# Coal Liquefaction Fundamentals

D. Duayne Whitehurst

ACS Symposium Series 139

# Coal Liquefaction Fundamentals

**D. Duayne Whitehurst**, EDITOR
*Mobil Research and Development Corporation*

[redacted]

Based on symposia sponsored
by the Division of Fuel Chemistry
at the ACS/CSJ Chemical Congress,
Honolulu, Hawaii, April 2–5, 1979
and at the 178th Meeting of the
American Chemical Society,
Washington, D.C.,
September 10–14, 1979.

ACS SYMPOSIUM SERIES **139**

AMERICAN CHEMICAL SOCIETY
WASHINGTON, D. C. 1980

Library of Congress CIP Data

Coal liquefaction fundamentals.
(ACS symposium series; 139 ISSN 0097-6156)

Includes bibliographies and index.

1. Coal liquefaction—Congresses.
I. Whitehurst, Darrell Duayne, 1938- . II. American Chemical Society. Division of Fuel Chemistry. III. ACS/CSJ Chemical Congress, Honolulu, 1979. IV. Series: American Chemical Society. ACS symposium series; 139.

TP352.C64 662'.6622 80-20585
ISBN 0-8412-0587-6 ACSMC8 139 1-411 1980

Copyright © 1980

American Chemical Society

All Rights Reserved. The appearance of the code at the bottom of the first page of each article in this volume indicates the copyright owner's consent that reprographic copies of the article 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. 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 new collective works, for resale, or for information storage and retrieval systems.

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.

PRINTED IN THE UNITED STATES OF AMERICA

# ACS Symposium Series

**M. Joan Comstock,** *Series Editor*

# 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 since symposia may embrace both types of presentation.

# PREFACE

This book is composed predominantly of a compilation of papers presented in two symposia of the Fuel Division of the American Chemical Society. These symposia were held originally at the joint ACS/CSJ Chemical Congress in Honolulu, Hawaii, session on coal liquefaction fundamentals, April 1979, and the 178th Meeting of the American Chemical Society, at the Storch Award Symposium in Washington, D.C., September 1979.

One purpose of the former symposium was to bring together scientists from different parts of the world to discuss their beliefs on the critical features of coals found in their countries that are relevant to liquefaction behavior. The first chapter provides an excellent general background on the biological and geological origin of coals from different parts of the world and the significance of this to liquefaction potential.

In the rest of this section, coal liquefaction researchers of the United States, South Africa, Australia, Japan, Canada, and Great Britain describe their country's coal reserves and origins, and the significance of coal composition to liquefaction behavior.

The second section of this volume describes several potentially new liquefaction processes which may have higher efficiencies than today's developing technologies. The theme of the Storch Award Symposium, featured throughout these six chapters, was new process potentials through the use of short-contact-time thermal processes followed by catalytic upgrading.

The mechanisms by which coal is converted to soluble or liquid form and the nature of the products of such reactions have been the subjects of a great deal of effort throughout the world. In the last two sections, researchers from Australia, Japan, South Africa, and the United States describe their findings in these areas. The reader will note that no unanimous agreement exists on the chemical mode by which coal is converted although kinetic descriptions are often similar.

This book is intended primarily for those who have some expertise in coal liquefaction but the first six chapters should be very valuable to persons just entering the field. The international flavor of the text is somewhat unique and will provide the readers with a feeling for goals and philosophies for coal liquefaction in various parts of the world.

D. DUAYNE WHITEHURST

Mobile Research and Development
Corporation
P.O. Box 1025
Princeton, NJ 08540

May 21, 1980

# CONTENTS

RELATIONSHIPS BETWEEN COAL COMPOSITIONS AND LIQUEFACTION BEHAVIOR

NOVEL LIQUEFACTION PROCESSES

COMPOSITIONAL CHANGE ON COAL CONVERSION

LIQUEFACTION MECHANISMS

# RELATIONSHIPS BETWEEN COAL COMPOSITIONS AND LIQUEFACTION BEHAVIOR

persons just entering the field. The international flavor of the text is somewhat unique and will provide the readers with a feeling for goals and philosophies for coal liquefaction in various parts of the world.

