Petroleum-Derived Carbons

EDITED BY
John D. Bacha,
John W. Newman,
and J. L. White

ACS SYMPOSIUM SERIES **303**

Petroleum-Derived Carbons

John D. Bacha, EDITOR
Chevron Research Company

John W. Newman, EDITOR
Ashland Petroleum Company

J. L. White, EDITOR
The Aerospace Corporation

American Chemical Society, Washington, DC 1986

Library of Congress Cataloging-in-Publication Data

Petroleum-derived carbons.
(ACS symposium series; 303)

Includes bibliographies and indexes.

1. Carbon—Congresses. 2. Petroleum coke—Congresses. 3. Carbon black—Congresses.

I. Bacha, John D., 1921- . II. Newman, John W., 1937- . III. White, J. L., 1925- . IV. American Chemical Society. V. Series.

TP245.C4P43 1986 661'.0681 86-7894
ISBN 0-8412-0964-2

Copyright © 1986

American Chemical Society

All Rights Reserved. The appearance of the code at the bottom of the first page of each chapter in this volume indicates the copyright owner's consent that reprographic copies of the chapter may be made for personal or internal use or for the personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay the stated per copy fee through the Copyright Clearance Center, Inc., 27 Congress Street, Salem, MA 01970, for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to copying or transmission by any means—graphic or electronic—for any other purpose, such as for general distribution, for advertising or promotional purposes, for creating a new collective work, for resale, or for information storage and retrieval systems. The copying fee for each chapter is indicated in the code at the bottom of the first page of the chapter.

The citation of trade names and/or names of manufacturers in this publication is not to be construed as an endorsement or as approval by ACS of the commercial products or services referenced herein; nor should the mere reference herein to any drawing, specification, chemical process, or other data be regarded as a license or as a conveyance of any right or permission, to the holder, reader, or any other person or corporation, to manufacture, reproduce, use, or sell any patented invention or copyrighted work that may in any way be related thereto. Registered names, trademarks, etc., used in this publication, even without specific indication thereof, are not to be considered unprotected by law.

PRINTED IN THE UNITED STATES OF AMERICA

ACS Symposium Series

M. Joan Comstock, *Series Editor*

Advisory Board

FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

PREFACE

THE ECONOMIC CRISIS of the early 1970s upset petroleum supply and price patterns throughout the world and led to an uncertain outlook for carbon precursor development. Nevertheless, promising concepts were emerging for a wider range of carbon products, including the idea that the "bottom-of-the-barrel" petroleum residues should not be viewed as a disposal problem but as a valuable source of heavy molecular species.

In 1975 the American Chemical Society (ACS) sponsored the first symposium on petroleum-derived carbons as part of the 169th National Meeting. This first symposium was organized by M. L. Deviney and T. M. O'Grady; the strong favorable response of the participants led these cochairmen to edit the papers for publication in the ACS Symposium Series. This volume (*1*) has become a standard reference work for carbon scientists and organizations with vested interests in the refining of petroleum precursors, the fabrication of carbon and graphitic materials, and the use of carbon and graphitic materials in our increasingly high-technological environment.

Since 1975, the increased intensity of research on carbon materials and precursors has been evidenced by the growth of various conferences on carbon, including those conducted biennially by the American Carbon Society (*2–6*) as well as the international conferences in Europe (*7–11*) and Japan (*12*). The number of published abstracts on carbon materials nearly doubled from the 12th American Conference (1975) to the 16th Conference (1983). Furthermore, new patterns of petroleum supply have formed a more stable basis for carbon precursor development and thus foster an optimistic outlook for the development of high-technological carbon products.

A second symposium on petroleum-derived carbons was held as part of the 187th National ACS Meeting. The primary objectives were to discuss research progress since the first symposium and to appreciate the potential of the higher added-value carbon products that are or could be based on petroleum-derived precursors. By inviting selected speakers, we sought to cover most topics of interest to the petroleum industry, and the papers included in this volume fall into five general categories:

- Chemistry and industrial processing of carbon precursors
- Chemical and plastic behavior of the carbonaceous mesophase, which is the liquid crystalline phase where the microstructure of coke and many other carbon products is established
- Petroleum coke and coking processes

- Carbon products ranging from conventional materials, such as electrodes for the aluminum and steel industries, to new high-technological applications, such as biomedical implants
- Carbon fibers and carbon–carbon composite materials

The topic of graphitic intercalation compounds was intentionally omitted because intercalation science has become a major field, encompassing disciplines beyond those conventionally associated with petroleum chemistry.

