

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

Progress Report no. 4  
(covering the period July 1 - September 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

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**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 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 period July 1 - September 30, 1987, covered by the present report, research activities were performed on the following subjects: (A) Continuation of the systematic studies of low-temperature depolymerization and liquefaction of a Pittsburgh (PA) HVB coal; (B) Structural analysis of

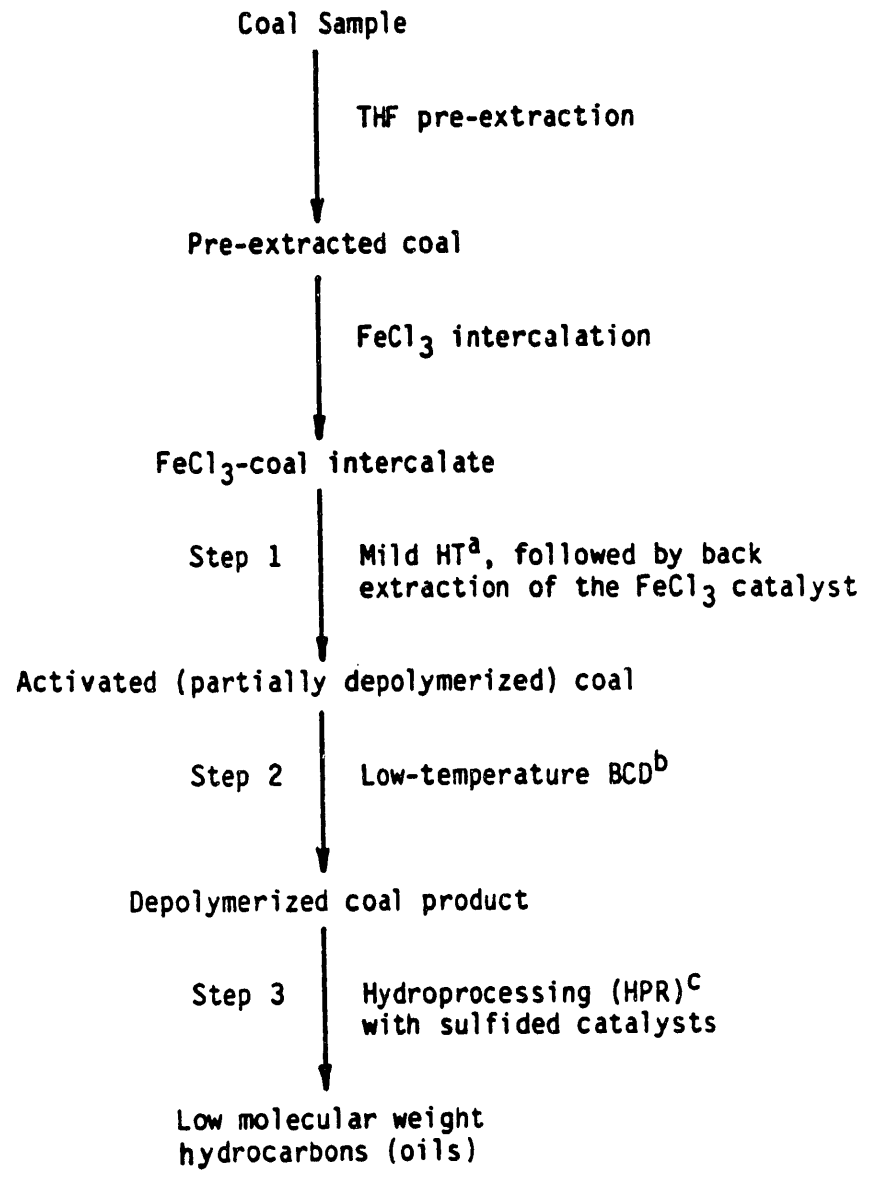
depolymerized products obtained from a Burning Star, Illinois, no. 6 coal; and (C) Initiation of low-temperature depolymerization-liquefaction studies of a Beulah-Zap (ND) lignite. Following is a description of results obtained.

## RESULTS

### A. Depolymerization-Liquefaction of a Pittsburgh #8 (Pennsylvania) Coal

A Pittsburgh #8 (Pennsylvania) coal sample, referred to below as PB(PA) coal, was supplied by the Argonne National Laboratory premium coal program. This coal had (according to data provided by the supplier) the following ultimate analysis (MAF basis), in wt. %: C, 83.0; H, 5.5; N, 1.8; O, 8.1; and S, 1.6. The ash content (dry basis) was 9.0 wt. %.

The PB(PA) coal 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  $\text{FeCl}_3$ , followed by mild hydrotreatment (HT) of the coal- $\text{FeCl}_3$  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.



<sup>a</sup>HT = hydrotreatment (250 - 290°C; H<sub>2</sub> pressure, 1000 - 1500 psig)

<sup>b</sup>BCD = base-catalyzed depolymerization (250 - 290°C; initial N<sub>2</sub> pressure, 1000 psig)

<sup>c</sup>HPR = hydroprocessing (350 - 370°C; H<sub>2</sub> pressure, 2700 psig)

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

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

### 1. THF Pre-Extraction

The PB(PA) coal was first extracted for 48 hr with THF in a Soxhlet extractor, yielding 14.1 wt.% of soluble products. This was the highest yield of THF-soluble pre-extract obtained from various coals studied in this Laboratory, as summarized in Figure 2. As seen, the yield of THF pre-extract gradually increases with increase in the carbon content of the coal, i.e., from 3.8 wt.% for the Beulah-Zap (ND) lignite (C, 73.0%) to 14.1 wt.% for the PB(PA) coal (C, 83.0%). The pre-extract yield decreases somewhat for Elkhorn (KY) coal (C, 85.4%) and then drops sharply to 0.3% for semi-anthracite coal (PSOC-161; C content, 92.0%) and <0.01% for anthracite coal (PSOC-867; C content, 97.0%). In view of the unusually high yield of THF-soluble pre-extract from PB(PA) coal, the composition of this extract is presently being studied in some detail.

### 2. Mild Hydrotreatment (HT) Step

In order to determine a suitable set of conditions for the HT step of the depolymerization procedure, FeCl<sub>3</sub>-impregnated PB(PA) coal samples were subjected to mild hydrotreatment, and the yield of THF-soluble products were determined as a function of HT temperature (between 275-310°C) for three different FeCl<sub>3</sub> concentrations, i.e., 5, 10, and 15 wt.%. Results obtained are summarized in Figure 3. As seen, application of FeCl<sub>3</sub> concentrations in the range of 5-15 wt.% and HT temperatures between 275-310°C result in PB(PA) coal solubilization yields of about 9 to 18 wt.%. Such relatively

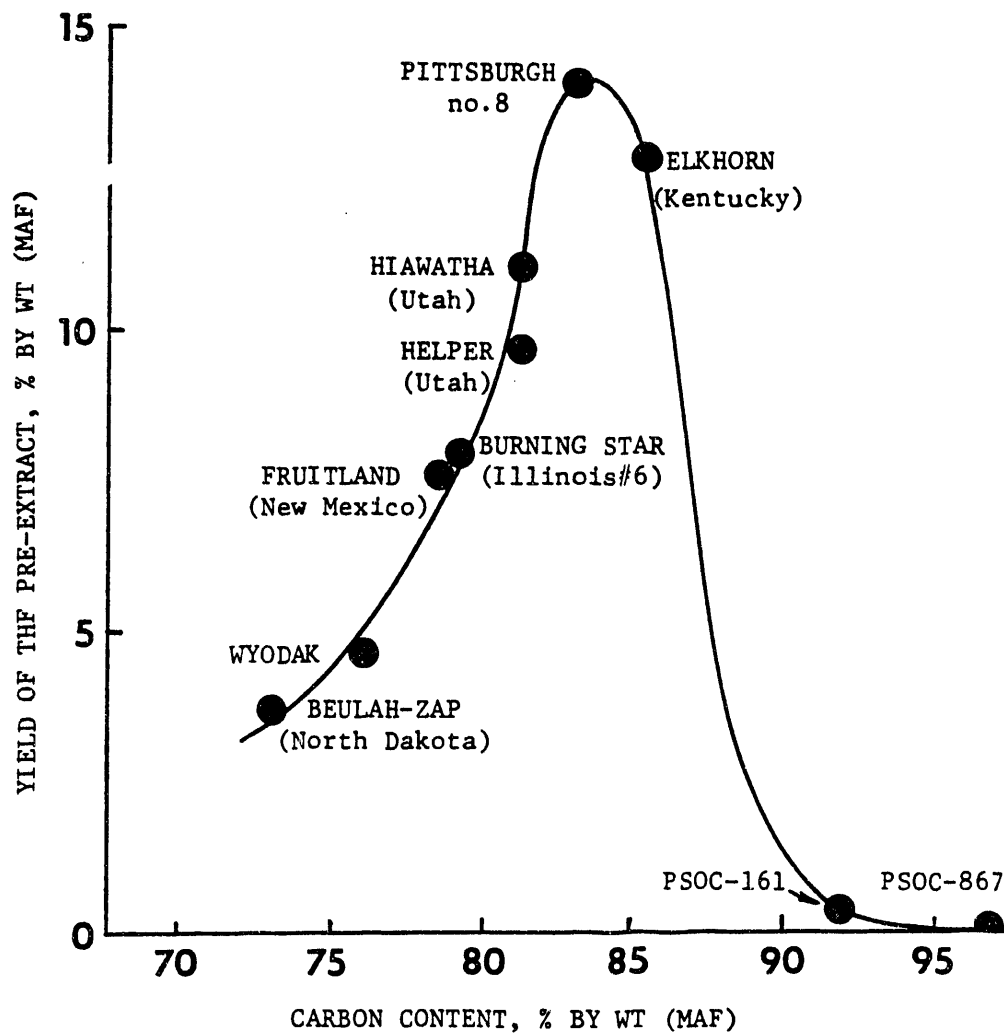


Figure 2. Change in yield of THF pre-extract from different U.S. coals, as a function of carbon content.