D. DUAYNE WHITEHURST

Mobil Research and Development
Corporation
P.O. Box 1025
Princeton, NJ 08540

May 21, 1980

# 1

# Some Proved and Unproved Effects of Coal Geochemistry on Liquefaction Behavior with Emphasis on U.S. Coals

P. H. GIVEN, W. SPACKMAN, A. DAVIS, and R. G. JENKINS

College of Earth and Mineral Sciences, The Pennsylvania State University,
University Park, PA 16802

## 1. Introductory Remarks on Coal Paleobotany, Geology and Geochemistry

The purpose of the collection of papers in this volume is to review what can be said about the susceptibility to liquefaction of coals from different parts of the world. We and later authors will present data relative to coals of the areas with which we are familiar. However, with the Editor's approval, we are going to devote the first part of this paper to making some general remarks about coal geology and geochemistry, in the hope that this will provide a useful background to what comes later.

### 1.1 Paleobotany of Coal Origins

On the evidence of coalified organs and tissues of the higher plants identifiable under the microscope in some coals (1), or petrified plan tissue found as "coal balls" in some coals (2), and on the basis of the pollen and spore content characteristic of coals, it is generally accepted that they are derived mostly from the organic matter of the higher plants, altered to a greater or lesser extent by microorganisms (3,4), and partly in some cases from the lower plants (algae).

The hydrologic, geologic and climatic conditions necessary for the formation of extensive coal measures are evidently rather specific, because the periods in geologic time in which major episodes of coal formation occurred were sporadic in any one geographic area (see Table I). Thus is many areas, there have been large gaps in time when no major coal measures were formed. Since the evolution of the plant kingdom proceeded continuously, whether or not coal measures were being laid down, the coals that formed after a gap in time were formed from plants quite different to those that gave rise to coals before the gap. Table II summarizes a few important events in the evolution of the plant kingdom.

0-8412-0587-6/80/47-139-003$08.00/0

Table I. Major Eras of Coal Formation

| | North America | Europe | Far East | Southern Hemisphere | in m. years B.P. approximately |
|---|---|---|---|---|---|
| Cenozoic | | | | | |
| Pliocene | + (Alaska) | + | — | — | 10 |
| Miocene | — | ++ | — | + (Australia) | 20 |
| Eocene | ++ | + | ++ | — | 45 |
| Mesozoic | | | | | |
| Cretaceous | ++ | — | ++ (Japan) | ++ | 100 |
| Jurassic | — | — | ++ | ++ (Australia) | 165 |
| Triassic | — | + | — | ++ (Australia) | 200 |
| Paleozoic | | | | | |
| Permian | — | — | — | ++ (All Gondwanaland) | 250 |
| Carboniferous | ++ | ++ | — | — | 310 |

++ coals very abundant   + abundant   — absent

Table II. An Outline of Plant Evolution

| Period | Approx. m. years before present | |
|---|---|---|
| Late Silurian | 400 | first appearance of lignified land plants |
| Carboniferous | 350-270 | large, diverse flora, of spore-dispersing plants, including ferns and slender trees with varying amounts of branching and leaf development |
| Permian | 270-225 | seed-fern flora (Glossopteris) flourishes all over Gondwanaland |
| Triassic & Jurassic | 225-180 | seed-bearing plants flourish with conifers and cycadophytes prominent |
| Cretaceous | 135- 70 | flowering plants evolved (Angiosperms) |
| Late Cretaceous | say 80 | essentially modern flora |