Thirty papers were presented at the 1984 symposium. Speakers were free to develop their topics, but encouraged to focus on their own work and to provide full reference lists for readers who wish to pursue particular topics in further depth. The twenty-five papers appearing in this volume were completed after the symposium so that authors could write with the benefits of the questions and discussions at the symposium. One paper entitled "Feedstocks for Carbon Black, Needle Coke, and Electrode Pitch," was published elsewhere, and readers are referred to that publication (*13*) for an analysis of market trends and an outlook for heavy aromatic oil supplies. Two other papers were also published elsewhere, and these appeared substantially in the same form as in the symposium preprints (*14, 15*).

We believe that three factors contributed to the success these symposia have achieved. The first factor is the growing recognition that the high-carbon "bottom-of-the-barrel" residues offer enormous potential for higher added-value carbon products. The second factor is the general appreciation that success in the development of carbon products depends on improved understanding of carbonization chemistry. These views are certainly well justified by the development of such products as high-modulus carbon fibers spun from refined petroleum (or coal-tar) pitches.

The third factor was the attendance of nine well-known carbon scientists from Europe and Japan in the 1984 symposium. Support for their attendance was obtained by a grant from The Petroleum Research Fund supplemented by contributions from the following industrial sponsors: Aluminum Company of America, Ashland Petroleum Company, Arco Petroleum Products Company, Exxon Research & Development Laboratories, GA Technologies Inc., Gulf Canada, Ltd., Gulf Research & Development Company, Koppers Company, Inc., Mobil Oil Corporation, The Standard Oil Company (Ohio), and UOP, Inc.

The active participation by European and Japanese scientists contributed to the scientific quality of the symposium and provided an international perspective that will be increasingly significant to future carbon technology. We were particularly impressed by the vigor of Japanese research and development on carbon materials in the absence of stimulus by large aerospace and defense industries. Reflecting the dedicated activity of many workers, the Japanese effort also seems to result from clear recognition by government and industry of the important role of carbon products in future technology.

In addition to the foregoing industrial sponsors, we also wish to thank the reviewers of the papers. Although they must remain anonymous, we wish to join a number of authors in expressing gratitude for their contributions by careful review, constructive criticism, and good questioning. Finally we thank our respective organizations for the opportunity to undertake the duties of symposium cochairmen as well as coeditors of the present volume.

JOHN D. BACHA
Chevron Research Company
Richmond, CA 94802

JOHN W. NEWMAN
Ashland Petroleum Company
Ashland, KY 41114

J. L. WHITE
The Aerospace Corporation
Los Angeles, CA 90009

Literature Cited

1. *Petroleum-Derived Carbons;* Deviney, M. L.; O'Grady, T. M., Eds.; ACS Symposium Series 21; American Chemical Society: Washington, DC, 1976.
2. Extended Abstracts, 12th Conference on Carbon, Pittsburgh, PA; American Carbon Society, 1975.
3. Extended Abstracts, 13th Conference on Carbon, Irvine, CA; American Carbon Society, 1977.
4. Extended Abstracts, 14th Conference on Carbon, University Park, PA, American Carbon Society, 1979.
5. Extended Abstracts, 15th Conference on Carbon, Philadelphia, PA; American Carbon Society, 1981.
6. Extended Abstracts, 16th Conference on Carbon, San Diego, CA; American Carbon Society, 1983.
7. Preprints, Carbon '76, Baden-Baden, Federal Republic of Germany; Deutsche Keramische Gesellschaft, 1976.
8. Proceedings, 5th London International Carbon and Graphite Conference; London, England, 1978.
9. Preprints, Carbon '80, Baden-Baden, Federal Republic of Germany; Deutsche Keramische Gesellschaft, 1980.
10. Proceedings, 6th London International Carbon and Graphite Conference; London, England, 1982.

