry*, *68*, 5–12. doi:10.1016/j.orggeochem.2013.12.011

Pomerantz, A. E., Hammond, M. R., Morrow, A. L., Mullins, O. C., & Zare, R. N. (2008). Two-Step Laser Mass Spectrometry of Asphaltenes. *Journal of the American Chemical Society*, *130*(23), 7216–7217. doi:10.1021/ja801927v PMID:18484722

Pomerantz, A. E., Hammond, M. R., Morrow, A. L., Mullins, O. C., & Zare, R. N. (2009). Asphaltene Molecular-Mass Distribution Determined by Two-Step Laser Mass Spectrometry. *Energy & Fuels*, *23*(3), 1162–1168. doi:10.1021/ef8006239

Pomerantz, A. E., Seifert, D. J., Bake, K. D., Craddock, P. R., Mullins, O. C., & Kodalen, B. G. et al. (2013). Sulfur chemistry of asphaltenes from a highly compositionally graded oil column. *Energy & Fuels*, *27*(8), 4604–4608. doi:10.1021/ef400773f

Poon, C. S., Kou, S. C., Lam, L., & Lin, Z. S. (2001). Activation of fly ash/cement systems using calcium sulfate anhydrite ($CaSO_4$). *Cement and Concrete Research*, *31*(6), 873–881. doi:10.1016/S0008-8846(01)00478-1

Poon, C. S., Qiao, X. C., & Lin, Z. S. (2004). Effects of flue gas desulphurization sludge on the pozzolanic reaction of reject-fly-ash-blended cement pastes. *Cement and Concrete Research*, *34*(10), 1907–1918. doi:10.1016/j.cemconres.2004.02.027

Pope, C. A. III, Burnett, R. T., Thun, M. J., Calle, E. E., Krewski, D., Ito, K., & Thurston, G. D. (2002). Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *Journal of the American Medical Association*, *287*(9), 1132–1141. doi:10.1001/jama.287.9.1132 PMID:11879110

Popov, V. N. (2004). Carbon nanotubes: Properties and applications. *Materials Science and Engineering R Reports*, *43*(3), 61–102. doi:10.1016/j.mser.2003.10.001

Poulet, O., Hubaut, R., Kasztelan, S., & Grimblot, J. (1991). Experimental Evidences of the Direct Influence of Phosphorus on Activity and Selectivity of a MoS2-γAl2O3 Hydrotreating Catalyst. *Bulletin des Sociétés Chimiques Belges*, *100*(11-12), 857–863. doi:10.1002/bscb.19911001110

Pourmohammadbagher, A., Jamshidi, E., Ale-Ebrahim, H., Dabir, B., & Mehrabani-Zeinabad, M. (2011). Simultaneous removal of gaseous pollutants with a novel swirl wet scrubber. *Chemical Engineering and Processing: Process Intensification*, *50*(8), 773–779. doi:10.1016/j.cep.2011.06.001

Prasad, V. V. D. N., Jeong, K. E., Chae, H. J., Kim, C. U., & Jeong, S. Y. (2008). Oxidative desulfurization of 4,6-dimethyl dibenzothiophene and light cycle oil over supported molybdenum oxide catalysts. *Catalysis Communications*, *9*(10), 1966–1969. doi:10.1016/j.catcom.2008.03.021

Prins, R., & Bussell, M. E. (2012). Metal Phosphides: Preparation, Characterization and Catalytic Reactivity. *Catalysis Letters*, *142*(12), 1413–1436. doi:10.1007/s10562-012-0929-7

Prins, R., de Beer, V. H. J., & Somorjai, G. A. (1989). Structure and Function of the Catalyst and the Promoter in Co—Mo Hydrodesulfurization Catalysts. *Catalysis Reviews. Science and Engineering*, *31*(1-2), 1–41. doi:10.1080/01614948909351347

Purcell, J. M., Juyal, P., Kim, D.-G., Rodgers, R. P., Hendrickson, C. L., & Marshall, A. G. (2007). Sulfur speciation in petroleum: Atmospheric pressure photoionization or chemical derivatization and electrospray ionization fourier transform Ion cyclotron resonance mass spectrometry. *Energy & Fuels*, *21*(5), 2869–2874. doi:10.1021/ef700210q

Qin, S., Hansen, B. B., & Kiil, S. (2014). Effects of foaming and antifoaming agents on the performance of a wet flue gas desulfurization pilot plant. *AIChE Journal. American Institute of Chemical Engineers*, *60*(7), 2382–2388. doi:10.1002/aic.14428

Qi, R., Wang, Y., Chen, J., Li, J., & Zhu, S. (2007a). Pervaporative desulfurization of model gasoline with Ag2O-filled PDMS membranes. *Separation and Purification Technology*, *57*(1), 170–175. doi:10.1016/j.seppur.2007.04.001

Qi, R., Wang, Y., Chen, J., Li, J., & Zhu, S. (2007b). Removing thiophenes from n-octane using PDMS–AgY zeolite mixed matrix membranes. *Journal of Membrane Science*, *295*(1–2), 114–120. doi:10.1016/j.memsci.2007.02.047

Qi, R., Wang, Y., Li, J., Zhao, C., & Zhu, S. (2006). Pervaporation separation of alkane/thiophene mixtures with PDMS membrane. *Journal of Membrane Science*, *280*(1–2), 545–552. doi:10.1016/j.memsci.2006.02.008

Qi, R., Zhao, C., Li, J., Wang, Y., & Zhu, S. (2006). Removal of thiophenes from n-octane/thiophene mixtures by pervaporation. *Journal of Membrane Science*, *269*(1–2), 94–100. doi:10.1016/j.memsci.2005.06.022

Qiu, J., Wang, G., Bao, Y., Zhang, Y., & Zeng, D. (2012). Catalytic Oxidative desulfurization of model fuel oil with phosphomolybdic acid loaded on $SiO_{2.}$ *Advanced Materials*, *512-515*, 2110–2114. doi:10.4028/www.scientific.net/AMR.512-515.2110

Qiu, L., Zou, K., & Xu, G. (2013). Investigation on the sulfur state and phase transformation of spent and regenerated S zorb sorbents using XPS and XRD. *Applied Surface Science*, *266*, 230–234. doi:10.1016/j.apsusc.2012.11.156

Quintana-Melgoza, J. M., Cruz-Reyes, J., & Avalos-Borja, M. (2001). Synthesis and characterization of $NiWO_4$ crystals. *Materials Letters*, *47*(4-5), 314–318. doi:10.1016/S0167-577X(00)00272-X

Radke, M., Welte, D. H., & Wilsch, H. (1982). Geochemical study on a well in the Western Canada Basin: Relation of the aromatic distribution pattern to maturity of organic matter. *Geochimica et Cosmochimica Acta*, *46*(1), 1–10. doi:10.1016/0016-7037(82)90285-X

Rahmat, N., Zuhairi Abdullah, A., & Rahman Mohamed, A. (2010). A Review: Mesoporous Santa Barbara Amorphous-15, Types, Synthesis and Its Applications towards Biorefinery Production. *American Journal of Applied Sciences*, *7*(12), 1579–1586. doi:10.3844/ajassp.2010.1579.1586

Raj Mohan, B., & Meikap, B. C. (2010). Control of so2 from industrial effluents by a spray-cum bubble column scrubber. *Journal of Applied Sciences*, *10*(24), 3277–3282. doi:10.3923/jas.2010.3277.3282

Rajmohan, B., Reddy, S. N., & Meikap, B. C. (2008). Removal of SO2 from industrial effluents by a novel twin fluid air-assist atomized spray scrubber. *Industrial & Engineering Chemistry Research*, *47*(20), 7833–7840. doi:10.1021/ie800712a

Ralph, Y. T., Takahashi, A., & Yang, F. H. (2001). New Sorbents for Desulfurization of Liquid Fuels by π –Complexation. *Industrial & Engineering Chemistry Research*, *40*(26), 6236–6239. doi:10.1021/ie010729w

Ramachandran, P. A., & Sharma, M. M. (1969). Absorption with fast reaction in a slurry containing sparingly soluble fine particles. *Chemical Engineering Science*, *24*(11), 1681–1686. doi:10.1016/0009-2509(69)87033-8

Ramana, M. V., Ramanathan, V., Feng, Y., Yoon, S.-C., Kim, S.-W., Carmichael, G. R., & Schauer, J. J. (2010). Warming influenced by the ratio of black carbon to sulphate and the black-carbon source. *Nature Geoscience*, *3*(8), 542–545. doi:10.1038/ngeo918

Ramanathan, V., Chung, C., Kim, D., Bettge, T., Buja, L., & Kiehl, J. T. et al. (2005). Atmospheric brown clouds: Impacts on South Asian climate and hydrological cycle. *Proceedings of the National Academy of Sciences of the United States of America*, *102*(15), 5326–5333. doi:10.1073/pnas.0500656102 PMID:15749818

Ramaswamy, V., Bhagwat, M., Srinivas, D., & Ramaswamy, A. V. (2004). Structural and spectral features of nanocrystalline copper-stabilized zirconia. *Catalysis Today*, *97*(1), 63–70. doi:10.1016/j.cattod.2004.06.141

Ramı´rez, J., Fuentes, S., Dı’az, G., Vrinat, M., Breysse, M., & Lacroix, M. (1989). Hydrodesulphurization activity and characterization of sulphided molybdenum and cobalt—molybdenum catalysts: Comparison of Alumina-, Silica-Alumina- and Titania-Supported Catalysts. *Applied Catalysis*, *52*, 211–224.

Ramirez, J., Castano, V. M., Leclercq, C., & Lopez, A. (1992). High-resolution electron microscopy study of phosphorus-containing $MoS_2/A1_2O_3$ hydrotreating catalysts. *Applied Catalysis A*, *83*, 251–261. doi:10.1016/0926-860X(92)85038-D

Ramirez-Verduzco, L. F., De los Reyes, J. A., & Torres-Garcia, E. (2008). Solvent Effect in Homogeneous and Heterogeneous Reactions to Remove Dibenzothiophene by an Oxidation-Extraction Scheme. *Industrial & Engineering Chemistry Research*, *47*(15), 5353–5361. doi:10.1021/ie701692r

Rana, M. S., Sa’mano, V., Ancheyta, J., & Diaz, J. A. I. (2007). A review of recent advances on processing technologies for upgrading of heavy oils and residual. *Fuel*, *86*(9), 1216–1231. doi:10.1016/j.fuel.2006.08.004

Rao, C. N. R., Sood, A. K., Subrahmanyam, K. S., & Govindaraj, A. (2009). Graphene: The new two-dimensional nanomaterial. *Angewandte Chemie International Edition*, *48*(42), 7752–7777. doi:10.1002/anie.200901678 PMID:19784976

Rath, K., & Upadhyay, A. (2014). Role of pH in biodesulfurization of dibenzothiophene. *International Journal of Latest Technology in Engineering, Management and Applied Science, 3,* ISSN 2278-2540.

Rauchfuss, T. B. (1991). The Coordination Chemistry of Thiophenes (Vol. 39, pp. 259-329). New York: John Wiley & Sons doi:10.1002/9780470166406.ch5

Ray, S. S., & Okamoto, M. (2003). Polymer/layered silicate nanocomposites: A review from preparation to processing. *Progress in Polymer Science*, *28*(11), 1539–1641. doi:10.1016/j.progpolymsci.2003.08.002

Reichmuth, D. S., Hittle, J. L., Blanch, H. W., & Keasling, J. D. (2000). Biodesulfurization of dibenzothiophene in *Escherichia coli* is enhanced by expression of a *Vibrio harveyi* oxidoreductase gene. *Biotechnology and Bioengineering*, *67*(1), 72–79. doi:10.1002/(SICI)1097-0290(20000105)67:1<72::AID-BIT8>3.0.CO;2-C PMID:10581437

Reid, E. E. (1966). *Organic Chemistry of Bivalent Sulfur*. Chemical Pub. Co.

Reina, A., Jia, X., Ho, J., Nezich, D., Son, H., & Bulovic, V. et al. (2009). Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. *Nano Letters*, *9*(1), 30–35. doi:10.1021/nl801827v PMID:19046078

Reneker, D. H., & Chun, I. (1996). Nanometre diameter fibres of polymer, produced by electrospinning. *Nanotechnology*, *7*(3), 216–223. doi:10.1088/0957-4484/7/3/009

Reneker, D. H., & Yarin, A. L. (2008). Electrospinning jets and polymer nanofibers. *Polymer*, *49*(10), 2837–2425. doi:10.1016/j.polymer.2008.02.002

Riaz, U., Curnow, O. J., & Curtis, M. D. (1994). Desulfurization of Organic Sulfur Compounds Mediated by a Molybdenum /Cobalt / Sulfur Cluster. *Journal of the American Chemical Society*, *116*(10), 4357–4363. doi:10.1021/ja00089a025

Rioux, P., & Berard, P. A. (1928). The rate of absorption of sulfur dioxide in alkaline solutions. *Compt. Rend*., 186(1433).

Ritter, H. L., & Drake, L. C. (1945). Pore size distribution in porous materials. *Industrial & Engineering Chemistry Fundamentals*, *17*, 782–787.

Rivas Mercury, J., Cabra, A. A., Paiva, A. E. M., Angelica, R. S., Neves, R. F., & Scheller, T. (2011). Thermal behavior and evolution of the mineral phases of Brazilian red mud. *Journal of Thermal Analysis and Calorimetry*, *104*(2), 635–643. doi:10.1007/s10973-010-1039-7

Rivera, J. L., Navarro-Santos, P., Guerra-Gonzalez, R., & Lima, E. (2014). Interaction of refractory dibenzothiophenes and polymerizable structures. *International Journal of Polymer Science*, *2014*, 1–11. doi:10.1155/2014/103945

Rivera-Muñoz, E. M., Pawelec, B., Nava, R., Cortés, J. A., & Huirache-Acuña, R. (2015). SBA-16 Mesoporous Silica as Catalytic Support for Hydrodesulfurization Catalysts. In *Comprehensive Guide for Mesoporous Materials: Application and Commercialization* (Vol. 4, pp. 343–361). Hauppauge, New York, USA: Nova Science Publishers, Inc.

Robert, C. S. (2004 Spring). TransFiningTM – a novel process for low sulfur fuels. Proceedings of the American institute of chemical engineers.

Roberts, J. T., & Friend, C. M. (1987). Ring size and strain as a control of reaction selectivity: Ethylene sulfide on molybdenum (110). *Journal of the American Chemical Society*, *109*(25), 7899–7900. doi:10.1021/ja00259a058

Rochelle, G. T., & King, C. J. (1977). The effect of additives on mass transfer in $CaCO_3$ or CaO slurry scrubbing of SO_2 from waste gases. Industrial & Engineering Chemistry Fundamentals, *16*(1), 67–75. doi:10.1021/i160061a015

Rodemerck, U., & Linke, D. (2009). High-throughput experimentation. In K. P. De Jong (Ed.), *Synthesis of solid catalysts* (pp. 217–240). Weinheim, Germany: Wiley-VCH. doi:10.1002/9783527626854.ch11

Rodgers, R. P., Hughey, C. A., Hendrickson, C. L., & Marshall, A. G. (2002). Advanced characterization of petroleum crude and products by high field Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Am. Chem. Soc. Fuel Chemistry Division Preprints*, *47*(2), 636–698.

Rodgers, R. P., & Marshall, A. G. (2005). *Petroleomics: Advanced Characterization of Petroleum-Derived Materials by Fourier Transform Ion-Cyclotron Resonance mass Spectrometry* (pp. 63–93). New York: Springer.

Rodrigues, L. R., & Teixeira, J. A. (2010). *Biomedical and therapeutic applications of biosurfactants* (pp. 75–87). New York: Springer.

Rodrigues, L., Banat, I. M., Teixeira, J., & Oliveira, R. (2006). Biosurfactants: Potential applications in medicine. *The Journal of Antimicrobial Chemotherapy*, *57*(4), 609–618. doi:10.1093/jac/dkl024 PMID:16469849

Rodríguez-Cabo, B., Rodríguez, H., Rodil, E., Arce, A., & Soto, A. (2014). Extractive and oxidative-extractive desulfurization of fuels with ionic liquids. *Fuel*, *117A*, 882–889.

Rodríguez-Cabo, B., Rodríguez, H., Rodil, E., Arce, A., & Soto, A. (2014). Extractive and oxidative-extractive desulfurization of fuels with ionic liquids. *Fuel*, *117*, 882–889. doi:10.1016/j.fuel.2013.10.012

Rodriguez-Gattorno, G., Galano, A., & Torres-Garcia, E. (2009). Surface acid-basic properties of WOX-ZrO2 and catalytic efficiency in oxidative desulfurization. *Applied Catalysis B: Environmental*, *92*(1-2), 1–8. doi:10.1016/j.apcatb.2009.07.031

Rodriguez, J. A., Liu, P., Takahashi, Y., Nakamura, K., Vines, F., & Illas, F. (2009). Desulfurization of Thiophene on Au/TiC(001): Au-C Interactions and Charge Polarization. *Journal of the American Chemical Society*, *131*(24), 8595–8602. doi:10.1021/ja901522a PMID:19530731

Ron, G., Paul, B., & Visnja, G. (2004). Oxidative desulfurization: A new technology for UISD. *Prepr Pap Am Chem Soc. Div Fuel Chem*, *49*(2), 577–579.

Ronkainen, N. J., Halsall, H. B., & Heineman, W. R. (2010). Electrochemical biosensors. *Chemical Society Reviews*, *39*(5), 1747–1763. doi:10.1039/b714449k PMID:20419217

Roquero, F. J., Roquerol K. S., W. Sing, P. Llewellyn, & Maurin, G. (2014). Adsorption by powders and porous solids: Principles, Methodology and Applications (2nd Edition). Elsevier UK.