A comparison of Tables I and II shows that the major coal measures of the world were derived from several quite different floristic assemblages. Thus the plants that gave rise to coals in Europe and the east and midwest of North America in the Carboniferous were part of a complex flora that included ferns, seed ferns, horsetails, lycopods and conifer precursors. Except for the conifer precursors, lignified xylem tissues tended to be minimal in these plant groups and unusually large leaves with extensive waxy cuticles were characteristic of three of the groups. The abundant lycopods emphasized the development of a "corky" periderm or bark which, presumably, was formed of cell walls that were heavily impregnated with suberin as well as lignin. (Both cutin and suberin appear to be polymers of long chain hydroxy acids and dicarboxylic acids. Suberin is a waxy substance developed in the thickened cell walls characteristic of cork tissues.) Most of the plants were prolific spore-formers and generated large quantities of thick-walled microspores and megaspores whose waxy exines proved particularly resistant to decay and decomposition. Finally, the ratio of purely cellulosic cell walls to walls impregnated with lignin or suberin was much higher than at any subsequent time.

The term "Gondwanaland" in Table I refers to a once-existing supercontinent consisting of what are now known as Africa, South America, Antarctica, Australasia and India (5). The Permian coals of this supercontinent in the southern hemisphere were all formed under climatic conditions differing from those that prevailed in the northern hemisphere during the Carboniferous, with important consequences for the petrographic make-up of Gondwanaland coals (5). Also, these coals were formed from a less diverse flora than that described above, with a particular group of seed ferns and pre-conifers playing a conspicuous role in the vegetation. The seed habit began to affect the volume and type of spore production and the ratio of lignified to non-lignified tissues probably increased. Lycopods with their suberin-rich "barks" were no longer significant components of the swamp floras.

Little paleobotanic study has been made of the coal-forming plants of the Triassic and Jurassic in Australia and Africa, but in the rest of the world two plant groups ascended to positions of dominance. These were the conifers and the cycadophytes. The cycadophytes emphasized non-lignified parenchymatous tissue (i.e., containing living, protoplasmic cells) and large fern-like leaves with well developed waxy cuticles. The conifers emphasized the development of massive lignified stem and root cylinders with a significant amount of suberized periderm. Most of the plants in both groups were of arboreal habit, although the cycadophytes were often short and stocky, with much of their mechanical support as engineering structures being provided by heavily lignified leaf bases. All were seed producers, meaning that they no longer formed large quantities of the thick-walled megaspores that are so characteristic of many Carboniferous coal types.

The Angiosperms evolved in the Cretaceous, and from that period on the coals were formed from floras much like those we see today. In any period, the floral origin of the coals in one basin was not necessarily precisely the same as that of coals formed in other basins at the same time.

The above outline of the evolution of the plant kingdom during coal-forming eras has been presented largely in the language of botanical anatomy. However, the alert chemist will note that the anatomical differences imply considerable quantitative and spatial differences in the distribution of the principal plant constituents [cellulose, lignin, cutin, suberin and other waxes, contents of protoplasmic cells, pigments, resins, sporopollenin. The latter substance is thought to be the principal constituent of the outer layer (exine) of both spores and pollen grains; it is said to be a co-polymer of oxygenated carotenoid compounds with long-chain fatty acids (6,7)]. The differences may be qualitative also. It is a prime characteristic of the higher plants, as opposed to other types of organism, that they contain a wide variety of phenolic substances, of which lignin is only one (8,9). Other important phenolic constituents of plants include the hydrolyzable and condensed tannins (9) which as cell fillings are thought to give rise to the rather rare coal maceral, phlobaphenite (10). The structure and nature of these various phenolic substances differ considerably in plants that represent differing degrees of evolution (11,12,13,14). Thus the "paleo-biochemistry" of coal-forming plants in different periods and areas differed in several respects.

