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

Progress Report no. 3

(covering the period April 1 - June 30, 1987)

Joseph S. Shabtai and Wendell H. Wiser
(801-581-5161) (801-581-8602)

Principal Investigators

Department of Fuels Engineering

University of Utah

Salt Lake City, UT 84112

Prepared for the United States Department of Energy
under Grant no. DE-FG-22-86PC90537

July, 1987

MASTER

dx

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

This report was prepared with the support of the U. S. Department of Energy, Grant No. DE-FG-22-86PC90537. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of the DOE.

PERSONNEL

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

Mr. T. Skulthai, Graduate student

Mrs. Y. Zhang, 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 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 period April 1 - June 19, 1987, covered by the present report, systematic studies of the low-temperature depolymerization and liquefaction of a coal from Elkhorn (Kentucky) were performed, and parallel studies of a Pittsburgh #8 high volatile bituminous coal, supplied by the premium coal sample program at the Argonne National Laboratory, were continued. Following

is a description of results obtained.

RESULTS

A. Depolymerization-Liquefaction of an Elkhorn (Kentucky) Coal

The Elkhorn (Kentucky) coal sample, referred below as EH(Ky) coal, had the following ultimate analysis (MAF basis), in wt %: C, 85.36; H, 5.69; N, 1.75; Cl, 0.18; S, 0.72; O (diff) 6.30. H/C atomic ratio = 0.80; ash content (dry basis), 6.60 %. The sample showed a calorific value of 14,324 BTU/lb (dry basis). As indicated by its ultimate analysis and calorific value, the EH(Ky) coal was of somewhat higher rank as compared with the previously studied HVB coal sample from Burning Star (Illinois no. 6).

The EH (Ky) coal was subjected to the previously developed stepwise depolymerization-liquefaction procedure summarized in Figure 1 [for details see J. Shabtai, T. Skulthai and I. Saito, Am. Chem. Soc. Div. Fuel Chem. Prepr., 31 (4), 15-23 (1986)]. The procedure 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.

A systematic study was carried out with the purpose of determining the optimal range of processign conditions for EH (Ky) coal in each step of the above sequential procedure.

Mild Hydrotreatment (HT) Step

Figure 1 summarizes the change in the yield of THF-soluble products from mild hydrotreatment of EH(Ky) coal- FeCl_3 intercalates as a function of

^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.

Figure 1. Effect of FeCl_3 concentration and temperature used in the HT step upon the yield of THF-soluble products from EH(KY) coal.

reaction temperature, at three different FeCl_3 concentrations (5, 10 and 15 wt %). As seen, the solubilization yield increases linearly with increase in temperature from 250° to 310°C at all of the FeCl_3 concentrations used, under otherwise identical processing conditions (H_2 pressure, 1500 psig; reaction time, 3 hr). In view of the higher rank of the EH (Ky) coal (higher C content, lower O content) in comparison with the previously studied coal samples from Wyodak (Wyoming) and Burning Star (Illinois no. 6) it was anticipated that this coal will have a higher concentration of methylene (and other hydrocarbon) intercluster linkages. Consequently, a somewhat higher level of solubilization in the HT step, e.g., 15 - 20 % by wt, was considered as preferable, in comparison with the previously indicated optimal HT solubilization level of 8-10 wt % for lower rank coals (see Progress Reports no. 1 and 2). Figure 1 shows that such higher solubilization level for EH (Ky) coal is attained at HT temperatures of 290-310°C. To determine further the optimal FeCl_3 catalyst concentration in this temperature range the yield of THF-soluble products from EH (Ky) coal was examined at 290° and 310°C as a function of FeCl_3 concentration between 5 to 15 wt %. Results obtained are summarized in Figure 2. As seen, solubilization yields of 15 - 20 wt % at these temperatures are found for FeCl_3 concentrations between 10 - 15 wt %. A temperature of 290°C and a FeCl_3 concentration of 15 wt % were selected as suitable conditions for the purpose of the study. It should be noted that this temperature and metal halide catalyst concentration are considerably higher than those indicated as optimal for lower rank coals (from the point of view of the overall efficiency of the HT-BCD-HPR procedure).

Base-Catalyzed Depolymerization (BCD) Step

Table 1 and Figure 3 show the effect of reaction temperature used in the HT step upon the yield of THF-soluble products in the subsequent BCD step. As

Figure 2. Yield of THF-soluble products from hydrotreatment (HT) of EH(KY) coal, as a function of FeCl_3 concentration and HT temperature.

Table 1
Effect of temperature used in the HT step upon the yield
of THF-soluble products in the subsequent BCD step

Run no.	31	32	33	34
<u>HT step^a</u>				
HT temp., °C	250	275	290	310
Yield of THF-solubles, wt %	12.4	15.8	17.3	19.7
<u>BCD step^b</u>				
BCD temp. °C	275	275	275	275
Yield of THF-solubles, % by wt ^c	36.9	49.8	62.6	48.1

^aIn each HT run was used 4.0 g of EH (Ky) coal-FeCl₃ impregnate as feed (FeCl₃ concentration, 15 %; H₂ pressure, 1500 psig; reaction time, 3 hr).