11. Extended Abstracts, Carbone '84, Bordeaux, France, 1984.
12. Extended Abstracts, International Symposium on Carbon, Toyohashi University; Carbon Society of Japan, 1982.
13. Stokes, C. A.; Guercio, V. J. *Erdöl und Kohle* **1985,** *38,* 31.
14. Riggs, D. M. In *Polymers for Fibers and Elastomers;* Arthur, Jett C., Jr., Ed.; ACS Symposium Series 260; American Chemical Society: Washington, DC, 1984; pp 245–262.
15. Janssen, H. R.; Leaman, Gordon L. *Oil & Gas J.* **1984,** June 25, 79–83.

August 1, 1985

CONTENTS

1

The Chemistry of Mesophase Formation

Harry Marsh and Carolyn S. Latham

Northern Carbon Research Laboratories, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England

The origins and development of the concept of carbonaceous mesophase, as derived from discotic aromatic nematic liquid crystals, enable applications to be made to industrial processes. The world availability of pitch materials is such that there is an abundance of pitch which produces cokes of little commercial value. A major incentive for research into the chemistry of mesophase formation is the commercial up-grading of such pitches and the development of specialized pitches. Structure in cokes is described in terms of optical texture. The importance of viscosity of pyrolyzing pitch in controlling size of optical texture is stressed. Pitch viscosity itself is related to chemical composition of the parent material. Those rich in oxygen and sulphur tend to produce cokes with small sized optical texture; those rich in hydrogen tend to produce cokes with large sized optical texture related to needle coke formation. Generally, cokes with small sized optical texture tend to have higher strength, higher reactivity and higher CTE values. Cokes with larger sized optical texture, e.g. needle cokes, have lower reactivity and CTE values. The important role of transferable hydrogen in carbonizing systems is stressed. Attention is drawn to the fact that inerts or quinoline-insoluble material in pitch may not be inert, but can be chemically and physically active in the carbonization system. Future research and development is outlined.

The carbonaceous mesophase is the intermediate material formed during carbonization of parent pitch and leading to the resultant coke. The discovery and development of the concept of mesophase over the last twenty years must represent one of the most significant advances in carbon science. Mesophase is a term borrowed from the science of conventional liquid crystals and means "intermediate phase". The term "carbonaceous mesophase" is distinguished from the term 'nematic

0097–6156/86/0303–0001$08.25/0

liquid crystal' the former being a polymerized liquid crystal system. Mesophase is composed of lamellar molecules the structures of which are based on the hexagonal network of carbon atoms of the graphite lattice. Currently, carbonaceous mesophases can be produced with a range of solubilities, in e.g. quinoline. The term 'mesophase pitch' with thermotropic properties has been introduced recently. Here the carbonaceous mesophase is formed by cooling the fluid isotropic pitch. Prior to the recognition of mesophase, the formation of anisotropic coke from a fluid phase was described in terms of a coking principle (1).

As early as 1944, Blayden, Gibson and Riley (2) looked for significant changes in structure between non-graphitizing and graphitizing carbons during the carbonization process, using X-ray diffraction techniques. Diffraction patterns were interpreted in terms of the concept that lamellar constituent molecules within the carbonizing system formed stacked units, called crystallites. Although the X-ray diffraction approach showed that essential differences existed between the mechanisms of formation of non-graphitizing and graphitizing carbons (definitions adopted from the study of Rosalind Franklin (3)), the method was not specific enough to be able to identify clearly "the coking principle". Wandless (4), in 1971, was anticipating the future quite clearly when he wrote that the basic strength of coke is determined in the plastic phase and the very early stages of resolidification.

Although Taylor (5) discussed the development of optical properties of anisotropic material formed during carbonization in 1961, and together with Brooks (6) reviewed the concept of liquid crystals as an intermediate to coke formation in 1968, it was not until well into the 1970's that the potential of this knowledge was realised.