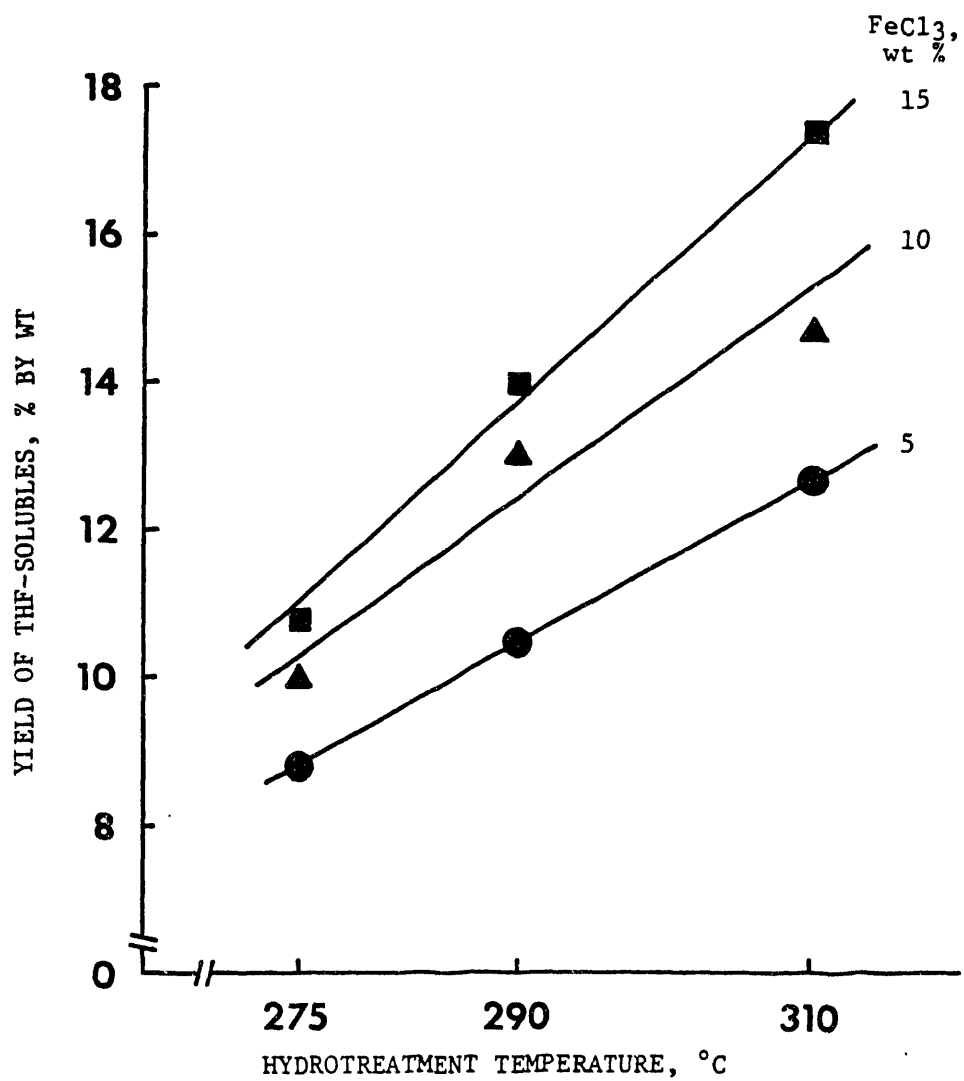


Figure 3. Effect of FeCl<sub>3</sub> concentration and temperature used in the HT step upon the yield of THF-soluble products from PB(PA) coal.



low solubilization yields in the HT step were previously found to be optimal from the point of view of the efficiency of the overall depolymerization process, as applied to other HVB coals, e.g., Fruitland, San Juan (NM), Helper (UT), and Burning Star (IL no. 6) coals. It is noteworthy, that for the PB(PA) coal, a very low  $\text{FeCl}_3$  concentration of 5 wt.% is sufficient for solubilization yields of 9-13 wt.% in the HT temperature range of 275-310°C (Figure 3), whereas with the previously studied, higher rank Elkhorn (KY) coal as feed the yields under the same conditions were only 6-9 wt.% (Progress Report no. 3, p. 5). This is probably indicative of a higher concentration of alkylene, e.g., methylene linkages (and other groups easily susceptible to acid-catalyzed hydrogenolysis) in the PB(PA) coal as compared with the Elkhorn (KY) coal.

On the basis of the results in Figure 3, a  $\text{FeCl}_3$  concentration of 5.0 wt.% and a HT temperature of 290°C were selected and used prior to the subsequent BCD step (see below). However, other sets of suitable conditions for the HT step are also being investigated.

### 3. Base-Catalyzed Depolymerization (BCD) Step

Figure 4 shows the effect of the reaction temperature used in the HT step upon the yield of THF-soluble products in the subsequent BCD step. A BCD temperature of 275°C was used in these runs. As seen, the highest yield of THF-solubles (63.0% by wt.) in the BCD step is obtained in the run using a temperature of 290°C in the preceding HT step. Although the yield of THF-solubles in the HT step is higher at 310°C, the THF-solubles yield in the subsequent BCD step (after HT at 310°C) is markedly lower (48.6%). Consequently, the total THF-solubles yield from the combined HT and BCD