Rouse, J. D., Sabatini, D. A., Suflita, J. M., & Harwell, J. H. (1994). Influence of surfactants on microbial degradation of organic compounds. *Critical Reviews in Environmental Science and Technology*, *24*(4), 325–370. doi:10.1080/10643389409388471

Rozanska, X., van Santen, R. A., Hutschka, F., & Hafner, J. (2003). A periodic density functional theory study of thiophenic derivative cracking catalyzed by mordenite. *Journal of Catalysis*, *215*(1), 20–29. doi:10.1016/S0021-9517(02)00148-3

Ruiz-Guerrero, R., Vendeuvre, C., Thiebaut, D., Bertoncini, F., & Espinat, D. (2006). Comparison of comprehensive two-dimensional gas chromatography coupled with sulfur-chemiluminescence detector to standard methods for speciation of sulfur-containing compounds in middle distillates. *Journal of Chromatographic Science*, *44*(9), 566–573. doi:10.1093/chromsci/44.9.566 PMID:17059685

Ruiz, M., Sastre, A. M., & Guibal, E. (2000). Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin. *Reactive & Functional Polymers*, *45*, 155–173. doi:10.1016/S1381-5148(00)00019-5

Ryan, J. G. (1942). Influence of Sulfur Compounds on Octane Number and Lead Susceptibility of Gasolines. *Industrial & Engineering Chemistry*, *34*(7), 824–832. doi:10.1021/ie50391a013

Ryu, H.-J., Grace, J. R., & Lim, C. J. (2006). Simultaneous CO_2/SO_2 capture characteristics of three limestones in a fluidized-bed reactor. *Energy & Fuels*, *20*(4), 1621–1628. doi:10.1021/ef050277q

Ryu, K., Heo, J., & Yoo, I. K. (2002). Removal of dibenzothiophene and its oxidized product in anhydrous water-immiscible organic solvent by immobilized cytochrome c. *Biotechnology Letters*, *24*(2), 143–146. doi:10.1023/A:1013806830105

Ryzhikov, A., Bezverkhyy, I., & Bellat, J. (2008). Reactive adsorption of thiophene on Ni/ZnO: Role of hydrogen pretreatment. *Applied Catalysis B: Environmental*, *84*(3-4), 766–772. doi:10.1016/j.apcatb.2008.06.009

Sabbah, H., Morrow, A. L., Pomerantz, A. E., & Zare, R. N. (2011). Evidence for Island Structures as the Dominant Architecture of Asphaltenes. *Energy & Fuels*, *25*(4), 1597–1604. doi:10.1021/ef101522w

Sada, E., Kumazawa, H., & Butt, M. A. (1977). Single gas absorption with reaction in a slurry containing fine particles. *Chemical Engineering Science*, *32*(10), 1165–1170. doi:10.1016/0009-2509(77)80048-1

Sada, E., Kumazawa, H., & Butt, M. A. (1979a). Chemical absorption into a finite slurry. *Chemical Engineering Science*, *34*(5), 715–718. doi:10.1016/0009-2509(79)85118-0

Sada, E., Kumazawa, H., & Butt, M. A. (1979b). Single and simultaneous absorptions of lean SO_2 and NO_2 into aqueous slurries of $Ca(OH)_2$ or $Mg(OH)_2$ particles. *Journal of Chemical Engineering of Japan*, *12*(2), 111–117. doi:10.1252/jcej.12.111

Saha, S. K., & Pramanik, P. (1995). Aqueous sol-gel synthesis of cordierite and cordierite-zirconia composite powders. *Journal of Materials Science*, *30*(11), 2855–2858. doi:10.1007/BF00349655

Saladino, R., Crucianelli, M., & De Angelis, F. (2010). Methyltrioxorhenium catalysis in nonconventional solvents: A great catalyst in safe reaction medium. *Chemistry and Sustainability*, *3*, 524–540. PMID:20391453

Saleh, T. A., Siddiqui, M. N., & Al-Arfaj, A. A. (2014). Synthesis of Multiwalled Carbon Nanotubes-Titania Nanomaterial for Desulfurization of Model Fuel. *Journal of Nanomaterials*, *2014*, 6. doi:10.1155/2014/940639

Salem, A. B. S. H. (1994). Naphtha desulfurization by adsorption. *Industrial & Engineering Chemistry Research*, *33*(2), 336–340. doi:10.1021/ie00026a025

Salem, A. B. S. H., & Hamid, H. S. (1997). Removal of sulfur compounds from naphtha solutions using solid adsorbents. *Chemical Engineering & Technology*, *20*(5), 342–347. doi:10.1002/ceat.270200511

Salernitanoa, E., Giorgi, L., & Dikonimos, M. (2014). Direct growth of carbon nanofibers on carbon-based substrates as integrated gas diffusion and catalysts layer for polymer electrolytes fuel cells. *International Journal of Hydrogen Energy*, *39*(27), 15005–15016. doi:10.1016/j.ijhydene.2014.07.060

Salmones, J., Galicia, J. A., Wang, J. A., Valenzuela, M. A., & Aguilar-Rios, G. (2000). Synthesis and characterization of nanocrystallite MgAl2O4 spinels as catalysts support. *Journal of Materials Science Letters*, *19*(12), 1033–1037. doi:10.1023/A:1006734902538

Sami, M., & Hatch, L. F. (1994). Chemistry of petrochemical processes, Gulf publishing company, Houston, Texas, p11-17.Monticello, D.J. (2000). Biodesulfurization and the upgrading of petroleum distillates. *Current Opinion in Biotechnology*, *11*, 540–546.

Samokhvalov, A., & Tatarchuk, B. J. (2010). Review of experimental characterization of active sites and determination of molecular mechanisms of adsorption, desorption and regeneration of the deep and ultradeep desulfurization sorbents for liquid fuels. *Catalysis Reviews*, *52*(3), 381–410. doi:10.1080/01614940.2010.498749

Sampanthar, J. T., Dou, J., Joo, G. G., Widjaja, E., & Eunice, L. Q. H. (2007). Template-free low temperature hydrothermal synthesis and characterization of rod-shaped manganese oxy-hydroxides and manganese oxides. *Nanotechnology*, *18*(2), 525–601. doi:10.1088/0957-4484/18/2/025601

Sampanthar, J. T., Xiao, H., Dou, J., Nah, T. Y., Rong, X., & Kwan, W. P. (2006). A novel oxidative desulfurization process to remove refractory sulfur compounds from diesel fuel. *Applied Catalysis B: Environmental*, *63*(1–2), 85–93. doi:10.1016/j.apcatb.2005.09.007

Sanchez-Delgado, R. A. (2002). *Organometallic Modeling of the Hydrodesulfurization and Hydrodenitrogenation Reactions*. Boston: Kluwer Academic Publishers. doi:10.1007/0-306-47619-3

Sánchez-Segado, S., Lozano, L. J., de Los Ríos, A. P., Hernández-Fernández, F. J., Godínez, C., & Juan, D. (2012). Process design and economic analysis of a hypothetical bioethanol production plant using carob pod as feedstock. *Bioresource Technology*, *104*, 324–328. doi:10.1016/j.biortech.2011.10.046 PMID:22100234

Sano, Y. (2004a). Adsorptive removal of sulfur and nitrogen species from a straight run gas oil over activated carbons for its deep hydrodesulfurization. *Applied Catalysis B: Environmental*, *49*(4), 219–225. doi:10.1016/j.apcatb.2003.12.007

Sano, Y., Choi, K. K., Korai, Y., & Mochida, I. (2004b). Selection further activation of activated carbons for removal of nitrogen species in gas oil as a pretreatment for its deep hydrodesulfurization. *Energy & Fuels*, *18*(3), 644–651. doi:10.1021/ef034080e

Sano, Y., Sugahara, K., Choi, K. H., Korai, Y., & Mochida, I. (2005). Two-step adsorption process for deep desulfurization of diesel oil. *Fuel*, *84*(7-8), 903–910. doi:10.1016/j.fuel.2004.11.019

Sarda, K. K., Bhandari, A., Pant, K. K., & Jain, S. (2012). Deep desulfurization of diesel fuel by selective adsorption over Ni/Al_2O_3 and Ni/ZSM-5 extrudates. *Fuel*, *93*, 86–91. doi:10.1016/j.fuel.2011.10.020

Sareen, N., Singh, S., & Bhattacharya, S. (2014). A Cu(II) mediated new desulfurization pathway involving elimination of ethylene sulphide. *Dalton Transactions (Cambridge, England)*, *43*(12), 4635–4638. doi:10.1039/c3dt53395f PMID:24509718

Sarret, G., Conna, J., Kasrai, M., Bancroft, G. M., Charrié-Duhaut, A., & Lemoine, S. et al. (1999). Chemical forms of sulfur in geological and archeological asphaltenes from Middle East, France, and Spain determined by sulfur K- and L-edge X-ray absorption near-edge structure spectroscopy. *Geochimica et Cosmochimica Acta*, *63*(22), 3767–3779. doi:10.1016/S0016-7037(99)00205-7

Satterfeld, C. N. (1991). *Heterogeneous Catalysis in Industrial Practice.* New York, NY: McGraw-Hill Book Company.

Satterfield, C. N. (1996). *Heterogeneous Catalysis in Industrial Practice: Catalyst Preparation and Manufacture* (2nd ed., pp. 87–129). Malabar, FL, USA: Krieger Publishing Co.

Satterfield, C. N., Modell, M., & Wilkens, J. A. (1980). Simultaneous Catalytic Hydrodenitrogenation of Pyridine and Hydrodesulfurization of Thiophene. *Industrial & Engineering Chemistry Process Design and Development*, *19*(1), 154–160. doi:10.1021/i260073a027

Sattler, A., & Parkin, G. (2011). Carbon−Sulfur Bond Cleavage and Hydrodesulfurization of Thiophenes by Tungsten. *Journal of the American Chemical Society*, *133*(11), 3748–3751. doi:10.1021/ja111034g PMID:21348517

Savage, D. W., Kaul, B. K., Dupre, G. D., O'Bara, J. T., Wales, W. E., & Ho, T. C. (1995). Deep desulfurization of distillate fuels. *US Patent*, 5454933.

Savithra, G. H. L., Muthuswamy, E., Bowker, R. H., Carrillo, B. A., Bussell, M. E., & Brock, S. L. (2013). Rational Design of Nickel Phosphide Hydrodesulfurization Catalysts: Controlling Particle Size and Preventing Sintering. *Chemistry of Materials*, *25*(6), 825–833. doi:10.1021/cm302680j

Saxton, R. J., & Minhas, B. S. (2002). Patent WO 02/053682 A1.

Schilling, B. M., Alvarez, L. M., Wang, D. I. C., & Cooney, C. L. (2002). Continuous desulfurization of dibenzothiophene with *Rhodococcus rhodochrous* IGTS8 (ATCC 53968). *Biotechnology Progress*, *18*(6), 1207–1213. doi:10.1021/bp0200144 PMID:12467453

Schlapbach, L., & Züttel, A. (2001). Hydrogen-storage materials for mobile applications. Hydrogen-storage materials for mobile applications. *Nature*, *414*(6861), 353–358. doi:10.1038/35104634 PMID:11713542

Schuetz, R. D., & Jacobs, R. L. (1961). The Preparation and Desulfurization of Some Unsymmetrically Substituted Thiiranes. *The Journal of Organic Chemistry*, *26*(9), 3467–3471. doi:10.1021/jo01067a106

Schuit, G. C. A., & Gates, B. C. (1973). Chemistry and engineering of catalytic hydrodesulfurization. *AIChE Journal. American Institute of Chemical Engineers*, *19*(3), 417–438. doi:10.1002/aic.690190303

Schulz, H., Böhringer, W., Ousmanov, F., & Waller, P. (1999). Refractory sulfur compounds in gas oils. *Fuel Processing Technology*, *61*(1-2), 5–41. doi:10.1016/S0378-3820(99)00028-4

Schulz, H., Böhringer, W., Waller, P., & Ousmanov, F. (1999). Gas oil deep hydrodesulfurization: Refractory compounds and retarded kinetics. *Catalysis Today*, *49*(1-3), 87–97. doi:10.1016/S0920-5861(98)00412-X

Scott, K., Jachuck, R. J., & Hall, D. (2001). Crossflow microfiltration of water-in-oil emulsions using corrugated membranes. *Separation and Purification Technology*, *22*(1-2), 431–441. doi:10.1016/S1383-5866(00)00180-5

Scott, T. C., & Wham, R. M. (1989). An electrically driven multistage countercurrent solvent extraction device: The emulsion-phase contactor. *Industrial & Engineering Chemistry Research*, *28*(1), 94–97. doi:10.1021/ie00085a016

Seah, C. M., Chai, S. P., & Mohamed, A. R. (2014). Mechanisms of graphene growth by chemical vapour deposition on transition metals. *Carbon*, *70*, 1–21. doi:10.1016/j.carbon.2013.12.073

Seewald, J. S. (1998). Sulfur greases the wheels. *Nature*, *391*(6663), 128–129. doi:10.1038/34301 PMID:9428759

Segawa, K., Takahashi, K., & Satoh, S. (2000). Development of new catalysts for deep hydrodesulfurization of gas oil. *Catalysis Today*, *63*(2–4), 123–131. doi:10.1016/S0920-5861(00)00452-1

Sellergren, B. (2001). *In molecularly imprinted polymers: man-made mimics of antibodies and their applications in analytical chemistry, techniques and instrumentation in analytical chemistry* (Vol. 23, pp. 113–184). Amsterdam: Elsevier.

Sengupta, A., Kamble, P. D., Basu, J. K., & Sengupta, S. (2012). Kinetic study and optimization of oxidative desulfurization of benzothiophene using mesoporous titanium silicate-1 catalyst. *Industrial & Engineering Chemistry Research*, *51*(1), 147–157. doi:10.1021/ie2024068

Seredych, M., & Bandosz, T. J. (2011). Removal of dibenzothiophene from model diesel fuel on sulfur rich activated carbons. *Applied Catalysis B: Environmental*, *106*, 133–141.

Seredych, M., & Bandosz, T. J. (2013). Visible light photoactivity of sulfur and phosphorus doped monoporous carbons in oxidation of dibenzothiophenes. *Fuel*, *108*, 846–849. doi:10.1016/j.fuel.2012.12.064

Seredych, M., Deliyanni, E., & Bandosz, T. J. (2010). Role of microporosity and surface chemistry in adsorption of 4, 6-dimethyldibenzothiophene on polymer-derived activated carbons. *Fuel*, *89*(7), 1499–1507. doi:10.1016/j.fuel.2009.09.032

Seredych, M., Khine, M., & Bandosz, T. J. (2011). Enhancement in dibenzothiophene reactive adsorption from liquid fuel via incorporation of sulfur heteroatoms into nanoporous carbon matrix. *Chemistry and Sustainability*, *4*, 139–147. PMID:21226224

Seredych, M., Khine, M., & Bandosz, T. J. (2011). Enhancement in dibenzothiophene reactive adsorption from liquid fuel via incorporation of sulfur heteroatoms into the nanoporous carbon matrix. *ChemSusChem*, *4*(1), 139–147. doi:10.1002/cssc.201000366 PMID:21226224

Seredych, M., Lison, J., Jans, U., & Bandosz, T. J. (2009). Textural and chemical factors affecting adsorption capacity of activated carbon in highly efficient desulfurization of diesel fuel. *Carbon*, *47*(10), 2491–2500. doi:10.1016/j.carbon.2009.05.001

Setti, L., Lanzarini, G., & Pifferi, P. G. (1997). Whole cell biocatalysis for an oil desulfurization process. *Fuel Processing Technology*, *52*(1-3), 145–153. doi:10.1016/S0378-3820(97)00023-4

Seung-Tae, Y., Kwang-Eun, J., Soon-Yong, J., & Wha-Seung, A. (2012). Synthesis of mesoporous TS-1 using a hybrid SiO2-TiO2 xerogel for catalytic oxidative desulfurization. *Materials Research Bulletin*, *47*(12), 4398–4402. doi:10.1016/j.materresbull.2012.09.041

Severino, F., Laine, J., & López-Agudo, A. (2000). Compensation effect and dual promotion effect in activated carbon-supported CoNiMo hydrodesulfurization catalysts. *Journal of Catalysis*, *189*(1), 244–246. doi:10.1006/jcat.1999.2683

Shaabani, A., Behnam, M., & Rezayan, A. H. (2009). Tungstophosphoric Acid (H3PW12O40) Catalyzed Oxidation of Organic Compounds with NaBrO3. *Catalysis Communications*, *10*(7), 1074–1078. doi:10.1016/j.catcom.2008.12.059

Shafi, R., & Hutchings, G. J. (2000). Hydrodesulfurization of hindered dibenzothiophenes: An overview. *Catalysis Today*, *59*(3–4), 423–442. doi:10.1016/S0920-5861(00)00308-4

Shahadat, H. A. M. H., & Tatarchuk, B. J. (2013). Adsorptive desulfurization of jet and diesel fuels using Ag/TiOx–Al_2O_3 and Ag/TiOx–SiO_2 adsorbents. *Fuel*, *107*, 465–473. doi:10.1016/j.fuel.2012.11.030

Shakirullah, M., Ahmad, W., Ahmad, I., & Ishaq, M. (2010). Oxidative desulphurization study of gasoline and kerosene: Role of some organic and inorganic oxidants. *Fuel Processing Technology*, *91*(11), 1736–1741. doi:10.1016/j.fuproc.2010.07.014

Shakirullah, M., & Imtiaz Ahmad, M. (2009). Study on the Role of Metal Oxides in Desulphurization of Some Petroleum Fractions. *Journal of the Chilean Chemical Society*, *56*(1), 107–114. doi:10.1002/jccs.200900015

Shalaby, C., Ma, X., Zhou, A., & Song, C. (2009). Preparation of organic sulfur adsorbent from coal for adsorption of dibenzothiophene-type compounds in diesel fuel. *Energy & Fuels*, *23*(5), 2620–2627. doi:10.1021/ef801135t

Shan, G., Xing, J., Zhang, H., & Liu, H. (2005). Biodesulfurization of Dibenzothiophene by Microbial Cells Coated with Magnetite Nanoparticles. *Applied and Environmental Microbiology*, *71*(8), 4497–4502. doi:10.1128/AEM.71.8.4497-4502.2005 PMID:16085841

Shangguan, J., Zhao, Y., Fan, H., Liang, L., Shen, F., & Miao, M. (2013). Desulfurization behavior of zinc oxide based sorbent modified by the combination of Al_2O_3 and K_2CO_3. *Fuel, 108*, 80-84.

Shang, H., Liu, C., & Wei, F. (2004). FT-IR study of carbon nanotube supported Co-Mo catalysts. *Journal of Natural Gas Chemistry*, *13*(2), 95–100.

Shan, J. H., Liu, X. Q., Sun, L. B., & Cui, R. (2008). Cu-Ce Bimetal ion-exchanged Y-Zeolites for selective adsorption of thiophenic sulfur. *Energy & Fuels*, *22*(6), 3955–3959. doi:10.1021/ef800296n

Sharifzadeh Baei, M., & Rezvani, M. A. (2011). An Efficient, New, Simple and Rapid Method for Synthesis and Isomerization of Heteropolyanion B-[PW9O34]9. *Asian Journal of Chemistry*, *23*, 5381–5389.

Sharipov, A. K., & Nigmatullin, V. R. (2005). Finishing of Diesel Fuel to Remove Sulfur Compounds after Hydrotreating. *Chemistry and Technology of Fuels and Oils*, *41*(4), 309–312. doi:10.1007/s10553-005-0071-y

Sharma, B. K. *Environmental Chemistry*: Krishna Prakashan.

