

Chemical Structure and Liquefaction Reactivity of Coal

Volume 2: Moderate-Temperature Coal Liquefaction



Prepared by
Rockwell International Corporation
Canoga Park, California

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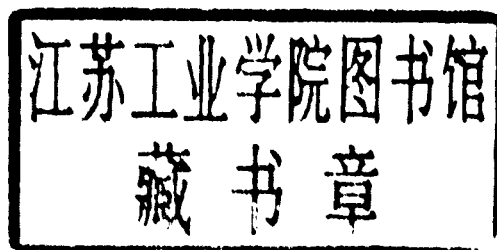
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R E P O R T S U M M A R Y

SUBJECTS Coal-derived liquids / Coal preparation and analysis

TOPICS	Coal structure	Coal conversion
	Subbituminous coal	Coal liquefaction
	Lignite	Coal preparation

AUDIENCE R&D scientists / Fuels engineers

Chemical Structure and Liquefaction Reactivity of Coal

Volumes 1 and 2

Characterizations of a Wyoming subbituminous coal and a Texas lignite have provided detailed data on the chemical structure of low-rank coals. This information will allow control and optimization of conversion and beneficiation processes. A parallel study with bituminous coal extends understanding of coal liquefaction at low temperatures.

BACKGROUND Conventional technologies for upgrading or converting coals do not take into account the chemical changes that occur during conversion or beneficiation processes. Thorough knowledge of a coal's structure would make it possible to manipulate its chemical behavior and to control and optimize these processes.

OBJECTIVES To determine the chemical composition and structure of several coals and to establish the relationship between coal structure and coal chemistry.

APPROACH Researchers characterized a Wyoming subbituminous coal and a Texas lignite in terms of aromatic clusters, linkages between clusters, oxygen-functional groups, and side chains on the clusters. Characterization tasks included controlled low-temperature solubilization of the coal, fractionation of the solubilized product according to cluster size, and analysis of the fractions. The research team then examined the reactivity of the coals to establish a relationship between their structural characteristics and their chemical behavior under conversion conditions.

Under a parallel effort, another research team investigated the low-temperature hydrogenation potential of bituminous coal. The researchers performed experimental studies without using an external solvent and at 300–350°C, which allowed selective bond-cleavage reactions. This approach avoided high-temperature retrogressive reactions and permitted a thorough investigation of hydrogenation mechanisms.

RESULTS Characterizations of the two low-rank coals, described in volume 1 of this report, show that they consist primarily (75%) of one- and two-ring aromatic and hydroaromatic clusters. The Texas lignite contained fewer large clusters

(four or more fused aromatic rings) than the subbituminous coal. Oxygen-functional groups and oxygen linkages, although different in distribution and arrangement in the two coals, are abundant in both and participate almost exclusively in the low-temperature dissolution reactions. The coal is solubilized in a well-defined manner: hydrolysis at 215°C, decarboxylation at 260°C, and another hydrolysis at 300°C.

In the low-temperature hydrogenation experiments described in volume 2, catalysis played a major role both in converting the coal and in making distillable products. Significant gas-phase hydrogenation occurred, giving oil yields ranging from 40–72%, maf (moisture ash-free) coal basis, whenever nickel catalyst was available.

EPRI PERSPECTIVE

This project determined the chemical structure and reactive nature of a Wyoming subbituminous coal and a Texas lignite. The extreme reactivity of these coals has drawn special attention to the reactions that occur at quite mild conditions. Beneficiation of low-rank coals must take into consideration the nature of these coals and the role oxygen-functional groups and oxygen linkages play during the beneficiation process. The scope of this project has been extended to the characterization of Illinois no. 6 coal (EPRI project RP8003-4).

The second part of this project demonstrated the importance of low-temperature gas-phase catalytic hydrogenation in conversion and beneficiation processes. Future work in hydroliquefaction should investigate in detail the chemistry that occurs at these conditions.

