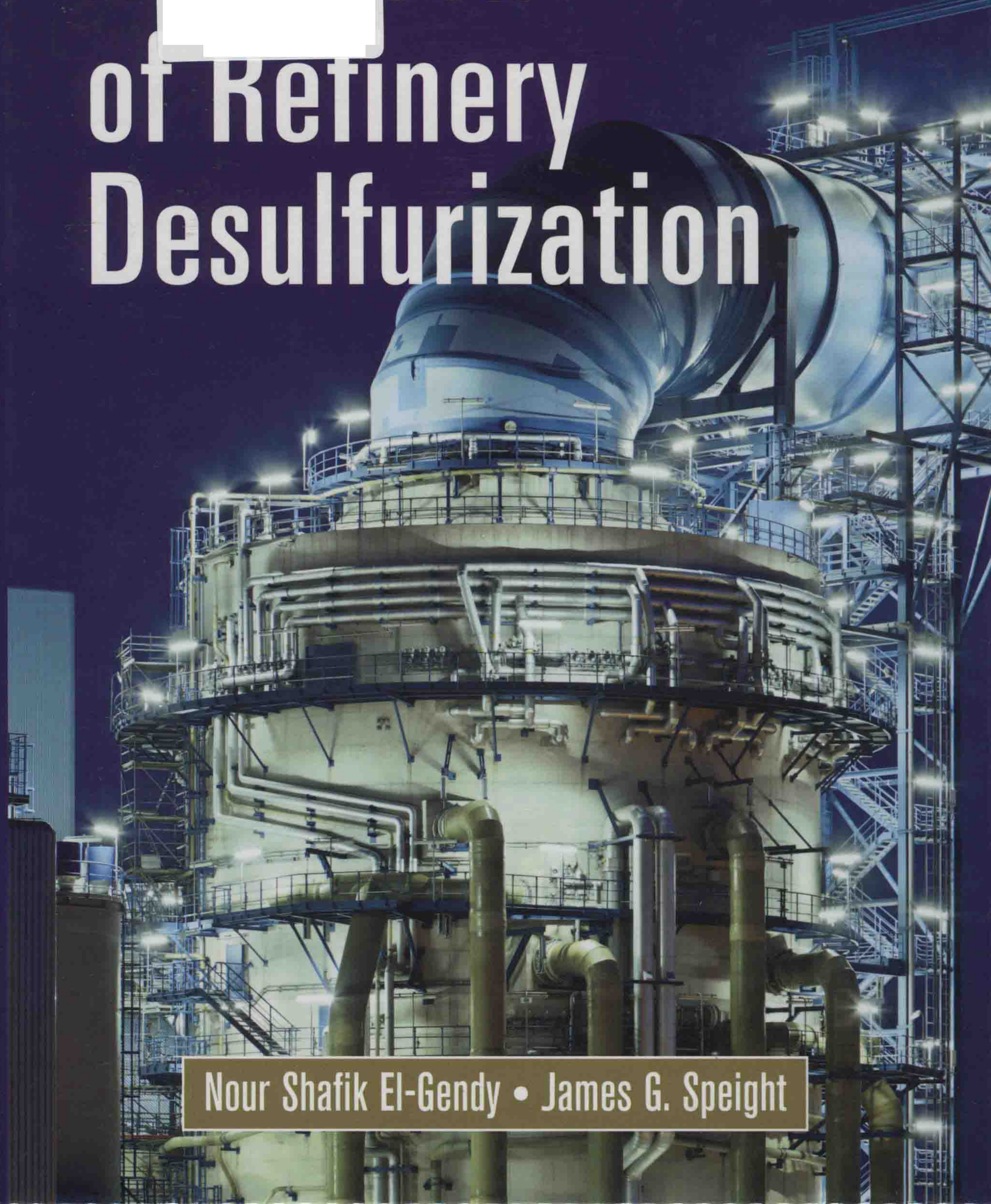
CHEMICAL INDUSTRIES/140

CRC Press
Taylor & Francis Group

Handbook of Refinery Desulfurization



Nour Shafik El-Gendy • James G. Speight

Handbook of Refinery Desulfurization

Nour Shafik El-Gendy
Egyptian Petroleum Research Institute, Cairo, Egypt

James G. Speight
CD&W Inc., Laramie, Wyoming, USA

CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

Printed on acid-free paper by CPI Group (UK) Ltd, Croydon
Version Date: 20150617

International Standard Book Number-13: 978-1-4665-9671-9 (Hardback)