The work of Brooks and Taylor led to a resurgence of research activity into the carbonization process with the advancement of knowledge leading to changes and developments within the carbon and graphite manufacturing industries. The tantalising prospect of cheap carbon fibres by spinning mesophase was one possibility, see Figure 1 (7). A window was opened into the mysteries of the delayed coker (8). The microstructure of carbon-carbon fibre composites using pitch carbon as the matrix material became better understood, see Figure 2 (9). Improved isotropic graphites of high density could be prepared by isostatic pressurised carbonizing techniques. The theory of coal co-carbonization processes was advanced considerably, and the use of pitch additives to up-grade effective coal rank was understood (10). Aspects of coke strength and physical properties e.g. the thermal expansivities of graphites were more fully understood. The role of quinoline insolubles (QI), both primary and secondary, in pitch carbonizations was explained, leading to the manufacture of prime needle cokes from coal-tar pitch (11, 12) by filtration of the QI material. A knowledge of the conditions of formation of mesophase from coal liquefaction products enabled a more precise control of operating conditions thus preventing, in this case, the retrogressive formation of mesophase and coke in pipe-work leading to plant closure (13). Improvements became possible in the manufacture of baked anodes for aluminium production as a knowledge of the structure of binder coke became available and the relationships between pitch properties and resultant cokes were further clarified. This in turn enabled pitch producers to begin to 'tailor-make' pitch materials relative to

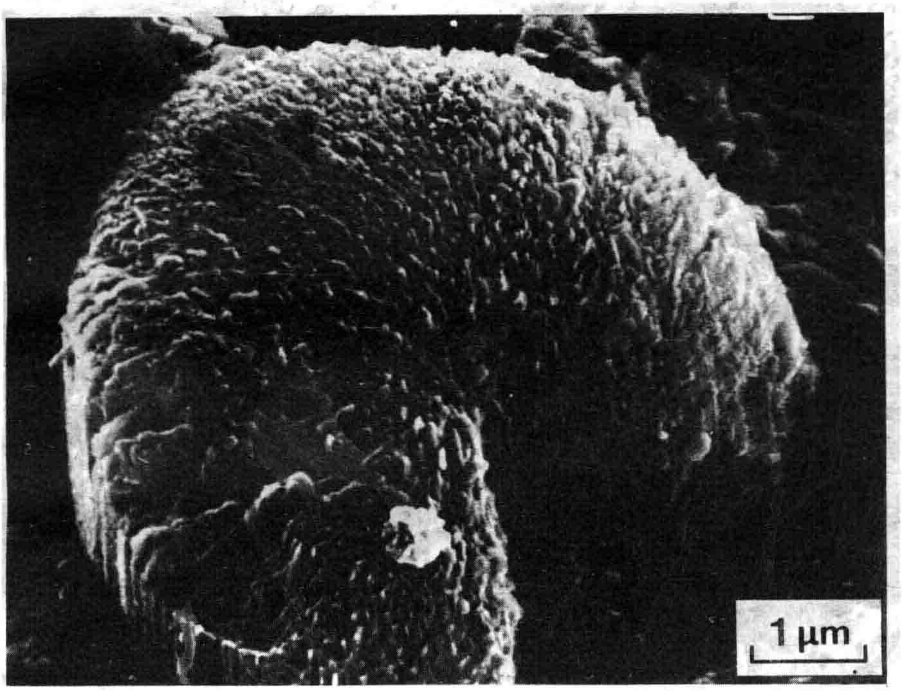

Figure 1. Scanning electron micrograph of fracture surface of a mesophase pitch carbon fiber etched with chromic acid to reveal the radial arrangement of constituent lamellar molecules.

