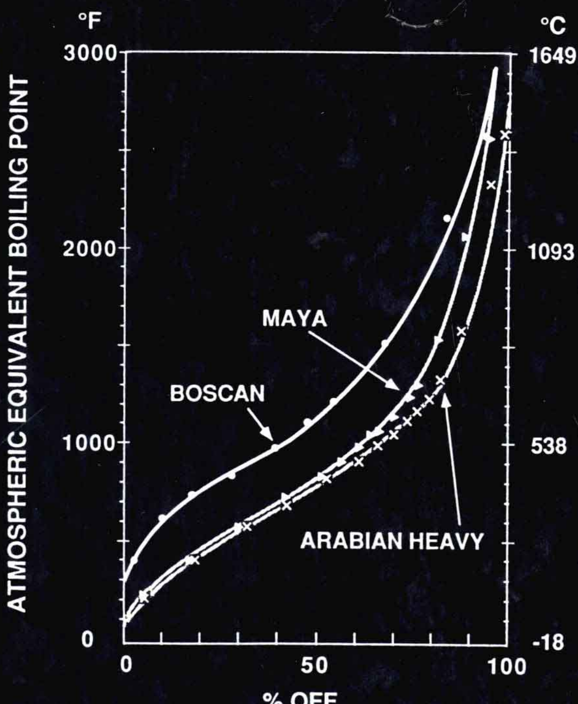
COMPOSITION AND ANALYSIS OF HEAVY PETROLEUM FRACTIONS



Klaus H. Altgelt
Mieczyslaw M. Boduszynski

COMPOSITION AND ANALYSIS OF HEAVY PETROLEUM FRACTIONS

Klaus H. Altgelt
Consultant
San Rafael, California

Mieczyslaw M. Boduszynski
Chevron Research and Technology Company
Richmond, California

江苏工业学院图书馆
藏书章

Marcel Dekker, Inc. New York • Basel • Hong Kong

Library of Congress Cataloging-in-Publication Data

Altgelt, Klaus H.
Composition and analysis of heavy petroleum fractions / Klaus H. Altgelt. Mieczyslaw M. Boduszynski.
p. cm. — (Chemical industries ; v. 54)
Includes bibliographical references and index.
ISBN 0-8247-8946-6
1. Petroleum—Analysis. I. Boduszynski, Mieczyslaw M. II. Title. III. Series.
TP691.A45 1994 93-39037
665.5—dc20 CIP

The publisher offers discounts on this book when ordered in bulk quantities. For more information, write to Special Sales/Professional Marketing at the address below.

This book is printed on acid-free paper.

Copyright © 1994 by Marcel Dekker, Inc. All Rights Reserved.

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

COMPOSITION AND ANALYSIS OF HEAVY PETROLEUM FRACTIONS

Preface

Almost five years ago, one of us (KHA) was approached by Marcel Dekker, Inc. to write a new edition of an earlier work, *Chromatography in Petroleum Analysis*. Instead we chose the topic of the present book, for two reasons: (1) the rising economic significance of heavy crude oils and their residues and (2) the recent progress in heavy crude oil analysis. This is a "hot" field, with great promise and not without controversy.

This field is economically important because most of the new crude oil produced is heavy, with relatively small amounts of light (low-boiling) components. On the other hand, the demand for light distillates is growing rapidly. Thus, increasing amounts of low-boiling fuel must be produced from high-boiling feed. Furthermore, sulfur, nitrogen, and even aromatic rings must be drastically reduced. Compositional analysis of heavy (high-boiling) petroleum fractions is an indispensible tool for the petroleum chemist in the search for improved methods for the conversion of messy heavy material to clean, low-boiling fuels.

Great progress has been made in instrumentation and methodology. Sensitivity and speed of analytical instruments (e.g., mass, nuclear magnetic resonance, and infrared spectrometers) have greatly improved during

此为试读，需要完整PDF请访问：www.ertongbook.com

the last 10–15 years. New approaches in the use and combination of analytical methods have also been important. We strongly feel that careful separation of heavy petroleum fractions before spectroscopic and other measurements is mandatory for reliable results. Even the type and sequence of the diverse separation methods are crucial. The first step should always be distillation, as discussed in the book. Depending on the task, several chromatographic techniques in specific sequences may be necessary. The right combination of separation and measuring techniques will give optimal results at reasonable cost.

Another recent innovation is the introduction of the atmospheric equivalent boiling point (AEBP) scale, which spans the entire boiling range of a crude oil, including nondistillable residue. This concept enables us to recognize the gradual change in composition from one boiling range to the next. It helps the analytical chemist choose the appropriate methods for a certain fraction based on the knowledge of the lower-boiling fractions. It also allows the refining engineer to visualize the composition of an entire crude oil in uniform terms. The AEBP concept is a major theme in our book and its application and appeal will be explored.

We have tried to present an in-depth view of the current analytical methodology. Also included is a survey of our present knowledge of the composition of heavy petroleum fractions. For some readers, it may be amazing to see how much detail is now accessible for certain fractions. For others, it may be disappointing to recognize how limited our understanding is of the highest-boiling fractions, especially the nondistillable residue, despite the enormous efforts expended over the last 25 years.

We could not have succeeded in our endeavor without the support from many people. First and foremost, we thank our families—especially our spouses—for their heavily taxed (yet seemingly unlimited) patience despite our extended neglect of their rightful title to our companionship in daily life, joys, and chores.

We are also deeply indebted to our colleagues and friends from Chevron Research and Technology Company, who have so willingly and ably assisted us with reading our drafts and providing us with helpful comments, corrections, and even written contributions. Dr. John Shinn read the entire manuscript, a momentous task, and gave us innumerable, valuable suggestions. Dr. T. H. Gouw rewrote major parts of our discussion concerning the practice and theory of distillation (Chapter 3). Dr. Carl Rechsteiner made many important improvements to our chapter on mass spectrometry (Chapter 7). Dr. Don Wilson critically read our chapter on NMR techniques (Chapter 8), and Dr. Don Young reviewed the section on IR (Chapter 9).

Our thanks also to the publishers and authors who gave us permission to reproduce figures and tables from their papers, and especially to those authors who kindly sent us high-quality copies of their original figures for our book: Drs. Biggs, Cookson, Farrall, Green, Snape, and Swain. Finally, Mr. David Grudoski introduced one of us (KHA) to the art of making illustrative diagrams by Macintosh computer, which was both useful and enjoyable.

We appreciate the patience and courtesy extended by our publisher, Marcel Dekker, Inc. Finally, we thank the management of Chevron Reserch and Technology Company for permission to publish some of the material developed under their sponsorship and for allowing one of us (KHA) the use of their library and other facilities.

Klaus H. Altgelt
Mieczyslaw M. Boduszynski

CHEMICAL INDUSTRIES

A Series of Reference Books and Textbooks

Consulting Editor

HEINZ HEINEMANN
Berkeley, California

1. *Fluid Catalytic Cracking with Zeolite Catalysts,* Paul B. Venuto and E. Thomas Habib, Jr.
2. *Ethylene: Keystone to the Petrochemical Industry,* Ludwig Kniel, Olaf Winter, and Karl Stork
3. *The Chemistry and Technology of Petroleum,* James G. Speight
4. *The Desulfurization of Heavy Oils and Residua,* James G. Speight
5. *Catalysis of Organic Reactions,* edited by William R. Moser
6. *Acetylene-Based Chemicals from Coal and Other Natural Resources,* Robert J. Tedeschi
7. *Chemically Resistant Masonry,* Walter Lee Sheppard, Jr.
8. *Compressors and Expanders: Selection and Application for the Process Industry,* Heinz P. Bloch, Joseph A. Cameron, Frank M. Danowski, Jr., Ralph James, Jr., Judson S. Swearingen, and Marilyn E. Weightman
9. *Metering Pumps: Selection and Application,* James P. Poynton
10. *Hydrocarbons from Methanol,* Clarence D. Chang
11. *Form Flotation: Theory and Applications,* Ann N. Clarke and David J. Wilson
12. *The Chemistry and Technology of Coal,* James G. Speight
13. *Pneumatic and Hydraulic Conveying of Solids,* O. A. Williams
14. *Catalyst Manufacture: Laboratory and Commercial Preparations,* Alvin B. Stiles
15. *Characterization of Heterogeneous Catalysts,* edited by Francis Delannay
16. *BASIC Programs for Chemical Engineering Design,* James H. Weber
17. *Catalyst Poisoning,* L. Louis Hegedus and Robert W. McCabe
18. *Catalysis of Organic Reactions,* edited by John R. Kosak
19. *Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application,* edited by Frank L. Slejko
20. *Deactivation and Poisoning of Catalysts,* edited by Jacques Oudar and Henry Wise

