CATALYTIC NAPHTHA REFORMING SECOND EDITION, REVISED and EXPANDED



^{edited by} George J. Antos Abdullah M. Aitani

Also available as a printed book see title verso for ISBN details

CATALYTIC NAPHTHA REFORMING

CHEMICAL INDUSTRIES

A Series of Reference Books and Textbooks Founding Editor

HEINZ HEINEMANN

- 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. Modem 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 linoya, 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 Bielanski 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 Willam 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
- 55. NMR Techniques in Catalysis, edited by Alexis T.Bell and Alexander Pines
- 56. Upgrading Petroleum Residues and Heavy Oils, Murray R.Gray
- 57. Methanol Production and Use, edited by Wu-Hsun Cheng and Harold H. Kung
- 58. Catalytic Hydroprocessing of Petroleum and Distillates, edited by Michael C.Oballah and Stuart S.Shih

- 59. *The Chemistry and Technology of Coal: Second Edition, Revised and Expanded,* James G.Speight
- 60. Lubricant Base Oil and Wax Processing, Avilino Sequeira, Jr.
- 61. *Catalytic Naphtha Reforming: Science and Technology*, edited by George J.Antos, Abdullah M.Aitani, and José M.Parera
- 62. Catalysis of Organic Reactions, edited by Mike G.Scaros and Michael L.Prunier
- 63. Catalyst Manufacture, Alvin B.Stiles and Theodore A.Koch
- 64. Handbook of Grignard Reagents, edited by Gary S.Silverman and Philip E.Rakita
- 65. Shape Selective Catalysis in Industrial Applications: Second Edition, Revised and Expanded, N.Y.Chen, William E.Garwood, and Francis G.Dwyer
- 66. Hydrocracking Science and Technology, Julius Scherzer and A.J. Gruia
- 67. Hydrotreating Technology for Pollution Control: Catalysts, Catalysis, and Processes, edited by Mario L.Occelli and Russell Chianelli
- 68. Catalysis of Organic Reactions, edited by Russell E.Malz, Jr.
- 69. Synthesis of Porous Materials: Zeolites, Clays, and Nanostructures, edited by Mario L.Occelli and Henri Kessler
- 70. Methane and Its Derivatives, Sunggyu Lee
- 71. Structured Catalysts and Reactors, edited by Andrzei Cybulski and Jacob Moulijn
- 72. Industrial Gases in Petrochemical Processing, Harold Gunardson
- 73. Clathrate Hydrates of Natural Gases: Second Edition, Revised and Expanded, E.Dendy Sloan, Jr.
- 74. Fluid Cracking Catalysts, edited by Mario L.Occelli and Paul O'Con-nor
- 75. Catalysis of Organic Reactions, edited by Frank E.Herkes
- 76. *The Chemistry and Technology of Petroleum, Third Edition, Revised and Expanded,* James G.Speight
- 77. Synthetic Lubricants and High-Performance Functional Fluids, Second Edition: Revised and Expanded, Leslie R.Rudnick and Ronald L. Shubkin
- 78. The Desulfurization of Heavy Oils and Residua: Second Edition, Revised and Expanded, James G.Speight
- 79. *Reaction Kinetics and Reactor Design: Second Edition, Revised and Expanded,* John B.Butt
- 80. *Regulatory Chemicals Handbook,* Jennifer M.Spero, Bella Devito, and Loius Theodore
- 81. Applied Parameter Estimation for Chemical Engineers, Peter Englezos and Nicolas Kalogerakis
- 82. Catalysis of Organic Reactions, edited by Michael E.Ford
- 83. *The Chemical Process Industries Infrastructure: Function and Economics,* James R.Couper, O.Thomas Beasley, and W.Roy Penney
- 84. Transport Phenomena Fundamentals, Joel L.Plawsky
- 85. Petroleum Refining Processes, James G.Speight and Baki Özüm
- 86. Health, Safety, and Accident Management in the Chemical Process Industries, Ann Marie Flynn and Louis Theodore
- 87. *Plantwide Dynamic Simulators in Chemical Processing and Control*, William L.Luyben
- 88. Chemicial Reactor Design, Peter Harriott
- 89. Catalysis of Organic Reactions, edited by Dennis Morrell

- 90. Lubricant Additives: Chemistry and Applications, edited by Leslie R. Rudnick
- 91. Handbook of Fluidization and Fluid-Particle Systems, edited by WenChing Yang
- 92. Conservation Equations and Modeling of Chemical and Biochemical Processes, Said S.E.H.Elnashaie and Parag Garhyan
- 93. Batch Fermentation: Modeling, Monitoring, and Control, Ali Cinar, Satish J.Parulekar, Cenk Ündey, and Gülnur Birol
- 94. Industrial Solvents Handbook: Second Edition, Nicholas P.Cheremisinoff
- 95. *Petroleum and Gas Field Processing*, H.K.Abdel-Aal, Mohamed Aggour, and M.A.Fahim
- 96. Chemical Process Engineering: Design and Economics, Harry Silla
- 97. Process Engineering Economics, James R.Couper
- 98. *Re-Engineering the Chemical Processing Plant: Process Intensification*, Andrzej Stankiewicz and Jacob A.Moulijn
- 99. Thermodynamic Cycles: Computer-Aided Design and Optimization, Chih Wu
- 100. Catalytic Naphtha Reforming: Second Edition, Revised and Expanded, edited by George J.Antos and Abdullah M.Aitani
- 101. Handbook of MTBE and Other Gasoline Oxygenates, edited by S. Halim Hamid and Mohammad Ashraf Ali

ADDITIONAL VOLUMES IN PREPARATION

CATALYTIC NAPHTHA REFORMING

SECOND EDITION, REVISED and EXPANDED

edited by

George J.Antos UOP, LLC Des Plaines, Illinois, U.S.A.

Abdullah M.Aitani

King Fahd University of Petroleum and Minerals

Dhahran, Saudi Arabia



MARCEL DEKKER, INC. NEW YORK • BASEL

This edition published in the Taylor & Francis e-Library, 2005.

"To purchase your own copy of this or any of Taylor & Francis or Routledge's collection of thousands of eBooks please go to http://www.ebookstore.tandf.co.uk/."

The first edition of this book was published as *Catalytic Naphtha Reforming: Science and Technology*, edited by George J.Antos, Abdullah M.Aitani, and José M.Parera (Marcel Dekker, Inc., 1995).

Although great care has been taken to provide accurate and current information, neither the author(s) nor the publisher, nor anyone else associated with this publication, shall be liable for any loss, damage, or liability directly or indirectly caused or alleged to be caused by this book. The material contained herein is not intended to provide specific advice or recommendations for any specific situation.

Trademark notice: Product or corporate names may be trademarks or registered trade marks and are used only for identification and explanation without intent to infringe.

Library of Congress Cataloging-in-Publication Data A catalog record for this book is available from the Library of Congress.

ISBN 0-203-91350-7 Master e-book ISBN

ISBN - (Adobe e-reader Format) ISBN: 0-8247-5058-6 (Print Edition)

Headquarters

Marcel Dekker, Inc., 270 Madison Avenue, New York, NY 10016, U.S.A. tel: 212–696–9000; fax: 212–685–4540

Distribution and Customer Service

Marcel Dekker, Inc., Cimarron Road, Monticello, New York 12701, U.S.A. tel: 800–228–1160; fax: 845–796–1772

Eastern Hemisphere Distribution

Marcel Dekker AG, Hutgasse 4, Postfach 812, CH-4001 Basel, Switzerland tel: 41–61–260–6300; fax: 41–61–260–6333

World Wide Web http://www.dekker.com/

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

Copyright © 2004 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.

Preface to the Second Edition

Nearly a decade has passed since the publication of the first edition of *Catalytic Naphtha Reforming*. That book was a survey of the technology encompassing the first 45 years of the use of this process in the refining industry. In preparing the second edition, perspective on this refining process was again considered. It is still true that catalytic reforming is the primary process in the refinery for producing high-octane gasoline to be blended into the gasoline pool. As needs for gasoline have risen, the demands on the reformer have also increased. What has changed is that additional drivers have surfaced, which have added to the demands on the process.

The first of these demands are the new environment-based regulations for fuel quality parameters. In particular, the targeted reduced-sulfiir content for gasoline and diesel fuel has had an impact on the catalytic reformer. Although sulfur in the gasoline pool does not originate with the reformer, sulfur content of naphtha from the fluid catalytic cracker does require significant treatment in order to continue inclusion in the pool. Most of the schemes to deal with this sulfur involve some level of hydrodesulfurization. Hydrogen is required, and the reformer is one of the few units to provide hydrogen in the refinery. The result is an increased demand on the catalytic reformer. Although many of these hydrotreating schemes attempt to minimize octane loss, any loss will need to be countered with more output from the octane machine—the reformer. Environmental regulations aimed at lowering sulfur in diesel fuel also increase the need for hydrogen in the refinery. Hydrogen demand has increased overall in the refinery, and the catalytic reformer is under pressure to produce more hydrogen by an increased severity of operation or by improved selectivity to aromatics.

In addition, in the United States, the drive to eliminate the use of MTBE as an oxygenate component in the gasoline pool will impact the reformer situation. Octane barrels are lost when MTBE is replaced by ethanol. The catalytic reformer will need to replace these lost octane barrels, largely through an increased severity of operation or through higher yields of high octane gasoline.

Over the past decade, refiners have been forced to maximize their existing asset utilization. With capital at a premium, refiners must deliver more from the units they already have. These twin pressures from environmental regulations and asset utilization have impacted the catalytic reformer. New technology, in the form of new catalysts or a minimal revamp of process improvements, was required. The catalyst vendors and process licensors have responded to these needs, thereby fulfilling predictions in the first edition and providing the basis for this book.

For this edition, prominent authors were again invited to either update an existing chapter or write a new chapter. The layout of the book is logical and similar to that of the first edition. Part I covers the chemistry of naphtha reforming, emphasizing basic reforming reactions, metal/acid catalysis, and naphtha hydrotreatment. Part II is a detailed review of reforming catalysts. The chapter on catalyst preparation has been extensively enhanced with an in-depth treatment of platinum impregnation chemistry, a topic that has

been extensively investigated over the past decade. When combined with the updated chapter on catalyst characterization, this section serves as a reference source for anyone involved in the preparation of or research on platinum-containing catalysts. Included in this section is a completely updated discussion of the commercial reforming catalysts available from vendors today. Two chapters that are more experimental have been included on the future direction of catalyst technology in pore structure optimization and zeolite-hybrid catalysts.

Part III focuses on catalyst deactivation by coking and regeneration. Added to this is a discussion on some of the issues that are important to continuous reformer operations involving catalyst movement and continuous regeneration as experienced by refinery personnel. A separate chapter is dedicated to the recovery of the precious metals from the reforming catalyst.

In Part IV, commercial process technology is covered. The licensed processes are reviewed in conjunction with chapters on control systems and modeling for commercial reformer units.

Once again it has been our pleasure to work with the contributors of this book. They paid much attention to reviewing the literature in the area, and then skillfully combined it with their own work and insights. It has been an extensive effort and has taken time to bring it to completion. We give special thanks to the contributors and the publisher for their patience. Our intent was to place our combined experience and knowledge of the technology of catalytic naphtha reforming into one book in order to share it with all those who need this information. We hope that this second edition will be recognized as a valuable resource for those involved in the reforming or related catalysis areas, whether as academics, graduate students, industrial researchers, chemical engineers, or refinery personnel. Knowledge and the time to gain it are two assets that we have attempted to help you manage to your advantage with this volume.