PROJECT

RP2147-4
EPRI Project Manager: Linda Atherton
Advanced Power Systems Division
Contractor: Rockwell International

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ABSTRACT

Coal hydrogenation experiments were conducted at 325°C and 3000 psi H₂ pressure. It was postulated that at this lower operating temperature more selective bond cleavage reactions will occur, promoting an efficient use of hydrogen and helping the identification of different hydrogenation and hydrocracking reactions. No donor solvent was used to simplify the analysis of the liquid products. Both catalytic and noncatalytic reactions were investigated. The following conclusions were reached:

- 1 Using a Pittsburgh seam coal (C = 82%), it was shown that the liner and impeller of the autoclave had a strong catalytic effect on the liquefaction reaction. The oil yield was 48% when the metallic surface was exposed and only 19% when these parts were replaced with a glass-coated liner and impeller.
- 2) Catalysis by nickel (applied as nickel acetate impregnated into the coal) gave significantly different results from those obtained when the uncoated liner and impeller catalyzed the reaction. Overall conversion to soluble products was higher using the nickel catalyst (94 versus 87%). However, nickel catalysis gave lower conversion to oil (40 versus 48%). The oil produced in the nickel-catalyzed hydrogenation was significantly more aliphatic in character (the aliphatic to aromatic ratio was 83/17 as compared with 74/26).
- 3) Comparing these tests with those made earlier with a lower rank coal (C = 80%), it was found that the latter was much more reactive and gave 50% higher oil yield than the higher rank coal (C = 82%). The oil yields were 72 and 48%, respectively.

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SUMMARY

Moderate temperature hydroliquefaction of two bituminous coals was explored to obtain information on the chemistry of liquefaction. Both catalytic and noncatalytic conditions were tested. No donor solvent was added to the feed coal to simplify product analysis and the evaluation of the results. The results and conclusions are summarized as follows:

1. Of the two bituminous coals tested, the lower rank coal (C = 80%) was much more reactive and gave 50% higher oil yield than the higher rank coal (C = 82%). The oil yields were 72 and 48%, respectively.
2. We showed in experiments made with the higher rank coal (C = 82%) that the Inconel and stainless steel components of the autoclave (liner and impeller) had a strong catalytic effect on the liquefaction reaction. The oil yield was reduced from 48 to 19% when the Inconel parts of the autoclave were replaced with a glass-coated liner and impeller.
3. Catalysis by nickel (applied as nickel acetate impregnated into the coal) gave significantly different results from those obtained in the Inconel-lined reactor. Overall conversion to soluble products was higher using the nickel catalyst (94 versus 87%). However, nickel catalysis gave lower conversion to oil (40 versus 48%).
4. The oil produced in the nickel-catalyzed hydrogenation was significantly more aliphatic in character than the product made by the catalytic effect of the Inconel/stainless steel autoclave components (the aliphatic to aromatic proton ratios were 83/17 and 74/26, respectively). Also, the nickel-catalyzed product had a much higher $\beta + \gamma/\alpha$ aliphatic proton ratio (55/29 versus 42/32). These data indicate that nickel catalysis strongly promoted hydrogenation of aromatic rings while the Inconel/stainless steel components more effectively catalyzed hydrocracking reactions, which result in oil formation.

Section 1

INTRODUCTION

An important basic research goal in coal liquefaction is to establish a well-defined correlation between coal structure, the reaction conditions of liquefaction, and the composition of the products. This goal has been very elusive because of the great complexity of the coal structure and the many side reactions that occur at the temperatures at which liquefaction takes place at commercially attractive rates. These side reactions include thermal fragmentation and condensation or polymerization of reactive intermediates, resulting in excessive gas and coke formation.

Further complications are caused by the practice that in most coal liquefaction processes a donor solvent vehicle is used. The use of solvent interferes with investigation of the reaction chemistry and characterization of the reaction products because the solvent forms adducts with the coal-derived intermediates, and because it is difficult separately to characterize the donor solvent and its dehydrogenation derivatives in the complex product mixture.

On the basis of these considerations, it appears that hydrogenation experiments conducted without using a solvent vehicle offer significant advantages in basic coal liquefaction investigations. This experimental technique has been extensively investigated and its usefulness has been well established (1). In this earlier investigation, however, all experiments were conducted at temperatures above 400°C where a number of side reactions leading to gas and coke formation are fast and take place indiscriminately.