Sharma, M., Vyas, R. K., & Singh, K. (2013). A review on reactive adsorption for potential environmental applications. *Adsorption*, *19*(1), 161–188. doi:10.1007/s10450-012-9436-9

Shefer, N., & Rozen, S. (2010). The Oxigenation of Thieno [2,3,-b]thiophenes. *The Journal of Organic Chemistry*, *75*(13), 4623–4625. doi:10.1021/jo100702f PMID:20521759

Shen, C., Wang, Y. J., Xu, J. H., & Luo, G. S. (2015). Synthesis of TS-1 on porous glass beads for catalytic oxidative desulfurization. *Chemical Engineering Journal*, *259*, 552–556. doi:10.1016/j.cej.2014.08.027

Shengyu, L., Wende, X., Pei, L., & Zhixiang, Y. (2008). Feasibility study of new limestone flue gas desulfurization process. *Clean - Soil, Air. Water (Basel)*, *36*(5-6), 482–487.

Shennan, J. L. (1996). Microbial attack on sulphur-containing hydrocarbons: Implications for the biodesulphurisation of oils and coals. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *67*(2), 109–123. doi:10.1002/(SICI)1097-4660(199610)67:2<109::AID-JCTB532>3.0.CO;2-Y

Shen, Y., Li, P., Xu, X., & Liu, H. (2012). Selective adsorption for removing sulfur: A potential ultra-deep desulfurization approach of jet fuels. *RSC Advances*, *2*(5), 1700–1711. doi:10.1039/C1RA00944C

Shen, Z., Chen, X., Tong, M., Guo, S., Ni, M., & Lu, J. (2013). Studies on magnesium-based wet flue gas desulfurization process with oxidation inhibition of the byproduct. *Fuel*, *105*(0), 578–584. doi:10.1016/j.fuel.2012.07.050

Shen, Z., Guo, S., Kang, W., Zeng, K., Yin, M., Tian, J., & Lu, J. (2012). Kinetics and Mechanism of Sulfite Oxidation in the Magnesium-Based Wet Flue Gas Desulfurization Process. *Industrial & Engineering Chemistry Research*, *51*(11), 4192–4198. doi:10.1021/ie300163v

Sherwood, T. K. (1925). Solubilities of sulfur dioxide and ammonia in water. *Industrial & Engineering Chemistry*, *19*(745).

Sherwood, T. K. (1952). *Absorption and Extraction*. New York: McGraw-Hill, Inc.

Sheu, Y., & Mullins, O. C. (Eds.). (1995). *Asphaltenes Fundamentals and Applications*. New York, London: Plenum.

Shih, S.-M., Lin, J.-P., & Shiau, G.-Y. (2000). Dissolution rates of limestones of different sources. *Journal of Hazardous Materials*, *79*(1-2), 159–171. doi:10.1016/S0304-3894(00)00253-3 PMID:11040393

Shin, W. H., Jeong, H. M., Kim, B. G., Kang, J. K., & Choi, J. W. (2012). Nitrogen-doped multi-walled carbon nanotubes for lithium storage with extremely high capacity. *Nano Letters*, *12*(5), 2283–2288. doi:10.1021/nl3000908 PMID:22452675

Shi, Q., Hou, D., Chung, K. H., Xu, C., Zhao, S., & Zhang, Y. (2010). Distribution of acids and neutral nitrogen compounds in a Chinese crude oil and its fractions: characterized by negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels*, *24*, 2545–2553. doi:10.1021/ef901564e

Shi, Q., Pan, N., Liu, P., Chung, K. H., Zhao, S., Zhang, Y., & Xu, C. (2010). Characterization of Sulfur Compounds in Oilsands Bitumen by Methylation Followed by Positive-Ion Electrospray Ionization and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels*, *24*(5), 3014–3019. doi:10.1021/ef9016174

Shiraishi, Y., Hara, H., Hirai, T., & Komasawa, I. (1999). A Deep Desulfurization Process for Light Oil by Photosensitized Oxidation Using a Triplet Photosensitizer and Hydrogen Peroxide in an Oil/Water Two-Phase Liquid−Liquid Extraction System. *Industrial & Engineering Chemistry Research*, *38*(4), 1589–1595. doi:10.1021/ie980651s

Shiraishi, Y., Tachibana, K., Hirai, T., & Komasawa, I. (2002). Desulfurization and Denitrogenation Process for Light Oils Based on Chemical Oxidation followed by Liquid−Liquid Extraction. *Industrial & Engineering Chemistry Research*, *41*(17), 4362–4375. doi:10.1021/ie010618x

Shiraishi, Y., Tachibana, K., Taki, Y., Hirai, T., & Komasawa, I. (2001). A Novel Desulfurization Process for Fuel Oils Based on the Formation and Subsequent Precipitation of S-Alkylsulfonium Salts. 2. Catalytic-Cracked Gasoline. *Industrial & Engineering Chemistry Research*, *40*(4), 1225–1233. doi:10.1021/ie000548e

Shiraishi, Y., Taki, Y., Hirai, T., & Komasawa, I. (2001). A Novel Desulfurization Process for Fuel Oils Based on the Formation and Subsequent Precipitation of S-Alkylsulfonium Salts. 1. Light Oil Feedstocks. *Industrial & Engineering Chemistry Research*, *40*(4), 1213–1224. doi:10.1021/ie000547m

Siagi, Z. O., & Mbarawa, M. (2009). Dissolution rate of South African calcium-based materials at constant pH. *Journal of Hazardous Materials*, *163*(2–3), 678–682. doi:10.1016/j.jhazmat.2008.07.014 PMID:18703281

Sigurdson, S., Sundaramurthy, V., Dalai, A. K., & Adjaye, J. (2008). Phosphorous promoted trimetallic NiMoW/γ-Al_2O_3 sulfide catalysts in gas oil hydrotreating. *Journal of Molecular Catalysis A Chemical*, *291*(1-2), 30–37. doi:10.1016/j.molcata.2008.05.011

Silva, C. R., Silva, M. L. C., Kamida, H. M., Goes-Neto, A., & Koblitz, M. G. B. (2014). Lytic enzyme production optimization using low-cost substrates and its application in the clarification of xanthan gum culture broth. *Food Science & Nutrition*, *2*(4), 299–307. doi:10.1002/fsn3.87 PMID:25473487

Silva, T. P., Paixão, S. M., Roseiro, J. C., & Alves, L. (2015). Jerusalem artichoke as low-cost fructose-rich feedstock for fossil fuels desulfurization by a fructophilic bacterium. *Journal of Applied Microbiology*, 118(3), 609–618. doi: 10.1111/jam.12721

Silva, T. P., Paixão, S. M., Teixeira, A. V., Roseiro, J. C., & Alves, L. (2013). Optimization of low sulfur carob pulp liquor as carbon source for fossil fuels biodesulfurization. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *88*(5), 919–923. doi:10.1002/jctb.3921

Sims, T. H. (1861). Contributions to the knowledge of the laws of gas-absorption, sulfurous acid in water. *Journal of the Chemical Society*, *14*(1).

Singh, A., & Agrawal, M. (2007). Acid rain and its ecological consequences. *Journal of Environmental Biology*, *29*(1), 15. PMID:18831326

Singh, A., Singh, B., & Ward, O. (2012). Potential applications of bioprocess technology in petroleum industry. *Biodegradation*, *23*(6), 865–880. doi:10.1007/s10532-012-9577-2 PMID:22829348

Singh, S., & Bhattacharya, S. (2011). Synthesis of triphenyltin(IV) hydrosulfide. *Inorganica Chimica Acta*, *367*(1), 230–232. doi:10.1016/j.ica.2010.12.014

Singh, S., Chaturvedi, J., & Bhattacharya, S. (2012). Studies of synthesis, structural features of Cu(I) thiophene-2-thiocarboxylates and unprecendented desulfurization of Cu(II) thiocarboxylate complexes. *Dalton Transactions (Cambridge, England)*, *41*(2), 424–431. doi:10.1039/C1DT10629E PMID:22024710

Sing, K. S. W., Everett, D. H., Haul, R. A., Moscou, L., Pierotti, R. A., Rouquerol, J., & Siemieniewska, T. (1985). Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure and Applied Chemistry*, *57*(4), 603–619. doi:10.1351/pac198557040603

Sing, K.S.W. (1982). Reporting Physiosorption Data Gas/Solid systems. *Pure and Applied Chemistry*, *54*(11), 2201–2218.

Sinninghe Damaste, J. S., & de Leeuw, J. W. (1990).. . *Organic Geochemistry*, *16*, 1077–1101.

Sinninghe Damste, J. S., Rijpstra, I. C., Kock-van Dalen, A. C., de Leeuw, J. W., & Schenck, P. A. (1989). Quenching of labile functionalized lipids by inorganic Sulphur species: Evidence for the formation of sedimentary organic sulphur compounds at the early stage of diagenesis. *Geochimica et Cosmochimica Acta*, *53*(6), 1343–1355. doi:10.1016/0016-7037(89)90067-7

Sinnott, S. B., & Andrews, R. (2001). Carbon nanotubes: Synthesis, properties and applications. *Critical Reviews in Solid State and Material Sciences*, *26*(3), 145–249. doi:10.1080/20014091104189

Si, X., Cheng, S., Lu, Y., Gao, G., & He, M. Y. (2008). Oxidative desulfurization of model oil over Au/Ti-MWW. *Catalysis Letters*, *122*(3-4), 321–324. doi:10.1007/s10562-007-9380-6

Smith, K., Booth, W., & Crevecoeur, S. *Evaluation of Wet FGD Technologies to Meet Requirements for Post CO_2 Removal of Flue Gas Streams*. Retrieved from http://www.mass.gov/eea/docs/dep/air/priorities/hazeapd25.pdf

Smith, S. J., Conception, E., Andres, R., & Lurz, J. (2004). Historical sulfur dioxide emissions 1850-2000: Methods and results. Pacific Northwest National Laboratory Report PNNL-14537.

Smith, S. J., Pitcher, H., & Wigley, T. M. L. (2001). Global and regional anthropogenic sulfur dioxide emissions. *Global and Planetary Change*, *29*(1-2), 99–119. doi:10.1016/S0921-8181(00)00057-6

Smith, T. S., & Johnson, K. H. (1994). A unified theory of periodic and promotion effects in transition metal sulphide hydrodesulphurization catalysts. *Catalysis Letters*, *28*(2-4), 361–372. doi:10.1007/BF00806067

Sobati, M. A., Dehkordi, A. M., & Shahrokhi, M. (2010). Extraction of Oxidized Sulfur-Containing Compounds of Non-Hydrotreated Gas Oil. *Chemical Engineering & Technology*, *33*(9), 1515–1524. doi:10.1002/ceat.200900622

Soled, S. L., Miseo, S., Krycak, R., Vroman, H., Ho, T. C., & Riley, K. L. (2000). Nickel Molybdotungstate Hydrotreating Catalysts. US Patent 6,156,695.

Soleimani, M., Bassi, A., & Margaritis, A. (2007). Biodesulfurization of refractory organic sulfur compounds in fossil fuels. *Biotechnology Advances*, *25*(6), 570–596. doi:10.1016/j.biotechadv.2007.07.003 PMID:17716849

Solem-Tishmack, J. K., McCarthy, G. J., Docktor, B., Eylands, K. E., Thompson, J. S., & Hassett, D. J. (1995). High-calcium coal combustion by-products: Engineering properties, ettringite formation, and potential application in solidification and stabilization of selenium and boron. *Cement and Concrete Research*, *25*(3), 658–670. doi:10.1016/0008-8846(95)00054-G

Solís, D., Agudo, A. L., Ramírez, J., & Klimova, T.Solı's. (2006). Hydrodesulfurization of hindered dibenzothiophenes on bifunctional NiMo catalysts supported on zeolite–alumina composites. *Catalysis Today*, *116*(4), 469–477. doi:10.1016/j.cattod.2006.06.029

Song, C. (1999). Sulfur-resistant noble metal catalysts based on shape-selective exclusion and hydrogen spillover. In C. Song, J.M. Garces, Y. Sugi, (Eds.), Shape-selective catalysis, chemicals synthesis and hydrocarbon processing (ACS Symposium Series 738), American Chemical Society, Washington, DC (pp. 381-390).

Song, C., Turaga, U. T., & Ma, X. (2006) Desulfurization. Encyclopedia of Chemical Processing pp. 651-661 Doi:10.1081/E-ECHP-120007732

Song, C. (1999). Designing sulfur-resistant, noble-metal hydrotreating catalysts. *Chemtech*, *29*(3), 26–30.

Song, C. (2003). An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel. *Catalysis Today*, *86*(1-4), 211–263. doi:10.1016/S0920-5861(03)00412-7

Song, C. S., & Ma, X. L. (2004). Ultra-deep desulfurization of liquid hydrocarbon fuels: Chemistry and process. *International Journal of Green Energy*, *1*(2), 167–191. doi:10.1081/GE-120038751

Song, C., & Ma, X. (2003). New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization. *Applied Catalysis B: Environmental*, *41*(1), 207–238. doi:10.1016/S0926-3373(02)00212-6

Song, C., & Reddy, K. M. (1999). Mesoporous molecular sieve MCM-41 supported Co–Mo catalyst for hydrodesulfurization of dibenzothiophene in distillate fuels. *Applied Catalysis A, General*, *176*(1), 1–10. doi:10.1016/S0926-860X(98)00230-0

Song, C., & Schmitz, A. D. (1997). Zeolite-Supported Pd and Pt Catalysts for Low-Temperature Hydrogenation of Naphthalene in the Absence and Presence of Benzothiophene. *Energy & Fuels*, *11*(3), 656–661. doi:10.1021/ef960179s

Song, J. L., Dong, Z. C., Zeng, H. Y., Zhou, W. B., Naka, T., & Wei, Q. et al. (2003). $[Cu(H_4C_3N_2S)Cl_2]n$, an Unprecedented Diazole-Bridged One-Dimensional Copper Halide: Synthesis, Structure, and Magnetic Properties. *Inorganic Chemistry*, *42*(6), 2136–2140. doi:10.1021/ic025976m PMID:12639152

Son, W. K., Youk, J. H., Lee, T. S., & Park, W. H. (2004). The effects of solution properties and polyelectrolyte on electrospinning of ultrafine poly(ethylene oxide) fibers. *Polymer*, *45*(9), 2959–2966. doi:10.1016/j.polymer.2004.03.006

Sorensen, O., Clausen, B. S., Candia, R., & Topsøe, H. (1985). Hrem and Aem studies of hds catalysts: Direct evidence for the edge location of cobalt in Co-Mo-S. *Applied Catalysis*, *13*(2), 363–372. doi:10.1016/S0166-9834(00)81154-9

Sound, H. N. (2000). *Developments in FGD*. London: IEA Coal Research Centre.

Speight, J. G., *The Chemsitry and Technology of Petroleum*, Marcel-Dekker, Inc., New York.

Speight, J. C. (1998). In M. Henz, (Ed.), *The Chemistry and Technology of Petroleum* (3rd ed.). New York, NY: Marcel Dekker.

Spojakina, A., Kraleva, E., Jiratova, K., & Petrov, L. (2005). TiO2-supported iron–molybdenum hydrodesulfurization Catalystd. *Applied Catalysis A, General*, *288*(1–2), 10–17. doi:10.1016/j.apcata.2005.02.034

Srivastav, A., & Srivastava, V. C. (2009). Adsorptive desulfurization by activated alumina. *Journal of Hazardous Materials*, *170*(2-3), 1133–1140. doi:10.1016/j.jhazmat.2009.05.088 PMID:19523762

Srivastava, R. K. (2000). *Controlling SO_2 emissions: a Review of Technologies*. Washington, United States: U.S. Environmental Protection Agency.

Srivastava, R. K., & Jozewicz, W. (2001). Flue Gas Desulfurization: The State of the Art. *Journal of the Air & Waste Management Association*, *51*(12), 1676–1688. doi:10.1080/10473289.2001.10464387 PMID:15666473

Srivastava, V. C. (2012). An evaluation of desulfurization technologies for sulfur removal from liquid fuels. *Royal Society of Chemistry Advances*, *2*, 759–783.

Srivastava, V. C. (2012). An evaluation of desulfurization technologies for sulfur removal from liquid fuels. *RSC Advances*, *2*(3), 759–783. doi:10.1039/C1RA00309G

Stanislaus, A., Marafi, A., & Rana, M. S. (2010). Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production. *Catalysis Today*, *153*(1–2), 1–68. doi:10.1016/j.cattod.2010.05.011

Stellenbosch Nanofiber Company. (n. d.). Retrieved from http://www.sncfibers.com/#!products/c1jm9

Stephanie, N. S., Goubert, R., Xiuling, Z., & Andrzej, W. (2010). Synthesis and characterization of carbon-supported transition metal oxide nanoparticles-Cobalt porphyrin as catalysts for electroreduction of oxygen in acids. *Electrochemistry Communications*, *12*(11), 1457–1461. doi:10.1016/j.elecom.2010.06.004

Stoner, D. L., Wey, J. E., Barrett, K. B., Jolley, J. G., Wright, R. B., & Dugan, P. R. (1990). Modification of water-soluble coal-derived products by dibenzothiophene-degrading microorganisms. *Applied and Environmental Microbiology*, *56*(9), 2667–2676. PMID:16348275

Stouffer, M. R., Rosenhoover, W. A., & Withum, J. A. (1993). Advanced coolside desulfurization process. *Environment and Progress*, *12*(2), 133–139. doi:10.1002/ep.670120211

Stouffer, M. R., Yoon, H., & Burke, F. P. (1989). An investigation of the mechanisms of flue gas desulfurization by in-duct dry sorbent injection. *Industrial & Engineering Chemistry Research*, *28*(1), 20–27. doi:10.1021/ie00085a005

Strel Ko, V. V., Kutz, V. S., & Thrower, P. A. (2000). On the mechanism of possible influence of heteroatoms of nitrogen, boron and phosphorus in a carbon matrix on the catalytic activity of carbon in electron transfer reactions. *Carbon*, *38*(10), 1499–1524. doi:10.1016/S0008-6223(00)00121-4

Stumpf, A., Tolvaj, K., & Juhasz, M. (1998). Detailed analysis of sulfur compounds in gasoline range petroleum products with high-resolution gas chromatography–atomic emission detection using group-selective chemical treatment. *Journal of Chromatography. A*, *819*(1-2), 67–74. doi:10.1016/S0021-9673(98)00444-0

Su, D. S., Maksimova, N., Delgado, J. J., Keller, N., Mestl, G., Ledoux, M. J., & Schlögl, R. (2005). Nanocarbons in selective oxidative dehydrogenation reaction. *Catalysis Today*, *102*, 110–114. doi:10.1016/j.cattod.2005.02.012

Sughrue, E. L., Khare, G. P., Bertus, B. J., & Johnson, M. M. (2001). US Patent 6.254.766.