George J.Antos Abdullah M.Aitani

Preface to the First Edition

The use of catalytic naphtha reforming as a process to produce high-octane gasoline is as important now as it has been for over the 45 years of its commercial use. The catalytic reformer occupies a key position in a refinery, providing high value-added reformate for the gasoline pool; hydrogen for feedstock improvement by the hydrogen-consuming hydrotreatment processes; and frequently benzene, toluene, and xylene aromatics for petrochemical uses. The technology has even further impact in the refinery complex. The processes of hydrogenation, dehydrogenation, and isomerization have all benefited from the catalyst, reactor, and feed treatment technologies invented for catalytic reforming processes. The long-term outlook for the reforming catalyst market remains strong. The conditions of operation of catalytic reforming units are harsh and there is an increasing need for reformate. Presently, the catalytic reforming process is currently operated to produce research octane numbers of 100 and more.

Since its introduction, catalytic reforming has been studied extensively in order to understand the catalytic chemistry of the process. The workhorse for this process is typically a catalyst composed of minor amounts of several components, including platinum supported on an oxide material such as alumina. This simplification masks the absolute beauty of the chemistry involved in combining these components in just the proper manner to yield a high-performance, modern reforming catalyst. The difficulty in mastering this chemistry and of characterizing the catalyst to know what has been wrought is the driving force behind the many industrial and academic studies in reforming catalysis available today.

Several questions come to mind. Why are scientists continuing to research this area of catalysis? What have all the preceding studies taught us about these catalysts, and what remains unknown? Given the numerous studies reported in the patent literature and in technical journals, it is surprising that a survey aimed at answering these questions summarizing the preceding experiences is not readily found. All the editors and contributors of this book are experienced in the study of reforming catalysts, and each one of them would have employed such a survey in his own research program. This volume provides information not currently available from one single literature source. The chapters are written by well-known authorities in the fields encompassed by catalytic reforming, starting with the process chemistry and focusing on the preparation, characterization, evaluation, and operation of the catalyst itself. The unknown aspects of catalyst chemistry and fundamental studies attempting to provide an understanding are also presented. Some attempt is made to predict the future for this catalyst technology, a task made complicated by the conflicting demand for more transportation fuels and petrochemicals, and the resolution to reduce the pollution resulting from their use.

It has been our pleasure to work with the contributors involved in this book. Their effort in combining their own research with the recent literature in the field of catalytic naphtha reforming is highly appreciated. This effort would not have been possible without their willingness to share valuable knowledge and experience. Moreover, we express our gratitude for their responsiveness to deadlines and review comments.

The editors hope that veteran industrial researchers will recognize this volume as an important resource and that novice researchers in the field of reforming and related catalysts—industrial chemists assigned to their first major catalysis project, graduate students embarking on the study of catalysis, and chemical engineers in the refinery responsible for full-scale commercial catalytic reforming—will find this a valuable reference volume and tool for their future endeavors in this exciting area.

George J.Antos Abdullah M.Aitani José M.Parera

Contents

Preface to the Second Edition	ix
Preface to the First Edition	xi
Contributors	xv

Part I: Naphtha Reforming Chemistry

1.	Compositional Analysis of Naphtha and Reformate Rune Prestvik, Kjell Moljord, Knut Grande, and Anders Holmen	1
2.	Basic Reactions of Reforming on Metal Catalysts Zoltán Paál	34
3.	Chemistry of Bifunctional Metal-Acid Catalysis José M.Parera and Nora S.Fígoli	71
4.	Naphtha Hydrotreatment Syed Ahmed Ali	100
Part I	I: Reforming Catalysts	
5.	Preparation of Reforming Catalysts J.R. Regalbuto and George J.Antos	133
6.	Characterization of Naphtha-Reforming Catalysts Burtron H.Davis and George J.Antos	187
7.	Optimization of Catalyst Pore Structure by Kinetics and Diffusion Analysis Jerzy Szczygieł	258
8.	The New Generation of Commercial Catalytic Naphtha-Reforming Catalysts <i>George J.Antos, Mark D.Moser, and Mark P.Lapinski</i>	309
9.	Naphtha Reforming Over Zeolite-Hybrid-Type Catalysts <i>Grigore Pop</i>	326

Part III: Catalyst Deactivation and Regeneration

10.	Deactivation by Coking	356
	Octavio Novaro, Cheng-Lie Li, and Jin-An Wang	

11. Catalyst Regeneration and Continuous Reforming Issues Patricia K.Doolin, David J.Zalewski, and Soni O.Oyekan	397
12. Precious Metals Recovery from Spent Reforming Catalysts Horst Meyer and Matthias Grehl	419
Part IV: Technology and Applications	
13. Licensed Reforming Processes <i>Abdullah M.Aitani</i>	435
14. Control Systems for Commercial Reformers Lee Turpin	453
15. Modeling Catalytic Naphtha Reforming: Temperature Profile Selection Benzene Reduction Rafael Larraz and Raimundo Arvelo	and 502
Index	545

Contributors

Abdullah M.Aitani King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia Syed Ahmed Ali King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arahia George J.Antos UOP, LLC, Des Plaines, Illinois, U.S.A. Raimundo Arvelo University of La Laguna, Laguna, Spain Burtron H.Davis University of Kentucky, Lexington, Kentucky, U.S.A. Patricia K.Doolin Marathon Ashland Petroleum, LLC, Catlettsburg, Kentucky, U.S.A. Nora S.Fígoli Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE), Santa Fe, Argentina Knut Grande STATOIL Research Centre, Trondheim, Norway Matthias Grehl W.C. Heraeus GmbH & Co., Hanau, Germany Anders Holmen Norwegian University of Science and Technology, Trondheim, Norway Mark P.Lapinski UOP, LLC, Des Plaines, Illinois, U.S.A. **Rafael Larraz**^{*} University of La Laguna, Laguna, Spain **Cheng-Lie Li**[†] *National University of Mexico, Mexico City, Mexico* Horst Meyer W.C.Heraeus GmbH & Co., Hanau, Germany Kiell Moljord STATOIL Research Centre, Trondheim, Norway Mark D.Moser UOP, LLC, Des Plaines, Illinois, U.S.A.

* Current affiliation: CEPSA, Madrid, Spain

[†] Current affiliation: East China University of Science and Technology, Shanghai, China

Octavio Novaro National University of Mexico, Mexico City, Mexico
Soni O.Oyekan Marathon Ashland Petroleum, LLC, Catlettsburg, Kentucky, U.S.A.
Zoltán Paál Hungarian Academy of Sciences, Budapest, Hungary
José M.Parera Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE), Santa Fe, Argentina
Grigore Pop S.C.Zecasin S.A., Bucharest, Romania
Rune Prestvik SINTEF Applied Chemistry, Trondheim, Norway
J.R.Regalbuto University of Illinois at Chicago, Chicago, Illinois, U.S.A.
Jerzy Szczygieł Wroclaw University of Technology, Wroclaw, Poland
Lee Turpin Aspen Technology Inc., Bothell, Washington, U.S.A.

Jin-An Wang National Polytechnic Institute, Mexico City, Mexico

David J.Zalewski Marathon Ashland Petroleum, LLC, Catlettsburg, Kentucky, U.S.A.

CATALYTIC NAPHTHA REFORMING

Compositional Analysis of Naphtha and Reformate

Rune Prestvik

SINTEF Applied Chemistry Trondheim, Norway Kjell Moljord and Knut Grande

> STATOIL Research Centre Trondheim, Norway Anders Holmen

Norwegian University of Science and Technology Trondheim, Norway

1 INTRODUCTION

Naphtha is transformed into reformate by catalytic reforming. This process involves the reconstruction of low-octane hydrocarbons in the naphtha into more valuable high-octane gasoline components without changing the boiling point range. Naphtha and reformate are complex mixtures of paraffins, naphthenes, and aromatics in the C_5-C_{1-2} range. Naphthas from catalytic or thermal cracking also contain olefins. Naphthas of different origin contain small amounts of additional compounds containing elements such as sulfur and nitrogen. These elements affect the performance of the bifunctional noble metal catalyst used in catalytic reforming and must be removed to low levels prior to entering the reformer unit. The composition of hydrocarbons and the concentration of additional elements determine the quality as reforming feedstock or as a gasoline blending component.

This chapter describes the chemistry of naphtha and reformate. It includes the origin from crude oil, the overall composition, and key parameters with respect to processing ability and product quality. Finally, analytical methods available for performing a complete compositional analysis and parameter detection are described.

2 THE NAPHTHA FRACTION

2.1 Origin from Crude Oil Distillation and Processing

Hydrocarbons are the major constituents of crude oil, or petroleum, and account for up to 97% of the total mass.^[1] These are paraffinic, naphthenic, or aromatic structures ranging from light gaseous molecules (C_1 – C_4 alkanes) to heavy waxes or asphaltenic matter. The

rest are organic compounds of sulfur, nitrogen, and oxygen, as well as water, salt, and a number of metal containing constituents such as vanadium, nickel, and sodium. Although elemental concentrations of carbon and hydrogen vary only slightly within narrow limits, typically 82–87 wt % C and 10–14 wt % H, the individual concentrations of the different compounds that determine the physical properties are highly variable and depend on the crude oil origin.

Full-range naphtha is the fraction of the crude oil boiling between 30°C and 200°C, and constitutes typically 15–30% by weight of the crude oil. This includes hydrocarbons ranging from C_5 to $C1_2$, some sulfur, and small amounts of nitrogen. Metal containing compounds are usually not present. The naphtha obtained directly from the atmospheric crude distillation column is termed *straight run* (SR). However, naphtha is also produced during processing of heavier parts of the crude oil (e.g., catalytic cracker naphtha, visbreaker naphtha, coker naphtha). As opposed to the straight-run streams, these naphthas also contain olefinic hydrocarbons. *Light naphtha* is the fraction boiling from 30°C to 200°C. The term *'medium naphtha'* is sometimes used for the fraction of this heavy cut that boils below 150°C and includes mostly C_7 – C_9 hydrocarbons. Table 1 illustrates how naphtha fractions can range from highly

Oil field	Paraffins (wt %)	Naphthenes (wt %)	Aromatics (wt %)	Sulfur (wt ppm)	Nitrogen (wt ppm)
Troll (Norway)	13.9	75.2	10.8	20	<1
Norne (Norway)	27.7	34.8	37.5	10	< 1
Heidrun (Norway)	35.4	51.2	13.5	10	<1
Lufeng (China)	69.5	27.5	2.9	<10	1

Table 1 Composition of Medium Naphtha Cutsfrom Different Crude Oils [2]

paraffinic to highly naphthenic and from low in sulfur to high in sulfur, depending on the crude oil.

Hydrotreated (desulfurized) medium naphtha is the favored feedstock for catalytic reforming, although full-range stocks are sometimes processed if benzene is a desired product. The light naphtha is preferentially upgraded by isomerization whilst the heaviest part of the naphtha is often included in the light gas oil fraction (jet fuel/diesel). Figure 1 gives an example of a processing scheme for refinery gasoline production with catalytic reforming.