The objective of this work is to explore this hydrogenation technique at a lower temperature where the side reactions are less extensive. At lower operating temperatures, in the range of 300 to 350°C, more selective bond cleavage reactions occur, which may make possible a more efficient use of costly hydrogen. Furthermore, selective bond cleavage helps the identification of different hydrogenation and hydrocracking reactions; this gives better insight into the mechanisms of liquefaction.

In a previous coal liquefaction research program (2) conducted at Rockwell, an exceptionally high oil yield (72%) was obtained by hydrogenating a bituminous coal without added donor solvent at 325°C and 3000 psig for 48 h in a stirred autoclave. Proton NMR analysis of this oil indicated that it contains high concentrations of hydroaromatic compounds, which are very effective hydrogen donor solvent components.

The objective of the present program were (1) to test the reproducibility of the initial moderate temperature liquefaction experiment carried out by Rockwell and (2) to determine to what extent the high conversion to oil in that experiment was catalyzed by the metal components (liner and impeller) of the autoclave. To achieve these objectives, first the initial experiment was repeated using a new sample of the same coal type and the same reaction parameters. Then, the liner and impeller were coated with glass to eliminate any potential catalytic effect and the experiment was repeated. In the final experiment, a different method of catalysis was tested using the glass-coated liner and impeller and 1% nickel (as nickel acetate) impregnated into the coal.

This report presents the results of the moderate temperature coal hydrogenation experiments. Section 1 provides an introduction to the work. Section 2 describes the materials, equipment, and experimental and analytical procedures used. Section 3 presents and discusses the results of the research. Section 4 gives a summary and the conclusions reached in this work.

Section 2

EXPERIMENTAL

2.1 Materials

Loveridge Mine, Pittsburgh seam coal was used. Elemental analysis of this coal indicates that it is 82.1% carbon, 5.9% hydrogen, 3.3% sulfur, 1.6% nitrogen, and 7.1% oxygen (maf basis). (The composition of the Loveridge Mine coal used in Experiment A was 80.1% carbon, 5.1% hydrogen, 3.6% sulfur, 1.6% nitrogen, and 9.6% oxygen.) The coal was ground to -200 U.S. mesh and dried at 115°C in a 40-torr (5.3 KPa) vacuum before use. High-purity hydrogen (99.99% according to the supplier's specifications) was obtained in 2200-psig (15.0 MPa) cylinders from Airco, Inc.

The benzene, hexane isomer mixture, and tetrahydrofuran (THF) solvents used for the solvent-fractionation were all Baker reagent grade. The CDCl_3 (99.8%) used for the NMR spectrometric analyses was obtained from the Aldrich Chemical Company, Inc., and was stored over molecular sieve.

2.2 Equipment

High-pressure hydrogenation experiments were conducted using the 1-liter, top-stirred Autoclave Engineers MagneDrive reaction vessel pictured in Figure 2-1. The autoclave was equipped with an anchor-type stirrer positioned very close to the autoclave liner walls. This stirring technique reduced the possibility of coal agglomeration during the early stages of the reaction, and assured effective contact between the reacting coal mass and the hydrogen gas. The coal was loaded into an Inconel liner inside the autoclave before the experiment. The liner was used to facilitate product recovery.

Product gases from the autoclave experiments were analyzed using a Hewlett-Packard Model 5840A gas chromatograph. This unit is equipped with Porapak N and molecular sieve 5A columns and a thermal conductivity detector.

2.3 Experimental Procedure

The 1-liter hydrogenation system was assembled with 25 g of coal in the liner. It is to be noted that no donor solvent was added to the coal. The use of a donor

