Practical Advances in Petroleum Processing

Volume 1

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Front cover photo and back cover photo insert: Two views of the OMV plant in Schwechat, Austria, one of the most environmentally friendly refineries in the world, courtesy of OMV. Front cover insert photo: The Neste Oil plant in Porvoo, Finland includes process units for fluid catalytic cracking, hydrocracking, and oxygenate production. The plant focuses on producing high-quality, low-emission transportation fuels. Courtesy of Neste Oil.

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Tribute to Dr. Esber I. Shaheen
(1937-2003)

Born in 1937 in a remote village in Lebanon, Dr. Esber Ibrahim Shaheen became a much-honored educator, mentor and consultant, both for technology and international affairs. He received his B.S. in chemical engineering from Oklahoma State University, his M.S. in chemical engineering from the University of Arizona in Tuscon, and his Ph.D. from the University of Tennessee in Knoxville.

He was a professor and distinguished lecturer at more than 6 universities, including the University of Wisconsin, the King Fahd University of Petroleum and Minerals in Saudi Arabia, the Illinois Institute of Technology, Chicago, and the University of Tennessee. He also served as Director of Educational Services for the Institute of Gas Technology and Director of International

Education Programs for the Gas Developments Corporation in Chicago, Illinois. He assisted and encouraged students from all over the world and was instrumental in helping many of them in developing careers throughout the world.

Dr. Shaheen authored 7 textbooks, 3 of which were on international relations and more than 50 technical articles. He was the author, co-author or editor of nearly 20 training manuals on engineering, energy, the environment and petrochemical processing.

He received many awards, including Outstanding Educator of America. Most significantly, Dr. Shaheen received medals from President Ronald Reagan and from the Governor of the Eastern Province in Saudi Arabia.

We are pleased to include, with the permission of Dr. Esber I. Shaheen's wife, Shirley K. Shaheen, selections from his writings in this volume.

Paul R. Robinson
Chang Samuel Hsu

Foreword

Petroleum has remained an important aspect of our lives and will do so for the next four or five decades. The fuels that are derived from petroleum supply more than half of the world's total supply of energy. Gasoline, kerosene, and diesel oil provide fuel for automobiles, tractors, trucks, aircraft, and ships. Fuel oil and natural gas are used to heat homes and commercial buildings, as well as to generate electricity. Petroleum products are the basic materials used for the manufacture of synthetic fibers for clothing and in plastics, paints, fertilizers, insecticides, soaps, and synthetic rubber. The uses of petroleum as a source of raw material in manufacturing are central to the functioning of modern industry.

Petroleum refining is now in a significant transition period as the industry has moved into the 21st century and the demand for petroleum products has shown a sharp growth in recent years, especially with the recent entry of China into the automobile market. This means that the demand transportation fuels will, without doubt, show a steady growth in the next decade, contributing to petroleum product demand patterns that can only be fulfilled by the inclusion of heavier feedstocks into refinery operations.

In fact, the increasing supply of heavy crude oils as refinery feedstocks is a serious matter and it is essential that refineries are able to accommodate these heavy feedstocks. Indeed, in order to satisfy the changing pattern of product demand, significant investments in refining conversion processes will be necessary to profitably utilize these heavy crude oils. The most efficient and economical solution to this problem will depend to a large extent on individual country and company situations. However, the most promising technologies will likely involve the conversion of heavy crude oil, vacuum bottom residua, asphalt from deasphalting processes, and bitumen from tar sand deposits. Therefore, a thorough understanding of the benefits and limitations of petroleum processing is necessary and is introduced within the pages of this book.

The book is divided into two volumes. The first volume contains covers the origin and characterization of petroleum, major processes for fuel-production, and environmental pollution control. The second volume focuses on lubricants, hydrogen production, process modeling, automation, and online optimization.

The 50 contributors hail from three continents – Asia, Europe, and North America. This allows the book to contain within its pages a variety of experiences that are truly worldwide in breadth and scope. Contributions come from several sources, including integrated oil companies, catalyst suppliers, licensors, consultants, and academic researchers.

I am pleased to have been asked to write the Forward to this book. In light of the world energy situation, it is a necessary and timely addition to the literature that covers the technology of petroleum.

Dr. James G. Speight

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Preface

In 1964, Bob Dylan released an album and song named, *The Times They Are A-Changin'*. He was right. Times were changing, but nobody, not even Dylan, could have foreseen just how dramatically the great, wide world – and the smaller world of petroleum processing – would change during the next forty years.

In 1964, a wall divided Berlin. The moon was free of foot-prints. And in America we said, "Fill 'er up with ethyl" as a team of fueling-station attendants hurried to wash the windows of our thirsty Fords and Chevies.