2.2 Naphtha Composition

Hydrocarbons

Paraffins or *alkanes* are saturated aliphatic hydrocarbons with the general formula $C_n H_2$ _{*n*+2}. They are either straight-chain (*n*-paraffins) or branched structures (*i*-paraffins). The boiling point increases by about 25–30°C for each carbon





atom in the molecule, and the boiling point of an *n*-paraffin is always higher than that of the *i*-paraffin with the same carbon number. The density increases with increasing carbon number as well. **Olefins** or *alkenes* are unsaturated aliphatic hydrocarbons. Like the paraffins, they are either straight chains or branched structures, but contain one or more double bonds. Monoolefins have the general formula $C_n H_{2n}$. **Naphthenes** or *cycloalkanes* are saturated cyclic hydrocarbons that contain at least one ring structure. The general formula for mononaphthenes is $C_n H_{2n}$. The most abundant naphthenes in petroleum have a ring of either five or six carbon atoms. The rings can have paraffinic side chains attached to them. The boiling point and the density is higher than for any paraffin with the same number of carbon atoms. **Aromatics** have the general formula C_n

 $H_{2 n-6}$ and contain one or more polyunsaturated rings (conjugated double bonds). These benzene rings can have paraffinic side chains or be coupled with other naphthenic or aromatic rings. The boiling points and the densities of these polyunsaturated compounds are higher than that of both paraffins and naphthenes with the same carbon number. The reactivity of the unsaturated bonds make the C₆, C₇, and C₈ aromatics or *BTX* (benzene, toluene, xylenes) important building blocks for the petrochemical industry. Aromatics have high octane numbers.

The composition of a given naphtha depends on the type of crude oil, the boiling range of the naphtha, and whether it is obtained directly from crude oil distillation or produced by catalytic or thermal cracking of heavier oil fractions. A typical straight-run medium naphtha contains 40–70 wt % paraffins, 20–50 wt % naphthenes, 5–20 wt % aromatics, and only 0–2 wt % olefins. Naphtha produced by fluid catalytic cracking (FCC), coking, or visbreaking may contain 30–50 wt % olefins. Table 2 shows the hydrocarbon composition for different naphtha streams originating from a given crude.

In general, the paraffinicity decreases when the boiling point of the naphtha increases (Fig. 2). At the same time the complexity grows because the number of possible isomers increases exponentially with the carbon number. The number of detectable individual compounds in naphthas ranges typically from 100–300 for straight-run medium naphthas to beyond 500 for full-range stocks containing cracked material (additional olefins). In Table 3 the concentration of individual compounds detected in a medium straight-run naphtha is listed. Components like *n*-heptane, *n*-octane, methylcyclohexane, toluene, ethylbenzene, and xylenes are usually present in significant concentrations, whereas a number of C_7 – C_{9+} paraffin and naphthene isomers are usually present in much smaller amounts.

Heteroatomic Organic Compounds, Water, and Metallic Constituents

Sulfur is an important heteroatomic constituent in petroleum. The concentration is highly dependent on the type of crude oil and may range from virtually zero to

Stream	Paraffins (wt %)	Olefins (wt %)	Naphth. (wt %)	Aromatics (wt %)	Density (g/ml)	IBP— FBP (°C)	Crude (wt %)
Light SR	55	_	40	5	0.664	C ₅ -90	3.2
Medium SR	31	_	50	19	0.771	90-150	8.6
Heavy SR	30	-	44	26	0.797	150-180	4.7
FCC	34	23	11	32	0.752	C ₅ -220	20
Light VB	64	10	25	1	0.667	C ₅ -90	_
Heavy VB	46	30	16	8	0.750	90-150	_

Table 2 Typical Compositions and Characteristics
of Refinery Naphtha Streams Originating from the
Same Crude Oil

SR, straight-run; FCC, fluid catalytic cracker; VB, visbreaker; IBP, initial boiling point; FBP, final boiling point.





more than 5% by weight. The sulfur tends to be more concentrated in the heavy end of the crude oil, which means that only ppm levels of sulfur are found in straight-run naphtha fractions. Still, even small concentrations are of great importance when it comes to processing the feedstock or using it directly as fuel. Sulfur poisons the noble-metal catalyst used in reforming and also promotes formation of undesirable SO $_x$ during combustion. Cracker and coker naphthas originating from heavier oil fractions often contain much more sulfur, up to a few thousand ppm. Sulfur is removed from naphtha by hydrotreating, which means conversion to H₂S over a hydrotreating catalyst under hydrogen pressure. Hydrotreating is described more extensively in Chapter 4. The types of sulfur compounds found in crude oil are many: mercaptans, sulfides, disulfides, cyclic sulfides, alkylthiophenes, benzothiophenes, sulfates, traces of sulfuric acid, and sulfur oxides. In the naphtha boiling range thiophenes, noncyclic mercaptans and sulfides are the major groups. Identified sulfur compounds in naphtha are shown in Figure 3.

Organic **nitrogen** is present in even smaller concentrations than sulfur in the crude oil (<1.0 wt %) and mostly in the higher boiling point fractions. The compounds are usually classified as basic or nonbasic. Basic compounds are

Compound	Wt %	Compound	Wt %	Compound	Wt %	Compound	Wt %
2,4-Dm-Pentane	0.018	c-1,4-Dm-CyC6	0.914	C ₉ naphthene 16	0.784	1-Me-2-Et- Benz	0.225
3,3-Dm-Pentane	0.078	<i>n</i> -Octane	5.263	C ₉ naphthene 18	0.152	3-Et-Octane	0.094
2-Me-Hexane	2.287	iPr-CyC5	0.065	C ₉ naphthene 20	0.269	C_{10} naphthene 10	0.014
2,3-Dm-Pentane	1.140	C ₈ naphthene 6	0.074	C ₉ naphthene 22	0.013	C ₁₀ naphthene 11	0.030
1,1-Dm-CyC5	0.716	c-2-Octane	0.066	C ₉ naphthene 23	0.039	C ₁₀ paraffin 8	0.040
3-Me-Hexane	3.216	c-1,2-Et-Me- CyC5	0.154	C ₉ naphthene 24	0.079	3-Me-Nonane	0.073
c-1,3-Dm-CyC5	1.742	2,2-Dm-Heptane	0.089	C ₉ naphthene 26	0.052	C ₁₀ paraffin 9	0.021
t-1,3-Dm-CyC5	1.650	c-1,2-Dm-CyC6	0.279	C ₉ naphthene 29	0.036	1,2,4-Tm-Benz	0.281
t-1,2-Dm-CyC5	3.328	2,2,3-Tm- Hexane	0.106	C ₉ naphthene 31	0.070	C ₁₀ naphthene 14	0.067
C ₇ Olefin 7	0.017	2,4-Dm-Heptane	0.276	<i>n</i> -Nonane	2.226	C ₁₀ naphthene 15	0.081
<i>n</i> -Heptane	7.885	4,4-Dm-Heptane	0.035	C ₉ naphthene 32	0.062	<i>i</i> -But-CyC6	0.010
Me-CyC6	17.38	Et-CyC6	3.052	C ₉ naphthene 33	0.046	C ₁₀ naphthene 16	0.012
1,1,3-Tm-CyC5	0.866	2-Me-4-Et- Hexane	0.038	iPr-Benzene	0.205	C ₁₀ naphthene 17	0.013
2,2-Dm-Hexane	0.105	2,6-Dm-Heptane	0.719	C ₉ olefin 13	0.342	C ₁₀ naphthene 18	0.013
Et-CyC5	1.056	1,1,3-Tm-CyC6	0.918	C ₉ naphthene 35	0.206	<i>i</i> -But-Benzene	0.037
2,2,3-Tm- Pentane	0.409	1,1,4-Tm-CyC6	0.136	iPr-CyC6	0.009	s-But-Benzene	0.055
2,4-Dm-Hexane	0.595	2,5-Dm-Heptane	0.394	2,2-Dm- Octane	0.067	<i>n</i> -Decane	0.258

Table 3 Hydrocarbon Composition^a in a Straight-Run Naphtha from North Sea Crude, Identified by GC

ct-124-Tm- CyC5	0.990	3,5-Dm-Heptane	0.205	C ₁₀ paraffin 1	0.109	C ₁₀ naphthene 20	0.013
3,3-Dm-Hexane	0.137	C ₉ naphthene 3	0.179	C_{10} paraffin 2	0.015	1,2,3-Tm-Benz	0.079
tc-123-Tm- Pentane	1.051	C ₉ naphthene 4	0.078	C ₉ naphthene 36	0.053	1,3-Me-iPr- Benz	0.087
2,3,4-Tm- Pentane	0.162	Ethylbenzene	1.265	<i>n</i> -Pr-CyC6	0.519	1,4-Me-iPr- Benz	0.132
Toluene	6.765	C ₉ naphthene 5	0.226	C ₁₀ paraffin 3	0.090	C ₁₀ naphthene 22	0.119
1,1,2-Tm-CyC5	0.308	tt-1,2,4-Tm- CyC6	0.472	<i>n</i> -But-CyC5	0.096	Indane	0.070
2,3-Dm-Hexane	0.452	C ₉ naphthene 7	0.050	C_{10} naphthene 2	0.074	C ₁₀ naphthene 24	0.016
2-Me-3-Et- Pentane	0.180	C ₉ naphthene 8	0.031	C_{10} naphthene 3	0.020	C ₁₀ naphthene 25	0.030
2-Me-Heptane	2.741	<i>m</i> -Xylene	3.039	C_{10} naphthene 4	0.041	C ₁₁ paraffin 2	0.040
Compound	Wt %	Compound	Wt %	Compound	Wt %	Compound	Wt %
4-Me-Heptane	0.888	<i>p</i> -Xylene	0.927	3,3-Dm- Octane	0.250	<i>n</i> -But-CyC6	0.036
3,4-Dm-Hexane	0.123	2,3-Dm- Heptane	0.860	C ₁₀ paraffin 4	0.059	C ₁₀ naphthene 30	0.011
C ₈ naphthene 1	0.064	C ₉ naphthene 9	0.048	n_Pr_Benzene	0.278	1 3-De-	0.012
		· •	0.010	<i>n</i> -11-Delizene	0.278	Benzene	
C ₈ naphthene 2	0.065	3,3-Dm- Heptane	0.090	C_{10} naphthene 5	0.065	Benzene 1,3-Me-nPr- Benz	0.026
C ₈ naphthene 2 c-1,3-Dm-CyC6	0.065 2.904	3,3-Dm- Heptane 4-Et-Heptane	0.090 0.105	C ₁₀ naphthene 5 2,6-Dm- Octane	0.065	Benzene 1,3-Me-nPr- Benz 1,4-Me-nPr- Benz	0.026 0.009
C ₈ naphthene 2 c-1,3-Dm-CyC6 3-Me-Heptane	0.065 2.904 1.699	3,3-Dm- Heptane 4-Et-Heptane 4-Me-Octane	0.090 0.105 0.433	C_{10} naphthene 5 2,6-Dm- Octane C_{10} naphthene 7	0.065 0.145 0.039	Benzene 1,3-Me-nPr- Benz 1,4-Me-nPr- Benz <i>n</i> -But-Benzene	0.026 0.009 0.012
C ₈ naphthene 2 c-1,3-Dm-CyC6 3-Me-Heptane 3-Et-Hexane	0.065 2.904 1.699 1.664	3,3-Dm- Heptane 4-Et-Heptane 4-Me-Octane 2-Me-Octane	0.090 0.105 0.433 0.570	C_{10} naphthene 5 2,6-Dm- Octane C_{10} naphthene 7 1-Me-3-Et- Benz	0.065 0.145 0.039 0.383	Benzene 1,3-Me-nPr- Benz 1,4-Me-nPr- Benz <i>n</i> -But-Benzene 13-Dm-5Et- Benz	0.026 0.009 0.012 0.009
C ₈ naphthene 2 c-1,3-Dm-CyC6 3-Me-Heptane 3-Et-Hexane 1,1-Dm-CyC6	0.065 2.904 1.699 1.664 0.454	3,3-Dm- Heptane 4-Et-Heptane 4-Me-Octane 2-Me-Octane C ₉ naphthene 11	0.090 0.105 0.433 0.570 0.124	C ₁₀ naphthene 5 2,6-Dm- Octane C ₁₀ naphthene 7 1-Me-3-Et- Benz 1-Me-4-Et- Benz	0.065 0.145 0.039 0.383 0.150	Benzene 1,3-Me-nPr- Benz 1,4-Me-nPr- Benz <i>n</i> -But-Benzene 13-Dm-5Et- Benz C ₁₀ naphthene 31	0.026 0.009 0.012 0.009 0.014
C ₈ naphthene 2 c-1,3-Dm-CyC6 3-Me-Heptane 3-Et-Hexane 1,1-Dm-CyC6 t-13-Et-Me- CyC5	0.065 2.904 1.699 1.664 0.454 0.374	3,3-Dm- Heptane 4-Et-Heptane 4-Me-Octane 2-Me-Octane C ₉ naphthene 11 3-Et-Heptane	0.090 0.105 0.433 0.570 0.124 0.157	C ₁₀ naphthene 5 2,6-Dm- Octane C ₁₀ naphthene 7 1-Me-3-Et- Benz 1-Me-4-Et- Benz C ₁₀ naphthene 9	0.065 0.145 0.039 0.383 0.150 0.063	Benzene 1,3-Me-nPr- Benz 1,4-Me-nPr- Benz <i>n</i> -But-Benzene 13-Dm-5Et- Benz C ₁₀ naphthene 31 1,2-Me-nPr- Benz	0.026 0.009 0.012 0.009 0.014 0.015