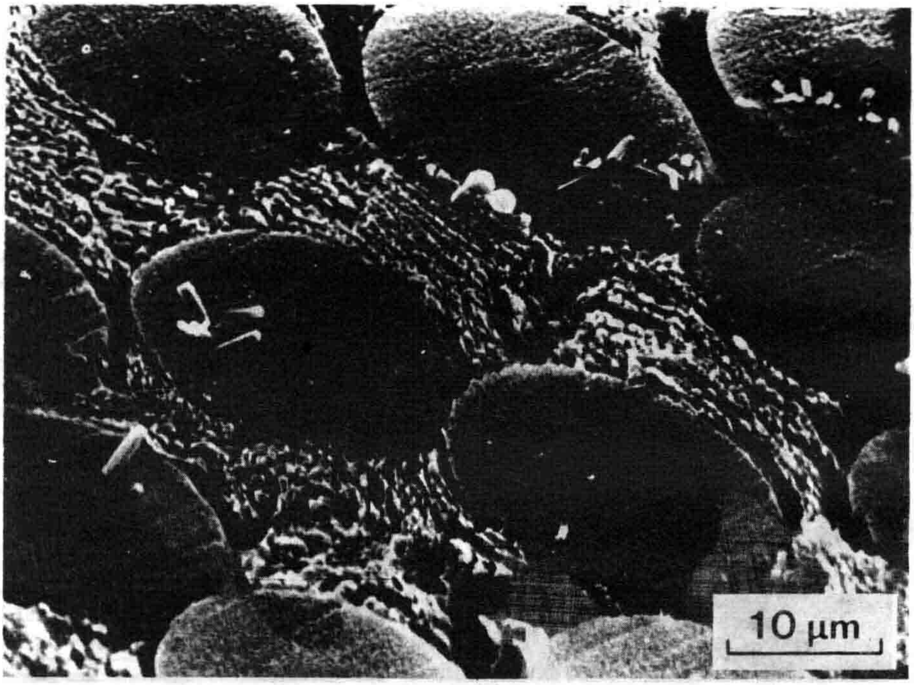

Figure 2. Scanning electron micrograph of a polished surface subsequently etched with chromic acid, of a carbon fiber-pitch carbon composite showing the orientation of a constituent lamellar molecules of pitch carbon parallel to surfaces of the carbon fiber.

a desired type of carbon product (14). Thus, the decade 1974-1984 has been one of intense interest and development of knowledge of many aspects of the conversion of pitch materials, with their various origins, to the structures of the many grades of cokes.

During this period, useful reviews were published. White (15) and Zimmer and White (16) describe the disclinations present in mesophase microstructures and their relation to coke properties. Lewis and Singer (17) overview the role and importance of stable free radicals in carbonization processes. Fitzer et al (18) provide a comprehensive description of the chemistry involved in the conversion of specific organic compounds to carbon. Marsh (19-23) and Forrest and Marsh (24) relate the chemistry of mesophase formation to its properties and applications. The journal CARBON published an issue devoted specially to studies of mesophase and its applications (25). The world availability of pitch materials is such that there is an abundance of pitch which produces cokes of little industrial value. A major incentive into research of mesophase is the commercial upgrading of such pitches.

Mesophase and Coke Structure

Petroleum and coal are the dominant parent sources of carbons, cokes and graphites. Apart from such exceptions as the carbonization of sucrose and related materials, the carbonization systems leading to graphitizable carbons (for definitions see Ref. 26) all pass through a fluid phase and all produce the liquid crystal/mesophase material. The cokes produced from such materials, e.g. filler coke, needle coke, shot coke, metallurgical coke and fluid coke, may not be distinguishable structurally in a meaningful way by X-ray diffraction. A powerful analytical tool in studies of coke structure is the polarized light optical microscope (16, 21) which, whether operating with cross-polarized light or making use of reflection interference colours (27, 28), very definitely categorizes carbons according to their optical texture. This optical texture is a measure of the size and coalescence behaviour of mesophase developing from the isotropic parent pitch and enables structure and orientation of lamellae within the mesophase to be established. A nomenclature (24) used to describe optical texture in cokes derived from petroleum and coal is in Table 1. The microscopic appearance of optical texture can be quantified in an arbitrary way (29) by making use of an optical texture index (OTI) calculated using the formula:-

$$\text{OTI} = \Sigma f_i \times (\text{OTI})_i$$

where: f_i = fraction of component of optical texture in the overall appearance of polished surfaces of the coke

$(\text{OTI})_i$ = an arbitrary (29) factor for each recognizable component of optical texture related to the relative sizes of the component as in Table 1. For example, for an isotropic carbon OTI = 0; for an anisotropic carbon composed entirely of domains, OTI = 30. All other anisotropic carbons have OTI values in the range 0-30 being summation of $(\text{OTI})_i$ values. Examples of optical textures are the micrographs of Figures 3-6.