In 1970, the Nixon administration created the U.S. Environmental Protection Agency (EPA), which, in 1973, initiated a lead phase-down program for gasoline. By the end of the decade, thanks to an oil embargo in 1973-74 and a revolution in Iran in 1978-79, fuel-efficient Japanese cars were displacing home-made brands in the United States and Europe.

In the 1980s, refiners built new process units to close the "octane gap" created by ever-tighter limits on lead in gasoline. Due to record-high prices, the worldwide demand for petroleum actually was decreasing. The drive to conserve energy created a market for rigorous models and advanced process control in refineries and petrochemical plants.

The Clean Air Act Amendments (CAAA) of 1990 again changed the industry. For gasoline, the CAAA required the addition of oxygenates such as MTBE. Billions of dollars, francs, marks, and yen were spent building methanol and MTBE plants. For on-road diesel, the CAAA emulated California by limiting sulfur content to 500 wppm. Across the Atlantic, the European Commission imposed a different set of limits. By the end of 2003, refiners were making low-sulfur gasoline and preparing to make ultra-low-sulfur diesel. Ironically, in 1999, Governor Gray Davis issued an executive order banning the use of MTBE in California gasoline. Soon thereafter, Davis was replaced by Arnold Schwarzenegger.

Purpose of this Book. This historical digression illustrates, we hope, that petroleum processing is a dynamic industry driven by global political, economic, and environmental forces. That's one of the reasons we're writing this book: to explain how the industry has changed during the past 40 years, particularly since 1994. We also wanted to cover cutting-edge topics usually missing from other general books on refining – FCC gasoline post-treatment, catalytic production of lubes, optimization of hydrogen and utility networks, process modeling, model-predictive control, and online optimization. And in addition: pollution control, staffing, reliability and safety.

Target Audience. Our target audience includes engineers, scientists and students who want an update on petroleum processing. Non-technical readers, with help from our extensive glossary, will benefit from reading Chapter 1 and the overview chapters that precede each major section.

Contributors. We are pleased to have contributions from several sources, including integrated oil companies, catalyst suppliers, licensors, consultants, and academic researchers. Our 50 contributors hail from three continents – Asia, Europe, and North America.

Many of the chapters are based on presentations given at a symposium at the 222nd National Meeting of the American Chemical Society (ACS), which was held in Chicago, Illinois in 2001. The symposium was entitled, "Kinetics and Mechanisms of Petroleum Processes." We thank ACS and the Division of Petroleum Chemistry, Inc. for allowing us to co-chair that session.

Organization and Overview. The book is divided into two volumes. The first contains 14 chapters, which cover the origin and characterization of petroleum, major processes for fuel-production, and environmental pollution control. The second volume contains 13 chapters, which focus on lubricants, hydrogen production, process modeling, automation, and refining management.

Chapter 1 introduces the book by giving an overview of petroleum and petroleum processing. Chapters 2-4 focus on the origin and characterization of oil and gas. Chapter 5 reports recent advances in the production of light olefin feedstocks for petrochemicals by catalytic processes, especially the balance between propylene and ethylene. Chapter 6 gives an overview of the kinetics and mechanism of fluidized catalytic cracking, an important process for producing gasoline.

The next five chapters discuss hydroprocessing and alternative ways to remove sulfur from fuels. Chapter 7 gives an overview of hydrotreating and hydrocracking and Chapter 8 gives more detail on hydrocracking. Chapters 9-11 discuss aspects of hydrotreating catalysts and processes, especially those related to meeting clean fuel specifications. Chapter 12 describes an extractive desulfurization process, and Chapter 13 discusses improvements in reactor design for hydroprocessing units.

One of the most important elements in modern petroleum refining is to keep the environment clean. Chapter 14 covers a wide range of pollution control issues: regulations, types of pollutants, informative examples of major environmental incidents, and pollution control technology.

The first four chapters in Volume 2 describe processes for making lubricating oils, including synthetic lubes. Chapter 15 gives an overview of conventional manufacturing processes for lube base-stocks, Chapter 16 discusses selective hydroprocessing for making high quality lubricants to meet new standards, Chapter 17 discusses synthetic lube base stocks, and Chapter 18 describes additives and formulation technology for engine oils.

As the world's supplies of light crude oils dwindle, processes for refining heavy oils and bitumen are becoming increasingly important. Chapter 19 deals with heavy oil processing. It reviews the chemical composition, physical and chemical properties, and upgrading chemistry of bitumen and heavy oils.