Sun, M. Z., Zhao, D. Z., & Sun, W. W. (2008). Study on the oxidative desulfurization of diesel fuel with power ultrasound. . *Chemistry and adhension, 30*(2), 65-68.

Sundaraman, R., Peduzzi, E., & Song, C. (2009). Catalytic cracking of oxidized sulfur compounds in gas oil stream. *Prepr Pap Am Chem Soc Div Fuel Chem*, *54*(2), 954–955.

Sundaramurthy, V., Dalai, A. K., & Adjaye, J. (2008). Thetraalkylthiomolybdates-derived Co(Ni)Mo/γ-Al_2O_3 sulfide catalysts for gas oil hydrotreating. *Journal of Molecular Catalysis A Chemical*, *294*(1-2), 20–26. doi:10.1016/j.molcata.2008.07.004

Sundararaman, R., Ma, X., & Song, C. (2010). Oxidative Desulfurization of Jet and Diesel Fuels Using Hydroperoxide Generated in Situ by Catalytic Air Oxidation. *Industrial & Engineering Chemistry Research*, *49*(12), 5561–5568. doi:10.1021/ie901812r

Sun, F., Yin, Z., Wang, Q. Q., Sun, D., Zeng, M. H., & Kurmao, M. (2013). Tandem Postsynthetic Modification of a Metal–Organic Framework by Thermal Elimination and Subsequent Bromination: Effects on Absorption Properties and Photoluminescence. *Angewandte Chemie International Edition*, *52*(17), 4538–4543. doi:10.1002/anie.201300821 PMID:23564565

Sun, M., Nicosia, D., & Prins, R. (2003). The effects of fluorine, phosphate and chelating agents on hydrotreating catalysts and catalysis. *Catalysis Today*, *86*(1-4), 173–189. doi:10.1016/S0920-5861(03)00410-3

Sun, Z., Zhao, Y., Gao, H., & Hu, G. (2010). Removal of SO_2 from Flue Gas by Sodium Humate Solution. *Energy & Fuels*, *24*(2), 1013–1019. doi:10.1021/ef901052r

Su, P., Xiao, H., Zhao, J., Yao, Y., Shao, Z., Li, C., & Yang, Q. (2013). Nitrogen-doped carbon nanotubes derived from Zn–Fe-ZIF nanospheres and their application as efficient oxygen reduction electrocatalysts with in situ generated iron species. *Chemical Sciences*, *4*, 2941–2946.

Sviridova, T. V., Stepanova, L. I., & Sviridov, D. V. (2012). Molybdenum: characteristics, production and applications. In M. Ortiz & T. Herrera (Eds.), *Nova Science* (pp. 147–179). New York, NY.

Svoboda, K., Lin, W., Hannes, J., Korbee, R., & van den Beek, C. M. (1994). Low temperature flue gas desulfurization by alumina-CaO regenerable sorbents. *Fuel*, *73*(7), 1144–1150. doi:10.1016/0016-2361(94)90251-8

Swain, E. J. (1998). US refining crude slates continue towards heavier feeds, high sulfur contents. *Oil & Gas Journal*, *96*(40), 43–48.

Ta-Chen, L., Chang, J.-S., & Young, C.-C. (2008). Exopolysaccharides produced by *Gordonia alkanivorans* enhance bacterial degradation activity for diesel. *Biotechnology Letters*, *30*(7), 1201–1206. doi:10.1007/s10529-008-9667-8 PMID:18286235

Taerakul, P., Sun, P., Golightly, D. W., Walker, H. W., Weavers, L. K., Zand, B., & Fan, L.-S. (2007). Characterization and re-use potential of by-products generated from the Ohio State Carbonation and Ash Reactivation (OSCAR) process. *Fuel*, *86*(4), 541–553. doi:10.1016/j.fuel.2006.08.012

Taguchi, A., & Schuth, F. (2005). Ordered mesoporous materials in catalysis. *Microporous and Mesoporous Materials*, *77*(1), 1–45. doi:10.1016/j.micromeso.2004.06.030

Takada, M., Nomura, N., Okada, H., Nakajima-Kambe, T., Nakahara, T., & Uchiyama, H. (2005). De-repression and comparison of oil-water separation activity of the dibenzothiophene desulfurizing bacterium, *Mycobacterium* sp. G3. *Biotechnology Letters*, *27*(12), 871–874. doi:10.1007/s10529-005-6721-7 PMID:16086250

Takahashi, A., Yang, R. T., Munson, C. L., & Chinn, D. (2001). Cu(I)−Y-Zeolite as a Superior Adsorbent for Diene/Olefin Separation. *Langmuir*, *17*(26), 8405–8413. doi:10.1021/la011196z

Talvy, S., Cockx, A., & Line, A. (2005). Global modelling of a gas–liquid–solid airlift reactor. *Chemical Engineering Science*, *60*(22), 5991–6003. doi:10.1016/j.ces.2005.04.067

Tam, P. S., & Kittrell, J. R. (1984). *Process for purifying hydrocarbonaceous oils*.U.S. Patent 4, 485, 007.

Tam, P. S., Kittrell, J. R., & Eldridge, J. W. (1990a). Desulfurization of fuel oil by oxidation and extraction. 1. Enhancement of extraction oil yield. *Industrial & Engineering Chemistry Research*, *29*(3), 321–324. doi:10.1021/ie00099a002

Tam, P. S., Kittrell, J. R., & Eldridge, J. W. (1990b). Desulfurization of fuel oil by oxidation and extraction. 2. Kinetic modeling of oxidation reaction. *Industrial & Engineering Chemistry Research*, *29*(3), 324–329. doi:10.1021/ie00099a003

Tanaka, Y., Yoshikawa, O., Maruhashi, K., & Kurane, R. (2002). The cbs mutant strain of *Rhodococcus erythropolis* KA2-5-1 expresses high levels of Dsz enzymes in the presence of sulfate. *Archives of Microbiology*, *178*(5), 351–357. doi:10.1007/s00203-002-0466-7 PMID:12375103

Tanev, P. T., Chibwe, M., & Pinnavaia, T. J. (1994). Titanium-containing mesoporous molecular sieves for catalytic oxidation of aromatic compounds. *Nature*, *368*(6469), 321–323. doi:10.1038/368321a0 PMID:8127366

Tangestaninejad, S., Mirkhani, V., Moghadam, M., Mohammadpoor-Baltork, I., Shams, E., & Salavati, H. (2008). Hydrocarbon oxidation catalyzed by vanadium polyoxometalate supported on mesoporous MCM-41 under ultrasonic irradiation. *Ultrasonics Sonochemistry*, *15*(4), 438–447. doi:10.1016/j.ultsonch.2007.06.009 PMID:17692553

Tang, K., & Hong, X. (2014). A characterization of bacterium for fcc diesel oil desulfurization. *Petroleum Science and Technology*, *32*(13), 1545–1552. doi:10.1080/10916466.2012.689795

Tang, K., Song, K. L., Duan, L., Li, X., Gui, J., & Sun, Z. (2008). Deep desulfurization by selective adsorption on a heteroatoms zeolite prepared by secondary synthesis. *Fuel Processing Technology*, *89*(1), 1–6. doi:10.1016/j.fuproc.2007.06.002

Tang, M., Zhou, L., Du, M., Lyu, Z., Wen, X.-D., Li, X., & Ge, H. (2015). A novel reactive adsorption desulfurization Ni/MnO adsorbent and its hydrodesulfurization ability compared with Ni/ZnO. *Catalysis Communications*, *61*, 37–40. doi:10.1016/j.catcom.2014.11.005

Tang, Q., Lin, S., Cheng, Y., Liu, S., & Xiong, J.-R. (2013). Ultrasound-assisted oxidative desulfurization of bunker-C oil using tert-butyl hydroperoxide. *Ultrasonics Sonochemistry*, *20*(5), 1168–1175. doi:10.1016/j.ultsonch.2013.02.002 PMID:23538118

Tang, T., Yin, C., Wang, L., Ji, Y., & Xiao, F.-S. (2007). Superior performance in deep saturation of bulky aromatic pyrene over acidic mesoporous Beta zeolite-supported palladium catalyst. *Journal of Catalysis*, *249*(1), 111–115. doi:10.1016/j.jcat.2007.03.031

Tang, X.-, Meng, X., & Shi, L. (2011). Desulfurization of Model Gasoline on Modified Bentonite. *Industrial & Engineering Chemistry Research*, *50*(12), 7527–7533. doi:10.1021/ie200475x

Tatsumi, T., & Jappar, N. (1998). Properties of Ti-beta zeolites synthesized by dry-gel conversion and hydrothermal methods. *Journal of Physical Chemistry*, *102*(37), 7126–7131. doi:10.1021/jp9816216

Tawara, K., Nishimura, T., & Iwanami, H. (2000). Ultra-deep hydrodesulfurization of kerosene for fuel cell system (Part 2) regeneration of sulfurpoisoned nickel catalyst in hydrogen and finding of autoregenerative nickel catalyst. Sekiyu Gakkaishi. *Journal of the Japan Petroleum Institute*, *43*(2), 114–120. doi:10.1627/jpi1958.43.114

Tawara, K., Nishimura, T., Iwanami, H., Nishimoto, T., & Hasuike, T. (2001a). New hydrodesulfurization catalyst for petroleum-feed fuel cell vehicles and cogenerations. *Industrial & Engineering Chemistry Research*, *40*(10), 2367–2370. doi:10.1021/ie000453c

Tawara, K., Nishimura, T., Iwanami, H., Nishimoto, T., & Hasuike, T. (2001b). Ultra-deep hydrodesulfurization of kerosene for fuel cell system (Part 3) Development and evaluation of Ni/ZnO catalyst. *Sekiyu Gakkaishi*, *44*(1), 43–51. doi:10.1627/jpi1958.44.43

Taylor, M. R., Rubin, E. S., & Hounshell, D. A. (2005). Control of SO_2 emissions from power plants: A case of induced technological innovation in the U.S. *Technological Forecasting and Social Chan*ge, 72(6 SPEC. ISS.), 697–718.

Taylor, M. R., Rubin, E. S., & Hounshell, D. A. (2005). Regulation as the mother of innovation: The case of SO_2 control. *Law & Policy*, *27*(2), 348–378. doi:10.1111/j.1467-9930.2005.00203.x

Teichmuller, M. (1982). Origin of petrographic constituents of coal. In E. Stach, M-T. Mackowsky, M. Teichmuller, G.H. Taylor, D. Chandra, & R. Teichmuller, (Eds.), Stach's Textbook on Coal Petrology (Trans., English ed. by D.G. Murchison, G.H. Taylor, & F. Zierke). Gebruder Borntraeger, Berlin, Stuttgart.

Teixeira, I. F., Oliveira, A. A., Christofani, T., & Moura, F. C. C. (2013). Biphasic oxidation promoted by magnetic amphiphilic nanocomposites undergoing a reversible emulsion process. *Journal of Material Chemistry A*, *1*(35), 10203–10208. doi:10.1039/c3ta11535f

Te, M., Fairbridge, C., & Ring, Z. (2001). Oxidation reactivities of dibenzothiophenes in polyoxometalate/H_2O_2 and formic acid/H_2O_2 systems. *Applied Catalysis A, General*, *219*(1–2), 267–280. doi:10.1016/S0926-860X(01)00699-8

Teo, W. E., & Ramakrishna, S. (2005). Electrospun fibre bundle made of aligned nanofibres over two fixed points. *Nanotechnology*, *16*(9), 1878–1884. doi:10.1088/0957-4484/16/9/077

Teo, W. E., & Ramakrishna, S. (2006). A review on electrospinning design and nanofibre assemblies. *Nanotechnology*, *17*(14), 89–106. doi:10.1088/0957-4484/17/14/R01 PMID:19661572

Terrones, M. (2003). Science and technology of twenty-five century: Synthesis, properties and applications. *Annual Review of Materials Research*, *33*, 419. doi:10.1146/annurev.matsci.33.012802.100255

Teunissen, W., Bol, A. A., & Geus, J. W. (1999). Magnetic catalyst bodies. *Catalysis Today*, *48*(1-4), 329–336. doi:10.1016/S0920-5861(98)00389-7

Theron, S. A., Yarin, A. L., Zussman, E., & Kroll, E. (2005). Multiple jets in electrospinning: Experiment and modelling. *Polymer*, *46*(9), 2889–2899. doi:10.1016/j.polymer.2005.01.054

Thess, A., Smalley, R. E., Roland, L., Nikolaev, P., Dai, H., & Petit, P. et al. (1996). Crystalline ropes of metallic carbon nanotubes. *Science*, *273*(5274), 483–487. doi:10.1126/science.273.5274.483 PMID:8662534

Thode, H. G. (1965). In A. Young & J. E. Galley (Eds.), *Fluids in Subsurface Environments* (pp. 367–377). AAPG Press.

Thomas, D., Colle, S., & Vanderschuren, J. (2003a). Designing wet scrubbers for SO_2 absorption into fairly concentrated sulfuric acid solutions containing hydrogen peroxide. *Chemical Engineering & Technology*, *26*(4), 497–502. doi:10.1002/ceat.200390074

Thomas, D., Colle, S., & Vanderschuren, J. (2003b). Kinetics of SO_2 absorption into fairly concentrated sulphuric acid solutions containing hydrogen peroxide. *Chemical Engineering and Processing: Process Intensification*, *42*(6), 487–494. doi:10.1016/S0255-2701(02)00070-3

Thomazeau, C., Geantet, C., Lacroix, M., Danot, M., Harlé, V., & Raybaud, P. (2007). Predictive approach for the design of improved HDT catalysts: γ-Alumina supported (ni, Co) promoted $Mo_{1-x}W_xS_2$ active phases. *Applied Catalysis A, General*, *322*, 92–97. doi:10.1016/j.apcata.2007.01.016

Thompson Smith, W. M., & Parkhurst, R. B. (1922). The solubility of sulfur dioxide in suspensions of calcium and magnesium hydroxides. *Journal of the American Chemical Society*, *44*(9), 1918–1927. doi:10.1021/ja01430a010

Tian, F., Li, C., Jiang, Z., & Weicheng, W. U. (2005). Adsorption of Sulphur containing compounds from FCC Gasoline on Cerium-Exchanged Y Zeolite. *Chinese Journal of Catalysis*, *26*(9), 734–736.

Tian, W.-H., Sun, L.-B., Song, X.-L., Liu, X.-Q., Yin, Y., & He, G.-S. (2010). Adsorptive Desulfurization by Copper Species within Confined Space. *Langmuir*, *26*(22), 17398–17404. doi:10.1021/la101856d PMID:20882950

Tian, Y., Yao, Y., Zhi, Y., Yan, L., & Lu, S. (2015). Combined Extraction−Oxidation System for Oxidative Desulfurization (ODS) of a Model Fuel. *Energy & Fuels*, *29*, 618–625.

Tiers, G. V. D., & Brostrom, M. L. (2000). Lead mercaptides: Materials useful as powder secondary standards and internal references for calibration of X-ray diffractometers at small and medium angles. *Journal of Applied Crystallography*, *33*(3 Part 2), 915–920. doi:10.1107/S0021889800002806

Tissot, B. P., & Welte, D. H. (1984). *Petroleum Formation and Occurrence* (2nd ed., p. 699). Berlin: Springer-Verlag. doi:10.1007/978-3-642-87813-8

Tokalic, R., Marinkovic, S., Trifunovic, P., Devic, G., & Zildzovic, S. (2013). Preliminary Examination of the System Fly Ash-Bottom Ash-Flue Gas Desulphurization Gypsum-Portland Cement-Water for Road Construction. *Journal of Chemistry*, *2013*, 421480. doi:10.1155/2013/421480

Tokumura, M., Baba, M., Znad, H. T., Kawase, Y., Yongsiri, C., & Takeda, K. (2006). Neutralization of the acidified seawater effluent from the flue gas desulfurization process: Experimental investigation, dynamic modeling, and simulation. *Industrial & Engineering Chemistry Research*, *45*(18), 6339–6348. doi:10.1021/ie0603619

Tomskii, I. S., Vishnetskaya, M. V., & Rufov, Y. N. (2009). The oxidation of toluene on transition metal oxides. *Russian Journal of Physical Chemistry A*, *83*(11), 1868–1872. doi:10.1134/S0036024409110107

Topsøe, H., & Clausen, B. S. (1984). Importance of Co-Mo-S Type Structures in Hydrodesulfurization. *Catalysis Reviews. Science and Engineering*, *26*, 395–420. doi:10.1080/01614948408064719

Topsøe, H., Clausen, B. S., & Massoth, F. E. (1996). *Catalysis-Science and Technology* (J. R. Anderson & M. Boudard, Eds.). Vol. 11). Berlin: Springer.

Topsoe, H., Clausen, B. S., & Massoth, F. E. (1996). *Hydrotreating Catalysis*. Berlin: Springer. doi:10.1007/978-3-642-61040-0_1

Topsoe, H., Clausen, B. S., & Massoth, F. E. (1996). Hydrotreating catalysis. In *Science and Technology* (p. 310). Berlin: Springer-Verlag.

Topsøe, H., Clausen, B. S., & Massoth, F. E. (1996). *Hydrotreating Catalysis. Science and Technology* (J. R. Anderson & M. Boudart, Eds.). Vol. 11). Berlin Heidelberg Germany: Springer-Verlang.

Topsøe, H., Clausen, B. S., Topsøe, N.-Y., & Pederson, E. (1986). Recent basic research in hydrodesulfurization catalysis. *Industrial & Engineering Chemistry Fundamentals*, *25*(1), 25–36. doi:10.1021/i100021a004

Topsøe, H., Hinnemann, B., Nørskov, J. K., Lauritsen, J. V., Besenbacher, F., & Hansen, P. L. et al. (2005). The role of reaction pathways and support interactions in the development of high activity hydrotreating catalysts. *Catalysis Today*, *107-108*, 12–22. doi:10.1016/j.cattod.2005.07.165

Topsøe, N.-Y., & Topsøe, H. (1983). Characterization of the structures and active sites in sulfided Co-Mo/Al2O3 and Ni-Mo/Al2O3 catalysts by NO chemisorption. *Journal of Catalysis*, *84*(2), 386–401. doi:10.1016/0021-9517(83)90010-6

Torres-García, E., Galano, A., & Rodriguez-Gattorno, G. (2011). Oxidative desulfurization (ODS) of organosulfur compounds catalysed by peroxo-metallate complexes of WOx–ZrO_2: Thermochemical, structural, and reactivity indexes analyses. *Journal of Catalysis*, *282*(1), 201–208. doi:10.1016/j.jcat.2011.06.010

Trakarnpruk, W., & Seentrakoon, B. (2007). Hydrodesulfurization Activity of MoS_2 and Bimetallic Catalysts Prepared by in Situ Decomposition of Thiosalt. *Industrial & Engineering Chemistry Research*, *46*(7), 1874–1882. doi:10.1021/ie061176y

Triantafyllidis, K. S., & Deliyanni, E. A. (2014). Desulfurization of diesel fuels: Adsorption of 4, 6-DMDBT on different origin and surface chemistry nanoporous activated carbons. *Chemical Engineering Journal*, *236*, 406–414. doi:10.1016/j.cej.2013.09.099

Tsang Mui Ching, M.-J., Pomerantz, A. E., Andrews, A. B., Dryden, P., Schroeder, R., Mullins, O. C., & Harrison, C. (2010). On the nanofiltration of asphaltene solutions, crude oils, and emulsions. *Energy & Fuels*, *24*(9), 5028–5037. doi:10.1021/ef100645b

Tuli, D., & Kumar, A. (2008). Non-conventional technologies for fuel desulphurization. Proceedings of the *19th World Petroleum Congress*.

