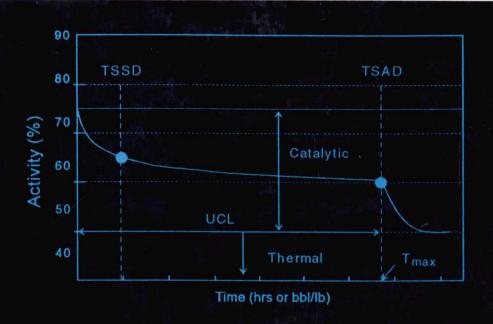
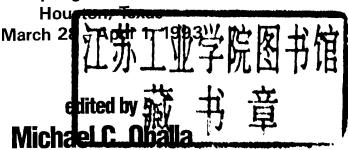
CATALYTIC HYDROPROCESSING OF PETROLEUM AND DISTILLATES



edited by Michael C. Oballa Stuart S. Shih

CATALYTIC HYDROPROCESSING OF PETROLEUM AND DISTILLATES

Based on the Proceedings of the AIChE Spring National Meeting,



Novacor Research and Technology Corporation Calgary, Alberta, Canada

Stuart S. Shih

Mobil Research and Development Corporation Paulsboro, New Jersey

Library of Congress Cataloging-in-Publication Data

National Meeting of AIChE (1993: Houston, Tex.)

Catalytic hydroprocessing of petroleum and distillates: proceedings of the AIChE Spring National Meeting, Houston, Texas, March 28-April 1, 1993 / edited by Michael C. Oballa and Stuart S. Shih.

p. cm. -- (Chemical industries; v. 58) Includes bibliographical references and indexes. ISBN 0-8247-9255-6 (acid-free)

1. Catalytic cracking--Congresses. 2. Hydrotreating catalysts--Congresses. I. Oballa, Michael C. II. Shih, Stuart S. III. Title. IV. Series.

TP690.4.N38 1993 665.5'33--dc20

94-12079

CIP

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

This book is printed on acid-free paper.

Copyright © 1994 by MARCEL DEKKER, INC. All Rights Reserved.

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

MARCEL DEKKER, INC. 270 Madison Avenue, New York, New York 10016

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

PRINTED IN THE UNITED STATES OF AMERICA

CATALYTIC HYDROPROCESSING OF PETROLEUM AND DISTILLATES

Preface

The era of refineries that process only light oils is almost over. There is a strong push for the processing of heavy oils, bitumen and/or residue, which in commercial jargon are combined and termed "bottom-of-the-barrel." The processing of "bottom-of-the-barrel" carries with it some problems. These are connected with obtaining state-of-the-art technologies at reasonable capital and operating costs to the refiner. Then there are problems associated with choosing the best catalyst—one specially designed to lower considerably the high content of heteroatoms (S, N, O) and metals (V, Ni, Fe) in the "bottom-of-the-barrel." The effective life of such catalysts becomes a factor to be reckoned with, especially when the economics of the various processes is being looked at. Recent regulations on the content of aromatics and sulfur in diesel fuels, as well as environmental concerns on SO_x and NO_x emissions from mobile and stationary combustion facilities, have made it imperative for engineers and scientists to think of ways to economically process middle distillates to meet new product specifications or more stringent emission regulations.

To address the above consideration, we organized a symposium at the AIChE Spring National Meeting in Houston, March 28–April 1, 1993. Engineers and scientists working in the processing of petroleum and distillates from different parts of the world presented papers covering different facets of residue upgrading and distillate hydrotreating. We thank the Fuels and Petrochemicals Division of the American Institute of Chemical Engineers for sponsoring this symposium. This book is a compilation of most of the papers presented in the five sessions of the symposium. We have broadly classified the papers in terms of content into the following four categories:

- a) Catalyst Deactivation
- b) Upgrading of Heavy Oils and Residue
- c) Hydrotreating of Distillates
- d) General Papers

We would like to thank all the people who contributed to make the publication of this book possible, including the authors, speakers and various organizations

iv Preface

that provided the necessary support. We give special thanks to the authors for preparing the manuscripts in the requested form and of such high quality that little editorial work was necessary.

We also express our appreciation to Professor Carle H. Bartholomew, who, as an invited guest speaker at the symposium, agreed to prepare a review paper on Catalyst Deactivation for this publication. Finally, the secretarial help of Ms. Karen Armellino and Ms. Kerri Dauphinee of Novacor Research & Technology Corporation is gratefully acknowledged.