During the past twenty years, competitive pressures, including industry consolidation, forced the closure of some refineries even as others expanded. More and more, surviving refiners are using automation – model-predictive control, composition-based modeling, and computerized analysis of analytical data – to gain or maintain a competitive edge. Chapter 20 describes the application of kinetic modeling tools based on molecular composition to the development of a mechanistic kinetic model for the catalytic hydrocracking of heavy paraffins. Chapter 21 provides a general survey of process models based on two types of kinetic lumping: partition-based lumping and total lumping. Chapter 22 describes how model-predictive control can increase throughput, product quality, and stability in refining operations. Chapter 23 describes the real-time, online refinery-wide optimization application at Suncor-Sarnia.

As refiners reconfigure their plants to produce clean fuels, they are looking at ways to optimize the value of the hydrogen they now produce. They are also looking at different ways to supply the extra hydrogen required to make clean fuels. Chapter 24 discusses the online application of models of hydrogen production from the steam reforming of naphtha and other hydrocarbons. Chapter 25 addresses the issues of hydrogen demand, production and supply in refineries, and Chapter 26 tells refiners why they should think of their hydrogen as an asset, not a liability.

Chapter 27 reviews a new methodology to generate complete and reliable crude oil assays from limited laboratory data. Better crude quality control can improve refinery planning to ensure the profitability to survive in highly competitive global markets. It has also potential to be used in upstream operations for preliminary assessment of the oil quality of new reservoirs and new wells.

Putting this book together has been a rewarding challenge. We hope that you, our readers, will find it useful.

Acknowledgements. We wish to thank Dr. Kenneth Howell, Senior Editor for Chemistry at Springer, for his guidance and limitless patience. We also want to thank our many contributors for their time and effort. Obviously, without them, this book would not exist.

Most of all, we wish to thank our devoted, magnificent wives, Grace Miao-Miao Chen and Carrie, for putting up with our absences – mental if not physical – during so many nights and lost weekends throughout the past two years.

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Chapter 1

PETROLEUM PROCESSING OVERVIEW

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1. INTRODUCTION

The ground begins to rumble, then shake. The hero of the film – a lean ex-cowboy with a square jaw under his hat and a gorgeous brunette on his arm – reaches out to brace himself against his horse. A smile creases his face as the rumbling grows louder. Suddenly, a gush of black goo spurts into the air and splashes down on him, his side-kick and his best gal. They dance with ecstasy until the music swells and the credits start to roll.

Why is our hero so happy? Because he's rich! After years of drilling dry holes in every county between the Red River and the Rio Grande, he finally struck oil.

1.1 History of Petroleum Production

So why is he rich? What makes oil so valuable?

Actually, crude oil straight from the ground has some value, but not a lot. *Table 1* shows the history of petroleum before 1861. Before 1859, oil that was mined or that simply seeped up out of the ground was used to water-proof ships, as an adhesive in construction, for flaming projectiles, and in a wide variety of ointments.[1-4]

After 1859, petroleum became more and more important to the world's economy, so important that today, without a steady flow of oil, most human activities on this planet would grind to a halt. Petroleum accounts for 60% of the world's shipping on a tonnage basis.[3] It provides fuels and lubricants for our trucks, trains, airplanes, and automobiles. Ships are powered by fuel oil derived from petroleum. Bottom-of-the-barrel petroleum derivatives pave our roads and provide coke for the steel industry. Together with natural gas, petroleum provides precursors for the world's petrochemical industries. At the end of 2003, the world was consuming 78 million barrels of oil per day.[5] In August 2005, that volume of petroleum was worth $4.6 billion per day, or $1.7 trillion per year.

Table 1. History of Petroleum Before 1861

Date	Description
3000 BC	Sumerians use asphalt as an adhesive for making mosaics. Mesopotamians use bitumen to line water canals, seal boats, and build roads. Egyptians use pitch to grease chariot wheels, and asphalt to embalm mummies.
1500 BC	The Chinese use petroleum for lamps and for heating homes.
600 BC	Confucius writes about the drilling of 100-foot (30-meter) natural gas wells in China. The Chinese build pipelines for oil using bamboo poles.
600-500 BC	Arab and Persian chemists mix petroleum with quicklime to make Greek fire, the napalm of its day.
1200-1300 AD	The Persians mine seep oil near Baku (now in Azerbaijan).
1500-1600 AD	Seep oil from the Carpathian Mountains is used in Polish street lamps. The Chinese dig oil wells more than 2000 feet (600 meters) deep.
1735 AD	Oil is extracted from oil sands in Alsace, France.
Early 1800s	Oil is produced in United States from brine wells in Pennsylvania.
1847	James Oakes builds a "rock oil" refinery in Jacksdale, England.[6] The unit processes 300 gallons per day to make "paraffin oil" for lamps. James Young builds a coal-oil refinery in Whitburn, Scotland.[7]
1848	F.N. Semyenov drills the first "modern" oil well near Baku.
1849	Canadian geologist Abraham Gesner distills kerosene from crude oil.
1854	Ignacy Lukasiewicz drills oil wells up to 150 feet (50 meters) deep at Bóbrka, Poland.
1857	Michael Dietz invents a flat-wick kerosene lamp (Patent issued in 1859).
1858	Ignacy Lukasiewicz builds a crude oil distillery in Ulaszowice, Poland.[8] The first oil well in North America is drilled near Petrolia, Ontario, Canada.
1859	Colonel Edwin L. Drake triggers the Pennsylvania oil boom by drilling a well near Titusville, Pennsylvania that was 69-feet deep and produced 35 barrels-per-day.
1859	An oil refinery is built in Baku (now in Azerbaijan).
1860-61	Oil refineries are built near Oil Creek, Pennsylvania; Petrolia, Ontario, Canada; and Union County, Arkansas.

