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

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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 October 1 - December 31, 1987 period, covered by the present report, a systematic study was performed on the low-temperature depolymerization and liquefaction of a Beulah-Zap (North Dakota) lignite. Following is a description of results obtained.

RESULTS

Low-Temperature Depolymerization-Liquefaction of a Beulah-Zap (North Dakota) Lignite

A Beulah-Zap (North Dakota) lignite sample, designated below as BZ(ND) lignite, was obtained from the Argonne National Laboratory premium coal program. This lignite had the following ultimate analysis (MAF basis) in wt.%: C, 71.05; H, 5.58; N, 1.17; S, 1.60; O (diff), 20.6. The ash content (dry basis) was 6.0 wt.%. As expected, the BZ(ND) lignite had a considerably higher oxygen content (-20.6%) in comparison with that of previously studied coals (Progress Reports nos. 1-4).

The BZ(ND) lignite was subjected to a previously developed stepwise depolymerization-liquefaction procedure [for details and recent applications see J. Shabtai and T. Skulthai, Proc. 1987 Internat. Confer. Coal Science, Elsevier, Amsterdam (J.A. Moulijn, K.A. Nater, and H.A.G. Chermin, Eds.), 1987, pp. 761-764; and J. Shabtai, T. Skulthai, and I. Saito, Am. Chem. Soc. Div. Fuel Chem. Prepr., 31 (4), 15-23 (1986)]. The procedure, as summarized in Figure 1, consists essentially of the following sequential steps: (1) intercalation of the coal sample with catalytic amounts (5 - 20 %) of FeCl_3 , followed by mild hydrotreatment (HT) of the coal- FeCl_3 intercalate; (2) base-catalyzed depolymerization (BCD) of the product from step 1, under super-critical conditions; and (3) hydroprocessing (HPR) of the depolymerized product from the two preceding steps, using a sulfided 6Co8Mo catalyst.

Following are the results obtained in processing the BZ(ND) lignite according to the above procedure:

^aHT = hydrotreatment (250 - 290°C; H₂ pressure, 1000 - 1500 psig)

^bBCD = base-catalyzed depolymerization (250 - 290°C; initial N₂ pressure, 1000 psig)

^cHPR = hydroprocessing (350 - 370°C; H₂ pressure, 2700 psig)

Figure 1. Low-temperature Coal Depolymerization-Liquefaction Procedure.

1. THF Pre-Extraction

Samples of BZ(ND) lignite were pre-extracted for 48 h with THF in a Soxhlet apparatus, yielding an average of 3.8 wt.% of soluble products. This was the lowest yield of THF-soluble pre-extract obtained from representative U.S. coals of varying rank (see Progress Report no. 4, Figure 2).

2. Mild Hydrotreatment (HT) Step

FeCl_3 -impregnated BZ(ND) lignite samples were subjected to mild hydrotreatment (HT), and the yield of THF-soluble products (at 290°C) was determined as a function of FeCl_3 concentration in the range of 5-20 wt.%. Results obtained are summarized in Table 1. As seen, application of FeCl_3 catalyst concentrations in the range of 5-20 wt.% and a hydrotreatment temperature of 290°C results in BZ(ND) lignite solubilization yields in the narrow range of 6.0-7.9 wt.%. This indicates that in comparison with previously studied HVB coals, the effect of FeCl_3 concentration upon the solubilization yields in the HT step is relatively minor. Furthermore, the observed yields of THF-solubles from BZ(ND) lignite in the HT step are lower than those obtained from HVB coals using identical FeCl_3 catalyst concentrations.

On the basis of the above results, a FeCl_3 concentration of 20 wt.% and a temperature of 290°C were used as suitable conditions for the HT step. However, in current studies on the BZ(ND) lignite lower FeCl_3 concentrations (5-10 wt.%) are being applied.

Table 1

Effect of FeCl_3 Concentration Used in the HT Step Upon
the Yield of THF-Soluble Products from BZ(ND) Lignite

Run no.	1	2	3	4
FeCl_3 conc., wt.%	5	10	15	20
HT temperature, °C	290	290	290	290
Yield of THF-solubles, wt.%	6.0	6.5	7.0	7.9

Table 2

Effect of Temperature Used in the HT Step Upon the Yield
of THF-Soluble Products in the Subsequent BCD Step

Run no.	5	6	7	8
<u>HT Step^a</u>				
Temperature, °C	250	275	290	310
Yield of THF-solubles, wt.%	6.8	7.3	7.9	8.5
<u>BCD Step^b</u>				
Temperature, °C	275	275	275	275
Yield of THF-solubles, wt.%	64.0	78.9	84.8	65.0

^aHydrotreatment was performed using BZ(ND) lignite impregnated with 20% FeCl_3 .