t-12-Et-Me- CyC5	0.733	C ₉ naphthene 11	0.050	C_{10} paraffin 5	0.076	12-Dm-4Et- Benz	0.013
1-Me-1-Et- CyC5	0.107	o-Xylene	1.260	C ₁₀ paraffin 6	0.042	<i>n</i> -Undecane	0.018
t-1,2-Dm-CyC6	1.649	C ₉ naphthene 12	0.061	C_{10} paraffin 7	0.030		
cc-123-Tm- CyC5	0.023	C ₉ naphthene 14	0.023	4-Me-Nonane	0.025		

^aStructures not fully identified are numbered according to type of compound and carbon number.



Figure 3 Identified sulfur compounds in naphtha.

pyridine, piperidine, or indoline derivatives whereas the nonbasic are pyrrole derivatives. Straight-run naphtha fractions usually contain sub-ppm concentrations of nitrogen, whereas cracker and coker naphthas may contain typically 10–100ppm by weight. Nitrogen is poisonous to the reforming catalyst as it adsorbs strongly on its acidic sites. Common N-containing components in the naphtha boiling range are shown in Figure 4.

Oxygen-containing organic compounds are normally present only in the heavy fractions of the crude. These are phenols, furanes, carboxylic acids, or esters. The different acids account for the petroleum's acidity. High acidity can cause serious corrosion problems in the refinery. Little or no organic oxygen is found in the naphtha fractions.

Water is normally present in crude oil to some extent, partly dissolved in the oil and possibly as a separate water phase. Naphtha fractions will to some extent dissolve moisture during handling and storage. Water has a high heat of



Figure 4 Identified nitrogen compounds in straight-run naphtha.

vaporization compared to petroleum and complicates distillation.^[3] Water also results in catalyst deactivation by neutralizing the acidic sites of the reforming catalyst.

The heaviest oil fractions rich in resins and asphaltenes contain **metallic compounds.** These are usually organometallic complexes in the form of porphyrins with Ni^{2+} or vanadium oxide (1+) cations. These compounds are not found in the naphtha boiling range. However, other metallic constituents, such as iron (dust or scale or organometallic compounds) from pipeline corrosion or silicon compounds (siloxanes) originating from antifoam chemicals, might cause problems in catalytic reforming. Iron dust can cause pressure drop problems whereas the silicon compounds adsorb onto and deactivate the reforming catalyst.

3 EFFECT OF NAPHTHA COMPOSITION ON PROCESS PERFORMANCE AND PRODUCT QUALITY IN CATALYTIC REFORMING

The hydrocarbon composition, the naphtha boiling range, and the concentration of *impurities* affect the quality of the reformate product. The same feedstock characteristics also influence the reforming process, including the performance and lifetime of the catalyst. In order to understand these relationships it is useful first to define some quality requirements of the product (gasoline specifications, octane ratings) and to describe briefly the reactions involved in the catalytic reforming process.

3.1 Gasoline Quality Requirements

The purpose of catalytic reforming is primarily to increase the octane number of the naphtha feedstock to a level that makes the reformate product suitable as a gasoline blend stock. The octane number represents the ability of a gasoline to resist *knocking* during combustion of the air-gasoline mixture in the engine cylinder. European gasoline today must have research octane number (RON) ratings of 95–98. Such high octane numbers allow compression ratios needed for optimal fuel economy of present gasoline engines.

Gasoline must have a number of other properties in order to function properly and to avoid damage to the environment. Olefins have a tendency to form gums by polymerization and oxidation of olefins, and can foul the engine. In order to avoid emission of volatile light hydrocarbons, the vapor pressure (often measured as Reid vapor pressure, RVP) must be limited. Certain compounds, such as benzene, are classified as carcinogenic and represent a health hazard. Tetraalkyllead has long been used as an octane booster, but will accumulate in

Max values	USA	EU	Japan
RVP (kPa)	_	60	78
Sulfur (wppm)	50	150 ^a	100
Oxygen (wppm)	2.2	2.7	_
Benzene (vol %)	1.0	1	
Aromatics (vol %)	35	45	_
Olefins (vol %)	15	18	_
Lead (g/L)	_	0.005	_

Table 4 Present Gasoline Specifications	for 1	the
United States, Europe, and Japan ^{$[4-6]$}		

^a50 wppm from 2005.

nature, and is today strictly regulated and largely eliminated. Combustion of carbon leads to CO_2 (global warming problem) and poisonous CO. Combustion of sulfur and nitrogen (from air) leads to production of SO_x and NO_x that cause acid rain pollution. The volatile organic compounds produced during combustion of heavy aromatics are toxic in nature and are involved also in the photochemical reaction with NO_x to form ground-level ozone (smog). Exhaust catalysts have reduced emissions of NO_x to some extent, but present catalysts are sensitive to sulfur. Stringent regulations on the sulfur level of gasoline are therefore being developed. The present gasoline specifications (Table 4) set upper limits for the allowable concentrations of sulfur, benzene, olefins, and aromatics. Some countries have tax incentives for 50 or 10 ppm sulfur.

3.2 The Octane Number

In practice two octane ratings are measured, the research octane number (RON) and the motor octane number (MON), which differ in test procedure used. RON represents the engine performance at low speed whereas MON is representative for high-speed driving. By definition, the octane number of n-heptane is zero and the octane number of isooctane (2,2,4-trimethylpentane) is 100. The octane number for a gasoline is defined as the volume percent of isooctane in blending with *n*-heptane that equals the knocking performance of the gasoline being tested. Some gasoline components have octane numbers exceeding 100 and have to be characterized by use of mixtures. A common mixture contains 20% of the actual compound and 80% of an *n*-heptane/isooctane (40:60)

mixture. A hypothetical blending octane number is then obtained by extrapolating from 20% to 100% concentration. The blending octane number is specific for the mixture and usually different from the octane number of the pure component, as seen for a range of different hydrocarbons with octane numbers less than 100 in Table 5.

Hydrocarbon	RON pure	RON blending	Hydrocarbon	RON	RON blending
Paraffins	pure	orenang	Nanhthenes	pure	orenang
n Dutono	04.0	112	Cuelementene	>100	1.4.1
	94.0	115	Cyclopentalle	>100	141
Isobutane	>100	122	Cyclohexane	83.0	110
<i>n</i> -Pentane	61.8	62	Methylcyclopentane	91.3	107
2-Methylbutane	92.3	100	Methylcyclohexane	74.8	104
<i>n</i> -Hexane	24.8	19	t-l,3-Dimethylcyclopentane	80.6	90
2-MethylPentane	73.4	82	1,1,3- Trimethylcyclopentane	87.7	94
2,2-Dimethylbutane	91.8	89	Ethylcyclohexane	45.6	43
<i>n</i> -Heptane	0.0	0	Isobutylcyclohexane	33.7	38
3-Methylhexane	52	56	Aromatics		
2,3-DimethylPentane	91.1	88	Benzene	_	98
2,2,3-Trimethylbutane	>100	112	Toluene	>100	124
<i>n</i> -Octane	<0	-18	Ethylbenzene	>100	124
3,3-Dimethylhexane	75.5	72	o-Xylene	_	120
2,2,4-TrimethylPentane	100.0	100	<i>m</i> -Xylene	>100	145
n-Nonane	<0	-18	<i>p</i> -Xylene	>100	146
2,2,3,3- TetramethylPentane	>100	122	<i>n</i> -Propylbenzene	>100	127
<i>n</i> -Decane	<0	-41	Isopropylbenzene	>100	132
Olefins			l-Methyl-3-ethylbenzene	>100	162
1-Hexene	76.4	96	1,3,5-Trimethylbenzene	>100	170
1-Heptene	54.5	65	<i>n</i> -Butylbenzene	>100	114
2-Methyl-2-hexene	90.4	129	l-Methyl-3- isopropylbenzene	—	154
2,3-Dimethyl-l-pentene	99.3	139	1,2,3,4-Tetramethylbenzene	>100	146

Table 5 Pure and Blending^a Research Octane Numbers of Hydrocarbons^[7]

^aObtained using a 20% hydrocarbon -80% 60:40 mixture of isooctane and *n*-heptane.

Table 5 shows that aromatics generally have much higher octane numbers than naphthenes, olefins, and paraffins and are therefore desired reformate hydrocarbon components. The octane number of the aromatics (except for benzene) is always above 100. Straight-chain paraffins have very low octane numbers (RON<0 for *n*-octane and *n*-nonane), but the octane number increases markedly with the degree of branching (RON>100 for 2,2,3-trimethylbutane). Light olefins and naphthenes generally have higher RON than the paraffins, but as for the *n*-paraffins the octane number declines as the number of carbon atoms increases. This decline is much less pronounced for the above comparison, visualized in Figure 5, an increase in the octane number of the reformate can best be obtained by transformation of naphthenes into aromatics and of linear paraffins into branched paraffins or aromatics. These transformations are the key reactions of the catalytic reforming process.

3.3 Catalytic Reforming Process

Catalytic reforming is carried out at elevated temperature (450–520°C) and moderate pressure (4–30 bar). By use of a proper catalyst in three or four serial reactors and in the presence of hydrogen (H₂/oil equal to 4–6 mol/



Figure 5 Octane numbers vs. boiling point for hydrocarbon families.^[7,8]



reforming of naphtha.

mol), naphthenes are transformed into aromatics by dehydrogenation and straight-chain paraffins into branched paraffins by isomerization. Paraffins also undergo dehydrocyclization to form aromatics. Other important reactions are hydrogenolysis and hydrocracking (carbon–carbon bond scissions), which result in low molecular weight paraffins, and coke formation that will eventually deactivate the catalyst. Figure 6 shows the major reforming reactions.