So what happened in 1859? What began the transformation of petroleum from a convenience into the world's primary source of energy? As often is the case with major socioeconomic shifts, the move toward oil was instigated not by just a single event, but by the juxtaposition of several:

- In the 1850s, most home-based lamps burned whale oil or other animal fats. Historically, whale-oil prices had always fluctuated wildly, but they peaked in the mid-1850s due to the over-hunting of whales; by some estimates, in 1860 several species were almost extinct. Whale oil sold for an average price of US$1.77 per gallon between 1845 and 1855. In contrast, lard oil sold for about US$0.90 per gallon.[9,10] Lard oil was more abundant, but it burned with a smoky, smelly flame.

- Michael Dietz invented a flat-wick kerosene lamp in 1857. The Dietz lamp was arguably the most successful of several devices designed to burn something other than animal fats.
- The availability of kerosene got a sudden boost on August 27, 1859, when Edwin L. Drake struck oil with the well he was drilling near Titusville, Pennsylvania. By today's standards, the well was shallow – about 69 feet (21 meters) deep and it produced only 35 barrels per day. Drake was able to sell the oil for US$20 per barrel, a little less than the price of lard oil and 70% less than the price of whale oil. In 1861, US$700 per day was a tidy sum, equivalent to US$5 million per year in 2002 dollars.[11] Drake's oil well was not the first – according to one source, the Chinese beat Drake by about 2200 years – but it may have been the first drilled through rock, and it certainly triggered the Pennsylvania oil rush. Figure 1 shows some of the closely spaced wells that sprang up in 1859 in the Pioneer Run oil field a few miles from Titusville.

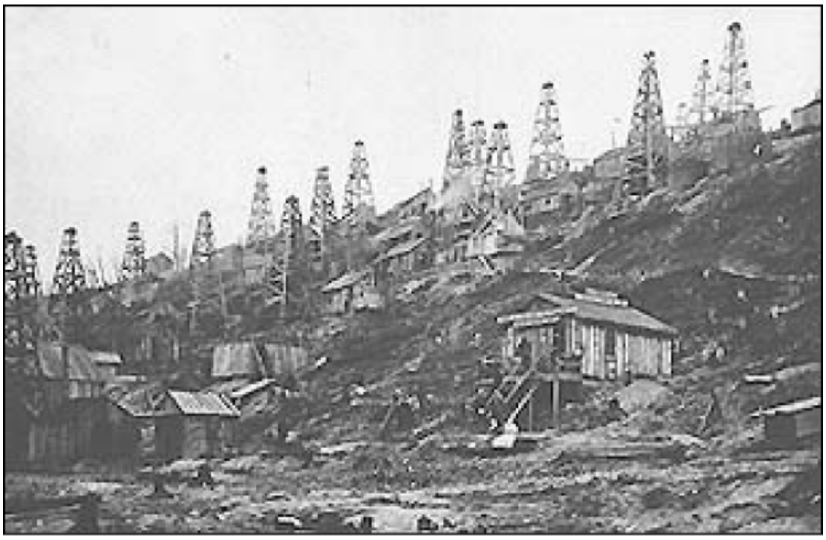

Figure 1. Pioneer Run oil field in 1859. Photo used with permission from the Pennsylvania Historical Collection and Musem Commission, Drake Well Museum Collection, Titusville, PA.

According to a report issued in 1860 by David Dale Owens,[12] the state geologist of Arkansas:

"On Oil Creek in the vicinity of Titusville, Pennsylvania, oil flows out from some wells at the rate of 75 to 100 gallons in 24 hours already fit for the market. At least 2000 wells are now in progress and 200 of these are already pumping oil or have found it."

According to *The Prize*,[13] a prize-winning book by Daniel Yergin: