SEQUENTIAL LOW-TEMPERATURE DEPOLYMERIZATION
AND LIQUEFACTION OF U.S. COALS

Progress Report no. 6
(covering the period January 1 - March 31, 1988)

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PERSONNEL

Junior research personnel participating in this project during the reporting period were:

Mrs. Y. Zhang, graduate student

Mr. Rick White, graduate student

OBJECTIVES AND SCOPE OF THE RESEARCH PROJECT

One of the main objectives of this project is to investigate the low-temperature ($\leq 290^{\circ}\text{C}$) depolymerization-liquefaction reactions of representative U.S. coals, using a 3-step procedure recently developed in our Laboratory. The procedure involves subjecting the coal first to two consecutive depolymerization steps in which different types of intercluster linkages are subjected to preferential cleavage. The depolymerized products obtained have low molecular weights and consist predominantly of monocluster and bicluster compounds. In the third step of the procedure these simplified depolymerization products are subjected to hydroprocessing and attendant exhaustive hydrodeoxygenation to yield light liquid hydrocarbon mixtures as main products. It is planned under the research program to adapt and optimize the above indicated procedure for U.S. coals of different rank, and to examine the feasibility of the new processing concept for conversion of these coals into light liquid hydrocarbon fuels.

A second major objective of the research program is to subject the low-temperature depolymerization products (obtained by the first two consecutive steps) to exhaustive structural analysis for the purpose of deriving average structural models for the coals under investigation. Such models are expected to be useful as fingerprints for identification and differentiation of various representative U.S. coals.

PROJECT STATUS

During the January 1 - March 31, 1988 period, covered by the present report, research activities included (a) an extension of the systematic study of the depolymerization-liquefaction reactions of a Pittsburgh no. 8 (PA) coal sample (see Progress Report no. 4); and (b) derivation of an

average molecular structure for the oil fraction of the depolymerized product obtained from an Elkhorn (KY) coal (Progress Report no. 3).

RESULTS

1. Low-Temperature Depolymerization-Liquefaction of a Pittsburgh #8 (PA) Coal

Earlier results on the reactions of a Pittsburgh #8 (PA) coal sample, designated below as PB(PA) coal, were described in Progress Report no. 4.

Additional work on this coal was performed during the reporting period, as follows:

Mild Hydrotreatment (HT) Step

The study of the effect of FeCl_3 catalyst concentration upon the efficiency of the HT depolymerization step was extended. Low FeCl_3 concentrations, in particular in the range of 3.0 to 7.5 wt%, were investigated at four different HT temperatures (275, 290, 300, and 310°C). It was found that even at the lowest concentration employed (3.0 wt%) FeCl_3 is efficient at 290-310°C in causing extensive depolymerization (*viz.* cleavage of alkylene, e.g., methylene linkages) in the PB(PA) coal framework, as reflected by partial solubilization in THF (7-11 wt%) and attendant high degree of activation of the coal for the subsequent BCD step. The concentration of 3.0 wt% of FeCl_3 for PB(PA) coal hydrotreatment (HT) indicates that this inexpensive catalyst could be effectively used in very low concentrations for depolymerization of higher rank (low oxygen and hydrogen content) coals.

Base-Catalyzed Depolymerization (BCD) Step

Additional BCD experiments with the mildly hydrotreated PB(PA) coal, i.e., with the partially depolymerized coal product from the HT step, were

also performed. In particular, the effect of increased BCD temperature, above 290°C, upon product composition was determined. It was found (see Figure 1) that increase in BCD temperature from 290° to 310°C results in a slight increase in the overall yield of THF solubles. On the other hand, this temperature increase causes a major decrease in the yield of the desirable cyclohexane-soluble (oil) fraction and a corresponding increase in the yield of asphaltol and asphaltene products. This clearly indicates that BCD temperatures above 290°C cause undesirable changes in the composition of the final depolymerized product from PB(PA) coal. A similar result was previously found with Elkhorn (KY) coal as feed. It was ascribed to the occurrence of resynthesis reactions at BCD temperatures > 300°C, leading to higher molecular weight products (see Progress Report no. 3, pp 12-13).

2. Structural Studies of the Oil Fraction from Depolymerization of Elkhorn (KY) Coal

The predominant cyclohexane-soluble (oil) fraction from depolymerization of the Elkhorn (KY) coal, representing ca 63 wt% of the starting MAF coal (see Progress Report no. 4, p. 11, run no. 42) was subjected to detailed structural analysis, using the modified Brown-Ladner method described in Progress Report no. 4 (pp 16-23). As schematically indicated in Figure 2 the elemental composition, average molecular weight and quantitative C¹³ NMR and PMR data on the above oil fraction of the depolymerized (HT-BCD) product from Elkhorn (KY) coal were input into a structural analysis computer program in order to derive structural parameters and thereby an average molecular structure for the fraction.

Figure 3 shows the derived average molecular structure for the above oil fraction, obtained from Elkhorn (KY) coal by HT at 290°C, followed by BCD at 290°C. As seen, the average structure has a formula of

Figure 1. Change in the composition of THF-soluble products from HT-BCD of PB(PA) coal, as a function of BCD temperature.

Figure 2. General scheme for structural analysis of soluble products from HT-BCD of Elkhorn (KY) coal.

Parameter	Theoretical Values	Values calculated from experimental data
C atoms	20	19.3
H atoms	22	24.4
O atoms	2	1.73
N atoms	-	0.71
M.W.	294	288
f_a, C	0.60	0.50
f_a, H	0.18	0.18
f_o	0.41	0.39
f_o	0.41	0.43
Total rings (RT)	3	3.5
Aromatic rings (RA)	2	1.7
Naphthenic rings (RN)	1	1.8
Degree of polymerization (M)	2	2.3
Avg. side-chain length, C atoms	2	2.3

Fig. 3. Average molecular structure for the oil fraction obtained by depolymerization of EH(KY) coal.

$C_{19.3}H_{24.4}O_{1.73}N_{0.17}$. The derived structure consists of a monocyclic aromatic cluster and a bicyclic aromatic-hydroaromatic cluster linked by means of a furanic ring. Such furanic ring linkages have been found to be very resistant to hydrogenolysis or hydrolysis (alcoholysis) under the conditions of the HT and BCD steps, respectively. However, this type of linkages are easily cleaved under the conditions of the hydroprocessing (HPR) step of the procedure (T. Skulthai, Ph.D. Dissertation, University of Utah, 1987).

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