The hydrogen produced in catalytic reforming has become increasingly valuable since it is used in hydroprocessing units for removal of sulfur and nitrogen as well as for hydrocracking. The formation of aromatics from naphthenes is a very rapid endothermic reaction. It is thermodynamically favored by high temperature and low pressure, as illustrated by the equilibrium between toluene and the C_7 naphthenes (Fig. 7). Olefins are readily hydrogenated and at equilibrium only small concentrations can exist with the hydrogen partial pressures normally used in reforming. The isomerization of paraffins is also rapid and mostly thermodynamically controlled. The dehydrocyclization of paraffins is a much slower reaction and kinetically controlled. Hydrocracking rates increase with the pressure and lower the reformate yield. Coking, which is the main cause for catalyst deactivation, is very slow but increases rapidly at low hydrogen pressure and high temperature. In order to optimize the hydrogen and aromatics formation, and to avoid severe yield loss due to hydrocracking, the choice is to operate at a high temperature and at the lowest possible hydrogen pressure, although the latter always is a trade-off with catalyst stability.

The catalyst is bifunctional in the sense that it contains both a metallic function (platinum) that catalyzes dehydrogenation reactions and an acidic





function (chlorided alumina) that catalyzes isomerization reactions. Platinum, which is usually used with a second metal, needs to be highly dispersed on the acidic carrier in order to maintain high activity and selectivity throughout a commercial cycle. In units designed for periodic regeneration of the catalyst (semiregenerative reforming), a cycle typically lasts 1–2 years. Most new units are designed with continuous catalyst regeneration implying that each catalyst particle has a cycle time of typically 6–8 days between regenerations. Two catalyst formulations prevail commercially: Pt-Re/Al2O3 and Pt-Sn/Al₂O₃. The former is the most stable and is preferred in semiregenerative units, whereas the latter has the highest selectivity at low pressure and is the best choice in continuous reforming units. These catalysts are sensitive to sulfur which adsorbs (reversibly) on the platinum crystallites. Sulfur can be removed by hydrotreatment of the naphtha feedstock. The water content must also be kept low to avoid leaching of chloride and thus loss of acid strength. Metallic poisons are relatively rare, but iron from plant corrosion and silicon originating from antifoam chemicals can affect catalyst activity.

Effect of Naphtha Hydrocarbon Composition

The distribution of paraffins (P), olefins (O), naphthenes (N), and aromatics (A) in the naphtha determines the *richness* of the feedstock. A high concentration of aromatics automatically means that the octane level is quite high. The naphthenes are transformed into aromatics with high selectivity and a high octane is therefore easily achieved. A paraffinic (or paraffinic—olefinic) feedstock will have a low octane number. Severe reaction conditions are required to reach a specified RON level, and the yield loss and coke laydown will be significant. The richness of a naphtha is therefore usually rated by its N+A or N+2A value. Figure 8 illustrates how the reforming reactor temperature decreases and the liquid yield of reformate increases when the feedstock N+A values increase.







The hydrocarbon composition in the naphtha does not affect the reformate composition much. The reformate consists mainly of paraffinic and aromatic hydrocarbons since the large part of the naphthenes is consumed in the reaction. There is a near-linear relationship between the RON value and the concentration of aromatics (Fig. 9). Thus, regardless of feedstock composition, when operating with a constant RON level in the product, the aromatic and paraffin concentrations are usually fixed within narrow limits. However, as shown in Figure 9, the RON—aromatics relationship changes somewhat with reaction pressure. At elevated pressures the concentration of high-octane cracked products (C_5 and C_6 isoparaffins) increases, and subsequently less aromatics are required to reach a specified RON in the product.

Effect of Naphtha Boiling Range

The boiling range of the naphtha feedstock is a key factor in catalytic reforming. The initial and final boiling points (IBPs and FBPs) and the boiling point distribution not only determine the carbon number distribution of the product but greatly affect reaction conditions, and thus reformate yields, as well as the rate of catalyst deactivation.

Although the carbon number distribution in the feedstock and in the reformate product are strongly related, the boiling points increase somewhat during reaction due to aromatics formation. As an illustration, the FBP typically increases by 20°C at low to intermediate reaction pressures (<20 bar). The increase in FBP from feedstock to product is slightly smaller at higher pressures because the heaviest components undergo additional hydrocracking. Based on boiling points of individual hydrocarbons in naphtha, Figure 10 shows the boiling range for each carbon number group. Although azeotropic phenomena among various compounds exist, it is still possible by distillation to separate the feedstock fairly well according to carbon number. Above 100°C the overlap in boiling range between the groups is significant and separation becomes increasingly difficult.

The choice of naphtha boiling range depends on the intended use of the reformate product. When catalytic reforming is used mainly for benzene, toluene, and xylenes (BTX) production, a C_6-C_8 cut (IBP-FBP 60–140°C), rich in C_6 , is usually employed. For high-octane gasoline production, especially when the reformate constitutes a major part of the gasoline pool, a C_7-C_9 cut (IBP-FBP 90–160°) is the preferred choice. The C_6 hydrocarbons may be removed to avoid the benzene in the naphtha and to avoid further benzene formation from the C_6 naphthenes. The benzene yield from cyclohexane and methylcyclohexane (primary production) is significant, as illustrated in Figure 11. These reactions are controlled by thermodynamics and favored by low pressure. Benzene is also formed by dealkylation of heavier aromatics (secondary production). This reaction is kinetically controlled and favored by high temperature and low space velocity (Fig. 12).

The benzene selectivity from substituted aromatics increases with the length of the side chain (n-butylbenzene>n-propylbenzene) and with the degree







Figure 11 Benzene selectivity (percentage of the components feed concentration found as wt % benzene yield) vs. pressure in semiregenerative reforming with PtRe catalyst. RON=101.



Figure 12 Benzene in reformate as a function of reaction temperature and space velocity using a feedstock with 0.23 wt % C₆ hydrocarbons.

of sidechain branching (*i*-propylbenzene>*n*-propylbenzene). Toluene has a relatively low selectivity to dealkylation. However, considering the very high concentrations in the reformate, the contribution from toluene and also from methylyclohexane (which forms toluene) to the secondary benzene production is significant.

The heavy end containing C_{10+} hydrocarbons is the least favorable with regard to processing, particularly in semiregenerative units, due to high deactivation rates. Figure 13 shows how the relative deactivation rate increases with the naphtha FBP. This effect is not related to the reaction temperature but to the amount of coke precursor in the feed.^[10] Alkyl-substituted C_{10+} aromatics (and polycyclics) have been identified as strong coke precursors. For continuous reforming units, heavy stocks can be processed if the coke burning capacity is sufficient. The cutpoint in the light end of the naphtha also affects the deactivation rate. When the IBP is increased the naphtha becomes richer and the same octane number can be achieved at lower reaction temperatures.

The legislative requirements for sulfur removal from gasoline and diesel have increased hydrogen use in the refineries; hence, refiners are looking for ways to maximize their hydrogen yields. The optimal feedstock to a reformer with respect to hydrogen yield is a C_6 - C_9 cut that contains the highest naphthene concentrations. No hydrogen can be produced from the C_5 fraction and little hydrogen is produced from the C_{10+} hydrocarbons, which are highly susceptible to hydrocracking. The highest yields of hydrogen are obtained at low pressures and high temperatures when the conversion of naphthenes and paraffins into



Figure 13 The deactivation rate (measured as the temperature rise needed to maintain 102.4 RON relative to a base naphtha) as a function of final boiling point (FBP).^[10]

aromatics is high. The temperature must, however, be kept below a point when hydrocracking becomes important, which would lower the yield of both hydrogen and

reformate. The octane number during maximized hydrogen production is typically in the order of 102–105 RON, and it follows that the deactivation rate is high.

Effect of Naphtha Sulfur Content

Reforming catalysts are sensitive to sulfur impurities in the naphtha feedstock. The surface platinum atoms of the catalyst convert the sulfur compounds into H_2S molecules that readily adsorb onto the surface metal atoms. The poisoned platinum atoms are no longer active and the temperature must be increased to maintain RON (i.e., produce aromatics by dehydrogenation). Reformate yield decreases somewhat due to the temperature rise but not as much as normally observed. This is due to the reduced methane production by the metal-catalyzed hydrogenolysis reaction. However, the rate of deactivation increases according to the temperature increase. The adsorption of sulfur is strong but reversible. A given sulfur concentration in the feedstock results in a specific sulfur coverage. However, if the sulfur is removed from the naphtha, the activity will eventually return to very near the initial level as shown in Figure 14.



4 ANALYSIS METHODS

The high complexity of naphtha and reformate fractions requires advanced techniques to obtain a complete compositional analysis and to determine the chemical and physical parameters needed for the refiner. Many different approaches exist, and the choice of analytical method depends on the needed resolution, the analysis time, and the cost. For industrial products that must meet defined specifications, refiners are required to follow standardized analysis procedures. The American Society for Testing and Materials (ASTM) is one of several recognized organizations for standardization. This chapter will concentrate on the most common methods for determining hydrocarbon composition, distillation range, octane numbers, and sulfur/nitrogen contents. Examples of both ASTM and nonstandardized methods are included.

4.1 Hydrocarbon Composition

The most powerful and widely used technique for analysis of hydrocarbons in naphthas or reformates is gas chromatography (GC). This is a separation method in which the sample is injected into a carrier gas stream, usually helium, and brought through a dedicated capillary column allowing transport of the different molecules at different rates (Fig. 15). The samples may be gaseous or liquid. Vaporized sampling is usually preferred for on-line product testing in research laboratories. An adjustable split injector can strongly reduce the sample amount and thereby avoid column overloading and subsequent separation problems. Nonpolar, cross-linked methylsiloxane columns



give elution times close to the order of increasing boiling point. The columns have diameters of 0.1-0.5 mm and the length ranges from a few meters up to 100 m. A flame ionization detector creates and detects a signal proportional to the concentration of each hydrocarbon as the components exit the column. It operates by collecting (by an electrode) the ions of the flame produced during combustion of the hydrocarbon. The detector response is approximately proportional to the weight of carbon present,^[11] which greatly simplifies quantitative analysis.

The rate of hydrocarbon transport through the column is dependent on the carrier gas velocity, adjusted for the injector pressure and the oven temperature. The lightest hydrocarbons (methane and ethane) are transported very quickly through the column and separation requires low temperature (ambient). On the



Figure 15 Schematic illustration of gas chromatography (GC) with gas/liquid sampling, split injection, and flame ionization detection (FID).

other hand, the heaviest aromatics need a temperature of 200°C or more in order not to adsorb strongly at the column front. Thus, an advanced temperature program and column pressure selection is required to optimize separation and time consumption of a GC analysis. The column material and length, the detector temperature, the carrier gas type, and the split flow rate also affect the separation.

Gas chromatography is not an identification method. In order to identify the large number of peaks in the chromatogram, the system must be calibrated. This can best be obtained by coupling a mass spectrometer to the column exit of an identical chromatographic setup (gas chromatography—mass spectrometry, GCMS). Most of the resolved peaks are identified from MS spectra libraries. The equipment is costly and such an analysis is time consuming, but a good 'peak library' for the GC user is obtained given that the column separation is good. In practice, the 'heavy region' of the chromatogram is never fully resolved,

Column	50 m cross-linked methylsiloxane
Temp. program	35°C (30 min)→200°C, 2°C/min (20 min)
Carrier gas	Helium, 215 kPa
Injector	Split, 200 ml/min; <i>T</i> =200°C
Detector	FID; <i>T</i> =250°C
Sample size	0.1 μ1 (liquid)

Table 6 Analysis of C_5 - C_{12} PONA HydrocarbonsAccording to ASTM D5134

especially when additional peaks created by the presence of olefins exist, as is the case for naphthas from catalytic cracking.