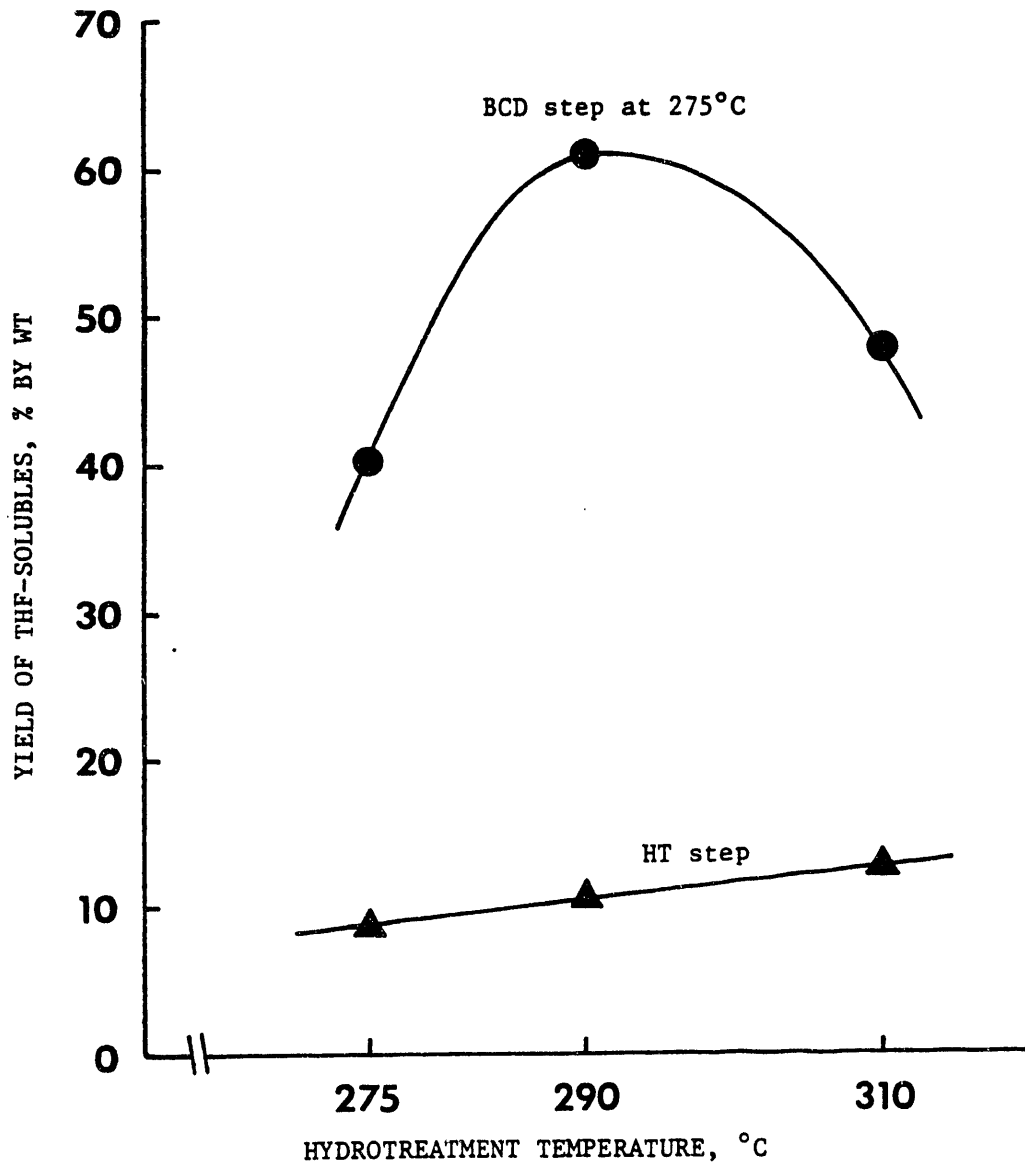


Figure 4. Effect of temperature used in the HT step upon the yield of THF-soluble products in the subsequent BCD step at 275°C (feed, PB(PA) coal-5% FeCl<sub>3</sub> impregnate).

steps is considerably higher (73.5 wt.%) for a HT temperature of 290°C as compared with that for a HT temperature of 310°C (61.3%).

Table 1 summarizes the effect of temperature in the BCD step (in the range of 250-290°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 (compare runs nos. 40-42). An additional run (no. 43) was performed without preliminary hydrotreatment, for the purpose of comparison. As seen, the total yield of THF-solubles increases markedly with increase in BCD temperature, *viz.* from 54.7% at 250°C to 71.5% at 290°C (MAF coal basis; excluding 14.1 wt.% of pre-extract). Run no. 43 shows that BCD alone, without the preceding HT step, results in markedly lower solubilization (57.6%) as compared to that obtained in run no. 42 (71.5%), in which an identical BCD temperature (290°C) was used.

Table 1 shows also the distribution of the THF-soluble products from PB(PA) coal into oils, asphaltenes, and asphaltols, as a function of the BCD temperature. As seen (runs no. 40-42), the proportion of asphaltols in the products sharply decreases, while that of oils correspondingly increases with increase in BCD temperature from 250° to 290°C. Asphaltenes, which are formed in low yields only, increase slightly with increase in BCD temperature. Products obtained from run no. 43 (BCD alone without preliminary HT) consist mostly of asphaltols. Relevant data in Table 1 are also plotted in Figure 4.