Turk, B. S., & Gupta, R. P. (2001). RTI's TReND Process for deep desulfurization of naphtha, Am. Chem. Soc. *Div. Fuel Chem. Prepr.*, *46*, 392.

U.S. Energy Information Administration. (2013). *International Energy Outlook 2014*. Retrieved from http://www.eia.gov/forecasts/ieo/

U.S. Energy Information Administration. (2014). *Annual Energy Outlook*. Retrieved from http://www.eia.gov/forecasts/aeo/

Uchida, S., Moriguchi, H., Maejima, H., Koide, K., & Kageyama, S. (1978). Absorption of Sulfur Oxide into limesone slurry in a stirred tank reactor. *Canadian Journal of Chemical Engineering*, *56*(6), 690–697. doi:10.1002/cjce.5450560607

Ukawa, N., Okino, S., Iwaki, T., Oshima, M., & Watanabe, Y. (1992). The effects of fluoride complexes in wet limestone flue gas desulfurization. *Journal of Chemical Engineering of Japan*, *25*(2), 146–152. doi:10.1252/jcej.25.146

Urum, K., & Pekdemir, T. (2004). Evaluation of biosurfactants for crude oil contaminated soil washing. *Chemosphere*, *57*(9), 1139–1150. doi:10.1016/j.chemosphere.2004.07.048 PMID:15504473

Vairavamurthy, M. A., Maletic, D., Wang, S., Monowitz, B., Eglington, T., & Lyons, T. (1997). Characterization of Sulfur-Containing Functional Groups in Sedimentary Humic Substances by X-ray Absorption Near-Edge Structure Spectroscopy. *Energy & Fuels*, *11*(3), 546–553. doi:10.1021/ef960212a

Vairavapandian, D., Vichchulada, P., & Lay, M. D. (2008). Preparation and modification of carbon nanotubes: Review of recent advances and applications in catalysis and sensing. *Analytica Chimica Acta*, *626*(2), 119–129. doi:10.1016/j.aca.2008.07.052 PMID:18790113

Valenza, J. J., Drenzek, N., Marques, F., Pagels, M., & Mastalerz, M. (2013). Geochemical controls on shale microstructure. *Geology*, *41*(5), 611–614. doi:10.1130/G33639.1

Varesano, A., Carletto, R. A., & Mazzuchetti, G. (2009). Experimental investigations on the electrospinning process. *Journal of Materials Processing Technology*, *209*(11), 5178–5185. doi:10.1016/j.jmatprotec.2009.03.003

Vargas, R., & Nunez, O. J. (2008). The photocatalytic oxidation of dibenzothiophene (DBT). *Journal of Molecular Catalysis A Chemical*, *294*(1-2), 74–81. doi:10.1016/j.molcata.2008.08.001

Varshney, C. K., Garg, J. K., Lauenroth, W. K., & Heitschmidt, R. K. (1979). Plant responses to sulfur dioxide pollution. *CRC Critical Reviews in Environmental Control*, *9*(1), 27–49. doi:10.1080/10643387909381667

Vasile, H., Francois, F., & Jacques, B. (2000). Mild Oxidation with H_2O_2 over Ti-Containing Molecular Sieves—A very Efficient Method for Removing Aromatic Sulfur Compounds from Fuels. *Journal of Catalysis*, *198*, 179–186.

Vasudevan, P. T., & Fierro, J. L. G. (1996). A Review of Deep Hydrodesulfurization Catalysis. *Catalysis Reviews*, *38*(2), 161–188. doi:10.1080/01614949608006457

Vaudagna, S. R., Canavese, S. A., Comelli, R. A., & Figoli, N. S. (1998). Platinum supported WOx–ZrO2: Effect of calcination temperature and tungsten loading. *Applied Catalysis A, General*, *168*(1), 93–111. doi:10.1016/S0926-860X(97)00343-8

Vazquez-Duhalt, R., Torres, E., Valderrama, B., & Le Borgne, S. (2002). Will biochemical catalysis impact the petroleum refining industry? *Energy & Fuels*, *16*(5), 1239–1250. doi:10.1021/ef020038s

Velu, s., Ma, X., Song, C. (2003). Selective adsorption for removing sulfur from jet fuel over zeolite based adsorbents. *Industrial Engineering and Chemical Research*, 42(21), 5293–5304.

Velu, S., Ma, X., & Song, C. (2003). Selective Adsorption for Removing Sulfur from Jet Fuel over Zeolite-Based Adsorbents. *Industrial & Engineering Chemistry Research*, *42*(21), 5293–5304. doi:10.1021/ie020995p

Venkateshwar Rao, T., Sain, B., Kafola, S., Nautiyal, B. R., Sharma, Y. K., Nanoti, S. M., & Garg, M. O. (2007). Oxidative Desulfurization of HDS Diesel Using the Aldehyde/Molecular Oxygen Oxidation System. *Energy & Fuels*, *21*(6), 3420–3424. doi:10.1021/ef700245g

Venturiello, C., Alneri, E., & Ricci, M. (1983). A new effective catalytic system for epoxidation of olefins by hydrogen peroxide under phase-transfer conditions. *The Journal of Organic Chemistry*, *48*(21), 3831–3833. doi:10.1021/jo00169a052

Vicente, M. A., Belver, C., Trujillano, R., Rives, V., Alvarez, A. C., & Lambert, J. F. et al. (2004). Preparation and characterization of Mn- and Co-supported catalysts derived from Al-pillared clays and Mn- and Co-complexes. *Appl. Catal. A*, *267*(1-2), 47–58. doi:10.1016/j.apcata.2004.02.023

Viculis, L. M., Mack, J. J., & Kaner, R. B. (2003, February28). A chemical route to carbon nanoscrolls. *Science*, *299*(5611), 1361. doi:10.1126/science.1078842 PMID:12610297

Vidal, B., Ollero, F., Gutiérrez, P., Ortiz, F. J., & Villanueva, A. (2007). Catalytic seawater flue gas desulfurization process: An experimental pilot plant study. *Environmental Science & Technology*, *41*(20), 7114–7119. doi:10.1021/es0706899 PMID:17993156

Vu, T. H. T., Nguyen, T. T. T., Nguyen, P. H. T., Do, M. H., Au, H. T., & Nguyen, T. B. et al. (2012). Fabrication of photocatalytic composite of multi-walled carbon nanotubes/TiO2 and its application for desulfurization of diesel. *Materials Research Bulletin*, *47*(2), 308–314. doi:10.1016/j.materresbull.2011.11.016

W., S. (2001, March 18–20). Paper presented at the National Petrochemical & Refiners Association (NPRA) annual meeting, AM-01-29, New Orleans.

Wachs, I. E. (1996). Raman and IR studies of surface metal oxide species on oxide supports: Supported metal oxide catalysts. *Catalysis Today*, *27*(3-4), 437–455. doi:10.1016/0920-5861(95)00203-0

Waldo, G. S., Carlson, R. M. K., Moldowan, J. M., Peters, K. E., & Penner-Hahn, J. (1991). Sulfur speciation in heavy petroleums: Information from X-ray absorption near-edge structure. *Geochimica et Cosmochimica Acta*, *55*(3), 801–814. doi:10.1016/0016-7037(91)90343-4

Waldo, G. S., Mullins, O. C., Penner-Hahn, J. E., & Cramer, S. P. (1992). Determination of the chemical environment of sulphur in petroleum asphaltenes by X-ray absorption spectroscopy. *Fuel*, *71*(1), 53–57. doi:10.1016/0016-2361(92)90192-Q

Wallin, M., & Bjerle, I. (1989). A mass transfer model for limestone dissolution from a rotating cylinder. *Chemical Engineering Science*, *44*(1), 61–67. doi:10.1016/0009-2509(89)85233-9

Walmsley, R. S., Hlangothi, P., Litwinski, C., Torto, N., Nyokong, T., & Tshentu, Z. R. (2012). Catalytic oxidation of thioanisole using oxovanadium(IV)-functionalized electrospun polybenzimidazole nanofibers. *Journal of Applied Polymer Science*, *127*(6), 4719–4725. doi:10.1002/app.38067

Walmsley, R. S., Ogunlaja, A. S., Coombes, M. J., Chidawanyika, W., Litwinski, C., Torto, N., & Tshentu, Z. R. et al. (2012). Imidazole-functionalized polymer microspheres and fibers – useful materials for immobilization of oxovanadium(IV) catalysts. *Journal of Materials Chemistry*, *22*(12), 5792–5800. doi:10.1039/c2jm15485d

Wan Abu Bakar, W. A., Ali, R., Abdul Kadir, A. A., & Wan Mokhtar, W. A. (2012). Effect of transition metal oxides catalyst on oxidative desulfurization of model diesel. *Fuel Processing Technology*, *101*, 78–84. doi:10.1016/j.fuproc.2012.04.004

Wang, L., Ma, Y., Yuan, G., & Hao, J. (2009). Study on the reaction characteristics of flue gas desulfurization by magnesia. Proceedings of the *3rd International Conference on Bioinformatics and Biomedical Engineering, iCBBE 2009*. Department of Environmental Science and Engineering, Tsinghua University, Beijing, China. doi:10.1109/ICBBE.2009.5163522

Wang, Z., & Luo, T. (2009). Experimental investigation on flue gas desulfurization by electrostatic spray. Proceedings of the *2009 International Conference on Energy and Environment Technology, ICEET 2009* (Vol. 3, pp. 44–47).

Wang, B., Zhu, J., & Ma, H. (2009). Desulfurization from thiophene by $SO^{(4)\,(2-)}/ZrO_2$ catalytic oxidation at room temperature & atmospheric pressure. *Journal of Hazardous Materials*, *164*(1), 256–264. doi:10.1016/j.jhazmat.2008.08.003 PMID:18799257

Wang, D., Qian, E. W., Amano, H., Okata, K., Ishihara, A., & Kabe, T. (2003). Oxidative desulfurization of fuel oil: Part I. Oxidation of dibenzothiophenes using tert-butyl hydroperoxide. *Applied Catalysis A, General*, *253*(1), 91–99. doi:10.1016/S0926-860X(03)00528-3

Wang, J. A., Chen, L. F., Valenzuela, M. A., Montoya, A., Salmones, J., & Del Angel, P. (2004). Rietveld refinement and activity of CO oxidation over Pd/Ce0.8Zr0.2O2 catalyst prepared via a surfactant-assisted route. *Applied Surface Science*, *230*(1-4), 34–43. doi:10.1016/j.apsusc.2003.08.111

Wang, J., Keener, T. C., Li, G., & Khang, S.-J. (1998). The dissolution rate of $Ca(OH)_2$ in aqueous solutions. *Chemical Engineering Communications*, *169*(1), 167–184. doi:10.1080/00986449808912726

Wang, J., Xu, L., Zhang, K., Peng, H., Wu, H., & Jiang, J. G. et al. (2012). Multilayer structured MFI-type titanosilicate: Synthesis and catalytic properties in selective epoxidation of bulky molecules. *Journal of Catalysis*, *288*, 16–23. doi:10.1016/j.jcat.2011.12.023

Wang, L., Cai, H., Li, S., & Mominou, N. (2013). Ultra-deep removal of thiophene compounds in diesel oil over catalyst TiO_2/Ni-ZSM-5 assisted by ultraviolet irradiating. *Fuel*, *105*, 752–756. doi:10.1016/j.fuel.2012.09.069

Wang, L., Sun, B., Yang, F. H., & Yang, R. T. (2012). Effects of aromatics on desulfurization of liquid fuel by p-complexation and carbon adsorbents. *Chem Engineering Science*, *7*, 208–217. doi:10.1016/j.ces.2012.01.056

Wang, L., Zhao, Z., Li, J., & Chen, C. (2006). Synthesis and characterization of fluorinated polyimides for pervaporation of n-heptane/thiophene mixtures. *European Polymer Journal*, *42*(6), 1266–1272. doi:10.1016/j.eurpolymj.2005.12.013

Wang, M. Z., & Ruan, Y. J. (2010). Study on process conditions of adsorption desulfurization reaction of FCC gasoline. *Petroleum Refinery Engineering*, *40*(9), 5–10.

Wang, M., Li, W., Shi, Y., Wang, D., & Feng, H. (2006). Effects of surfactant on biodesulfurization by *Corynebacterium* sp. ZD-1 in the presence of organic phase. *Journal of Zhejiang University SCIENCE A*, *7*(S2), 371–375. doi:10.1631/jzus.2006.AS0371

Wang, P., & Krawiec, S. (1996). Kinetic analyses of desulfurization of dibenzothiophene by *Rhodococcus erythropolis* in batch and fed-batch cultures. *Applied and Environmental Microbiology*, *62*(5), 1670–1675. PMID:16535315

Wang, R., Yu, F., Zhang, G., & Zhao, H. (2010). Performance evaluation of the carbon nanotubes supported Cs2.5H0.5PW12O40 as efficient and recoverable catalyst for the oxidative removal of dibenzothiophene. *Catalysis Today*, *150*(1-2), 37–41. doi:10.1016/j.cattod.2009.10.001

Wang, R., Zhang, G., & Zhao, H. (2010). Polyoxometalate as effective catalyst for the deep desulfurization of diesel oil. *Catalysis Today*, *149*(1–2), 117–121. doi:10.1016/j.cattod.2009.03.011

Wang, S. H., Chang, J. S., & Berezin, A. A. (1993). Atomization characteristics of electrohydrodynamic limestone-water slurry spray. *Journal of Electrostatics*, *30*(C), 235–246. doi:10.1016/0304-3886(93)90078-L

Wang, T. G., He, F. Q., & Li, M. J. (2005). Alkyl dibenzothiophenes: A biomarker tracing petroleum charge. *Science Bulletin*, *50*(2), 176–181.

Wang, W. D., Serp, P., Kalck, P., & Faria, J. L. (2005). Photocatalytic degradation of phenol on MWNT and titania composite catalysts prepared by a modified sol–gel method. *Applied Catalysis B: Environmental*, *56*(4), 305–312. doi:10.1016/j.apcatb.2004.09.018

Wang, W., Li, G., Liu, L., & Chen, Y. (2013). Synthesis and catalytic performance of hierarchical TS-1 directly using agricultural products sucrose as meso/macropores template. *Microporous and Mesoporous Materials*, *179*, 165–171. doi:10.1016/j.micromeso.2013.06.012

Wang, W., Li, G., Liu, L., & Liu, H. (2012). Titanium silicalite synthesized by dry gel conversion metrhod and its catalytic performance. *Chinese Journal of Catalysis*, *33*, 1236–1241.

Wang, X., Li, F., Liu, J., Kou, C., Zhao, Y., Hao, Y., & Zhao, D. (2012). Preparation of TiO2 in Ionic Liquid via Microwave Radiation on in situ Photocatalytic Oxidative Desulfurization of Diesel Oil. *Energy & Fuels*, *26*, 6777–6782.

Wang, X., Li, Z., Shi, J., & Yu, Y. (2014). One-Dimensional Titanium Dioxide Nanomaterials: Nanowires, Nanorods, and Nanobelts. *Chemical Reviews*, *114*(19), 9346–9384. doi:10.1021/cr400633s PMID:24725155

Wang, Y. H., Yang, F. H., Yang, R. T., Heinzel, J. M., & Nickens, A. D. (2006). Desulfurization of high sulfur jet fuel by π-Complexation with copper and palladium halide sorbents. *Industrial & Engineering Chemistry Research*, *45*(22), 7649–7655. doi:10.1021/ie060922w

Wang, Y. H., Yang, R. T., & Heinzel, J. M. (2008). Desulfurization of jet fuel by π-complexation with metal halides supported on MCM-41 and SBA-15 mesoporous materials. *Chemical Engineering Science*, *63*(2), 356–365. doi:10.1016/j.ces.2007.09.002

Wang, Y., & Yang, R. T. (2007). Desulfurization of liquid fuels by adsorption on carbon-based sorbents and ultrasound-assisted sorbent regeneration. *Langmuir*, *23*(7), 3825–3831. doi:10.1021/la063364z PMID:17315903

Wang, Y., Zhang, C., Bi, S., & Luo, G. (2010). Preparation of ZnO nanoparticles using the direct precipitation method in a membrane dispersion micro-structured reactor. *Powder Technology*, *202*(1-3), 130–136. doi:10.1016/j.powtec.2010.04.027

Wang, Z., Wang, D., Li, Q., Li, W., Tang, H., & Xing, J. (2011). Enhanced biodesulfurization by expression of dibenzothiophene uptake genes in *Rhodococcus erythropolis. World Journal of Microbiology & Biotechnology*, *27*(9), 1965–1970. doi:10.1007/s11274-011-0656-z

Wan, M.-W., & Yen, T.-F. (2007). Enhance efficiency of tetraoctylammonium fluoride applied to ultrasound-assisted oxidative desulfurization (UAOD) process. *Applied Catalysis A, General*, *319*(0), 237–245. doi:10.1016/j.apcata.2006.12.008

Wannatong, L., Sirivat, A., & Supaphol, P. (2004). Effects of solvents on electrospun polymeric fibers: Preliminary study on polystyrene. *Polymer International*, *53*(11), 1851–1859. doi:10.1002/pi.1599

Wappel, D., Khan, A., Shallcross, D., Joswig, S., Kentish, S., & Stevens, G. (2009). The Effect of SO2 on CO2 Absorption in an Aqueous Potassium Carbonate Solvent. In Energy Procedia (Vol. 1, pp. 125–131).