ASTM D5134 is a GC method for PONA analysis in naphthas and reformates (C₅-C₁₂). The method, described in Table 6, is limited to straight-run naphthas, reformates, and alkylates because the olefin content is limited to 2% and all components eluting after n-nonane (BP>150.8°C) are collected as one peak. The analysis time is 122 min. Table 7 describes an even more time-consuming method that applies a longer column, a lower initial temperature, and a more complex temperature program designed to separate most C_1 - $C_{1,2}$ hydrocarbons in naphthas and reformates. A chromatogram with identified peaks obtained using this method on a reformate sample is shown in Figure 16. Detection of most individual compounds is important for the understanding of the chemistry involved in catalytic reforming. As an example, a precise feedstock and product hydrocarbon analysis makes it possible by mass balance to calculate the amount of hydrogen produced by the reforming reactions. The data can also, based on simple models, be used to calculate density, vapor pressure, carbon and hydrogen content, and octane numbers. For the process engineer it is often sufficient to know the PONA group concentrations in order to verify the feedstock or product qualities, and the least time-consuming GC methods are chosen. Specialized methods for more precise analysis of single compounds are available.

Table 7 Comprhensive Laboratory Analysis forPONA C_1 - C_{12} Hydrocarbons

Column	100 m cross-linked methylsiloxane
Temp. program	30°C (30 min)→50°C, 1°C/min (10 min)→140°C, 2°C/min (0 min)→250°C, 10°C/min, (30 min)
Carrier gas	Helium, 300 kPa
Injector	Split, 800 ml/min; <i>T</i> =250°C
Detector	FID; <i>T</i> =280°C
Sample size	0.2 μ1 (liquid)



Figure 16 Chromatogram of reformate (liquid sample) using the GC method listed in Table 7. Page 1 of 2.



4.2 Distillation Range

Knowledge about the boiling point distribution of gasolines is most frequently obtained by distillation according to ASTM D86. A batch distillation is conducted at atmospheric pressure and the resulting curve shows the temperature as a function of percent volume distilled. Automated instruments perform the measurement. Figure 17 shows an ASTM D86 distillation curve and tabulated values for a reformate sample.

Another way of analyzing the boiling range characteristics is to simulate the distillation by use of GC. By using an inert column stationary phase, the components

elute in order of their boiling points. The ASTM D3710 method is specialized for gasoline fractions and gives the result within 15 min.

4.3 Sulfur and Nitrogen Analysis

The fact that only small concentrations of sulfur and nitrogen poison reforming catalysts calls for highly accurate analysis methods, capable of measuring down to sub-ppm levels. Non-hydrotreated naphthas from thermal or catalytic cracking



Figure 17 Results for an ASTM D86 distillation of a reformate sample.

Target	Technique	ASTM	Range (wppm) ^a
Ν	OC/chemiluminescence	D4629	0.3–100
Ν	OC/electrochemical detection	D6366	0.05-100
S	OC/microcoulometry	D3120	3–100
S	OC/UV fluorescence	D5453	1-8000
S	Hydrogenolysis	D4045	0.02–10
S	X-ray fluorescence	D4294	>1000
S	GC/selective sulfur detector	D5623	0.1–100 ^b

Table 8 Sulfur and Nitrogen Analysis Methods

^aAnalytical range suggested by ASTM method.

^bConcentration range of each individual sulfur compound.

OC, oxidative combustion.

processes may reach percent levels of sulfur and 100 ppm levels of nitrogen. Thus, versatile analysis methods covering sulfur and nitrogen from ppb up to percent levels are needed. A large number of methods and instrument types are available as shown in Table 8. Most analysis techniques are based on initial combustion of sulfur into SO_2 or SO_3 and of nitrogen into NO or NO₂. The amount of these oxides can then be measured by microcoulometry techniques such as (sulfur), UV fluorescence (sulfur). chemiluminescence (nitrogen), and electrochemical detection (nitrogen). Nonoxidative techniques for sulfur analysis include hydrogenolysis, X-ray fluorescence, and, finally, GC with sulfur-selective detection methods such as atomic emission detection (AED), sulfur chemiluminescence detection (SCD), and flame photometric detection (FPD). The GC technique not only measures total sulfur but may also detect and distinguish among different sulfur compounds in the sample.

Sulfur and nitrogen analyzers have improved in recent years when it comes to detection limits. Pyrochemiluminescent nitrogen and pyrofluorescent sulfur technology are such examples and can be combined in one instrument and used on the same sample injection simultaneously. The principal reactions for the measurement of sulfur by pyrofluorescence are shown in Figure 18. Modern instruments give total nitrogen determinations from low ppb to 20 wt % and total sulfur determinations from low ppb up to 40 wt %. The analysis takes only a few minutes.

For research laboratories studying the chemistry of sulfur and its reactions, as in hydrotreatment, the available GC methods are most appealing. By extensive precalibration of such a system it is possible to identify the different sulfur structures present in the sample. Figure 19 shows a chromatogram from analysis of a cracker naphtha using AED. Integration of all peaks in the chromatogram



Figure 18 Schematic illustration of total sulfur analysis by pyrofluorescence method.

yields the total sulfur concentration. Very good comparisons have been measured between total sulfur analysis by GC/AED and sulfur analysis by pyrofluorescence.^[12]

The new SCD instruments^[13] have extremely high sensitivity and are the choice for low-sulfur samples.^[14]



range catalytic cracker naphtha.

4.4 Octane Number Determination

Octane ratings are measured directly using a single-cylinder reference motor (CFR engine).^[15] The compression ratio and the fuel/air ratio are adjustable and the engine is solidly built to withstand knocking without damage. The basic procedure is to increase the compression ratio of the engine until a 'standard' knocking intensity is indicated by a pressure detector in the combustion chamber.^[15] The critical compression ratio is recorded and compared with two binary heptane—isooctane mixtures of neighboring composition. The fuel/air ratio is adapted in each case to obtain maximum knocking intensity; it is usually between 1.05 and 1.10. The octane number is calculated by linear interpolation, assuming the primary reference mixture has similar behavior as the fuel being tested. The distinctions between the two procedures of RON and MON measurement concern essentially the engine speed, temperature of admission, and spark advance as indicated in Table 9. The RON and MON methods simulate the engine performance when driving at low and high speed, respectively.

An alternative method for determination of the octane number of a gasoline is by means of calculation, using the hydrocarbon composition from GC analysis as input data. It is not a straightforward task to develop such a model because blending of different individual hydrocarbons does not result in an engine knocking performance as expected from the octane numbers of the individual components. Advanced models, both linear and nonlinear and based on a number of naphthas or reformates with variable compositions and cut points, have been put forward. An approach to calculate the octane number based only on the total aromatics content is possible.^[16] However, the RON—aromatics relationship is not accurate and changes significantly with reaction pressure as shown earlier in this chapter (Fig. 9). Walsh and coworkers^[17] developed a linear RON calculation model based on GC analysis with capillary columns. A grouping technique is used

Operating parameters	RON method ASTM D2699	MON method ASTM D2700
Engine speed (rpm)	600	90
Ignition advance (degrees before top dead center)	13	14 to 26 ^a
Inlet air temperature (°C)	48	—
Fuel mixture temperature (°C)	—	149
Fuel/air ratio	b	b

Table 9 Test Conditions for RON and MONDetermination in CFR Engines

^aVariable with the compression ratio.

^bAdapted in each case to obtain maximum knocking intensity.

to produce a manageable number of pseudocompounds. Thirty-one groups were defined by the order of elution in the GC chromatogram and given a regression coefficient (br) for calculation of RON after the simple equation $RON = \sum (b_r W_r)_{where}$ Wr is the weight fraction of group r. Durand and coworkers^[18] have demonstrated the versatility of this RON model using 60 different gasoline samples that were analyzed by GC and rated by ASTM engine tests. The difference in RON values turns out to be less than 1 RON unit in most cases. The defined model groups with regression coefficients are listed in Table 10.

Table 10 Group Definition and RegressionCoefficients of Linear RON Model Developed byWalsh and Coworkers^[17]

Group no.	Group definition by GC elution times	Regression coefficient
1	Components eluting before <i>n</i> -butane	103.9
2	<i>n</i> -Butane	88.1
3	Components eluting between <i>n</i> -butane and isopentane	144.3
4	Isopentane	84.0
5	Components eluting between isopentane and <i>n</i> -pentane	198.2
6	<i>n</i> -Pentane	67.9

7	Components eluting between <i>n</i> -pentane and 2-methylpentane	95.2
8	2- and 3-Methylpentane and components eluting between these	86.6
9	Components eluting between 3-methylpentane and <i>n</i> -hexane	95.9
10	<i>n</i> -Hexane	20.9
11	Components eluting between <i>n</i> -hexane and benzene	94.9
12	Benzene	105.2
13	Components eluting between benzene and 2-methylhexane	113.6
14	2- and 3-Methylhexane and components eluting between these	80.0
15	Components eluting between 3-methylhexane and <i>n</i> -heptane	97.8
16	<i>n</i> -Heptane	-47.8
17	Components eluting between <i>n</i> -heptane and toluene	62.3
18	Toluene	113.9
19	Components eluting between toluene and 2-methylheptane	115.1
20	2- and 3-Methylheptane and components eluting between these	81.7
21	Components eluting between 3-methylheptane and <i>n</i> -octane	109.7
22	<i>n</i> -Octane	10.5
23	Components eluting between n-octane and ethylbenzene	96.1
24	Ethylbenzene	122.6
25	Components eluting between ethylbenzene and <i>p</i> -xylene	45.4
26	<i>p-x</i> ylene+m-xylene	102.0
27	Components eluting between <i>m</i> -xylene and <i>o</i> -xylene	73.3
28	<i>o</i> -Xylene	123.6
29	Components eluting after <i>o</i> -xylene up to and including <i>n</i> -nonane	35.0
30	Components eluting between <i>n</i> -nonane and <i>n</i> -decane	112.0
31	n-Decane and components eluting after n-decane	85.6

Complex, nonlinear models in which the deviation from ideality (as expressed by the regression coefficients) of each component or component group is set as a function of the concentrations of the different hydrocarbon families can reduce the error of calculation to less than 0.5 RON unit. Such models will be especially useful for more complex gasolines in which the concentration of nonreformate material (alkylates, isomerates, cracker naphtha, polymerate, alcohols, and ethers) is high.

A fast and simple alternative to the previously described methods for octane number determination was proposed by BP^[19] and involves the use of infrared (IR) spectroscopy. The near-IR region of the spectrum (wavelength: 800–2500 nm) contains many bands that result from overtones and combinations of carbon—hydrogen stretching vibrations, which are particularly useful for analyzing gasoline (Fig. 20). The variations in IR spectra can be coupled to a range of gasoline properties including RON and MON numbers. Automated and computerized instruments offer fast (1 min) analysis and have the possibility of





on-site sampling. The error of calculation is not significantly higher than for the composition-octane models derived from GC analysis.