Library of Congress Cataloging-in-Publication Data

El-Gendy, Nour Shafik.
Handbook of refinery desulfurization / Nour Shafik El-Gendy and James G. Speight.
pages cm. -- (Chemical industries)
Includes bibliographical references and index.
ISBN 978-1-4665-9671-9 (hardcover : alk. paper) 1. Petroleum--Refining--Desulfurization. I. Speight, James G. II. Title.

TP690.45.E43 2016
665.5'3--dc23 2015021151

Visit the Taylor & Francis Web site at
http://www.taylorandfrancis.com

and the CRC Press Web site at
http://www.crcpress.com

Handbook of Refinery Desulfurization

CHEMICAL INDUSTRIES

A Series of Reference Books and Textbooks

Founding Editor

HEINZ HEINEMANN
Berkeley, California

Series Editor

JAMES G. SPEIGHT
CD & W, Inc.
Laramie, Wyoming

MOST RECENTLY PUBLISHED

Handbook of Refinery Desulfurization, Nour Shafik El-Gendy and James G. Speight

Refining Used Lubricating Oils, James Speight and Douglas I. Exall

The Chemistry and Technology of Petroleum, Fifth Edition, James G. Speight

Educating Scientists and Engineers for Academic and Non-Academic Career Success, James Speight

Transport Phenomena Fundamentals, Third Edition, Joel Plawsky

Synthetics, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology, Second Edition, Leslie R. Rudnick

Modeling of Processes and Reactors for Upgrading of Heavy Petroleum, Jorge Ancheyta

Synthetics, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology, Second Edition, Leslie R. Rudnick

Fundamentals of Automatic Process Control, Uttam Ray Chaudhuri and Utpal Ray Chaudhuri

The Chemistry and Technology of Coal, Third Edition, James G. Speight

Practical Handbook on Biodiesel Production and Properties, Mushtaq Ahmad, Mir Ajab Khan, Muhammad Zafar, and Shazia Sultana

Introduction to Process Control, Second Edition, Jose A. Romagnoli and Ahmet Palazoglu

Fundamentals of Petroleum and Petrochemical Engineering, Uttam Ray Chaudhuri

Advances in Fluid Catalytic Cracking: Testing, Characterization, and Environmental Regulations, edited by Mario L. Occelli

Advances in Fischer-Tropsch Synthesis, Catalysts, and Catalysis, edited by Burton H. Davis and Mario L. Occelli

Transport Phenomena Fundamentals, Second Edition, Joel Plawsky

Asphaltenes: Chemical Transformation during Hydroprocessing of Heavy Oils, Jorge Ancheyta, Fernando Trejo, and Mohan Singh Rana

Preface

Sulfur, nitrogen, and metals in petroleum cause expensive processing problems in the refinery. As conventional technology does not exist to economically remove these contaminants from crude oil, the problem is left for the refiners to handle downstream at a high cost. In addition, regulations in various countries restricting the allowable levels of sulfur in end products continue to become increasingly stringent. This creates an ever more challenging technical and economic situation for refiners, as the sulfur levels in available crude oils continue to increase, conferring a market disadvantage for producers of high-sulfur crudes. Lower-sulfur crudes continue to command a premium price in the market, while higher sulfur crude oils sell at a discount. Desulfurization would offer producers the opportunity to economically upgrade their resources.

The sulfur content of petroleum varies from <0.05% to >14% wt. but generally falls in the range of 1–4% wt. Petroleum having <1% wt. sulfur is referred to as *low-sulfur*, and that having >1% wt. sulfur is referred to as *high-sulfur*. Heavy oils, residua, and bitumen are generally considered to be high-sulfur feedstocks by the refining industry. In addition, petroleum refining has entered a significant transition period as the industry moves into the 21st century. Refinery operations have evolved to include a range of next-generation processes as the demand for transportation fuels and fuel oil has shown a steady growth. These processes are different from one another in terms of the method and product slates, and they will find employment in refineries according to their respective features. The primary goal of these processes is to convert the heavy feedstocks to lower-boiling products, and during the conversion there is a reduction in the sulfur content.