Michael C. Oballa Stuart S. Shih

Contributors

- M. Absi-Halabi Petroleum Technology Department, Kuwait Institute for Scientific Research, Safat, Kuwait
- **H.** Al-Zaid Petroleum Technology Department, Kuwait Institute for Scientific Research, Safat, Kuwait
- C. H. Bartholomew Department of Chemical Engineering, Brigham Young University, Provo, Utah

Chakib Bennouna Laboratoire de Chimie Organique Appliquée, Faculté des Sciences, Université Cadi Ayyad, Marrakech, Morocco

Abdennaji Benyamna Laboratoire de Chimie Organique Appliquée, Faculté des Sciences, Université Cadi Ayyad, Marrakech, Morocco

J. S. Brinen CYTEC Research and Development, CYTEC Industries, A Business Unit of American Cyanamid Company, Stamford, Connecticut

x Contributors

- Ph. Caillette Institut Français du Pétrole, Rueil-Malmaison, France
- C. N. Campbell Texaco Research and Development, Port Arthur, Texas
- J. D. Carruthers CYTEC Research and Development, CYTEC Industries, A Business Unit of American Cyanamid Company, Stamford, Connecticut
- G. A. Clausen Texaco Research and Development, Port Arthur, Texas
- Barry H. Cooper Haldor Topsøe A/S, Nymøllevej, Lyngby, Denmark
- E. P. Dai Texaco Research and Development, Port Arthur, Texas
- J.-C. Duchet Laboratoire Catalyse et Spectrochimie, Université de Caen, France
- Patrick Geneste Laboratoire de Chimie Organique Physique et Cinétique Chimique Appliquées, Ecole Nationale Supérieure de Chimie, Montpellier, France
- G. Germaine Shell Recherche SA, CRGC, Grand-Couronne, France
- M. Gjers Shell Raffinaderi AB, Gothenburg, Sweden
- S. Greenhouse CYTEC Research and Development, CYTEC Industries, A Business Unit of American Cyanamid Company, Stamford, Connecticut
- Teh C. Ho Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey
- J. R. Huang Texaco Research and Development, Port Arthur, Texas
- S. Kasztelan Institut Français du Pétrole, Rueil-Malmaison, France
- Z. Khan Petroleum Technology Department, Kuwait Institute for Scientific Research, Safat, Kuwait
- M. T. Klein Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware
- Peter Kokayeff Unocal Science and Technology Division, Brea, California
- D. A. Komar CYTEC Research and Development, CYTEC Industries, A Business Unit of American Cyanamid Company, Stamford, Connecticut
- S. C. Korré Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware

Contributors

Klaus Kretschmar VEBA OEL Technologie und Automatisierung GmbH, Gelsenkirchen, Germany

Andrzej Krzywicki Novacor Research and Technology Corporation, Calgary, Alberta, Canada

- **R. N. Landau** Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware
- J. Leglise Laboratoire Catalyse et Spectrochimie, Université de Caen, France

Leszek Lewkowicz Alberta Research Council, Edmonton, Alberta, Canada

- **J. P. Lucien** Companie Rhenane de Raffinage Reichstett, Reichstett Vandenheim, France
- N. Marchal Institut Français du Pétrole, Rueil-Malmaison, France
- V. K. Mathur Department of Chemical Engineering, University of New Hampshire, Durham, New Hampshire
- S. Mignard Institut Français du Pétrole, Rueil-Malmaison, Françe
- A. R. Mohamed Department of Chemical Engineering, University of New Hampshire, Durham, New Hampshire

Claude Moreau Laboratoire de Chimie Organique Physique et Cinétique Chimique Appliquées, Ecole Nationale Supérieure de Chimie, Montpellier, France

James Mudra Texaco Research and Development, Port Arthur. Texas

- M. Neurock[†] Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware
- F. T. Ng Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada
- Tuan A. Nguyen Unocal Fred L. Hartley Research Center, Brea, California

Peter Nielsen-Hannerup Haldor Topsøe A/S, Nymøllevej, Lyngby, Denmark

G. Nongbri Texaco Research and Development, Port Arthur, Texas

^{*}Current affiliation: Merck Chemical Manufacturing Division, Rahway, New Jersey

^{*}Current affiliation: Schuit Institute of Catalysis, Technical University of Eindhoven, Eindhoven, The Netherlands

xii Contributors

Michael C. Oballa Novacor Research and Technology Corporation, Calgary, Alberta, Canada