REFERENCES

- Speight, J.G. *The Chemistry and Technology of Petroleum*, 3rd Ed.; Chemical Industries Vol. 3; Marcel Dekker: New York, 1999.
- 2. http://www.statoil.com/ (Products and Services/Crude Oil and Condensate).
- Parera, J.M.; Figoli, N.S. In *Catalytic Naphtha Reforming*, 1st Ed.; Chemical Industries Vol. 61; Marcel Dekker: New York, 1995.

- Martino, G. Catalysis for oil refining and petrochemistry: recent developments and future trends. In *Studies in Surface Science and Catalysis*, Corma, A., Melo, F.V., Mendioroz, S., Fierro, J.L.G., Eds.; *Proceedings of the 12th* ICC, Granada, Spain, July 9–14, 2000; Vol. 130A; Elsevier: Amsterdam, 2000; 83–103.
- 5. Hartman, E.L.; Hanson, D.W.; Weber, B. Hydrocarbon Proc. 1998, 77.
- http://www.paj.gr.jp/html/english/index.html (Petroleum Association of Japan, Annual Review 1999).
- 7. American Institute Research Project 45, 16th annual report, 1954.
- 8. Weast, Ed. Handbook of Chemistry and Physics, 58th ed.; CRC Press: Boca Raton, 1978.
- Gjervan, T.; Prestvik, R.; Holmen, A. In *Basic Principles of Applied Catalysis*; Baerns, M., Ed.; in press.
- Moljord, K.; Grande, K.; Tanem, I.; Holmen, A. In *Deactivation and Testing of Hydrocarbon-Processing Catalysts* ', O'Connor, P., Takatsuka, T., Woolery, G.L., Eds.; ACS Symposium Series No. 634, 1995; 268–282.
- 11. Dietz, W.A.J. Gas Chromatogr. 1967, 5, 68.
- 12. Steiner, P.; Myrstad, R.; Thorvaldsen, B.; Blekkan, E., in preparation .
- 13. Benner, R.L.; Stedman, D.H.Anal. Chem. 1989, 61, 1268.
- 14. Adlard, E.R. Ed. *Chromotography in the refining industry*. J. Chromatogr. Lib., Vol. 56; Amsterdam, 1995.
- 15. Wauquier, J.-P. Ed. Petroleum Refining 1, Crude Oil, Petroleum Products, Process Flowsheets ; IFP Publications, Editions Technip: Paris, 1994.
- 16. McCoy, R.D. ISA AID 73442, 187, 1973.
- 17. Anderson, P.C.; Sharkey, J.M.; Walsh, R.P. J. Inst. Petr. 1972, 58 (560), 83.
- 18. Durand, J.P.; Boscher, Y.; Petroff, N.J. Chromatrogr. 1987, 395, 229.
- Descales, B.; Lambert, D.; Martens, A. Determination des nombres d'octane RON et MON des essences par la technique proche infrarouge, Revue de l'Association Francaise des Techniciens du Petrole, No 349, 1989.

Basic Reactions of Reforming on Metal Catalysts

Zoltán Paál

Hungarian Academy of Sciences, Budapest, Hungary

1 INTRODUCTION

Since the first industrial application of reforming for fuel upgrading using supported Pt catalysts, this large-scale commercial process has proved to be a driving force for research of metal-catalyzed hydrocarbon reactions. Laboratory studies, which frequently employed conditions vastly different from industrial ones, provided a scientific background for catalytic reforming, and these apparently remote investigations prepared the ground for several industrially important innovations in the past, and will do so in the future, too. This chapter concentrates on a few points of laboratory-scale studies that might be of value for industry.

Several catalytic reactions of reforming involve the rearrangement of the hydrocarbon skeleton; hence, they can be termed as 'skeletal reactions': aromatization, isomerization, C_5 cyclization, and hydrogenolysis. The first three reactions are 'useful' or value enhancing, the last one 'disadvantageous' for operation of a reforming plant, since products of lower value are produced.

This chapter concentrates on metal catalysts and mechanisms of reactions catalyzed by them. Relevant problems and the numerous hypotheses suggested for their solution will be pointed out rather than by presenting ready and apparently finalized theories. Interactions between metallic and support sites will also be mentioned. The diversity of ideas, methods, approaches, etc., reflects truly the present situation, where the experimental results as a function of several parameters lack well-established and generally valid interpretations. This is the reason why a relatively high number of references has been included; still, the literature covered is far from being comprehensive. Most of the basic information included in the first edition of this book^[1] has been retained, although several recent references have been added.

2 POSSIBLE MECHANISMS OF THE REACTIONS

The chemistry of the industrial reforming process has been extensively reviewed.^[2] All the valuable information from results obtained in the 1960s and 1970s will not be repeated here. Another, more concise review dealing with both chemistry and industrial aspects was published in 1991.^[3] The excellent book by Olah and Molnár^[4] summarized all relevant hydrocarbon reactions. *Every* reaction important in reforming

(aromatization, C_5 cyclization, isomerization, and fragmentation) can also proceed with catalysts possessing metallic activity only. This feature will be stressed in the present chapter. Laboratory measurements are often carried out in the temperature range of 500–650 K and pressures up to 1 bar, being much lower than the conditions of industrial reforming. Yet these studies will be useful in understanding underlying phenomena.

Aromatization (or C₆ dehydrocyclization) was first observed by a Russian group as the formation of a second aromatic ring from an alkylbenzene on monofunctional Pt/C catalyst; the same group reported also the formation of an aromatic C₆ ring from alkanes.^[5] Later they described the metal-catalyzed *C*₅ cyclization of alkanes to alkylcyclopentanes.^[6] The aromatic ring is very stable under these conditions but C₅ cyclization is reversible: a ring opening of the C5 ring to alkanes also takes place.^[7] Metal-catalyzed *isomerization* ^[8] may occur (1) via the formation and splitting of the C₅ ring;^[9] (2) in the case of hydrocarbons whose structure does not allow the formation of C₅ cyclic intermediate, by a so-called 'bond shift' mechanism.^[10], ^{11]} The former isomerization route is often termed as 'cyclic mechanism'.^[12] The present author prefers the name 'C₅ cyclic' intermediate. *Hydrogenolysis* of alkanes has also been a well-known and widely studied reaction.^[15] The reaction mechanisms of these reactions and their relative importance over various catalysts have been comprehensively reviewed.^{[13, 14, 16} - ²⁰]

Early ideas for *aromatization* ^[21] assumed the dehydrogenation of an open-chain hydrocarbon and the subsequent ring closure of the olefin directly to give a sixmembered ring. Aromatization on carbon-supported metals was interpreted in terms of a direct 1,6 ring closure of the alkane molecule without its preliminary dehydrogenation.^[5] ^{b]} Past and present state of the art has been discussed in the excellent review by Davis.^[22] With the appearance of bifunctional catalysts, the concept of this 1,6 ring closure has fallen temporarily into the background in favor of the two-dimensional mechanism.^[2] This described very satisfactorily the reactions observed under industrial conditions. Still, the possibility of the 1,6 ring closure has again surfaced due to new evidence. The stepwise dehydrogenation of heptanes to heptenes, heptadienes, and heptatriene followed by cyclization has been shown over oxidic catalysts.^[23] This idea was confirmed recently with *n*-octane aromatization over CrO _x clusters or Cr³⁺ ions as the catalyst, stabilized by La₂O₃.^[24] Another novel catalyst family included Zr, Ti, and Hf oxides on carbon support.^[25], ²⁶ These oxides were claimed to decompose upon pretreatment in Ar at 1273 K and were described as nonacidic 'Zr/C, Hf/C, Ti/C', producing aromatics with selectivities up to 67% from *n*-hexane^[25] and 80–92% from *n*-octane, likely *via* the 'triene route'.

Hexatriene as an intermediate has been shown also on unsupported Pt catalysts, partly by using ¹⁴C radiotracer.^[27, 28] This triene mechanism has also been regarded as one of the possible reaction pathways over Pt/Al₂O₃, together with another, direct C₆ ring closure.^[29] The assumption of dienes and trienes does not mean that these intermediates should appear in the gas phase. It is more likely that a 'hydrocarbon pool' is produced on the catalyst surface upon reactive chemisorption of the reactant(s). As long as sufficient hydrogen is present, all of the chemisorbed species are reactive and may undergo dehydrogenation, rehydrogenation, and, if they have reached the stage of surface olefins, double bond or cis—trans isomerization may also occur.^[13,28] Their desorption is possible in either stage; hence, hexenes, hexadienes, etc., may appear as intermediates. The true intermediates of aromatization are *surface* unsaturated species;^[30] those appearing in the gas phase are the products of surface dehydrogenation *and* desorption process. Desorption should be less and less likely with increasing unsaturation of the surface intermediates. The loss of hydrogen produces either *cis* or *trans* isomers. The *cis* isomer of hexatriene is expected to aromatize rapidly, the chance of its desorption being practically zero. The *trans* isomer, on the other hand, has to isomerize prior to cyclization and, during this process, it has also a minor chance to desorb to the gas phase.^[13,28] It is also a misunderstanding to suggest that *thermal* cyclization of triene intermediates would have any noticeable importance in heterogeneous reactions^[30] just because a gas-phase hexatriene molecule would cyclize spontaneously and very rapidly at or above about 400 K.^[28] The temperatures in any *catalytic* reaction exceed this value.

The 1–6 cyclization of hexane proceeds between two primary C atoms, but at least one secondary carbon must be involved with alkanes having seven or more C atoms in their main chain.^[22] Tracer studies using ¹⁴C labeled *n*-heptane indicated that, over Pt supported on a nonacidic A1₂O₃, 1,6 ring closure was the main reaction of aromatization; in addition, 1,5 ring closure, opening, and repeated cyclization might also occur.^[31] The aromatization of [1-¹³C]*n*-heptane on Te/NaX resulted in toluene with 93% of the label in the methyl group.^[32] Davis^[22] summarized the results of tracer methods as well as the peculiarities of 'monofunctional' aromatization. Random C₆ ring closure of *n*-octane would give *o*-xylene (oX) and ethylbenzene (EB) in a ratio of oX/EB=0.5. Isomerization of these primary alkylaromatics on acidic sites would shift this value while producing *p*-and *m*-xylene. The distribution of primary ring closure products is, however, different on various nonacidic catalysts: **OX/EB** \cong **1**_{on} Hf/C, Zr/C, Ti/C^[26] as well as on Pt/nonacidic alumina but ~0.7 on Pt/SiO₂ ^[-33 a] At 1 bar pressure the oX/EB values were about 1.3–1.5 on PtSn on both silica and alumina support.^[33 b] Adding Sn to a Pt/SiO₂ catalyst increased the oX/EB ratio from about 0.6 to about 1.6 when the experiment was carried out at 7.8 bar, with eight-fold H₂ excess,^[33 c] and the same trend was seen on Pt/Al₂O₃ as well.^[33 d] These results indicate that the activation of the primary and secondary C atoms is strongly dependent on the nature of the catalyst, and the reasons are still to be clarified.