With the inception of hydrogenation as a process by which both coal and petroleum could be converted into lighter products, it was also recognized that hydrogenation would be effective for the simultaneous removal of nitrogen, oxygen, and sulfur compounds from the feedstock. However, with respect to the prevailing context of fuel industries, hydrogenation seemed to be uneconomical for application to petroleum fractions. At least two factors dampened interest: (1) the high cost of hydrogen and (2) the adequacy of current practices for meeting the demand for low-sulfur products by refining low-sulfur crude oils, or even by alternative desulfurization techniques.

Nevertheless, it became evident that reforming processes instituted in many refineries were providing substantial quantities of by-product hydrogen, enough to tip the economic balance in favor of hydrodesulfurization processes. In fact, the need for such commercial operations has become more acute because of a shift in supply trends that has increased the amount of high-sulfur crude oils employed as refinery feedstocks.

Overall, there has, of necessity, been a growing dependence on high-sulfur heavier oils and residua as a result of continuing increases in the prices of the conventional crude oils coupled with the decreasing availability of these crude oils through the depletion of reserves in various parts of the world. Furthermore, the ever growing tendency to convert as much as possible lower-grade feedstocks to liquid products is causing an increase in the total sulfur content in refined products. Refiners must, therefore, continue to remove substantial portions of sulfur from the lighter products; however, residua and the heavier crude oils pose a particularly difficult problem. Indeed, it is now clear that there are other problems involved in the processing of the heavier feedstocks and that these heavier feedstocks, which are gradually emerging as the liquid fuel supply of the future, need special attention.

The hydrodesulfurization of petroleum fractions has long been an integral part of refining operations, and in one form or another, hydrodesulfurization is practiced in every modern refinery. The process is accomplished by the catalytic reaction of hydrogen with the organic sulfur compounds in the feedstock to produce hydrogen sulfide, which can be separated readily from the liquid (or gaseous) hydrocarbon products. The technology of the hydrodesulfurization process is well established, and petroleum feedstocks of every conceivable molecular weight range can be treated to remove sulfur. Thus, it is not surprising that an extensive knowledge of hydrodesulfurization has been acquired along with the development of the process during the last few decades. However, most of the available information pertaining to the hydrodesulfurization process has been obtained with the lighter and more easily desulfurized petroleum fractions, but it is, to some degree, applicable to the hydrodesulfurization of the heavier feedstocks such as the heavy oils and residua. On the other hand, the processing of the heavy oils and residua present several problems that are not found with distillate processing and that require process modifications to meet the special requirements that are necessary for heavy feedstock desulfurization.

In the last three decades, there have been many changes in the refining industry. The overall character of the feedstocks entering refineries has changed to such an extent that the difference can be measured by a decrease of several points on the API gravity scale. It is, therefore, the object of the present text to discuss the processes by which various feedstocks may, in the light of current technology, be treated to remove sulfur and, at the same time, afford maximum yields of low-sulfur liquid products. Thus, this text is designed for those scientists and engineers who wish to be introduced to desulfurization concepts and technology, as well as those scientists and engineers who wish to make more detailed studies of how desulfurization might be accomplished. Chapters relating to the composition and evaluation of heavy oils and residua are considered necessary for a basic understanding of the types of feedstock that will necessarily need desulfurization treatment. For those readers requiring an in-depth theoretical treatment, a discussion of the chemistry and physics of the desulfurization process has been included. Attention is also given to the concept of desulfurization during the more conventional refinery operations.

The effects of reactor type, process variables and feedstock type, catalysts, and feedstock composition on the desulfurization process provide a significant cluster of topics through which to convey the many complexities of the process. In the concluding chapters, examples and brief descriptions of commercial processes are presented and, of necessity, some indications of methods of hydrogen production are also included. In addition, environmental issues have become of such importance that a chapter on the cleanup of refinery gases is included. Moreover, the environmental effects of sulfur-containing gases are also addressed.