#### 4. Hydroprocessing (HPR) Step

A sample of the depolymerized PB(PA) coal obtained by the sequential HT-BCD procedure under the conditions of run no. 42 (Table 1) was subjected

**Table 1**  
**Effect of Temperature Upon the Yield and Distribution of**  
**Products from BCD of Mildly Hydrotreated PB(PA) Coal**

Run no.	40 <sup>a</sup>	41 <sup>a</sup>	42 <sup>a</sup>	43 <sup>b</sup>
HT temp., °C	290	290	290	--
BCD temp., °C	250	275	290	290
Total yield of THF-solubles, wt% <sup>c</sup>	54.7	63.0	71.5	57.6
Distribution of THF-solubles, wt% <sup>c</sup>				
Oils	34.4	49.5	62.7	22.1
Asphaltenes	6.5	7.2	12.5	18.2
Asphaltols	59.2	43.3	24.8	59.7

<sup>a</sup>The total yield of THF solubles from BCD includes 10.5% by wt of THF-solubles obtained in the HT step.

<sup>b</sup>In this run, the PB(PA) coal was not subjected to mild hydrotreatment (HT) prior to the BCD step.

<sup>c</sup>Yields of THF-solubles are calculated on the starting MAF coal and do not include 14.1% by wt of THF-soluble pre-extract.

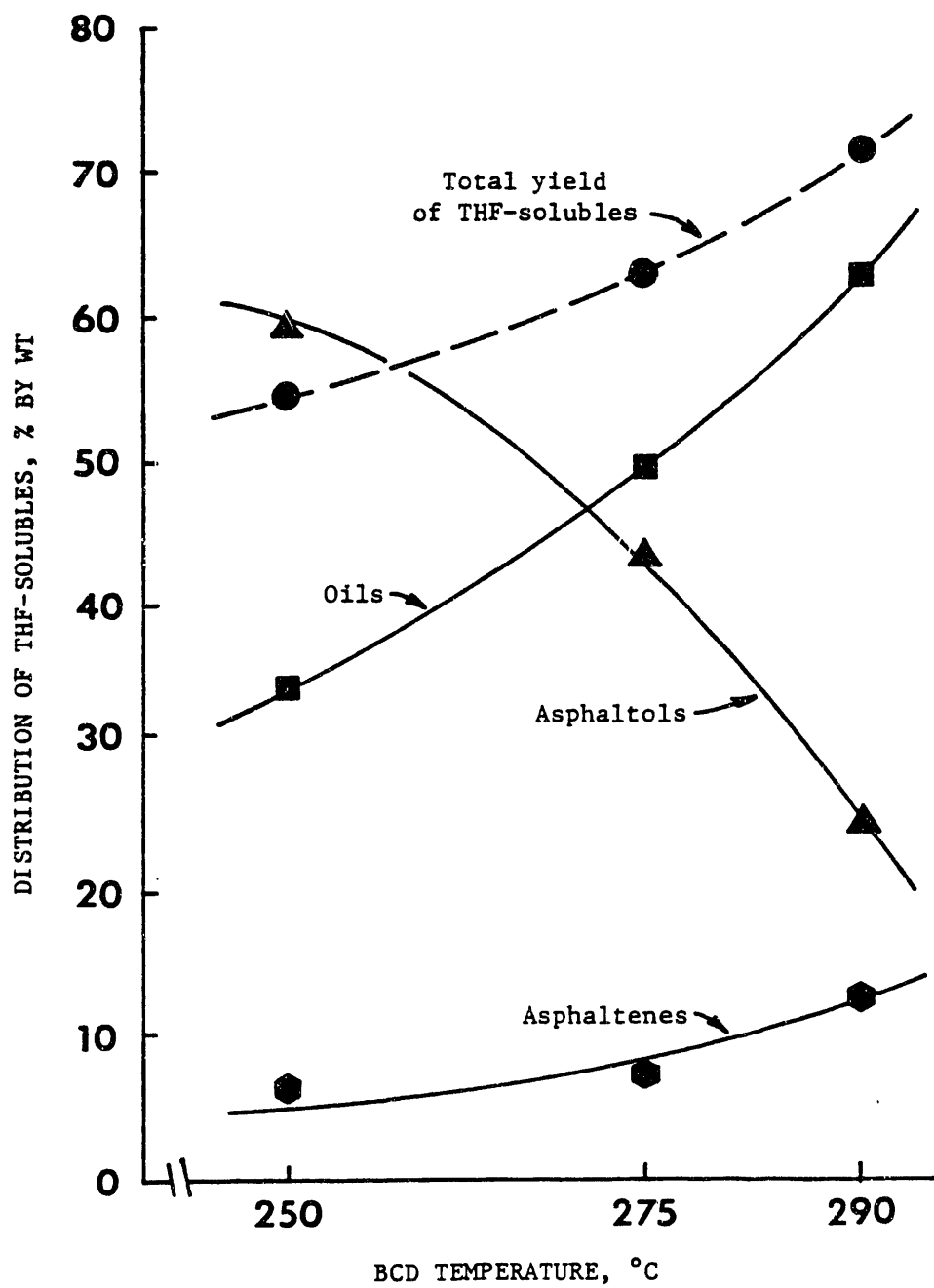


Figure 5. Change in the composition of THF-soluble products from HT-BCD of PB(PA) coal, as a function of BCD temperature.

to hydroprocessing (HPR) at 370°C and a H<sub>2</sub> pressure of 2700 psig, using sulfided 6Co8Mo as catalyst and mesitylene as a solvent.