Ward, P. L. (2009). Sulfur dioxide initiates global climate change in four ways. *Thin Solid Films*, *517*(11), 3188–3203. doi:10.1016/j.tsf.2009.01.005

Warych, J., & Szymanowski, M. (2001). Model of the wet limestone flue gas desulfurization process for cost optimization. *Industrial & Engineering Chemistry Research*, *40*(12), 2597–2605. doi:10.1021/ie0005708

Washburn, E. W. (1921). The dynamics of capillary flow. *Physical Review*, *17*(3), 273–283. doi:10.1103/PhysRev.17.273

Wasserscheid, P., & Jess, A. (2004). Deep desulfurization of oil refinery streams by extraction with ionic liquids. *Green Chemistry*, *6*(7), 316–322. doi:10.1039/b407028c

Watts, W. M. (1864). On the absorption of mixed gases in water; II. Sulfurous acid and carbonic acid in water. *Journal of the Chemical Society*, *17*(98).

Weitkamp, J., Schwark, M., & Ernst, S. (1991). Removal of thiophene impurities from benzene by selective adsorption in zeolite ZSM-5. *Chem. Soc. Chemical Communications*, (16): 1133–1134. doi:10.1039/c39910001133

Wells, A. E. (1917). An Investigation of the Wet Thiogen Process. *Journal of Industrial and Engineering Chemistry*, *9*(9), 872–873. doi:10.1021/ie50093a019

Welte, D. (1974). *Advances in Organic Geochemistry*, Editions Technip, 3-13.

Wen, Y., Wang, G., Wang, Q., Xu, C., & Gao, J. (2012). Regeneration characteristics and kinetics of Ni/ZnO-SiO_2-Al_2O_3 adsorbent for reactive adsorption desulfurization. *Industrial & Engineering Chemistry Research*, *51*(10), 3939–3950. doi:10.1021/ie202730w

Werther, J., Saenger, M., Hartge, E.-U., Ogada, T., & Siagi, Z. (2000). Combustion of agricultural residues. *Progress in Energy and Combustion Science*, *26*(1), 1–27. doi:10.1016/S0360-1285(99)00005-2

White, L. S., Wormsbecher, R. F., & Lesemann, M. (2004). Patent US 0211706 A1.

Whitehurst, D. D., Isoda, T., & Mochida, I. (1998). Present State of the Art and Future Challenges in the Hydrodesulfurization of Polyaromatic Sulfur Compounds. *Advances in Catalysis*, *42*, 345–471. doi:10.1016/S0360-0564(08)60631-8

Whitman, W. G. (1923). Preliminary experimental confirmation of the two-film theory of gas absorption. *Chemical and Metallurgical Engineering*, *29*, 146–148.

Willaert, R. G., & Baron, G. V. (1996). Gel entrapment and micro-encapsulation: Methods, applications and engineering principles. *Reviews in Chemical Engineering*, *12*(1), 1–205. doi:10.1515/REVCE.1996.12.1-2.1

Willey, C., Iwao, M., Castle, R. N., & Lee, M. L. (1981). Determination of sulfur heterocycles in coal liquids and shale oils. *Analytical Chemistry*, *53*(3), 400–407. doi:10.1021/ac00226a006

Williams, G., Seger, B., & Kamat, P. V. (2008). TiO_2-graphene nanocomposites. UV-assisted photocatalytic reduction of graphene oxide. *ACS Nano*, *2*(7), 1487–1491. doi:10.1021/nn800251f PMID:19206319

Wiltfong, R., Mitra-Kirtley, S., Mullins, O. C., Andrews, B., Fujisawa, G., & Larsen, J. (2005). Sulfur speciation in different kerogen by XANES spectroscopy. *Energy & Fuels*, *19*(5), 1971–1976. doi:10.1021/ef049753n

Wivel, C., Candia, R., Clausen, B. S., Mørup, S., & Topsøe, H. (1981). On the catalytic significance of a Co-Mo-S phase in Co-Mo/Al_2O_3 hydrodesulfurization catalysts: Combined *in situ* Mössbauer emission spectroscopy and activity studies. *Journal of Catalysis*, *68*, 453–463. doi:10.1016/0021-9517(81)90115-9

Woan, K., Pyrgiotakis, G., & Sigmund, W. (2009). Photocatalytic Carbon-Nanotube–TiO2 Composites. *Advanced Materials*, *21*(21), 2233–2239. doi:10.1002/adma.200802738

Wood, A. E., Sheely, C., & Trusty, A. W. (1925). Corrosion Effect of Naphtha Solutions of Sulfur and Sulfur Compounds. *Industrial & Engineering Chemistry*, *17*(8), 798–802. doi:10.1021/ie50188a008

World Energy Council. (2014). *World Energy Insight*. Retrieved from http://www.worldenergy.org/publications/2013/world-energy-insight-2013/

Wu, J., Iizuka, A., Kumagai, K., Yamasaki, A., & Yanagisawa, Y. (2008). Desulfurization Characteristics of Waste Cement Particles as a Sorbent in Dry Desulfurization. *Industrial & Engineering Chemistry Research*, *47*(24), 9871–9877. doi:10.1021/ie8009654

Wulff, G. (1993). The role of binding-site interactions in the molecular imprinting of polymers. *Trends in Biotechnology*, *11*(3), 85–87. doi:10.1016/0167-7799(93)90056-F PMID:7763512

Wu, Q., Pomerantz, A. E., Mullins, O. C., & Zare, R. N. (2014). Laser-Based Mass Spectrometric Determination of Aggregation Numbers for Petroleum- and Coal-Derived Asphaltenes. *Energy & Fuels*, *28*(1), 475–482. doi:10.1021/ef401958n

Wu, S., Lin, J., & Chan, S. I. (1994). Oxidation of dibenzothiophene catalyzed by heme-containing enzymes encapsulated in sol-gel glass. *Applied Biochemistry and Biotechnology*, *47*(1), 11–20. doi:10.1007/BF02788671 PMID:8203869

Wu, X.-C., Zhao, H.-F., Zhang, Y.-X., Zheng, C.-H., & Gao, X. (2014). Measurement of slurry droplets in coal-fired flue gas after WFGD. *Environmental Geochemistry and Health*, Sept., 25. PMID:25252634

Wu, Y., Li, Q., & Li, F. (2007). Desulfurization in the gas-continuous impinging stream gas–liquid reactor. *Chemical Engineering Science*, *62*(6), 1814–1824. doi:10.1016/j.ces.2006.01.027

Wu, Z., Jernström, S., Hughey, C. A., Rodgers, R. P., & Marshall, A. G. (2003). Resolution of 10,000 compositionally distinct components in polar coal extracts by negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels*, *17*(4), 946–953. doi:10.1021/ef030026m

Xia, J., Rumpf, B., & Maurer, G. (1999). Solubility of sulfur dioxide in aqueous solutions of acetic acid, sodium acetate, and ammonium acetate in the temperature range from 313 to 393 K at pressures up to 3.3 MPa: Experimental results and comparison with correlations/predictions. *Industrial & Engineering Chemistry Research*, *38*(3), 1149–1158. doi:10.1021/ie980529t

Xia, K., Weesner, F., Bleam, W. F., Bloom, P. R., Skyllberg, U. L., & Helmke, P. A. (1998). XANES studies of oxidation states in aquatic and soil humic substances. *Soil Science Society of America Journal*, *62*(5), 1240–1246. doi:10.2136/sssaj1998.03615995006200050014x

Xia, Y., Yang, P., Sun, Y., Wu, Y., Mayers, B., & Gates, B. et al. (2003). One-Dimensional Nanostructures: Synthesis, Characterization, and Applications. *Advanced Materials*, *15*(5), 353–389. doi:10.1002/adma.200390087

Xie, X. L., Mai, Y. W., & Zhou, X. P. (2005). Dispersion and alignment of carbon nanotubes in polymer matrix: A review. *Materials Science and Engineering R Reports*, *49*(4), 89–112. doi:10.1016/j.mser.2005.04.002

Xie, X., Ju, L., Feng, X., Sun, Y., Zhou, R., & Liu, K. et al. (2009). Controlled fabrication of high-quality carbon nanoscrolls from monolayer graphene. *Nano Letters*, *9*(7), 2565–2570. doi:10.1021/nl900677y PMID:19499895

Xi, L., Squires, C. H., Monticello, D. J., & Childs, J. D. (1997). A flavin reductase stimulates DszA and DszC proteins of Rhodococcus erytthropolis IGTS8 in vitro. *Biochemical and Biophysical Research Communications*, *230*(1), 73–75. doi:10.1006/bbrc.1996.5878 PMID:9020064

Xu, D., Zhu, W., Li, H., Zhang, J., Zou, F., Shi, H., & Yan, Y. (2009). Oxidative Desulfurization of Fuels Catalyzed by V2O5 in Ionic Liquids at Room Temperature. *Energy & Fuels*, *23*(12), 5929–5933. doi:10.1021/ef900686q

Xue, Y. Z., Wu, B., Guo, Y. L., Huang, L. P., Jiang, L., & Chen, J. Y. et al. (2011). Synthesis of large-area,few-layer graphene on iron foil by chemical vapor deposition. *Nano Research*, *4*(12), 1208–1214. doi:10.1007/s12274-011-0171-4

Xu, P., Feng, J., Yu, B., Li, F., & Ma, C. (2009). Recent developments in biodesulfurization of fossil fuels. *Advances in Biochemical Engineering/Biotechnology*, *113*, 255–274. PMID:19475378

Xu, X., Zhang, S., Li, P., & Shen, Y. (2014). Adsorptive desulfurization of liquid Jet-A fuel at ambient conditions with an improved adsorbent for on-board fuel treatment for SOFC applications. *Fuel Processing Technology*, *124*, 140–146. doi:10.1016/j.fuproc.2014.03.001

Yamada, K. O., Morimoto, M., & Tani, Y. (2001). Degradation of dibenzothiophene by sulfate-reducing bacteria cultured in the presence of only nitrogen gas. *Journal of Bioscience and Bioengineering*, *91*(1), 91–93. doi:10.1016/S1389-1723(01)80119-5 PMID:16232954

Yamada, K., Minoda, Y., Kodama, K., Nakatani, S., & Aesaki, T. (1998). Microbial conversion of petro-sulfur compounds. Part I Isolation and identification of dibenzothiophene utilizing bacteria. *Agricultural and Biological Chemistry*, *32*(7), 840–845. doi:10.1271/bbb1961.32.840

Yang, R. T., Yang, F. H., Takahashi, A., & Maldonado, A. J. H. (2002). *US Patent No. 7,029,574*. Washington DC: U.S. Patent and Trademark Office

Yang, C.-L., & Shaw, H. (1998). Aqueous Absorption of Nitric Oxide Induced by Sodium Chlorite Oxidation in the Presence of Sulfur Dioxide. *Environment and Progress*, *17*(2), 80–85. doi:10.1002/ep.670170213

Yang, F. H., Hernandez-Maldonado, A. J., & Yang, R. T. (2004). Selective adsorptipion of organosulfur compounds from transportation fuels by π-complexation. *Separation Science and Technology*, *39*(8), 1717–1731. doi:10.1081/SS-120035937

Yang, J., Hu, Y., Zhao, D., Wang, S., Lau, P. C. K., & Marison, I. W. (2007). Two-layer continuous-process design for the biodesulfurization of diesel oils under bacterial growth conditions. *Biochemical Engineering Journal*, *37*(2), 212–218. doi:10.1016/j.bej.2007.04.012

Yang, L., Li, J., Yuan, X., Shen, J., & Qi, Y. (2007). One step non-hydrodesulfurization of fuel oil: Catalyzed oxidation adsorption desulfurization over HPWA-SBA-15. *Journal of Molecular Catalysis A Chemical*, *262*(1–2), 114–118. doi:10.1016/j.molcata.2006.08.058

Yang, R. T. (2003). *Adsorbents: Fundamentals and Applications*. New York: Wiley. doi:10.1002/047144409X

Yang, R. T., Hernández-Maldonado, A. J., & Yang, F. H. (2003). Desulfurization of Transportation Fuels with Zeolites Under Ambient Conditions. *Science*, *301*(5629), 79–81. doi:10.1126/science.1085088 PMID:12843388

Yang, W., & Carleson, T. E. (1990). Several effects of electric fields on liquid extraction. *IEEE Transactions on Industry Applications*, *26*(2), 366–373. doi:10.1109/28.54265

Yang, W., Ratinac, K. R., Ringer, S. P., Thordarson, P., Gooding, J. J., & Braet, F. (2010). Carbon nanomaterials in biosensors: Should you use nanotubes or graphene? *Angewandte Chemie International Edition*, *49*(12), 2114–2138. doi:10.1002/anie.200903463 PMID:20187048

Yang, X., Cao, C., Klabunde, K. J., Hohn, K. L., & Erickson, L. E. (2007). Adsorptive desulfurization with xerogel-derived zinc-based nanocrystalline aluminum oxide. *Industrial & Engineering Chemistry Research*, *46*(14), 4819–4823. doi:10.1021/ie0701928

Yang, X., Erickson, L. E., Hohn, K. L., Jeevanandam, P., & Klabunde, K. J. (2006). Sol-Gel Cu-Al_2O_3 Adsorbents for Selective Adsorption of Thiophene out of Hydro carbon. *Industrial & Engineering Chemistry Research*, *45*(18), 6169–6174. doi:10.1021/ie060559t

Yang, X., Han, Y., Lin, K., Tian, G., Feng, Y., & Meng, X. (2012). Ordered mesoporous titanosilicates with catalytically stable and active four-coordinated titanium sites. *Chemical Communications (Cambridge)*, *60*, 1236–1241.

Yan, L., Lu, X., Wang, Q., Kang, Y., Xu, J., & Chen, Y. (2014). Research on sulfur recovery from the byproducts of magnesia wet flue gas desulfurization. *Applied Thermal Engineering*, *65*(1-2), 487–494. doi:10.1016/j.applthermaleng.2014.01.032

Yan, X. M., Mei, P., Lei, J., Mi, Y., Xiong, L., & Guo, L. (2009). Synthesis and characterization of mesoporous phosphotungstic acid/TiO2 nanocompositive as a novel oxidative desulfurization catalyst. *Journal of Molecular Chemical Catalysis A. Chemical*, *304*, 52–57.

Yan, X.-M., Lei, J.-H., Liu, D., Wu, Y.-C., & Guo, L.-P.Xue-Min Yan. (2007). Oxidative Desulfurization of Diesel Oil Using Mesoporous Phosphotungstic Acid/SiO2 as Catalyst. *Journal of the Chilean Chemical Society*, *54*(4), 911–916. doi:10.1002/jccs.200700131

Yazu, K., Furuya, T., Miki, K., & Ukegawa, K. (2003). Tungstophosphoric Acid-catalyzed Oxidative Desulfurization of Light Oil with Hydrogen Peroxide in a Light Oil/Acetic Acid Biphasic System. *Chemistry Letters*, *32*(10), 920–921. doi:10.1246/cl.2003.920

Yazu, K., Sato, S., Sugimoto, Y., Matsumura, A., & Saito, I. (2007). Tungstophosphoric acid–catalyzed oxidative desulfuriazation of naphtha with hydrogen peroxide in naphtha/acetic acid biphasic system. *Journal of the Japan Petroleum Institute*, *50*(6), 329–334. doi:10.1627/jpi.50.329

Yazu, K., Yamamoto, Y., Furuya, T., Miki, K., & Ukegawa, K. (2001). Oxidation of Dibenzothiophenes in an Organic Biphasic System and Its Application to Oxidative Desulfurization of Light Oil. *Energy & Fuels*, *15*(6), 1535–1536. doi:10.1021/ef0101412

Yen, T. F. (Ed.). (1975). *The Role of Trace Metals in Petroleum*. Michigan: Ann Arbor Science Inc.

Yin, C., & Xia, D. (2004). A study of the distribution of sulfur compounds in gasoline produced in China. Part 3. Identification of individual sulfides and thiophenes. *Fuel*, *83*(4–5), 433–441. doi:10.1016/j.fuel.2003.09.003

Yin, C., Zhu, G., & Xia, D. (2002). A study of the distribution of sulfur compounds in gasoline fraction produced in China: Part 2. The distribution of sulfur compounds in full-range FCC and RFCC naphthas. *Fuel Processing Technology*, *79*(2), 135–140. doi:10.1016/S0378-3820(02)00108-X

Yi, Y., Zhang, B., Jin, X., Wang, L., Williams, C. T., & Xiong, G. et al. (2011). Unsupported NiMoW sulfide catalysts for hydrodesulfurization of dibenzothiophene by thermal decomposition of thiosalts. *Journal of Molecular Catalysis A Chemical*, *351*, 120–127. doi:10.1016/j.molcata.2011.09.024

Yoon, H., Stouffer, M. R., Rosenhoover, W. A., Withum, J. A., & Burke, F. P. (1988). Pilot Process Variable Study of Coolside Desulfurization. *Environment and Progress*, *7*(2), 104–111. doi:10.1002/ep.3300070211

Yoshida, H., Shimizu, T., Uchiyama, T., Kohno, H., Homma, Y., & Takeda, S. (2009). Atomic-scaleanalysis on the role of molybdenum in iron-catalyzed carbon nanotube growth. *Nano Letters*, *9*(11), 3810–3815. doi:10.1021/nl9019903 PMID:19731921

Yoshikawa, O., Ishii, Y., Koizumi, K.-I., Ohshiro, T., Izumi, Y., & Maruhashi, K. (2002). Enhancement and stabilization of desulfurization activity of *Rhodococcus erythropolis* KA2-5-1 by feeding ethanol and sulfur components. *Journal of Bioscience and Bioengineering*, *94*(5), 447–452. doi:10.1016/S1389-1723(02)80223-7 PMID:16233332

Young, G. J. (1931). Reduction of sulfur dioxide. *Engineering and Mining Journal*, *131*(7).

Yuan, L., Saito, K., Hu, W., & Chen, Z. (2001). Ethylene flame synthesis of well-aligned multi-walled carbon nanotubes. *Chemical Physics Letters*, *346*(1-2), 23–28. doi:10.1016/S0009-2614(01)00959-9

Yuan, X. Y., Zhang, Y. Y., Dong, C. H., & Sheng, J. (2004). Morphology of ultrafine polysulfone fibers prepared by electrospinning. *Polymer International*, *53*(11), 1704–1710. doi:10.1002/pi.1538

Yudasaka, M., Komatsu, T., Ichihashi, T., & Iijima, S. (1997). Single wall carbon nanotube formation by laser ablation using double-targets of carbon and metal. *Chemical Physics Letters*, *278*(1-3), 102–106. doi:10.1016/S0009-2614(97)00952-4

Yue, Y., Sun, Y., & Gao, Z. (1997). Disordered mesoporous KIT-1 as a support for hydrodesulfurization catalysts. *Catalysis Letters*, *47*(2), 167–171. doi:10.1023/A:1019084400340

Yu, G., Lu, S., Chen, H., & Zhu, Z. (2005). Diesel fuel desulfurization with hydrogen peroxide promoted by formic acid and catalyzed by activated carbon. *Carbon*, *43*(11), 2285–2294. doi:10.1016/j.carbon.2005.04.008

Yu, G., Lu, S., Chen, H., & Zhu, Z. (2005). Oxidative Desulfurization of Diesel Fuels with Hydrogen Peroxide in the Presence of Activated Carbon and Formic Acid. *Energy & Fuels*, *19*(2), 447–452. doi:10.1021/ef049760b

Zaczepinski, S. (1996). Exxon Diesel Oil Deep Desulfurization (DODD). In R. A. Meyers (Ed.), *Handbook of Petroleum Refining Processes*. New York: McGraw-Hill.