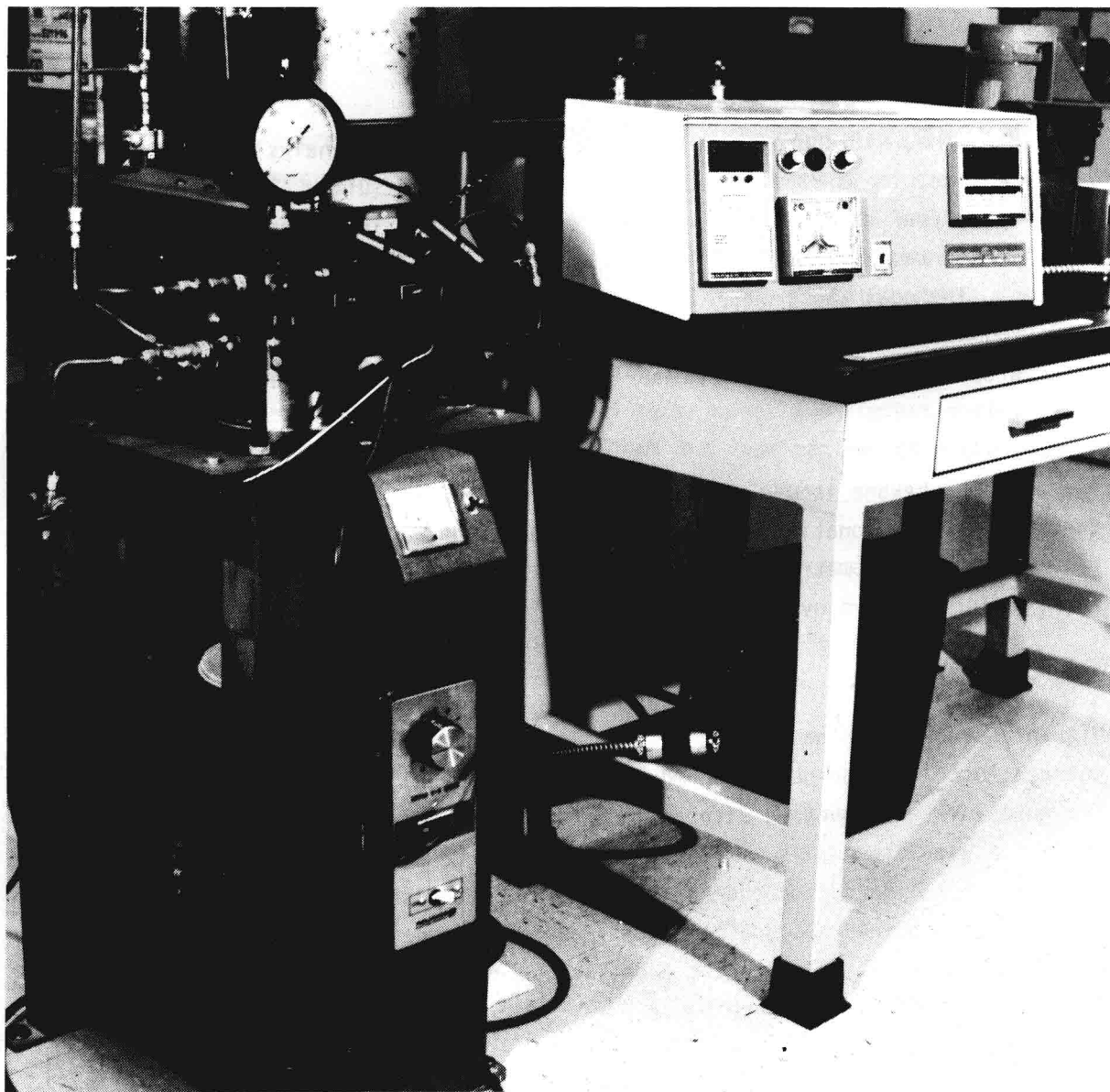


Figure 2-1. One-Liter Hydrogenation System

solvent complicates the investigation of reaction chemistry because the solvent forms adducts with the coal-derived intermediates; also, the donor solvent and its dehydrogenated derivatives are mixed with the coal products and this complicates the characterization of the coal liquids.

The system was leak-tested and then filled to 1425 psig with hydrogen. Agitation (100 rpm) and heating were begun. The contents of the autoclave were heated to 325°C, which required approximately 95 min. Temperature was maintained for 48 h. At the end of the reaction time, the power was turned off and the autoclave was allowed to cool to ambient temperature. The gas volume was then measured using a wet test meter, and product gas samples were taken for analysis. The system was then disassembled, and the liquid and solid products were collected.