## 1.2 Metamorphism or Catagenesis

There are geologic processes by which a peat formed at the earth's surface becomes buried progressively more and more deeply, and it is chiefly exposure to the elevated temperatures experienced at depth that is responsible for converting peat into the coals of various ranks, the rank attained depending on the maximum temperature reached by a stratum (15,16). The mean temperature gradient in the earth's crust is 3°C/100 m, but there is wide variation about the mean. Also, the length of time during which deeper and deeper burial takes place, before uplift brings the stratum back towards the surface, is quite variable. Thus coals in different basins may reach the same apparent rank through materially different temperature/time histories (as, for example, in the Appalachian and midwest areas of the U.S.) (16). The metamorphism of coals no doubt involves a large number of parallel reactions, each having its own enthalpy and entropy of activation. Available methods of assigning a degree of metamorphism, or rank, to a coal are so crude that it is very likely that we shall describe two coals as of the same rank when, even if the starting materials were identical, a different mix of products results from coal A being formed at temperature $T_1$ during the time interval $t_1$, while coal B was formed at the lower temperature $T_2$ during the longer time $t_2$. For pure substances there is in kinetics a considerable degree of temperature/time compensation: for coals, this cannot be so, because of their complexity.

It is customary to treat the kinetics of processes altering coals by the classical methods of chemical kinetics, as if a coal were a single chemical substance, whether from the point of view of the geochemistry of metamorphism (17), or laboratory pyrolysis (e.g.18), or liquefaction (e.g.19). In a study of coal liquefaction mechanisms and kinetics, Szladow has strongly objected to such procedures, arguing that any valid kinetic analysis must start from the proposition that any chemical process of alteration of a coal consists of a large number of reactions proceeding in parallel, each with its own rate and temperature coefficient (20,21). Accordingly, he developed his own kinetic analysis of liquefaction, which showed, *inter alia*, that the apparent overall energy of activation of coal liquefaction must vary with the degree of conversion of the coal to liquids + gases. Surely similar considerations must apply to the complex of chemical reactions that represent metamorphism, or, as the low-temperature thermal alteration of organic matter is increasingly being termed, catagenesis (22).

The various aspects of coal origins briefly reviewed above already strongly suggest that a world view of the interrelationships of coal properties, and of the relation of coal characteristics to behavior in processes, is likely to show a great deal of dispersion. Very few authors have obtained data that confirm or deny this conclusion. Tribute should be paid to Mott (23), who, 37 years ago, showed that the moisture-holding capacity of some 2000 coals is dependent on geological antecedents as well as on rank.

### 1.3 Some Macerals and their Origins

Certain compositional differences between coals of differing origins can be inferred from available data. Differing anatomical distributions of cellulose, lignin and suberin, with implications for the origins of vitrinites, and differing distribution of phenolic substances in plants of different orders and families, have been referred to above. Some biochemical investigations of modern representatives of ancient plants have been made (e.g., refs. 14, 24), which display taxonomic variations in lignin structure, flavonoid types and sugar anabolism.

Most of the plants that flourished in the Carboniferous and Permian reproduced by means of spores. This was a rather inefficient mode of reproduction, so that large numbers of spores were produced as a fail-safe reproductive strategy. Later plants (conifers and flowering plants) reproduced more efficiently via seed production. This involves elimination of the development and dispersal of large quantities of thick-walled megaspores and the production of smaller quantities of, often, thinner-walled pollen grains as the equivalent of the more ancient microspores. Thus the coals formed in the Triassic and later typically contain considerably smaller concentrations of sporinite (or exinite) maceral than earlier coals, and in biochemical terms the contribution of sporopollenin was therefore much less. Since it is assumed that sporinite is a highly reactive maceral in liquefaction, this is significant.

So far as is known, all of the higher plants contain terpenoid hydrocarbons and oxygen-containing compounds that are commonly described as resins. These may have various biological functions, such as sealing of wounds in the stem by exudation of liquid terpenoids and oxidative polymerization to a solid resin. Resin ducts containing such materials did occur in the plants that gave rise to coals in the Carboniferous, but were much more abundant in the conifers that were the precursors of many coals in the Cretaceous. Thus the distribution of resinite macerals differs in coals originating in different eras. The study of Murchison (25) suggests materially different chemical characteristics of resinites of differing geological age. Fragmentary unpublished observations of our own indicate that resinites are highly reactive macerals in liquefaction.

Fusinite macerals are generally held to be inert in coking, and in liquefaction, as will be seen below. In the production of metallurgical coke, they do not become fluid on heating, and