Zaera, F., Kollin, E. B., & Gland, J. L. (1987). Vibrational characterization of thiophene decomposition on the Mo(100) surface. *Surface Science*, *184*(1-2), 75–89. doi:10.1016/S0039-6028(87)80273-X

Zahedi, P., Rezaeian, I., Ranaei-Siadat, S. O., Jafari, S. H., & Supaphol, P. (2010). A review on wound dressings with an emphasis on electrospun nanofibrous polymeric bandages. *Polymers for Advanced Technologies*, *21*, 77–95.

Zaki, T., Mohamed, N.H., Nessim, M.I., Abd El Salam, H. (2013). Characterization and application of nano-alumina sorbents for desulfurization and dearomatization of Suez crude petrolatum. *Fuel Processing Technology*, *106*, 625–630. doi:10.1016/j.fuproc.2012.09.055

Zang, G., Yu, F., & Wang, R. (2009). Research Advances in Oxidative desulfurization technologies for the production of low sulphur fuel oils. *Petroleum and Coal*, *51*, 196–207.

Zannikos, F., Lois, E., & Stournas, S. (1995). Desulfurization of petroleum fractions by oxidation and solvent extraction. *Fuel Processing Technology*, *42*(1), 35–45. doi:10.1016/0378-3820(94)00104-2

Zapata, B., Pedraza, F., & Valenzuela, M. A. (2005). Catalyst screening for oxidative desulfurization using hydrogen peroxide. *Catalysis Today*, *106*(1-4), 219–221. doi:10.1016/j.cattod.2005.07.134

Zaykina, R. F., Zaykin, Y. A., Mamaonava, T. B., & Nadirov, N. K. (2002). Radiation methods for demercaptanization and desulfurization of oil products. *Radiation Physics and Chemistry*, *63*(3-6), 621–624. doi:10.1016/S0969-806X(01)00654-5

Zhang Y W, Shen J., & D., Y. X. (2005,). .Desulfurization by catalytic oxidation and adsorption over Ti3(PW12O)4. *Petroleum process and petrochemicals,*, *36*(3), 20-24.

Zhang, C. X., Yuan, X. Y., Wu, L. L., Han, Y., & Sheng, J. (2005). Study on morphology of electrospun poly(vinyl alcohol) mats. *European Polymer Journal*, *41*(3), 423–432. doi:10.1016/j.eurpolymj.2004.10.027

Zhang, F., Yan, Y., Yang, H., Meng, Y., Yu, C., Tu, B., & Zhao, D. (2005). Understanding Effect of Wall Structure on the Hydrothermal Stability of Mesostructured Silica SBA-15. *The Journal of Physical Chemistry B*, *109*(18), 8723–8732. doi:10.1021/jp044632+ PMID:16852033

Zhang, Gaofei, & Yu, Fengli, & Wang., R. (2009). Research advances in oxidative desulphurization technologies for the production of low sulfur fuel oils. *Petroleum and Coal*, *51*(3), 196–207.

Zhang, H., Liu, Q., Li, Y., Li, W., Xiong, X., Xing, J., & Liu, H. (2008). Selection of adsorbents for in-situ coupling technology of adsorptive desulfurization and biodesulfurization. *Science in China Series B: Chemistry*, *51*(1), 69–77. doi:10.1007/s11426-007-0118-5

Zhang, J., Liu, Y., Tian, S., Chai, Y., & Liu, C. (2010). Reactive adsorption of thiophene on Ni/ZnO adsorbent: Effect of ZnO textural structure on the desulfurization activity. *Journal of Natural Gas Chemistry*, *19*(3), 327–332. doi:10.1016/S1003-9953(09)60076-1

Zhang, J., You, C., Zhao, S., Chen, C., & Qi, H. (2008). Characteristics and reactivity of rapidly hydrated sorbent for semidry flue gas desulfurization. *Environmental Science & Technology*, *42*(5), 1705–1710. doi:10.1021/es702208e PMID:18441824

Zhang, J., Zhu, W., Li, H., Jiang, W., Jiang, Y., Huang, W., & Yan, Y. (2009). Deep oxidative desulfurization of fuels by Fenton-like reagent in ionic liquids. *Green Chemistry*, *11*(11), 1801–1807. doi:10.1039/b914130h

Zhang, Q., Huang, J. Q., Qian, W. Z., Zhang, Y. Y., & Wei, F. (2013). The Road for Nanomaterials Industry: A Review of Carbon Nanotube Production, Post-Treatment, and Bulk Applications for Composites and Energy Storage. *Small*, *9*(8), 1237–1265. doi:10.1002/smll.201203252 PMID:23580370

Zhang, Q., Yu, Z., Du, P., & Su, C. (2010). Carbon nanomaterials used as conductive additives in lithium ion batteries. *Recent Patents on Nanotechnology*, *4*(2), 100–110. doi:10.2174/187221010791208803 PMID:20415660

Zhang, S., & Conrad Zhang, Z. (2002). Novel properties of ionic liquids in selective sulfur removal from fuels at room temperature. *Green Chemistry*, *4*(4), 376–379. doi:10.1039/b205170m

Zhang, S., Zhang, Q., & Zhang, Z. C. (2004). Extractive desulfurization and denitrogenation of fuels using ionic liquids. *Industrial & Engineering Chemistry Research*, *43*(2), 614–622. doi:10.1021/ie030561+

Zhang, S., Zhang, Y., Huang, S., Wang, P., & Tian, H. (2012). Mechanistic investigations on the adsorption of thiophene over Zn3NiO4 bimetallic oxide cluster. *Applied Surface Science*, *258*(24), 10148–10153. doi:10.1016/j.apsusc.2012.06.096

Zhang, T., Li, W.-L., Chen, X.-X., Tang, H., Li, Q., Xing, J.-M., & Liu, H.-Z. (2010). Enhanced biodesulfurization by magnetic immobilized Rhodococcus erythropolis LSSE8-1-vgb assembled with nano-γ-Al2O3. *World Journal of Microbiology & Biotechnology*, *27*(2), 299–305. doi:10.1007/s11274-010-0459-7

Zhang, W., Froba, M., Wang, J., Tanev, P. T., Wang, J., & Pinnavaia, T. J. (1996). Mesoporous titanosilicate molecular sieve prepared at ambient temperature by electrostatic and neutral assembly pathways: A comparison of physical properties and catalytic activity for peroxide oxidations. *Journal of the American Chemical Society*, *118*(38), 9164–9171. doi:10.1021/ja960594z

Zhang, W., Xu, K., Zhang, Q., Liu, D., Wu, S., Verpoort, F., & Song, X.-M. (2010). Oxidative Desulfurization of Dibenzothiophene Catalyzed by Ionic Liquid [BMIm]HSO4. *Industrial & Engineering Chemistry Research*, *49*(22), 11760–11763. doi:10.1021/ie100957k

Zhang, W., Zhang, H., Xiao, J., Zhao, Z., Yu, M., & Zhong Li, Z. (2014). Carbon nanotube catalysts for oxidative desulfurization of a model diesel fuel using molecular oxygen. *Green Chemistry*, *16*(1), 211–220. doi:10.1039/C3GC41106K

Zhang, Y., Lü, H., Wang, L., Zhang, Y., Liu, P., & Han, H. et al. (2010). The oxidation of benzothiophene using the Keggin-type lacunary polytungstophosphate as catalysts in emulsion. *Journal of Molecular Catalysis A Chemical*, *332*(1–2), 59–64. doi:10.1016/j.molcata.2010.08.021

Zhang, Y.-W., Prabhu, P., & Lee, J.-K. (2010). Alginate immobilization of recombinant *Escherichia coli* whole cells harboring L-arabinose isomerase for L-ribulose production. *Bioprocess and Biosystems Engineering*, *33*(6), 741–748. doi:10.1007/s00449-009-0397-7 PMID:19946709

Zhang, Y., Yang, Y., Hana, H., Yang, M., Wang, L., & Zhang, Y. et al. (2012a). Ultra-deep desulfurization via reactive adsorption on Ni/ZnO: The effect of ZnO particle size on the adsorption performance. *Applied Catalysis B: Environmental*, *119-120*, 13–19. doi:10.1016/j.apcatb.2012.02.004

Zhang, Y., Yang, Y., Lin, F., Yang, M., Liu, T., Jiang, Z., & Li, C. (2013). Improvement of adsorptive desulfurization performance of Ni/ZnO adsorbent by doping with Mn additive. *Chinese Journal of Catalysis*, *34*(1), 140–145. doi:10.1016/S1872-2067(11)60513-5

Zhang, Z. C., Xu, B., & Wang, X. (2014). Engineering nanointerfaces for nanocatalysis. *Chemical Society Reviews*, *43*(22), 7870–7886. doi:10.1039/C3CS60389J PMID:24745032

Zhang, Z. X., Zhang, F. W., Zhu, Q. Q., Zhao, W., Ma, B. C., & Ding, Y. (2011). Magnetically separable polyoxometalate catalysts for the oxidation of dibenzothiophene with H2O2. *Journal of Colloid and Interface Science*, *360*(1), 189–194. doi:10.1016/j.jcis.2011.04.045 PMID:21546033

Zhang, Z. Y., Shi, T. B., Jia, C. Z., Ji, W. J., Chen, Y., & He, M. Y. (2008). Adsorptive removal of aromatic organosulfur compounds over the modified Na-Y zeolites. *Applied Catalysis B: Environmental*, *82*(1-2), 1–10. doi:10.1016/j.apcatb.2008.01.006

Zhao, X., Krishnaiah, G., & Cartwright, T. (2004). S-Brane technology brings flexibility to refiners' clean fuel solutions. *NPRA annual meeting*. San Antonio, TX.

Zhao, D., Feng, J., Huo, Q., Melosh, N., Fredrickson, H. G., Chmelka, F. B., & Stucky, D. G. (1998). Triblock copolymer synthesis of mesoporous silica with periodic 50 to 300 angstrom pores. *Science*, *279*(5350), 548–552. doi:10.1126/science.279.5350.548 PMID:9438845

Zhao, D., Li, F., Han, J., & Li, H. (2007). Photochemical oxidation of thiophene by O2 in an organic two-phase liquid-liquid extraction system. *Petroleum Chemistry*, *47*(6), 448–451. doi:10.1134/S0965544107060138

Zhao, D.-, Li, F.-, & Sun, Z.-. (2008). Study on photosensitized oxidative desulfurization of thiophene by riboflavin. *Journal of Fuel Chemistry and Technology*, *36*(2), 161–164. doi:10.1016/S1872-5813(08)60016-X

Zhao, D., Wang, J., & Zhou, E. (2007). Oxidative desulfurization of diesel fuel using a Bronsted acid room temperature ionic liquid in the presence of H2O2. *Green Chemistry*, *9*(11), 1219–1222. doi:10.1039/b706574d

Zhao, D., Zhang, J., Wang, J., Liang, W., & Li, H. (2009). Photocatalytic Oxidation Desulfurization of Diesel Oil Using Ti-containing Zeolite. *Petroleum Science and Technology*, *27*(1), 1–11. doi:10.1080/10916460802108314

Zhao, J., Jin, B., & Zhong, Z. (2007). The degree of desulphurization of a limestone/gypsum wet FGD spray tower using response surface methodology. *Chemical Engineering & Technology*, *30*(4), 517–522. doi:10.1002/ceat.200600347

Zhao, L., Chen, Y., Gao, J., & Chen, Y. (2010). Jinsen GAO, Yu Chen "Desulfurization mechanism of FCC gasoline: A review". *Chem. Eng. China*, *4*(3), 314–321. doi:10.1007/s11705-009-0271-9

Zheng, B., & Lu, C. (2009). Desulphurization Characteristic of Industry Alkaline Wastes during Coal Combustion. *Journal of Electromagnetic Analysis & Applications*, *1*(01), 36–41. doi:10.4236/jemaa.2009.11007

Zheng, Y., Kiil, S., & Johnsson, J. E. (2003). Experimental investigation of a pilot-scale jet bubbling reactor for wet flue gas desulphurisation. *Chemical Engineering Science*, *58*(20), 4695–4703. doi:10.1016/j.ces.2003.07.002

Zheng, Y., Kiil, S., Johnsson, J. E., & Zhong, Q. (2002). Use of spray dry absorption product in wet flue gas desulphurisation plants: Pilot-scale experiments. *Fuel*, *81*(15), 1899–1905. doi:10.1016/S0016-2361(02)00133-3

Zhou, G., Sun, W., Jiang, W., & Zhou, H. (2013). Deep desulfurization of hydro-gasoline by adsorption in H_2 atmosphere over Ni/ZnO-SiO_2-Al_2O_3. *Petroleum Processing and Petrochemicals*, *44*(7), 17–21.

Zhou, H., Li, G., Wang, X., Jin, C., & Chen, Y. (2009). Preparation of a kind of mesoporous carbon and its performance in adsorptive desulfurization. *Journal of Natural Gas Chemistry*, *18*(3), 365–368. doi:10.1016/S1003-9953(08)60117-6

Zhou, M., Ma, , & Song, . (2006). Liquid-Phase Adsorption of Multi-Ring Thiophenic Sulfur Compounds on Carbon Materials with Different Surface Properties. *The Journal of Physical Chemistry B*, *110*(10), 4699–4707. doi:10.1021/jp0550210 PMID:16526705

Zhou, W. W., Han, Z. Y., Wang, J. Y., Zhang, Y., Jin, Z., & Sun, X. et al. (2006). Copper catalyzing growth of single-walled carbon nanotubes on substrates. *Nano Letters*, *6*(12), 2987–2990. doi:10.1021/nl061871v PMID:17163745

Zhou, X., Gai, H., Wang, J., Zhang, S., Yang, J., & Zhang, S. (2009). Oxidation of Benzothiophenes Using Tert-amyl Hydroperoxide. *Chinese Journal of Chemical Engineering*, *17*(2), 189–194. doi:10.1016/S1004-9541(08)60192-5

Zhou, X., Li, J., Wang, X., Jin, K., & Ma, W. (2009). Oxidative desulfurization of dibenzothiophene based on molecular oxygen and iron phthalocyanine. *Fuel Processing Technology*, *90*(2), 317–323. doi:10.1016/j.fuproc.2008.09.002

Zhou, X., Zhao, C., Yang, J., & Zhang, S. (2006). Catalytic Oxidation of Dibenzothiophene Using Cyclohexanone Peroxide. *Energy & Fuels*, *21*(1), 7–10. doi:10.1021/ef060441p

Zhou, Y., Yang, D., Chen, X., Xu, Q., Lu, F., & Nie, J. (2008). Electrospun water-soluble carboxyethyl chitosan/poly(vinyl alcohol) nanofibrous membrane as potential wound dressing for skin regeneration. *Biomacromolecules*, *9*(1), 349–354. doi:10.1021/bm7009015 PMID:18067266

Zhou, Y., Zhang, M., Wang, D., & Wang, L. (2005). Study on a novel semidry flue gas desulfurization with multifluid alkaline spray generator. *Industrial & Engineering Chemistry Research*, *44*(23), 8830–8836. doi:10.1021/ie050457n

Zhou, Z., & Dayal, R. (1990). Characterization and leaching studies of FGD waste by-products. *Waste Management (New York, N.Y.)*, *10*(1), 53–59. doi:10.1016/0956-053X(90)90069-W

Zhou, Z., & Zhang, K. (2004). Development situation and prospect of oil fields in China. *Petroleum Exploration and Development*, *31*(1), 84–87.

Zhu, W., Li, H., Jiang, X., Yan, Y., Lu, J., He, L., & Xia, J. (2008). Commercially available molybdic compound-catalyzed ultra-deep desulfurization of fuels in ionic liquids. *Green Chemistry*, *10*(6), 641–646. doi:10.1039/b801185k

Zhu, W., Li, H., Jiang, X., Yan, Y., Lu, J., & Xia, J. (2007). Oxidative Desulfurization of Fuels Catalyzed by Peroxotungsten and Peroxomolybdenum Complexes in Ionic Liquids. *Energy & Fuels*, *21*(5), 2514–2516. doi:10.1021/ef700310r

Zong, X. H., Kim, K., Fang, D. F., Ran, S. F., Hsiao, B. S., & Chu, B. (2002). Structure and process relationship of electrospun bioabsorbable nanofiber membranes. *Polymer*, *43*(16), 4403–4412. doi:10.1016/S0032-3861(02)00275-6

Zuo, J. Y., Mullins, O. C., Freed, D., Elshahawi, H., Dong, C., & Seifert, D. J. (2013). Advances in the Flory–Huggins–Zuo Equation of State for Asphaltene Gradients and Formation Evaluation. *Energy & Fuels*, *27*(4), 1722–1735. doi:10.1021/ef301239h

Zuo, J. Y., Mullins, O. C., Mishra, V., Garcia, G., Dong, C., & Zhang, D. (2012). Asphaltene grading and tar mats in oil reservoirs. *Energy & Fuels*, *26*(3), 1670–1680. doi:10.1021/ef201218m

Zuo, W. W., Zhu, M. F., Yang, W., Yu, H., Chen, Y. M., & Zhang, Y. (2005). Experimental study on relationship between jet instability and formation of beaded fibers during electrospinning. *Polymer Engineering and Science*, *45*(5), 704–709. doi:10.1002/pen.20304

About the Contributors

Tawfik A. Saleh works, at present, as a faculty member in the Chemistry Department of King Fahd University of Petroleum and Minerals. He has published several papers in refereed journals and conference proceedings, authored and edited several books and book chapters, and he is a member of several local and international scientific societies. He has supervised many graduate students. His expertise includes, but is not limited to, synthesis, design and preparation of materials, nanomaterials, nanocomposites, hybrid materials and their applications. His expertise also includes materials characterization using various spectroscopic and electrochemical techniques.

* * *

Rafael Huirache Acuña studied Chemical Engineering at Faculty of Chemical Engineering, UMSNH, Mexico (2000) and is Master in Metallurgy and Materials Science (Institute of Metallurgical Research, UMSNH, Mexico)(2003). He obtained his Doctoral Degree in Materials Science at Advanced Materials Research Center (CIMAV, S.C.) (2007). Subsequently, he got a Postdoctoral fellow at Centro de Física Aplicada y Tecnología Avanzada-Universidad Nacional Autónoma de México (2008). Actually, he is a researcher and professor at Universidad Michoacana de San Nicolás de Hidalgo, México.