- C. A. Paul Texaco Research and Development, Port Arthur, Texas
- R. J. Quann Mobil Research and Development Corporation, Paulsboro, New Jersey
- R. T. Rintjema Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada
- A. I. Rodarte Texaco Research and Development, Port Arthur, Texas
- M. A. Salahuddin Department of Chemical Engineering, University of New Hampshire, Durham, New Hampshire
- D. E. Self Texaco Research and Development, Port Arthur, Texas
- Stuart S. Shih Mobil Research and Development Corporation, Paulsboro, New Jersey
- Milan Skripek Unocal Fred L. Hartley Research Center, Brea, California
- **Kevin J. Smith** Department of Chemical Engineering, University of British Columbia, Vancouver, British Columbia, Canada
- Peter Søgaard-Andersen Haldor Topsøe A/S, Nymøllevej, Lyngby, Denmark
- A. Stanislaus Petroleum Technology Department, Kuwait Institute for Scientific Research, Safat, Kuwait
- G. L. B. Thielemans Shell International Petroleum Mij., The Hague, The Netherlands
- J. P. van den Berg Shell International Petroleum Mij., The Hague, The Netherlands
- J. van Gestel Laboratoire Catalyse et Spectrochimie, Université de Caen, France
- H. M. J. H. van Hooijdonk Shell International Petroleum Mij., The Hague, The Netherlands
- Fritz Wenzel VEBA OEL Technologie und Automatisierung GmbH, Gelsenkirchen, Germany
- Chi Wong Novacor Research and Technology Corporation, Calgary, Alberta, Canada
- Sok M. Yui Research Center, Syncrude Canada Ltd., Edmonton, Alberta, Canada

CHEMICAL INDUSTRIES

A Series of Reference Books and Textbooks

Consulting Editor

HEINZ HEINEMANN Berkeley, California

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

- 21. Catalysis and Surface Science: Developments in Chemicals from Methanol, Hydrotreating of Hydrocarbons, Catalyst Preparation, Monomers and Polymers, Photocatalysis and Photovoltaics, edited by Heinz Heinemann and Gabor A. Somorjai
- 22. Catalysis of Organic Reactions, edited by Robert L. Augustine 23. Modern Control Techniques for the Processing Industries, T. H.
- Tsai, J. W. Lane, and C. S. Lin

 24. Temperature-Programmed Reduction for Solid Materials
 Characterization, Alan Jones and Brian McNichol
- Catalytic Cracking: Catalysts, Chemistry, and Kinetics, Bohdan W.
 Wojciechowski and Avelino Corma
 Chemical Posstian and Posstar Engineering addited by J. J.
- 26. Chemical Reaction and Reactor Engineering, edited by J. J. Carberry and A. Varma
- Filtration: Principles and Practices: Second Edition, edited by Michael J. Matteson and Clyde Orr
 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
- Hydrogen Effects in Catalysis: Fundamentals and Practical Applications, edited by Zoltán Paál and P. G. Menon
 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 Naiim
- 39. Clathrate Hydrates of Natural Gases, E. Dendy Sloan, Jr.
- 40. Catalysis of Organic Reactions, edited by Dale W. Blackburn
 41. Fuel Science and Technology Handbook, edited by James G.
- Speight
 42. Octane-Enhancing Zeolitic FCC Catalysts, Julius Scherzer
- 43. Oxygen in Catalysis, Adam Bielański and Jerzy Haber
- 44. The Chemistry and Technology of Petroleum: Second Edition, Revised and Expanded, James G. Speight

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

ADDITIONAL VOLUMES IN PREPARATION

Lubricant Base Oil and Wax Processing, Avilino Sequeira, Jr.

Catalytic Naphtha Reforming: Science and Technology, edited by George J. Antos, A. M. Aitani, and J. M. Parera

Contents

Preface		iii
Co	Contributors	
CATALYST DEACTIVATION		
1.	Catalyst Deactivation in Hydrotreating of Residua: A Review C.H. Bartholomew	1
2.	Catalyst Deactivation in Residue Hydrocracking Michael C. Oballa, Chi Wong and Andrzej Krzywicki	33
UP	GRADING OF HEAVY OILS AND RESIDUE	
3.	Resid Hydrocracking: New Frontiers G. Nongbri, G.A. Clausen, J.R. Huang, D.E. Self, C.A. Paul and A.I. Rodarte	55
4.	Upgrading of a Moroccan Deasphalted Shale Oil over Mechanical Mixtures of Sulfided Cobalt–Molybdenum and Nickel–Molybdenum Alumina Supported Catalysts Claude Moreau, Abdennaji Benyamna, Chakib Bennouna and Patrick Geneste	71
5.	Rapid Hydropyrolysis of Resid Oil V.K. Mathur, M.A. Salahuddin and A.R. Mohamed	87
6.	Residue Upgrading by Hydrovisbreaking and Hydrotreating Stuart S. Shih	111
7.	Mild Hydrocracking of Heavy Oils with Modified Alumina Based Catalysts E.P. Dai and C.N. Campbell	127

