Practical Advances in Petroleum Processing
Volume 1
Practical Advances in Petroleum Processing
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Edited by

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Springer
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
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 for 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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*Clifford C. Walters*

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Yevgenia Briker, Zbigniew Ring, and Hong Yang

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