^bDepolymerizing agent, 10 % methanolic KOH solution; catalyst solution/feed ratio 10:1; N₂ pressure, 1000 psig; reaction time, 1 hr.

^cTotal yield of THF-solubles from the sequential HT-BCD steps.

Figure 3. Effect of temperature used in the HT step upon the yield of THF-soluble products in the subsequent BCD step at 275°C (feed, EH(KY) coal-15 % FeCl_3 impregnate).

seen, the yield of THF-solubles in the BCD step (performed at the selected temperature of 275°C) passes through a maximum (~ 63 wt %) corresponding to the use of a temperature of 290°C in the preceding HT step. Although the yield of THF solubles in the HT step is higher at a HT temperature of 310°C (as compared with that at a HT temperature of 290°C), the yield of THF-solubles in the subsequent BCD step (reflecting the total overall yield from the sequential HT and BCD steps) is considerably lower (~ 48 wt %) as compared with that obtained when using the lower HT temperature of 290°C.

Table 2 summarizes the effect of temperature in the BCD step (in the range of 250-305°C) upon the total yield and distribution of THF-soluble products, using the above indicated optimal temperature of 290°C in the preceding HT step. Experiment 39 was performed without preliminary hydrotreatment (HT) of the EH (Ky) coal for the purpose of comparison. As seen from experiments 31 to 34, the total yield of THF-solubles from the sequential HT-BCD steps increases markedly with increase in BCD temperature from 250 to 290°C but then decreases sharply with further increase in temperature to 305°C. Run 39 shows that BCD alone, without the preceding HT step, results in very low extent of solubilization (27.5 wt % at 275°C).

Table 2 and Figure 4 show the distribution of the THF-soluble products (from sequential HT-BCD treatment of EH (Ky) coal) as a function of BCD temperature. As seen, the proportion of the oil (cyclohexane-soluble) fraction gradually increases, while that of the asphaltol fraction correspondingly decreases with increase in BCD temperature from 250° to 290°C. At higher BCD temperature (305°C), however, the trend is reversed and the yield of the oil fraction sharply decreases, while that of the asphaltol fraction markedly increases. This major change in product composition at a BCD temperature in excess of 300°C, can be tentatively ascribed to resynthesis

Table 2
Effect of BCD temperature upon the yield and distribution of
products from BCD of mildly hydrotreated EH (Ky) coal

Run no.	39 ^a	31 ^b	32 ^b	33 ^b	34 ^b
HT temp., °C	-	290	290	290	290
BCD temp., °C	275	250	275	290	305
Total yield of THF-solubles, wt % ^c	27.5	37.4	62.6	71.7	45.7
Distribution of THF-solubles, % by wt					
Oils	29.0	39.4	51.2	56.9	37.6
Asphaltenes	27.5	9.8	20.3	27.4	22.4
Asphalts	43.5	50.9	25.4	15.7	40.0

^aThe EH (Ky) coal was not subjected to mild hydrotreatment (HT) in this run.

^bThe total yield of THF solubles from BCD includes 19.7 % by wt of THF-solubles obtained in the HT step.

^cYields of THF-solubles are calculated on the starting MAF coal and do not include 7.3 % by wt of THF-soluble pre-extract.

Figure 4. Change in composition of THF-soluble products from HT-BCD of EH(KY) coal, as a function of BCD temperature.

reactions, e.g., etherification, of phenolic and other reactive compounds formed in the initial base-catalyzed hydrolysis (depolymerization) stage of the BCD treatment:

The results indicate the great advantage of using temperatures $< 290^{\circ}\text{C}$ in the BCD step. Conversely, for temperatures $> 300^{\circ}\text{C}$, a much shorter reaction time would be necessary.

The effects of the type and concentration of base catalyst upon the yield of THF-soluble products in the BCD step were also examined. For that purpose a comparative study of the activities of methanolic NaOH and KOH solutions having concentrations of 5-10 % by wt was performed. Results obtained are summarized in Table 3. As seen, the more strongly basic KOH is clearly a more efficient depolymerizing catalyst than NaOH in the BCD step, at all concentrations examined. Increase in NaOH concentration from 5 to 10 wt % increases only moderately the total yield of THF-soluble products. Furthermore, such an increase causes only a moderate change in the depth of depolymerization as reflected in a moderate increase in the proportion of the oil fraction (and corresponding decrease in the asphaltol fraction) of the product. On the other hand, an increase in KOH concentration from 5 to 10 wt % results in a considerable increase in the total yield of THF-solubles, and an attendant major increase (from 33.2 % at a concentration of 5 % to 59.0 % at a concentration of 10 %) in the proportion of the oil fraction. The effect of the type of solvent used upon the extent and depth of

Table 3

Effects of type and concentration of base catalyst upon the yield of THF-solubles in the BCD step^a

Catalyst	NaOH			KOH		
	5	7	10	5	7	10
Catalyst conc. in MeOH, wt %						
Yield of THF-solubles, wt % ^b	38.4	41.1	45.6	53.1	59.9	71.7
Distribution of THF-solubles, wt % ^c						
Oils	30.5	33.0	37.5	33.2	43.0	59.0
Asphaltenes	13.2	14.2	17.1	17.7	21.3	25.4
Asphalts	56.3	52.4	45.4	48.9	35.7	15.7

^aReaction conditions: temperature, 290°C; N₂ pressure, 1000 psig; reaction time, 1 hr.

^bWt % of starting EH (Ky) coal, excluding THF pre-extract.

^cWt % of total THF-soluble product.

depolymerization in the BCD step is also being studied, using various mono- and dialcohols. Results will be provided in the next progress report.

Since the total yields of THF-solubles from sequential HT-BCD treatment of EH (Ky) coal (Table 2) were generally somewhat lower than those obtained with lower rank coals (Progress Reports no. 1 and 2) the following additional treatment of the insoluble residue (non-depolymerized EH (Ky) coal) left in run no. 33 (Table 2) was performed: The residue was re-impregnated with 5 wt % of FeCl_3 and the impregnate was subjected to repeated mild hydrotreatment (HT) at 290°C. This resulted to an additional yield of 12.7 % of THF-soluble products, bringing the total yield of solubilized products in run no. 33 to 84.4 wt % (MAF basis) not including 7.3 % of THF-soluble pre-extract. This indicates that a more efficient coal-hydrogen contact (mixing) may be necessary in performing the HT step with higher rank coals. The construction of a small stirred autoclave is planned for that purpose.

Hydroprocessing (HPR) Step

A sample of depolymerized EH (Ky) coal obtained by sequential HT-BCD under the conditions of expt. 33 (Table 2) was subjected to hydroprocessing (HPR) at 370°C and a hydrogen pressure of 2700 psig, using a sulfided 6Co8Mo catalyst and mesitylene as a solvent. The conversion of the depolymerized coal under these conditions was essentially quantitative (98.5 wt %). Table 4 provides data on the boiling point distribution of the depolymerized EH (Ky) coal and of the hydroprocessed product derived from it in the HPR step. As seen, the depolymerized EH (Ky) coal is characterized by relatively low volatility as reflected in a proportion of total distillable fractions (< 538°C) of 45.2 %, viz a vacuum residue of 54.8 %. On the other hand, the hydroprocessed (HPR) product derived from the depolymerized coal is a hydrocarbon oil containing 75.0 % of distillables (b.p. < 538°C) including

Table 4

Boiling point distribution of depolymerized EH (Ky) coal
and of hydrocarbon product derived from it by hydroprocessing (HPR)

Fraction (b.p., °C) wt % ^a	Depolymerized coal ^b	Hydroprocessed (HPR) product
Gasoline (< 200°)	8.0	20.7
Kerosene (200-275°)	6.9	29.9
Gas Oil (275-325°)	7.3	9.4
	22.2	60.0
Heavy Gas Oil (325-400°)	10.3	5.7
Vacuum Gas Oil (400-538°)	12.7	9.3
Total Distillable (< 538°)	45.2	75.0
Atmospheric Residue (> 350°)	69.5	38.1
Vacuum Residue (> 538°)	54.8	25.0

^aBoiling point distributions were determined by simulated distillation.

^bObtained by mild hydrotreatment (HT) at 290°C of an EH(Ky) coal - 15 % FeCl₃ impregnate, followed by BCD of the derived product with 10 % methanolic KOH at 290°C and a reaction time of 1 hr. (see expt. 33, Table 2).

^cObtained by hydroprocessing (HPR) of the depolymerized EH (Ky) coal at 370°C and 2700 psig H₂ pressure, using a sulfided 6Co8Mo catalyst.

60.0 wt % of low-boiling fractions (gasoline, kerosene and light gas oil; b.p., up to 325°C/760 torr). The relatively low volatility of the depolymerized coal obtained by low-temperature HT-BCD procedure was previously ascribed to the fact that it still contains a major part of the original oxygen of the coal feed. However, the depolymerized coal consists mostly of simple, mostly monocluster compounds and the oxygen is in the form of non-bonding functional groups, e.g. phenolic groups (T. Skulthai, Ph.D. thesis, University of Utah 1987), which are easily susceptible to exhaustive hydrodeoxygenation in the hydroprocessing (HPR) step to yield a hydrocarbon oil product (Table 4).

The above results demonstrate the high efficiency of the sequential HT-BCD-HPR depolymerization-liquefaction procedure for converting a higher rank bituminous coal, e.g., the EH (Ky) coal, into a light hydrocarbon oil. Further improvement in product yields and boiling point distribution from the EH (Ky) coal is feasible and is presently being sought.

B. Work in Progress

The following studies are presently in progress:

- (a) Continuation of the studies with the EH (Ky) coal feed, including more detailed analysis of intermediate and final products obtained in the above HT-BCD-HPR studies.
- (b) Continuation of systematic studies of the depolymerization-liquefaction reactions of a Pittsburgh no. 8 HVB coal, supplied by the premium coal sample program of the Argonne National Laboratory. Results will be reported in the next progress report.
- (c) Structural analysis of depolymerized Wyodak (Wyoming) coal (see Progress Report no. 2).

END

**DATE
FILMED**

7 / 13 / 93