8.	Residuum Upgrading by High Pressure Slurry Phase Technology: Technical, Economic and Environmental Aspects Klaus Kretschmar and Fritz Wenzel	143			
9.	Fate of Asphaltenes During Hydroprocessing of Heavy Petroleum Residues A. Stanislaus, M. Absi-Halabi and Z. Khan	159			
10.	Catalyst Poisoning During Tar-Sands Bitumen Upgrading J.D. Carruthers, J.S. Brinen, D.A. Komar and S. Greenhouse	175			
11.	Comparison of Unimodal Versus Bimodal Pore Catalysts in Residues Hydrotreating M. Absi-Halabi, A. Stanislaus and H. Al-Zaid	203			
12.	A Study of Aluminophosphate Supported Ni-Mo Catalysts for Hydrocracking Bitumen Kevin J. Smith, Lezek Lewkowicz, Mike C. Oballa and Andrzej Krzywicki	219			
HY	HYDROTREATING OF DISTILLATES				
13.	Two-Stage Hydrotreating of a Bitumen-Derived Middle Distillate to Produce Diesel and Jet Fuels, and Kinetics of Aromatics Hydrogenation Sok M. Yui	235			
14.	Aromatics Saturation Over Hydrotreating Catalysts: Reactivity and Susceptibility to Poisons Peter Kokayeff	253			
15.	Production of Swedish Class I Diesel Using Dual-Stage Process Barry H. Cooper, Peter Søgaard-Andersen and Peter Nielsen-Hannerup	279			
16.	Shell Middle Distillate Hydrogenation Process J.P. Lucien, J.P. van den Berg, G. Germaine, H.M.J.H. van Hooijdonk, M. Gjers and G.L.B. Thielemans	291			
17.	A Comparative Study of Catalysts for the Deep Aromatic Reduction in Hydrotreated Gas Oil N. Marchal, S. Kasztelan and S. Mignard	315			

Contents		vii
18.	Unionfining: Technical Case Studies Tuan A. Nguyen and Milan Skripek	329
19.	Effect of H ₂ S on the Functionalities of a CoMo/Al ₂ O ₃ Hydrotreating Catalyst J. van Gestel, J. Leglise and JC. Duchet	357
GE	NERAL PAPERS	
20.	New Hydroprocessing Catalysts Prepared from Molecular Complexes Teh C. Ho	373
21.	Fluidized Catalytic Cracking of Hydrotreated Charge Stock for Naphtha Sulfur Reduction James Mudra	401
22.	Hydrocracking Phenanthrene and 1-Methyl Naphthalene: Development of Linear Free Energy Relationships R.N. Landau, S.C. Korré, M. Neurock, M.T. Klein and R.J. Quann	421
23.	A Novel Process for Upgrading Heavy Oil Emulsions F.T.T. Ng and R.T. Rintjema	433
24.	Hydroconversion of Methyl-Cyclohexane on a Bifunctional Catalyst S. Mignard, Ph. Caillette and N. Marchal	447
Author Index		459
Subject Index		461

1 Catalyst Deactivation in Hydrotreating of Residua: A Review

C. H. Bartholomew

Department of Chemical Engineering Brigham Young University Provo, Utah 84602

INTRODUCTION

Hydrotreating, the catalytic conversion and removal of organic sulfur, nitrogen, oxygen and metals from petroleum crudes at high hydrogen pressures and accompanied by hydrogenation of unsaturates and cracking of petroleum feedstocks to lower molecular hydrocarbons plays an ever increasing key role in the refinery. Indeed, hydrotreating capacity has been growing steadily (at about 6% per year since 1976) and represents today nearly 50% of the total refining capacity (1). The increased application of hydrotreating can be ascribed to (i) the ever decreasing availability of light, sweet crudes and thus the increasing fraction of heavy, sour crudes that must be processed and (ii) the trend to increase upgrading of feedstocks for improvement of downstream processing such as catalytic reforming and catalytic cracking.