The role of hydrogen in the scheme is twofold. First, the metal catalyzed *trans-cis* isomerization through half-hydrogenated surface intermediates^[20, 34] requires hydrogen. Second, the degree of dehydrogenation of the surface entities is often too deep, and thus their removal to the gas phase is a hydrogenative process, e.g.:

 $C_6H_4[ads]+2H[ads]\rightarrow C_6H_6[gas]$

The reality of such processes has been confirmed experimentally by at least two independent methods: temperature-programmed reaction $(TPR)^{[35]}$ and transient response method.^[36] Another TPR study, combined with infrared [RAIRS] and near-edge X-ray absorption fine structure (NEXAFS), confirmed the possible intermediate character of hexatriene in aromatization of 1-hexene on the Cu₃Pt(111) single-crystal surface^[37] (see also Sec. 5.2). Benzene formation from *trans*-3-hexene—requiring geometric isomerization—has also been confirmed. Only a fraction of unsaturated adsorbates formed benzene, with this fraction being higher starting with cyclohexene and

cyclohexadiene (about 100% vs. about 70% from both 1-hexene and 3-hexene). The $E_{\rm a}$ values were 24–25 kJ mol⁻¹ with open-chain and 14–17 kJ mol⁻¹ with cyclic feeds. The availability of surface hydrogen and its activation may also be important in activating primary and secondary C atoms in the direct C₆ ring closure.

The conformation of cis-hexatriene would permit an easy ring closure.^[13] Trans isomers, in turn, may be coke precursors.^[13], ^{28]} The trans \rightarrow cis isomerization involves half-hydrogenated species,^[20] and thus the transition can be promoted even by small amounts of hydrogen. When 1-hexene reacted on unsupported Pt precovered with HT,^[38] the unreacted hexene fraction exchanged on average one of its H atoms with T (Table 1). The relative radioactivity of *n*-hexane points to the uptake of two labeled H atoms from the retained surface hydrogen pool. Analogous values for other products showed incorporation of

Table 1 Selectivity and Relative Molar
Radioactivity of Products from 1-Hexene on
Tritiated Pt ^a

Effluent component	Composition (%)	Relative molar radioactivity (a.u.)
<c<sub>6</c<sub>	4	11
<i>n</i> -Hexane	12	2.0
Unreacted 1-hexene	62	0.2
2-Hexenes	14.5	1.0
Hexadienes	4.0	1.2
Benzene	3.5	3.4

^a *T*=633 K, 0.76 g Pt black pretreated with 3×0.5 ml tritiated hydrogen, 3 µl pulses into He carrier gas. Adapted after Ref. 38.

about one H atom per hexadiene and about three H atoms per benzene molecule.^[38] Thus, in addition to benzene as a π complex [produced, perhaps, directly from *cis*-hexatriene], more deeply dehydrogenated species could also been produced. Their hydrogenative desorption, such as

 $C_6H_3[ads]+3H[ads]\rightarrow C_6H_6[gas]$

may belong to the slow steps of the aromatization.^[35]

 C_5 cyclization and C_5 ring opening are closely related and likely have a common surface intermediate.^[7,39] An 'alkene-alkyl insertion' [like that mentioned for C₆ cyclization]^[40] as well as a 'dicarbene' and also a 'dicarbyne' mechanism involving surface intermediates attached by two double or two triple bonds to the surface^[12] were proposed for ring closure. An alternative pathway would involve a much less dehydrogenated intermediate where the position of the cycle would be roughly parallel to the catalyst surface.^[41] The relatively low degree of dehydrogenation of this latter intermediate has been shown by deuterium tracer studies.^[42] This type of intermediate of the C₅ cycle, which is to be formed or to be split, and its preferred 1,3 attachment to two sites of the catalyst has been suggested, ^[13] and supported experimentally by comparing several open-chain^[43] and C₅ cyclic hydrocarbons.^[44] At the same time, a 'dehydrogenative' C₅ cyclization of unsaturated molecules [hexenes, methyl-pentenes] is also possible.^[13,45] The C₅ ring opening can be hindered to various extents in the vicinity of an alkyl substituent [position a], with this hindrance depending on the nature of the metal and its dispersion.^[12,13,44,46,47] The selectivity of ring opening of methylcyclopentane [MCP] in this position can vary from the statistical value of 40% down to 1–2% depending on the nature of the metal and its support.^[22,46] Metal particles in narrow zeolite pores selectively catalyze the opening of MCP in position c.^{[48}]

The parallel occurrence of C_5 cyclic and bond shift isomerization has been shown by the use of ¹³C tracer.^[12, 39] Whenever the C₅ cyclic mechanism was possible, it was usually predominant; at the same time, strong sensitivity to the structure of the reactant and to the catalyst has been observed^[18] (see also later). Bond shift means a transfer of a C–C bond to the next carbon atoms ('1,2 bond shift'). This route has been demonstrated on Pt and Pd. These metals interact in different ways with the reactant.^[12] The product composition pointed to the interaction of two methyl groups of 2,2-dimethylbutane with Pt while one methyl group and the secondary C atom formed the preferred surface intermediate on Pd.^[49] A 1,3 bond shift of methylpentanes over Ir at 493 K was also shown by ¹³C tracer studies.^[50]

Hydrogenolysis is related to isomerization reactions.^[11,20,49,51] The Anderson— Avery mechanism^[19] assumed a rather deeply dehydrogenated surface intermediate. If the starting molecule has at least three carbon atoms, a 1,1,3 interaction with the surface is preferred. Pt, Pd, Ir, and Rh were found to split an alkane molecule predominantly into two fragments.^[52] A multiple hydrogenolysis prevailed over other metals. A fragmentation factor ζ has been defined as the average number of fragments per decomposed C_n hydrocarbon molecule. Its value is around 2 in the case of single hydrogenolysis and can go up to n with multiple hydrogenolysis. The variation of ζ with conversion was discussed in chapter 2 of Ref. 1. Hardly any change was seen in the value of ζ factor as a function of the degree of conversion with single hydrogenolyzing metals while it increased with higher conversions up to n in the case of multiple hydrogenolysis.^[] ⁵³] Hydrogenolysis *activity*^[15] can be quite high in the case of single hydrogenolysis, e.g., with Rh or Ir. The probability of the rupture of individual C-C bonds of an alkane molecule is not equal either. An ω factor has been defined as the ratio of actual rupture and random rupture at a given C-C bond.^[54] Its calculation is strictly valid for the case of single hydrogenolysis only; still, ω values provide useful information when the value of ζ is between 2 and 3 by considering the amounts of the larger fragments, i.e., the products C₅, C₄, and C₃ from a C₆ feed and disregarding the slight C₁ and C₂ excess. Such a calculation was provided, e.g., for fragmentation of 2,2-dimethylbutane.[55] Multiple fragmentation can occur via a true disruption of the molecule during one sojourn on the catalyst (e.g., with Os, Ref. 53) or, alternatively, by subsequent end-demethylation (e.g., with Ni). A way of distinguishing between these cases is to calculate the relative amounts of higher than C1 fragments and methane. Their ratio, the so-called fission parameter [Mf], permits one to distinguish between terminal, multiple, or random hydrogenolysis.^[56, 57] Both factors were strongly dependent on the nature of the metal (Mf was

determined for Pt, Ir, Ni, Cu, Pd;^[49] ω for Pt, Pd, Ir, Rh^[58]). The increase of temperature on Ir/Al₂O₃ increased the ζ value from n-hexane; the dropping of Mf below unity indicated a true multiple splitting at 603 K.^[59] Decreasing H₂ pressures had the same effect. As for more detailed discussion of the suggested surface intermediates and proposed mechanisms of metal catalyzed reactions, the reader is referred to the literature.^[3]

3 CATALYSTS AND THEIR ACTIVE SITES

Platinum is the most important catalyst capable of catalyzing all types of hydrocarbon reactions mentioned. Metals of group VIII of the periodic system [except for Fe and Os], as well as Re and Cu, have been found to catalyze aromatization to at least a slight extent.^[13] Hydrogenolysis and bond shift isomerization seem to be an inherent property of several metals.^[60] On the other hand, C₅ cyclization and related isomerization of 3-methylpentane was found^[52] to be restricted to a few metals.—Pt, Pd, Ir, and Rh— concomitant with their propensity to catalyze single hydrogenolysis. All these catalysts form facecentered cubic crystals and their atomic diameters are not far from each other. Figure 1 shows the nondegradative and fragmentation activity of these metals in the reaction of 3-methylpentane and methylcyclopentane, demonstrating the



Figure 1 The ratio of activity of four metals in nondegradative reaction (isomerization of 3-methylpentane and ring opening of MCP) and in fragmentation as a function of their atomic diameter. (Adapted after Ref. 16.) superiority of Pt for the former class of processes. Theoretical calculations on the correlation between adsorption properties, surface reactivity, and inherent properties of metals have reached a stage where the theoretical information can be useful for explaining reactions on real-world catalysts and, in particular, for explaining the difference between various transition metals.^[61] Bond^[62] pointed out the possible role of relativistic effects in determining structure, bond strength, and other properties of different metals. The increased 'speed' of the core 1s electrons leads to the shrinking of these orbitals above atomic number of about 50 [Sn] and the outer *s* orbitals will also contract. This will affect the atomic diameters and also the reactivities of the valence electrons in forming and splitting surface bonds. This may have been one of the reasons for the differences of chemisorption and catalytic properties of the Os, Ir, Pt triad as opposed to the group VIII–X metals of lower atomic number. The differences between Pd and Pt (e.g., prevailing π or σ adsorption) can perhaps also be attributed to such effects. Fundamental studies in the fields of solid-state physics and materials science will certainly contribute to better understanding of the inherent catalytic properties of different metals.

Various skeletal reactions may require different active sites. Those reactions whose active intermediate forms more than one chemical bond with the surface require active centers consisting of more than one atom. One Pt atom is sufficient to dehydrogenate propane to propene,^[63] but aromatization requires ensembles with up to three Pt atoms.^[64] Active sites for C₅ cyclic isomerization consist of more surface metal atoms than those for bond shift isomerization.^[57] Under certain conditions, however, single-atom active sites may also be operative.^[65]

Although the material and pressure gap between surface science and realworld catalysis still exists, ^[66] single-crystal studies permit one to elucidate the possible role of surfaces of various geometries by artificially creating various crystal surfaces.^[67] These results agree fairly well with the conclusions mentioned in the preceding paragraph: platinum crystal faces with sixfold (111) symmetry—where active ensembles of three atoms are abundant-exhibited an enhanced aromatization activity as compared with those with fourfold symmetry (100) planes. As a rule, single crystals with steps and corner sites were more active than flat planes.^[67,68] Much lower crystal plane sensitivity was observed in methylcyclopentane ring opening.^[69] two-atom ensembles can be present on any crystal plane configuration. Iridium single-crystal surfaces were less active than corresponding Pt surfaces in cyclohexane dehydrogenation and n-heptane dehydrocyclization at low pressures.^[70] Both C-H and C-C breaking occurred more easily on Ir than on Pt, which can explain the higher activity of Ir.^[15, 52] Present-day developments of surface science—among others, scanning tunneling microscopy (STM), in situ infrared (IR) spectroscopy,^[71] and sum-frequency generation vibrational spectroscopy (SFG)^[72]______contributed to bridge the pressure and material gap. However, the model systems are less complex than those involved in naphtha-reforming reactions, such as CO adsorption and oxidation^[71] or hydrogenation—dehydrogenation reactions.[[] ⁷²] The most relevant result revealed so far is the role of both 1,3- and 1,4cyclohexadiene in both hydrogenation and dehydrogenation of cyclohexane.^[72,73]

The catalytic properties of various single-crystal planes have been compared directly with those of Pt/Al_2O_3 catalysts with various metal loadings and different crystallite sizes.^[74,75] The importance of the so-called B₅ sites containing five atoms along a step,