21. *Catalysis and Surface Science: Developments in Chemicals from Methanol, Hydrotreating of Hydrocarbons, Catalyst Preparation, Monomers and Polymers, Photocatalysis and Photovoltaics,* edited by Heinz Heinemann and Gabor A. Somorjai
22. *Catalysis of Organic Reactions,* edited by Robert L. Augustine
23. *Modern Control Techniques for the Processing Industries,* T. H. Tsai, J. W. Lane, and C. S. Lin
24. *Temperature-Programmed Reduction for Solid Materials Characterization,* Alan Jones and Brian McNichol
25. *Catalytic Cracking: Catalysts, Chemistry, and Kinetics,* Bohdan W. Wojciechowski and Avelino Corma
26. *Chemical Reaction and Reactor Engineering,* edited by J. J. Carberry and A. Varma
27. *Filtration: Principles and Practices: Second Edition,* edited by Michael J. Matteson and Clyde Orr
28. *Corrosion Mechanisms,* edited by Florian Mansfeld
29. *Catalysis and Surface Properties of Liquid Metals and Alloys,* Yoshisada Ogino
30. *Catalyst Deactivation,* edited by Eugene E. Petersen and Alexis T. Bell
31. *Hydrogen Effects in Catalysis: Fundamentals and Practical Applications,* edited by Zoltán Paál and P. G. Menon
32. *Flow Management for Engineers and Scientists,* Nicholas P. Cheremisinoff and Paul N. Cheremisinoff
33. *Catalysis of Organic Reactions,* edited by Paul N. Rylander, Harold Greenfield, and Robert L. Augustine
34. *Powder and Bulk Solids Handling Processes: Instrumentation and Control,* Koichi Iinoya, Hiroaki Masuda, and Kinnosuke Watanabe
35. *Reverse Osmosis Technology: Applications for High-Purity-Water Production,* edited by Bipin S. Parekh
36. *Shape Selective Catalysis in Industrial Applications,* N. Y. Chen, William E. Garwood, and Frank G. Dwyer
37. *Alpha Olefins Applications Handbook,* edited by George R. Lappin and Joseph L. Sauer
38. *Process Modeling and Control in Chemical Industries,* edited by Kaddour Najim
39. *Clathrate Hydrates of Natural Gases,* E. Dendy Sloan, Jr.
40. *Catalysis of Organic Reactions,* edited by Dale W. Blackburn
41. *Fuel Science and Technology Handbook,* edited by James G. Speight
42. *Octane-Enhancing Zeolitic FCC Catalysts,* Julius Scherzer
43. *Oxygen in Catalysis,* Adam Bielański and Jerzy Haber
44. *The Chemistry and Technology of Petroleum: Second Edition, Revised and Expanded,* James G. Speight

45. *Industrial Drying Equipment: Selection and Application,* C. M. van't Land
46. *Novel Production Methods for Ethylene, Light Hydrocarbons, and Aromatics*, edited by Lyle F. Albright, Billy L. Crynes, and Siegfried Nowak
47. *Catalysis of Organic Reactions*, edited by William E. Pascoe
48. *Synthetic Lubricants and High-Performance Functional Fluids*, edited by Ronald L. Shubkin
49. *Acetic Acid and Its Derivatives*, edited by Victor H. Agreda and Joseph R. Zoeller
50. *Properties and Applications of Perovskite-Type Oxides*, edited by L. G. Tejuca and J. L. G. Fierro
51. *Computer-Aided Design of Catalysts*, edited by E. Robert Becker and Carmo J. Pereira
52. *Models for Thermodynamic and Phase Equilibria Calculations*, edited by Stanley I. Sandler
53. *Catalysis of Organic Reactions*, edited by John R. Kosak and Thomas A. Johnson
54. *Composition and Analysis of Heavy Petroleum Fractions*, Klaus H. Altgelt and Mieczyslaw M. Boduszynski

ADDITIONAL VOLUMES IN PREPARATION

NMR Techniques in Catalysis, edited by Alexis T. Bell and Alexander Pines

The Chemistry and Technology of Coal: Second Edition, Revised and Expanded, James G. Speight

Upgrading Petroleum Residues and Heavy Oils, Murray R. Gray

Contents

此为试读，需要完整PDF请访问：www.ertongbook.com

1

Introduction

I. INTENT AND SCOPE OF THIS BOOK

We believe that compositional analysis of heavy petroleum fractions will play a decisive role in improving refinery operations and will, thus, be a significant aid in saving energy and resources and in mitigating pollution problems. This book is an advocacy for its application as well as a guide to its implementation. Here are some reasons for our belief in the importance of this issue.