Table 2 summarizes the elemental compositions of the depolymerized PB(PA) coal and of the hydroprocessed product derived from it. As seen, HPR produces a hydrocarbon product having sharply reduced S, O, and N contents (and correspondingly increased C and H contents) as compared with those of the depolymerized PB(PA) coal.

Table 3 summarizes the boiling point distribution of the depolymerized PB(PA) coal and of the product derived from it in the HPR step. As seen, the oxygen-rich, depolymerized coal has a relatively low volatility as reflected by a large vacuum residue of 47.2 wt.%, and a moderate proportion of gasoline-, kerosene-, and gas oil-range fractions (a total of 22.9 wt.% up to 325°C). In contrast, the hydroprocessed product contains 76.9 wt.% of distillables, including 66.8 wt.% of low-boiling fractions (gasoline, kerosene, and gas oil; b.p. up to 325°C).

The above results, using Pittsburgh #8 coal as feed, provide an additional example of the high efficiency of the overall HT-BCD-HPR sequential procedure for converting a representative U.S. coal into light hydrocarbon liquids.

Samples of the fractionated, depolymerized PB(PA) coal product are presently being subjected to exhaustive analysis in order to derive average molecular structures for the oil, asphaltene, and asphaltic fractions. Data obtained will be used to obtain a structural model for this coal.

Table 2

Elemental Compositions of the Depolymerized PB(PA) Coal and  
of the Hydrocarbon Product Derived from it by Hydroprocessing (HPR)

	Depolymerized Coal <sup>a</sup>	Hydroprocessed (HPR) <sup>b</sup> Product
Element, % by wt.		
Carbon	79.86	88.51
Hydrogen	8.49	10.81
Nitrogen	0.94	0.08
Sulfur	0.39	<0.01
Oxygen (by difference)	10.32	0.60
H/C Atomic Ratio	1.27	1.46

<sup>a</sup>The depolymerized PB(PA) coal sample was obtained by HT at 290°C, followed by BCD at 290°C.

<sup>b</sup>The hydroprocessing (HPR) step was performed at 370°C and 2700 psig H<sub>2</sub> pressure, using a sulfided 6Co8Mo catalyst and mesitylene as a solvent.

Table 3

**Boiling Point Distribution of the Depolymerized PB(PA) Coal  
and of the Hydrocarbon Product Derived from it  
by Hydroprocessing (HPR)<sup>a</sup>**

Fraction (b.p., °C), wt %	Depolymerized Coal	Hydroprocessed (HPR) Product
Gasoline (<200 <sup>o</sup> )	3.7	13.3
Kerosene (200-275 <sup>o</sup> )	8.5	28.9
Gas Oil (275-325 <sup>o</sup> )	10.7	24.6
Heavy Gas Oil (325-400 <sup>o</sup> )	11.5	6.7
Vacuum Gas Oil (400-538 <sup>o</sup> )	18.4	3.4
Total Distillable (<538 <sup>o</sup> )	52.8	76.9
Atmospheric Residue (>350 <sup>o</sup> )	72.1	29.2
Vacuum Residue (>538 <sup>o</sup> )	47.2	23.1

<sup>a</sup>Boiling point distribution was determined by simulated distillation.

<sup>b</sup>For preparation conditions, see Table 2, footnote a.

<sup>c</sup>For hydroprocessing conditions, see Table 2, footnote b.



## B. Structural Studies of the Oil Fraction Obtained by

### Depolymerization of Burning Star, Illinois No. 6 Coal

Structural analysis of the oil fraction obtained by HT-BCD of a Burning Star, Illinois no. 6 coal, designated below as BS(IL) coal, was performed using the modified Brown-Ladner method. Figure 6 indicates the general procedure applied in the structural analysis. Elemental composition, molecular weight, and quantitative NMR data ( $C^{13}$  NMR and PMR) of the oil fraction were input into a structural analysis computer program to derive average structural parameters and, ultimately, an average molecular structure for the above-indicated oil fraction.

The validity of the method for the purpose of this study was first tested by derivation of structural parameters for several model structures. An example of such structures is shown in Figure 7. The latter shows the results of the computed structural analysis for the model structure 1, which consists of two aromatic clusters connected by an etheric linkage. From the input data, the derived values for the total rings in the structure (RT) was 5.2; for aromatic rings (RA), 4.2; and for naphthenic rings (RN), 1.0. Further, the derived value for HAU/CA (the ratio of the number of substitutable, viz., non-bridgehead aromatic carbons to the total number of aromatic carbons in the structure) was 0.79, indicating that the basic aromatic ring cluster consists of a naphthalene system. Since the derived degree of polymerization (M) was 1.99, the molecule should contain two aromatic clusters of this type. The derived structural parameters are found to fit closely the theoretical values for the model structure 1. Table 4 lists the structural parameters, while Table 5 provides a list of equations used in the structural analysis by the modified Brown-Ladner method.