^bThe BCD step was performed using a 10% methanolic solution of KOH as depolymerizing agent.

3. Base-Catalyzed Depolymerization (BCD) Step

The effect of reaction temperature in the HT step (in the range of 250-310°C) upon the yield of THF-soluble products from BZ(ND) lignite in the subsequent BCD step was examined. The BCD step in all runs was performed in a magnedrive autoclave, using a 10% methanolic solution of KOH as base catalyst under the following operating conditions: reaction temperature, 275°C; BZ(ND) lignite/methanolic KOH solution weight ratio = 0.1; initial N₂ pressure, 1000 psig; reaction time, 1 hr. Results obtained are summarized in Table 2 and in Figure 2. As seen, the yield of THF-soluble products from the BCD reaction increases from 64.0% to 84.5 wt.% with increase in HT temperature from 250 to 290°C. However, further increase in the HT temperature to 310°C causes a decrease in the yield of THF-soluble products in the subsequent BCD step (65.5%). Consequently, the total yield of THF-solubles (MAF basis) from the combined HT-BCD steps, using an HT temperature of 310°C, is markedly lower (73.5%) as compared with that obtained by HT-BCD using an HT temperature of 290°C (92.7 wt.%). A similar behavior was previously observed in the depolymerization of several HVB coals, although with such coals the optimal HT temperature for the overall depolymerization yield was usually lower (~ 275°C).

The effect of BCD temperature between 250-310°C upon the yield and distribution of THF-soluble products was also investigated. All runs were performed using as feed the mildly hydrotreated BZ(ND) lignite product obtained in the preceding HT step at 290°C, 1500 psig initial hydrogen pressure, and 3 hr reaction time. Except for the reaction temperature, all other conditions in the BCD runs were identical, i.e., 10% methanolic KOH solution/lignite ratio = 10:1; reaction time 1 hr; and initial N₂ pressure, 1000 psig. As seen in Table 3 and Figure 2, the total THF-solubles yield (MAF basis) is very high ($\geq$ 81 wt.%)

in the entire temperature range studied. It increases only slightly with increase in BCD temperature, i.e., from 81.0% at 250°C to 84.8% at 275°C, and 86.0% at 290°C. However, the THF-solubles yield decreases to 78.1% with further increase in BCD temperature to 310°C. Run no. 9 shows that BCD alone, without the HT step, results in markedly lower solubilization (59.1% at 275°C) as compared with runs 10-13, in which HT was performed as first depolymerization step.

Table 3 shows also the distribution of the THF-soluble products (from the combined HT-BCD treatment of BZ(ND) lignite) into oil, asphaltene, and asphaltol fractions as a function of BCD temperature. As seen from runs 10-12, the asphaltol fraction of the product, which predominates at 250°C (run 10), markedly decreases while the oil fraction correspondingly increases (up to 63.0 wt.%) with increase in BCD temperature from 250°C to 290°C. The asphaltene fraction remains almost at the same level. The product from run 9 (BCD alone, without HT) consists mostly of asphaltols, clearly demonstrating the need of sequential HT-BCD treatment for the purpose of achieving in-depth depolymerization of the lignite feed. The decrease in the yield of oils (and corresponding increase in the yield of asphaltols) observed at a BCD temperature of 310°C (Run 13, Table 3, and Figure 3), is similar to that observed previously with an Elkhorn (Kentucky) coal. This behavior was ascribed to an increase in the extent of resynthesis (recondensation) reactions of hydrolyzed products, e.g., phenols and carboxylic acids, at BCD temperatures above 300°C (see Progress Report no. 3, pp. 10-13).

Figure 2.

Effect of temperature used in the HT step upon the yield of THF-soluble products in the subsequent BCD step at 270°C (feed, BZ(ND) coal-20% FeCl_3 -impregnate).

Table 3

Effect of BCD Temperature Upon the Yield and Distribution of
Products from BCD of Mildly Hydrotreated BZ(ND) Lignite

Run no.	9 ^a	10	11	12	13
HT temperature, °C	-	290	290	290	290
BCD temperature, °C	275	250	275	290	310
Total yield of THF-solubles, wt.% ^{b,c}	59.1	81.0	84.8	86.0	78.1

Distribution of THF-solubles, wt.%					
Oils ^d	31.8	30.2	52.5	63.0	44.1
Asphaltenes ^e	19.0	13.5	16.9	17.8	12.3
Asphalts ^f	49.2	61.4	30.6	19.2	43.6

^aIn this run, the BZ(ND) lignite was not subjected to mild hydrotreatment (HT) prior to the BCD step.