According to recent reports, about 50% of the petroleum products consumed in the United States at the present time are gasoline and an additional 40% are other distillate fuels boiling below about 650°F (345°C). The Committee on Production Technologies for Liquid Transportation Fuels (1) states that "the US transportation sector . . . will depend almost completely for the foreseeable future on liquid fuels . . . and . . . any transition from the use of liquid transportation fuels (to compressed natural gas or electricity) is likely to be slow." Therefore, we can expect a continued high percentage of the petroleum products to be light distillate fuels boiling below 650°F. On the other hand, an increasing amount of the petroleum *produced* currently is of the "heavy" variety, containing large amounts of material boiling above 650°F (2,3). At least 85% of the world proven reserves of petroleum belong to this category (4). Figure 1.1 shows how the average API gravity of all the crudes refined in the United States decreased during the 10 years between 1980 and 1990. Related to this drop in API gravity is a constant rise in the sulfur content as illustrated in Fig. 1.2. These trends mean that most of the crude oil produced now and in the future must be converted from heavy material (>650°F) to light distillate products in multiple, complex refining steps (5).

Major conversion processes include catalytic cracking, hydrocracking, and coking. The yield and quality of the products resulting from these processes are quite variable and depend on feed type, process type, and processing conditions. Sulfur-, nitrogen-, and metal-containing compounds make the upgrading process difficult because of their propensity to poison catalysts. Heteroatoms must be removed in several steps with different catalysts. The ease of their removal depends on their chemical environment and functionality [e.g., aliphatic versus aromatic, thiophenic sulfur versus

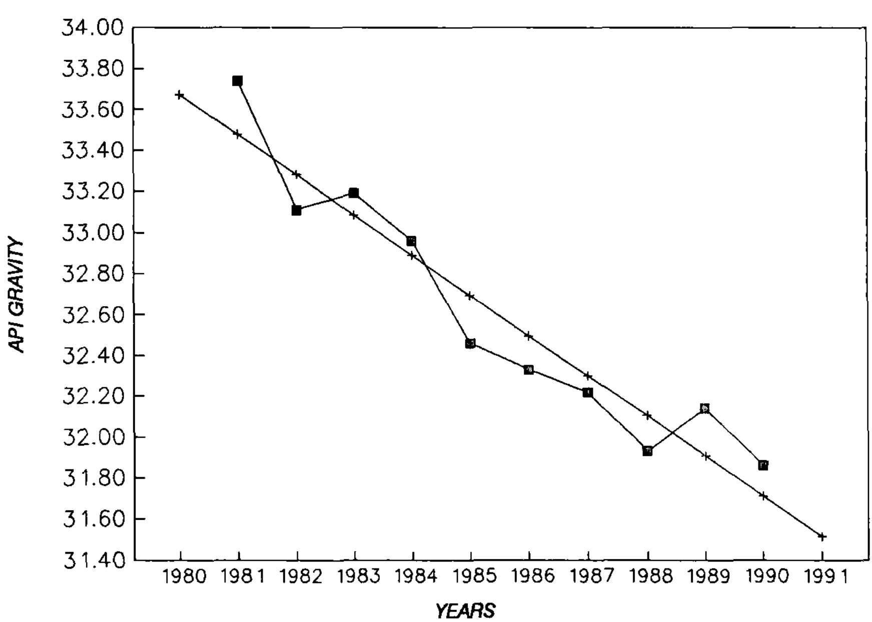


Figure 1.1 Change in API gravity of crude oils refined in the United States between 1980 and 1990. (From Ref. 5. Reproduced with permission of the publisher. Original data from the U.S. Department of Energy.)