There is a limitation to the use of optical microscopy in terms of its resolution. The correlation of anisotropy (optical activity) with graphitizability and of isotropy (zero optical activity) with

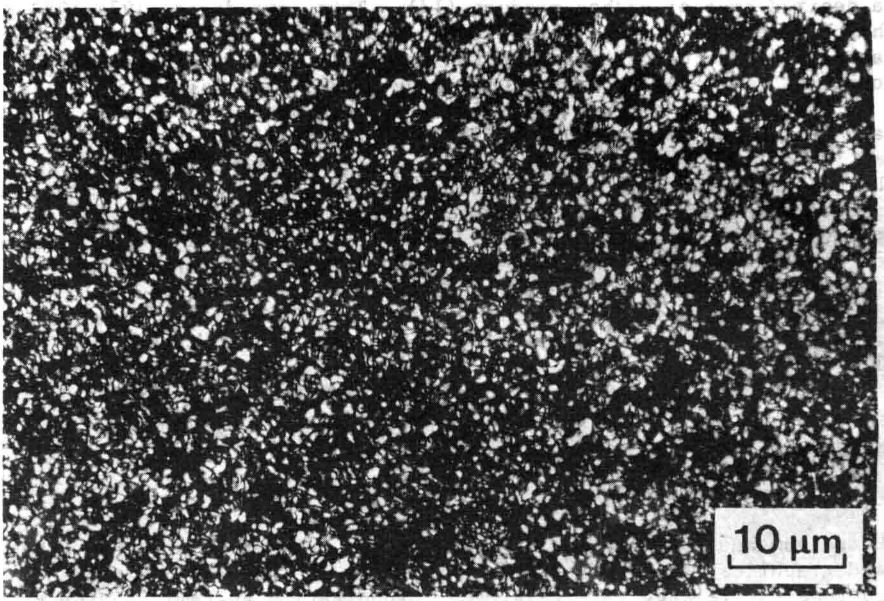

Figure 3. Optical micrograph of a coke surface showing an optical texture of fine-grained mosaics <1.5 µm diameter, OTI = 1.

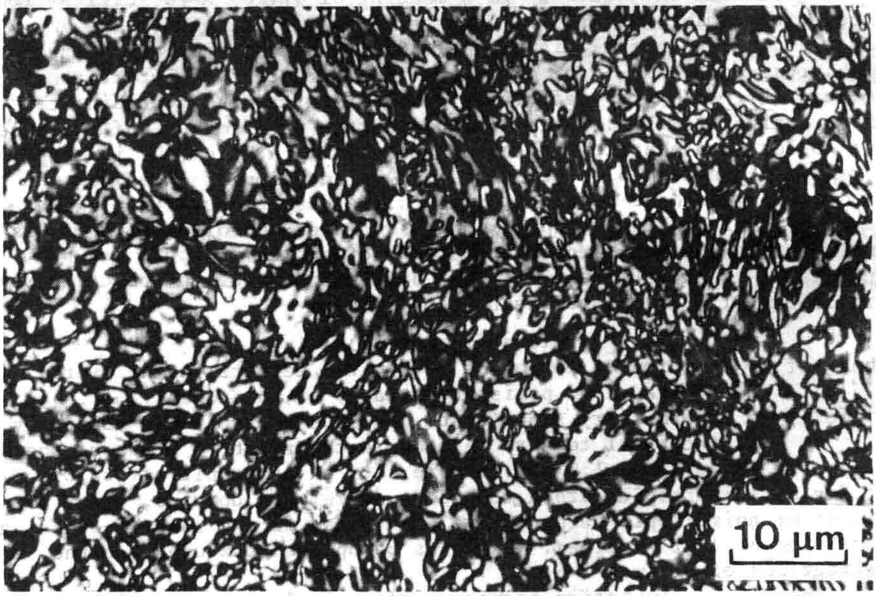

Figure 4. Optical micrograph of a coke surface showing an optical texture of medium-and coarse-grained mosaics, 1.5 - 10 µm diameter, OTI = 5.