2.4 Analytical Procedures

2.4.1 Product Gas Analysis

The product gases from the experiments were analyzed by gas-solid chromatography. The Poropak N column was held at 90°C for 1.65 min, the temperature was raised at the rate of 15°C/min to 145°C, and then held isothermally at 145°C until the C₃'s eluted. When the C₄'s and C₅'s were desired, the Poropak N was kept at 170°C to enable elution in a reasonable length of time. The molecular sieve 5A column was held at 125°C for 4.00 min, temperature raised at the rate of 15°C/min to 155°C, and then held isothermally until the C₆ eluted.

2.4.2 Solvent-Fractionation of the Hydrogenation Products

The combined solid and liquid products from each experiment were solvent-fractionated into the following four fractions:

- Benzene soluble, hexane soluble (oil)
- Benzene soluble, hexane insoluble (asphaltenes)
- THF soluble, benzene insoluble (preasphaltenes)
- THF insoluble (residue).

The procedure used to obtain this separation is outlined in Figure 2-2. It is based on the method recommended by the Pittsburgh Energy Technology Center (3). The benzene separation is carried out using a Soxhlet extraction apparatus. Separation of the oil and asphaltene fractions follows the recommended procedure except that the hexane isomer mixture is used instead of n-pentane. The THF separation is also conducted with a Soxhlet apparatus.

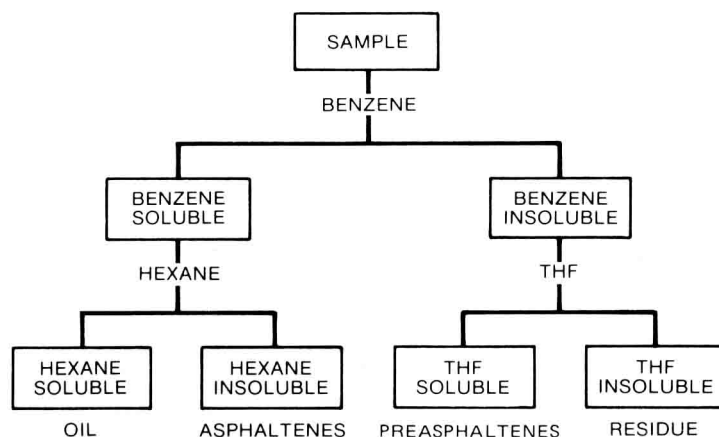


Figure 2-2. Solvent-Fractionation Scheme

2.4.3 Elemental Analysis

Oil fractions from each experiment and the distilled liquid from Experiment 1, as well as the reactant coal, were analyzed for carbon, hydrogen, nitrogen, oxygen, and sulfur. The analyses were conducted by Galbraith Analytical Laboratories, Inc., using a Perkin-Elmer Model 240 elemental analyzer. Approximately 2 mg of sample was used for each analysis. Ash content of the Loveridge Mine coal was determined on a 1-g sample in our laboratories.

2.4.4 Simulated Distillation

Simulated distillation analyses of the oil fractions from each experiment and the distilled liquid from Experiment 1 were conducted using a Varian 3700 gas chromatograph equipped with a flame ionization detector. A 6-ft glass column with a 2-mm ID was used. The column contained 80-100 mesh Supelcoport with a 3% OV-101 stationary phase. Temperature programming was carried out on each sample from 45 to 345°C at 10°C/min with no initial hold. These analyses were conducted by the IT Corporation.

2.4.5 Nuclear Magnetic Resonance (NMR) Spectrometry

Proton NMR spectra of the oil fractions from each experiment and the distilled liquid from Experiment 1 were obtained with a JEOL FX-60-Q Fourier transform NMR spectrometer using an observation frequency of 59.79 MHz. Spectra were recorded with an internal deuterium lock system. The NMR samples and reference were contained in 10-mm tubes, and the probe temperature was 30°C. A 45° pulse was utilized during multiple scan accumulation, which corresponds to 14 μ s. The pulse repetition time was 6.0 s. Spectra are referenced to tetramethylsilane at 0.0-ppm chemical shift (δ). Chloroform-d was used as the solvent. Spectra were