Finally, as refineries and feedstocks evolve, biocatalytic processes for reducing sulfur offers the petroleum industry potentially great rewards by use of such processes (biocatalytic desulfurization). Generally, biological processing of petroleum feedstocks offers an attractive alternative to conventional thermochemical treatment due to the mild operating conditions and greater reaction specificity afforded by the nature of biocatalysis. Efforts in microbial screening and development have identified microorganisms capable of petroleum desulfurization, denitrogenation, and demetallization.

Biological desulfurization of petroleum may occur either oxidatively or reductively. In the oxidative approach, organic sulfur is converted to sulfate and may be removed in process water. This route is attractive because it would not require further processing of the sulfur and may be amenable for use at the wellhead, where process water may then be reinjected. In the reductive desulfurization scheme, organic sulfur is converted into hydrogen sulfide, which may then be catalytically converted into elemental sulfur, an approach of utility at the refinery. Regardless of the mode of biodesulfurization, key factors affecting the economic viability of such processes are biocatalyst activity and cost, differential in product selling price, sale or disposal of coproducts or wastes from the treatment process, and the capital and operating costs of unit operations in the treatment scheme. Furthermore, biocatalytic approaches to viscosity reduction and the removal of metals and nitrogen are additional approaches to fuel upgrading.

Nour Shafik El-Gendy
Egyptian Petroleum Research Institute

James G. Speight
CD&W Inc.

Authors

Nour Shafik El-Gendy is an associate professor in the field of environmental biotechnology and head manager of Petroleum Biotechnology Lab, Egyptian Petroleum Research Institute, Cairo, Egypt. She is the author of two books in the fields of biofuels and petroleum biotechnology and more than 100 research papers in the fields of oil pollution, bioremediation, biosorption, biofuels, macro- and micro-corrosion, green chemistry, wastewater treatment, and nano-biotechnology and its applications in the petroleum industry and biofuels. Dr. El-Gendy is also an editor in 12 international journals in the field of environmental biotechnology and microbiology, and she has supervised 20 MSc and PhD theses in the fields of biofuels, micro–macro fouling, bioremediation, wastewater treatment, biodenitrogenation, and biodesulfurization. Dr. El-Gendy is a member of many international associations concerned with environmental health and sciences. She is also a lecturer and supervisor for undergraduate research projects at the British University in Egypt BUE and Faculty of Chemical Engineering, Cairo University, Egypt, and also teaches an environmental biotechnology course for postgraduates at the Faculty of Science, Monufia University, Egypt. Her biography is recorded in *Who's Who in Science and Engineering*, 9th edition, 2006–2007.

James G. Speight, who has doctoral degrees in chemistry, geological sciences, and petroleum engineering, is the author of more than 60 books on petroleum science, petroleum engineering, and environmental sciences. He has served as adjunct professor in the Department of Chemical and Fuels Engineering at the University of Utah and in the Departments of Chemistry and Chemical and Petroleum Engineering at the University of Wyoming. In addition, he has been a visiting professor in chemical engineering at the following universities: the University of Missouri, Columbia, the Technical University of Denmark, and the University of Trinidad and Tobago.

As a result of his work, Dr. Speight has been honored as the recipient of the following awards:

- Diploma of Honor, United States National Petroleum Engineering Society. For Outstanding Contributions to the Petroleum Industry. 1995.
- Gold Medal of the Russian Academy of Sciences. For Outstanding Work in the Area of Petroleum Science. 1996.
- Einstein Medal of the Russian Academy of Sciences. In recognition of Outstanding Contributions and Service in the field of Geologic Sciences. 2001.
- Gold Medal—Scientists without Frontiers, Russian Academy of Sciences. In recognition of His Continuous Encouragement of Scientists to Work Together across International Borders. 2005.
- Methanex Distinguished Professor, University of Trinidad and Tobago. In Recognition of Excellence in Research. 2006.
- Gold Medal—Giants of Science and Engineering, Russian Academy of Sciences. In Recognition of Continued Excellence in Science and Engineering. 2006.

Contents