^bThe total yield of THF-solubles from BCD includes 7.9 wt.% of THF-solubles obtained in the HT step.

^cYields of THF-solubles are calculated on the starting MAF coal and do not include 3.8 wt.% of THF-soluble pre-extract.

^dCyclohexane-solubles.

^eBenzene-solubles, cyclohexane-insolubles.

^fTHF-solubles, benzene-insolubles.

Figure 3. Change in composition of THF-soluble products from HT-BCD of BZ(ND) coal, as a function of BCD temperature.

5. Hydroprocessing (HPR) Step

A sample of the depolymerized product from the sequential HT-BCD depolymerization treatment of the BZ(ND) lignite, obtained under the conditions of run 12, Table 3, was subjected to hydroprocessing (HPR) with a sulfided 6Co8Mo/ Al_2O_3 catalyst at 370°C, 2700 psig hydrogen pressure, and 8 hr reaction time (with new catalyst introduced at the end of 4 hr). About 0.06 wt.% of CS_2 (wt.% of feed solution) was added after 4 hr of hydroprocessing in order to preserve the sulfided state of the catalyst. (Addition of CS_2 (H_2S) at the beginning of the run was found to decrease the initial rate of hydrodeoxygenation).

Table 4 summarizes the elemental compositions of (a) the original lignite, (b) the depolymerized product obtained by the sequential HT-BCD steps, and (c) of the final hydroprocessed product. As seen, the depolymerizing HT and BCD steps are accompanied by considerable reduction of heteroatom content, i.e., O, from 20.6 to 12.7 wt.%; N, from 1.17 to 0.62 wt.%; and S, from 1.60 to 0.23 wt.%. Hydroprocessing of the depolymerized lignite yields a hydrocarbon product having sharply reduced O, N, and S contents, and correspondingly increased C and H contents.

Table 5 summarizes the boiling point distribution of the depolymerized BZ(ND) lignite and of the hydrocarbon product derived from it in the hydroprocessing (HPR) step. As seen, the depolymerized BZ(ND) lignite sample is characterized by relatively moderate volatility as reflected by a vacuum residue of 27.0%, and a low proportion of gasoline, kerosene, and gas oil fractions (total of 24.6 wt.%). In contrast, the hydroprocessed product is almost fully (~ 98%) distillable and contains 97.0 wt.% of gasoline, kerosene, and gas oil fractions. This demonstrates the high efficiency of the overall HT-BCD-HPR

Table 4

Elemental Compositions of the Original BZ(ND) Lignite
of the Depolymerized Product and of the Hydrocarbon
Product Derived from it by Hydroprocessing (HPR)

	Original lignite	Depolymerized product ^a	Hydroprocessed (HPR) ^b product
Element, wt.%			
Carbon	71.05	78.57	88.73
Hydrogen	5.58	7.88	10.14
Nitrogen	1.17	0.62	0.08
Sulfur	1.60	0.23	0.05
Oxygen (by diff.)	20.6	12.7	1.0
H/C atomic ratio	0.94	1.21	1.38

^aThe depolymerized BZ(ND) lignite sample was obtained by HT at 290°C, followed by BCD at 290°C.

^bThe hydroprocessing (HPR) step was performed at 370°C and 2700 psig H₂ pressure, using a sulfided 6Co8Mo catalyst and mesitylene as a solvent.

Table 5

Boiling Point Distribution of the Depolymerized BZ(ND) Lignite
and of the Hydrocarbon Product Derived from it
by Hydroprocessing (HPR)^a

Fraction, (b.p., °C), wt.%	Depolymerized coal ^b	Hydroprocessed (HPR) product ^c
Gasoline (<200°C)	8.6	77.1
Kerosene (200-275°C)	3.8	17.6
Gas Oil (275-325°C)	12.2	2.3
Heavy Gas Oil (325-400°C)	25.0	0.6
Vacuum Gas Oil (400-538°C)	23.4	0.4
Total Distillable (<538°C)	73.0	98.0
Atmospheric Residue (>350°C)	66.2	< 0.1
Vacuum Residue (>538°C)	27.0	~ 2.0

^aBoiling point distribution was determined by simulated distillation.

^bFor preparation conditions, see Table 4, footnote a.

^cFor hydroprocessing conditions, see Table 4, footnote b.

procedure for converting a representative U.S. lignite into a low-boiling hydrocarbon fuel.

The markedly higher volatility of the final hydroprocessed product from the BZ(ND) lignite as compared with that of corresponding products from previously investigated HVB coals is consistent with the presence of smaller size clusters in the polymeric framework of the lignite.

Detailed structural analysis of the depolymerized BZ(ND) lignite is presently underway.

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