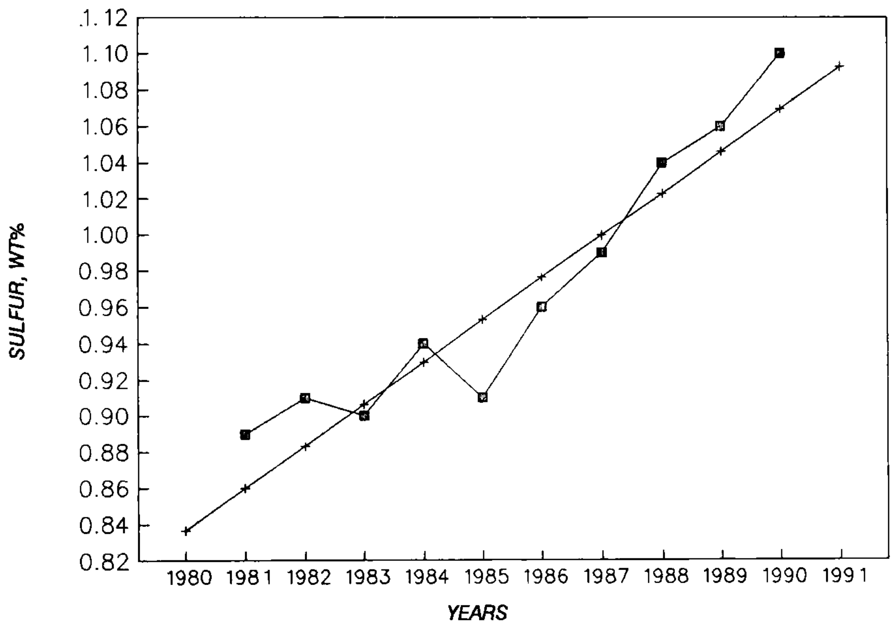


Figure 1.2 Change in sulfur content of crude oils refined in the United States between 1980 and 1990.(From Ref. 5. Reproduced with permission of the publisher. Original data from the U.S. Department of Energy.)

sulfide sulfur, neutral versus basic nitrogen, metals in low-molecular-weight (low-MW) free porphyrins versus high-MW structures]. The heteroatom content of the crudes to be processed is expected to increase dramatically, whereas the Conradson carbon residue content in the fluid catalytic cracker (FCC) feed also is expected to double or triple (see Fig. 1.3).

Measurements of compositional changes from feed to product to assess the effectiveness of an upgrading step for process optimization will involve much more detail than is presently common. The application of new technology together with new computational tools will offer a more fundamental approach to unraveling the chemical reactions that occur in catalytic processing of complex petroleum mixtures. Detailed compositional analysis will be vital in developing reaction networks and kinetic models of refining processes. Naber et al. (6) emphasize the need for detailed understanding on the molecular level of the product composition and its effect on performance properties in our efforts to improve product quality and process integration.

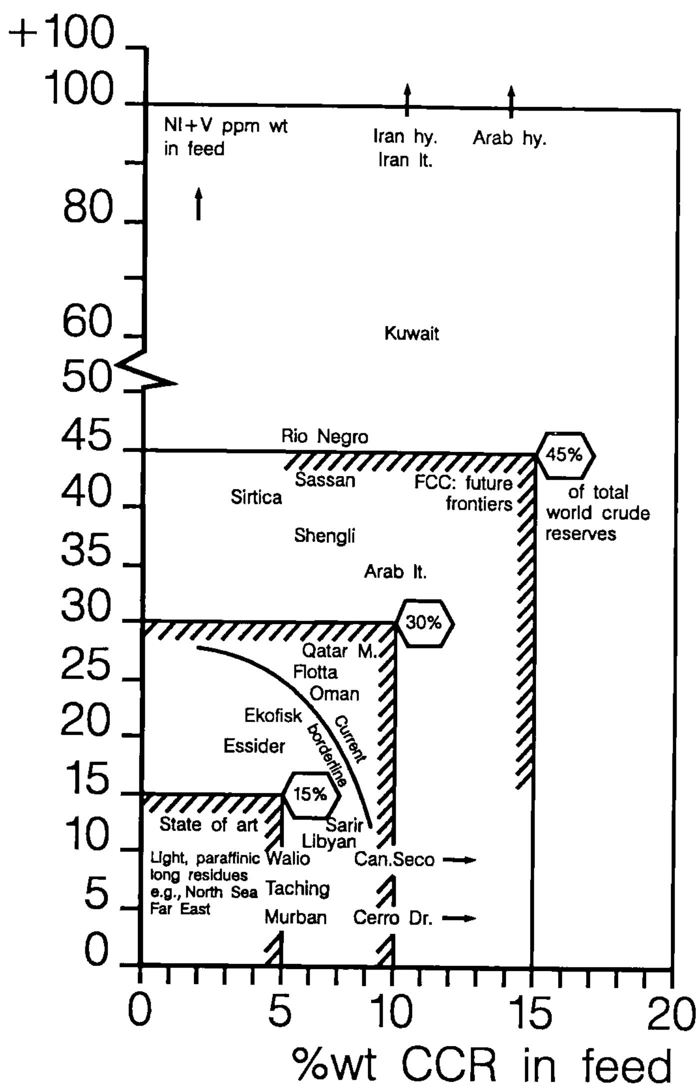


Figure 1.3 FCC feedstock "heaviness" diagram. Resid (>370°C) properties in relation to FCC processability. (From Ref. 6. Reproduced with permission of the publisher.)

此为试读,需要完整PDF请访问: www.ertongbook.com