Waqas Ahmad received an M.Sc from the University of Peshawar in 2001. He earned an M.Phil in 2008 and a PhD in 2013 in fuel chemistry, from the Institute of Chemical sciences, University of Peshawar. He carried out a part of his PhD research at the Department of Chemical and Material Engineering, University of Alberta, in Canada. His PhD research was based on oxidative desulfurization of petroleum using air assisted performic acid oxidation system. The research interest of Dr. Waqas Ahmad lie in catalytic oxidation, petroleum and coal desulfurization, heavy oil upgrading and Pyrolysis. Currently he is working as assistant professor at Institute of Chemical Sciences, University of Peshawar, Pakistan.

Gabriel Alonso obtained his BS degree (1987) in Chemistry from the Universidad Autónoma de Baja California at Tijuana, B. C., México, his MS degree (1994) in Organic Chemistry from the Instituto Tecnológico de Tijuana at Tijuana, B. C.,México and his PhD in Physics of Materials (1998) from the Centro de Investigación Científica y Estudios Superiores at Ensenada, México. Has Post-Doctoral Research (2002) in "Chemistry of transition metals sulfides" from the Chemistry Department of the University of Texas at El Paso, Texas, USA. At present, he works at the Universidad Nacional Autonóma de México, campus Ensenada, B. C., México. His research involve synthesis and characterization in organic chemistry and nanostructured materials (transition metal sulfides, oxides, nobles metals and carbon nanotubes) applied in catalysis and electrochemistry.

Luís Alves is a researcher at the Cell Factories & Enzymes Program of Bioenergy Unit at LNEG. PhD in Microbiology by the Faculty of Sciences - University of Lisbon, Portugal, he has experience in isolation and characterization of novel microorganisms and enzymes, application of fermentation techniques of SSF, SHF and CBP in batch or chemostat for the production of bioproducts (bioethanol, bioH2, lactic acid, carotenoids, biosurfactants, etc.) and biorefinery of fossil fuels. He has been participating in several national and international I&D projects as a team member or as the principal investigator. He has supervised several graduate, master and PhD thesis. He has published 27 peer-reviewed papers in ISI journals, and presented several communications at national/international scientific meetings.

Bruno F. Arez has a degree in Cellular Biology and Biotechnology by the Faculty of Sciences-University of Lisbon, and he is master student in Applied Microbiology in this faculty. Currently, he is developing his thesis entitled "Production and characterization of a novel yeast extracellular invertase activity towards improved dibenzotiophene biodesulfurization through SSF" in the ambit of the I&D project "Carbon4Desulf" at the Bioenergy unit at LNEG. He has experience in characterization and production of novel enzymes through the use of agroindustrial feedstocks and their application in different bioprocesses through techniques such as SSF and SHF. He published 1 peer-reviewed paper in ISI journals, and presented several communications at national/international scientific meetings.

Subrato Bhattacharya received master degree from Banaras Hindu University in 1990. In the same year, he qualified for the award of junior research fellowship (CSIR) and joined Prof. V.D. Gupta's group at Banaras Hindu University as a research fellow. He received his Ph.D. degree in 1994 and joined Sant Longowal Institute of Engineering and Technology (established by Govt. of India) the same year, as a lecturer. He moved to Post Graduate College in UP in the year 2000 and then to Banaras Hindu University in 2004. He became associate professor in 2008 and a full professor of Inorganic Chemistry in 2011. His main area of interest is organometallic chemistry, however, his research activities also include, structural studies of metal complexes, X-ray crystallography, synthesis and studies on molecular precursors of binary and ternary chalcogenides. He has authored/co-authored a number of research papers in reputed international journals and also a few popular science articles.

Giorgia Botta was born in Canada June 30th 1979. She obtained a degree in Medicinal Chemistry in 2005 and in 2008 a PhD in Pharmaceutical Sciences at University of Siena. From 2010 to now, she conducts research as a grant research at the laboratory of Bioorganic and Organic natural substances in collaboration with Professor Raffaele Saladino at the University of Tuscia, Viterbo. Currently, she is involved in several research areas including the study of catalysts and biocatalysts used in the synthesis of potentially active compounds, the study of the origin of life and the synthesis of peptidomimetic compounds using several new synthetic approaches.

Josep Maria Chimenos is associate professor at the University of Barcelona in the Materials Science and Metallurgical Engineering Department. He is a senior researcher and head of projects in the Environmental Technologies and Energy Sustainability division of the Center of Design and Optimization of Process and Materials, DIOPMA. The research group has been consolidated by the Government of Catalonia as a part of the network that brings together the leading technology transfer centers in Catalonia. He is author of more than 65 research papers in indexed journals (ISI; SCOPUS), mainly in the environmental engineering and environmental science categories.

Daniel de los Cobos-Vasconcelos He has a bachelor's degree in Biochemical Engineering from the National Polytechnic Institute of Mexico. He completed his master's degree and doctorate in the Chemical-Biological Sciences Program of the National Polytechnic Institute in the area of Environmental Biotechnology. Prior to his current appointment he was a post-doctoral research fellow at the Institute of Engineering of National Autonomous University of Mexico. Since 2014, he has been an academic staff member of the Environmental Engineering Laboratory of the same institution. His research interests are microbial population dymamics in biological wastewater treatment systems, microscopy imaging techniques of biological samples, bioprocess modeling and use of advanced techniques for characterization of complex matrices.

Marcello Crucianelli (Assistant Professor, University of L'Aquila) is a synthetic organic and organometallic chemist, with several years of experience in academic scientific research work. At the present, one of his research interests is focused on the study and development of new routes for the heterogenization of metal complexes or biocatalysts on hybrid organic/inorganic matrixes or carbon based structures in order to evaluate, under environment friendly catalytic conditions, their activity and selectivity towards the oxyfunctionalization of biologically active compounds.

Gaddafi Ibrahim Danmaliki earned his BSc in Biochemistry from Usmanu Danfodiyo University Sokoto in 2011. He is currently a Masters student of Environmental Science at King Fahd University of Petroleum and Minerals under the scholarship of Ministry of Higher Education of Saudi Arabia with thesis titled "Adsorptive evaluation of nanoparticles loaded carbon derived from used tires". He joined the Department of Biochemistry at Usmanu Danfodiyo University Sokoto as a Graduate Assistant in 2012.

Joan Formosa finished his PhD in 2012 at the University of Barcelona over the development of special mortars and cements formulated with magnesium by-products. He has over 20 research articles concerning the study of environmental routes for the revalorization of residues and by-products. He also has a broad experience in construction and building materials. He is currently working as a Lecturer in the Department of Materials Science and Metallurgical Engineering at the University of Barcelona.

Hui Ge was born in Taiyuan (China) in 1964. He studied biophysics at the Peking University (1881-185) and received his Ph.D. at Institute of Coal Chemistry, CAS in 2009. In the same year, he was appointed as a member of the Institute of Coal Chemistry where he joined the research group of Professor Xuekuan Li. He is currently an associate professor. The main focus of his work is the heterogeneous catalysis and application of hydrogenation and hydrodesulfurization catalysts.

Armando Gonzalez-Sanchez Research interests are focused on desulfurization of biogas and spent caustic streams, air and water pollution control, environmental biotechnology, biofiltation.

Omar Gutierrez Chemical Engineering, Faculty of Chemical Engineering, UMSNH, Mexico. 1998-2002. Master of Science in Chemical Engineering, Division of Graduate Studies, Faculty of Chemical Engineering, UMSNH, Mexico. 2004-2006. Doctor of Science in Chemical Engineering, Division of Graduate Studies, Faculty of Chemical Engineering, UMSNH, Mexico. 2008-2012. Researcher and Professor, Division of Biochemical Engineering, ITSCH, Mexico. From 2013 to present.

Mitra Kirtley is a professor in physics and optical engineering at the Rose-Hulman Institute of Technology. Her expertise lies in x-ray absorption spectroscopy with synchrotron radiation, with almost 30 years of experience in this area. She has worked synchrotron facilities at Brookhaven National Laboratory, Stanford Synchrotron Radiation Laboratory, Argonne National Laboratory, and Lawrence Berkeley Laboratory. She performed her post-doctoral research at the Lawrence Berkeley Laboratory, and Schlumberger-Doll Research, and received a Ph D in physics from the University of Kentucky. She has co-authored over 30 publications, and was the recipient of the Dean's Outstanding Research Award at the Rose-Hulman Institute of Technology.

Danai Montalvan-Sorrosa has a bachelor degree in Chemistry, Bacteriology, and Parasitology and she is a PhD student at the National Autonomous University of Mexico. As part of her PhD project, she has developed new bionanomaterials by using viral structures and inorganic nanoparticles. Her research interests includes the application of novel spectroscopic characterization techniques, and the use of biomolecules as part of functional bionanomaterials.

Oliver C. Mullins is a Science Advisor to Executive Management at Schlumberger, published 225 papers (half reviewed, half SPE & SPWLA). On Google Scholar Mullins has >9000 citations, H-index 54, authored 1 book, coedited 3 books & coauthored 13 book chapters on asphaltenes and related topics, and has 95 allowed US patents. He has various awards such as the SPWLA Technical Achievement Award, Distinguished lecturer SPE (4 times), the SPWLA, and 2 Schlumberger Gold Medals.

Adeniyi Ogunlaja is currently a Post-doctoral fellow at Nelson Mandela Metropolitan University, South Africa, Inorganic/Analytical Division working closely with Prof. Zenixole R. Tshentu. He graduated with a BSc (Hons) Industrial Chemistry from the University of Ilorin, Nigeria, MSc in Industrial Chemistry from the same university and a PhD in Inorganic/Analytical Chemistry from Rhodes University (South Africa). His research interests are (i) heterogeneous catalysis, (ii) designing molecularly imprinted nanomaterial essential for selective adsorption, and (iii) in computational molecular modelling. He received a Sasol Post-graduate Medal from the South African Chemical Institute in 2014 for his PhD work on "oxidative desulfurization of fuels".

Susana M. Paixão is a researcher at the Cell Factories & Enzymes Program of Bioenergy Unit at LNEG. A PhD in Microbiology by the Faculty of Sciences - University of Lisbon, Portugal, she has expertise in the fields of Environmental Microbiology (bioassays, ecotoxicity, biodegradability) and Bioenergy/Biotechnology (screening and characterization of novel microorganisms/enzymes, bioconversion studies, biomass for bioethanol, biorefinery, development of bioprocesses for bioenergy/bioproducts, experimental design, fermentation techniques such as SHF, SSF and CBP, fed-batch/continuous culture, clean technologies for fossil fuels - biodesulfurization). An experienced team member in several I&D projects, National and International (European) and experience in co-managing projects in Applied Microbiology/Enzymology/Bioenergy and in supervising graduate, master and PhD thesis. She has published more than 25 peer-reviewed papers (23 in ISI journals), and presented several works (oral communications and posters) at national/international scientific meetings.

Barbara Pawelec received her Ph. D. degree in Chemistry from the University Complutense of Madrid (Spain) in 1994. Her doctoral work under the supervision of Professor J.L.G. Fierro was on the development of catalysts for deep hydrodesulfurization of diesel feedstocks. In 2004 reached staff position as Tenure Scientist, then Research Scientist in 2008, in the Institute of Catalysis and Petrochemistry (ICP), which belongs to the Spanish National Council for Scientific Research (CSIC). Along the 25 years her research interests focused mainly in catalytic processes for heteroatom elimination (N and S) from gasoline and diesel, removal of oxygen from bio-oils via hydrodeoxygenation reaction to produce hydrocarbon fractions suitable for diesel fuel blending, total and preferential CO oxidation, and carbon dioxide reforming of methane to syngas. Her expertise includes: (i), preparation of catalysts; (ii), atmospheric and high-pressure flow-micro-reactor tests and gas chromatography analysis to evaluate catalyst performance and (iii), catalyst characterisation techniques such as FT-IR, TPR/TPD, XPS, XRD, TG and volumetric chemisorption of probe molecules over sulphide, reduced and oxide catalysts. She was director of 2 Doctoral Thesis, participated in 6 Projects supported by the EU Commission and other 23 Research Contracts supported by refining, gas and petrochemical companies, either of national or international dimensions. She is author or co-author of more 130 works published in specialised journals devoted to catalysis, material science and surface chemistry, and contributed with more than 100 presentations at international congresses and symposia.

Andrew E. Pomerantz is the Geochemistry Program Manager at Schlumberger-Doll Research. His research focuses on the development of novel techniques to characterize the chemical composition of kerogen and asphaltenes, including methods in mass spectrometry and X-ray spectroscopy. That molecular information is used to understand fundamental physical and chemical processes, such as petroleum generation, storage and transport in shales, and asphaltene compositional grading. He graduated from Stanford University with a PhD in chemistry in 2005 and has co-authored 50 peer-reviewed publications.

Eric M. Rivera He received his BSc in Physics (1987), his MSc (1992) and PhD (1997) in Materials Science from the National Autonomous University of Mexico. He made a postdoctoral stay in the Chemistry Department at the University of Texas at El Paso (USA) for two years. He is working as a scientist at the Center of Applied Physics and Advanced Technology of the National Autonomous University of Mexico (CFATA-UNAM). His present research interest includes Solid State Physics, Materials Science, Synthesis and characterization of materials, nanotechnology, etc. He is also working in diverse research in the field of catalysis.

Raffaele Saladino was born in Rome (Italy) August 31, 1964. Since 1992 he carries out teaching and research activity at the University of Tuscia (Viterbo, Italy), where he currently plays the role of Associate Professor of Organic Chemistry, Bioorganic Chemistry and Chemistry of Natural Substances. The main research fields of interest covered the organic synthesis, medicinal chemistry, biosensoring, organometallic catalysis and biocatalysis, with particular attention to the design, development and application of environmentally friendly procedures in the field of green chemistry and biotechnology.

Neha Sareen received a Master's of Science in Chemistry from Banaras Hindu University in 2011. She is currently working as a research scholar under Prof. Subrato Bhattacharya at Banaras Hindu University.

Taye D. Shuaib obtained a National Diploma in Chemical Engineering from The Federal Polytechnic, Bida in 2004 and a B.Tech in Chemistry with first class from Federal University of Technology, Minna, in 2010, both from Nigeria. Mr Shuaib is currently a graduate student at the Department of Chemistry, King Fahd University of Petroleum and Minerals, Kingdom of Saudi Arabia. His area of interest is preparation of nanomaterials for hydrocarbon processing and water treatment. He is an active member of a number of scientific societies both local and international.

Tiago P. Silva has a master's degree in Applied Microbiology by the Faculty of Sciences - University of Lisbon, Portugal, entitled "Utilization of agroindustrial materials as alternative carbon sources for the biodesulfurization of fossil fuels by Gordonia alkanivorans strain 1b". This work was performed in the ambit of the I&D project "Carbon4desulf", in which he was a part of the team. He has experience in processing agroindustrial feedstocks as well as application of fermentation techniques such as SSF in batch or chemostat for the production of microbial biomass towards application in the biorefinery of fossil fuels and production of bacterial pigments. He published 3 peer-reviewed papers in ISI journals, and presented several communications at national/international scientific meetings.

Zenixole Tshentu is currently an associate professor of analytical/inorganic chemistry at the Nelson Mandela Metropolitan University (NMMU) in South Africa. His research interests include (i) the development of inorganic/organic polymer materials for application in separation technology, (ii) bioinorganic chemistry and (iii) heterogeneous catalysis. He has been involved in several projects such as designing organic extractants for the separation of base metals and platinum group metals via solvent extraction and ion exchange processes, designing ligands for the stabilization of therapeutic metals in biological systems, designing catalysts for selective oxidation of sulfur compounds in fuels followed by selective adsorption of sulfones using molecularly imprinted polymers, and in the design of colorimetric probes for environmental pollutants and biological analytes. He has published more than 60 peer-reviewed papers in ISI journals. He terms his philosophy "the quest for selectivity and specificity". He currently holds a C2 rating from the National Research Foundation (South Africa) and has recently received a Research Excellence Award from NMMU.

Xiao-Dong Wen 05/2014-present: full professor, Institute of Coal Chemistry, Chinese Academy of Sciences 05/2014-present: Research Scientist, Synfuels China 05/2014-present: Guest Scientist, Los Alamos National Laboratory 12/2010-04/2014: Seaborg Fellow, Los Alamos National Laboratory 11/2007-11/2010: Postdoctoral Research Associate, Cornell University (Ithaca, 09/2002-07/2007: Ph.D. Institute of Coal Chemistry, Chinese Academy of Sciences 09/1998-07/2002: Bachelor of Science, Inner Mongolia Normal University.

Tang Ming Xing was born in 1982. 10/2008-present: assistant research fellow, Institute of Coal Chemistry, Chinese Academy of Sciences. The main research area is the fundamental & applied research of Ni/ZnO catalysts. 07/2005-09/2008: Master degree, Institute of Coal Chemistry, Chinese Academy of Sciences.

Ricardo del Valle Zermeño works as a researcher in the University of Barcelona since 2014 and his research is granted by the Catalonian Government. He graduated in Chemical Engineering in 2011 from the University of Barcelona and later finished his Master Degree in Energy Engineering in 2013 at the Technical University of Catalonia. In 2009, he started to work as a research assistant in the Center of Design and Optimization of Processes and Materials (DIOPMA) at the University of Barcelona where he has been involved in several industrial projects in collaboration with Spanish companies. His first research work was published in 2012 and since then several more articles and one patent in the waste management and environmental and chemical engineering field have been published. He has also been granted by the Communauté de Travail des Pyrénées and Montcelimar Foundation for developing his research in France and Spain.

Index

IRMA
INTERNATIONAL

Information Resources Management Association

Become an IRMA Member

Members of the **Information Resources Management Association (IRMA)** understand the importance of community within their field of study. The Information Resources Management Association is an ideal venue through which professionals, students, and academicians can convene and share the latest industry innovations and scholarly research that is changing the field of information science and technology. Become a member today and enjoy the benefits of membership as well as the opportunity to collaborate and network with fellow experts in the field.

IRMA Membership Benefits:

- **One FREE Journal Subscription**
- **30% Off Additional Journal Subscriptions**
- **20% Off Book Purchases**
- Updates on the latest events and research on Information Resources Management through the IRMA-L listserv.
- Updates on new open access and downloadable content added to Research IRM.
- A copy of the Information Technology Management Newsletter twice a year.
- A certificate of membership.

IRMA Membership $195

Scan code to visit irma-international.org and begin by selecting your free journal subscription.

Membership is good for one full year.

www.irma-international.org