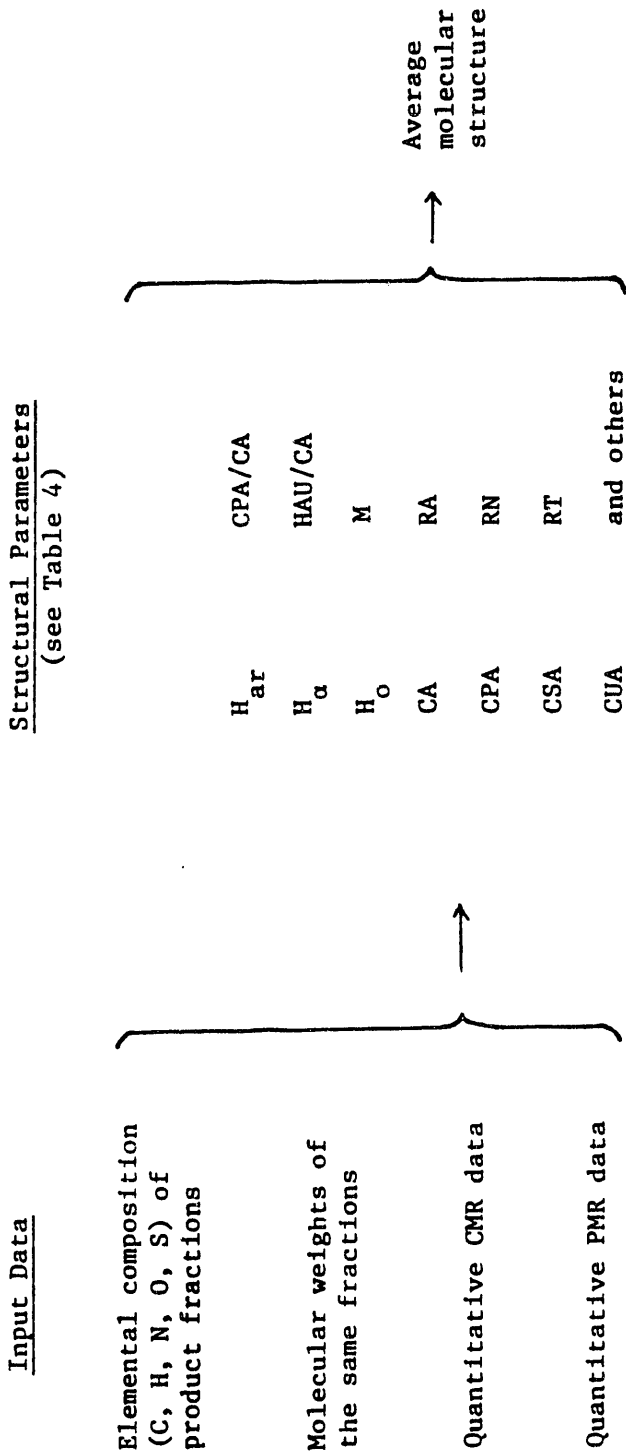
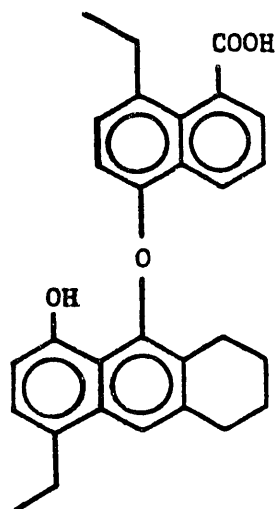


Figure 6. General scheme for structural analysis of soluble products from HT-BCD of BS(IL) coal.



Model Structure 1

Input Data:

C, 79.0%, H, 6.4%, O, 14.6%

M.W., 440

$H_{ar}=8$ ,  $H_{\alpha}=8$ ,  $H_o=10$

$C_{ar}=20$ ,  $C_{al}=8$

18

<u>Parameter</u>	<u>Theoretical Values</u>	<u>Computed Values</u>
C atoms	29	28.9
H atoms	28	27.9
O atoms	4	4.0
N atoms	-	-
Mol. wt.	440	439.9
$f_a, C$	0.69	0.71
$f_a, H$	0.28	0.30
$f_{\alpha}$	0.28	0.30
$f_o$	0.44	0.40
Total rings (RT)	5	5.2
Aromatic rings (RA)	4	4.2
Naphthanic rings (RN)	1	1.0
Degree of polymerization (M)	2	1.99
HAU/CA	0.80	0.79
Average side-chain length, C atoms	2	2.25

Figure 7. Test of applicability of computer program based on the modified Brown-Ladner method.

Table 4

List of Parameters used in Structural Analysis  
by Modified Brown-ladner Method

$f_a$	Carbon aromaticity
CA	Number of aliphatic carbons in the average structure
CPA	Number of peripheral aromatic carbons in the average structure
HAR	Number of aromatic protons in the average structure
H $\alpha$	Number of benzylic (alpha) protons in the average structure
HO	Number of aliphatic protons in the average structure not alpha to aromatic rings
$\frac{HAU}{CA}$	Ratio of the number of substitutable peripheral aromatic carbons to the total number of aromatic carbons in the unit structure
RA	Number of aromatic rings in the average structure
RN	Number of hydroaromatic and hydroaromatic rings in the average structure
RT	Total number of aromatic and hydroaromatic rings in the average structure
M	Degree of polymerization, or the number of unit structures in the average structure
n	Average length (carbon atoms) of the aliphatic side chains
$\delta$	Degree of ring substitution, or the fraction of the substitute aromatic carbons in the average structure that is substituted

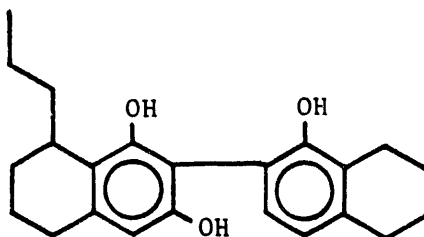
List of Equations used in Structural Analysis  
by Modified Brown-Ladner Method

1.  $f_a = C_a/C$  (NMR data)  
 $= \frac{C - 1/2 (H_\alpha + H_\beta) - 1/3 H_\gamma}{C}$  (PMR data)
2.  $HAU/CA = \frac{H_a + 1/2(H_\alpha) + O_{OH} + 2(O_{c-o-c} + N)}{C_a}$
3.  $\delta = \frac{1/2(H_\alpha) + O_{OH} + 2(O_{c-o-c} + N)}{H_a + 1/2(H_\alpha) + O_{OH} + 2(O_{c-o-c} + N)}$
4.  $C_{a,calc} = \frac{3}{\left(\frac{HAU}{CA}\right) - 1/2}$
5.  $MW_{calc} = \frac{MW}{N_p}$ , where  $N_p = \frac{C_a}{C_{a,calc}}$
6.  $CPA = \left(\frac{HAU}{CA}\right) \times C_{a,calc}$
7.  $RA = \frac{C_{a,calc} - CPA}{2} + 1$
8.  $R_A = RA \times N_p$
9.  $R_t = C - \frac{H}{2} + 1 - \frac{C_a}{2}$
10.  $R_n = R_t - R_a$
11.  $RN = \frac{R_n}{N_p}$
12.  $RT = RA + RN$
13.  $n = \frac{H_\alpha + H_\beta + H_\gamma}{H_\alpha}$

The application of the method to the oil fraction of a product obtained from BS(IL) coal by sequential HT-BCD (see Progress Report no. 1) is given in Figure 8 (A and B). The latter summarize the structural parameters derived for the oil fraction of the depolymerized BS(IL) coal product obtained by HT at 290°C followed by BCD at 290°C. The data derived on the basis of the analytical results show an average molecular formula  $C_{22.6}H_{29.1}O_{3.0}N_{0.24}$  for this fraction. The total number of rings is 3.9, out of which 1.9 are aromatic and 2.0 are naphthenic. The degree of polymerization is 2.3, which means that the above rings are part of a bicluster naphthenoaromatic system. The derived average structure contains 3 oxygen atoms per molecule. In actual molecules composing the oil fraction, these oxygen atoms could be in the form of phenolic, carboxylic, and etheric groups, as indicated by the FTIR spectrum (Figure 9).

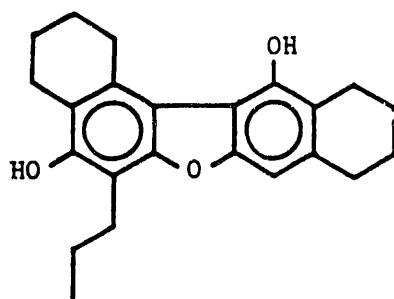
Figures 8A and 8B indicate two alternative average molecular structures derived for the oil fraction. Structure A consists of two clusters linked by means of a direct (Ar)C-C(Ar) bond, whereas structure B consists of two clusters linked by means of a furanic ring. Both types of linkages have been indicated as very resistant to cleavage under the conditions of the HT and BCD steps (T. Skulthai, Ph.D. Dissertation, University of Utah, 1987). These types of linkages, however, are easily cleaved in the final hydroprocessing step (HPR) of the procedure.

Work is continuing on the derivation of the average molecular structures for the asphaltene and asphaltol fractions of the depolymerized Burning Star (Illinois no. 6) coal.



<u>Parameter</u>	<u>Theoretical Values</u>	<u>Values Calculated from Experimental Data</u>
C atoms	23	22.6
H atoms	28	29.4
O atoms	3	3.0
N atoms	0	0.2
Mol. wt.	352	353
$f_a, C$	0.52	0.46
$f_a, H$	0.11	0.13
$f_\alpha$	0.25	0.34
$f_o$	0.54	0.53
Total rings (RT)	4	3.7
Aromatic rings (RA)	2	1.6
Naphthenic rings (RN)	2	2.1
Degree of polymerization (M)	2	2.3
Average side-chain length, C atoms	3	2.6

Figure 8 (A): Average molecular structure (structure A) for the oil fraction obtained by depolymerization of BS(IL) coal.



<u>Parameter</u>	<u>Theoretical Values</u>	<u>Values Calculated from Experimental Data</u>
C atoms	22.6	23
H atoms	26	29.4
O atoms	3	3.0
N atoms	0	0.2
Mol. wt.	350	353
$f_a, C$	0.52	0.46
$f_a, H$	0.04	0.13
$f_\alpha$	0.43	0.34
$f_o$	0.57	0.53
Total rings (RT)	4	3.7
Aromatic rings (RA)	2	1.6
Naphthenic rings (RN)	2	2.1
Degree of polymerization (M)	2	2.3
Average side-chain length, C atoms	3	3.03

Figure 8 (B): Average molecular structure (structure B) for the oil fraction obtained by depolymerization of BS(IL) coal.



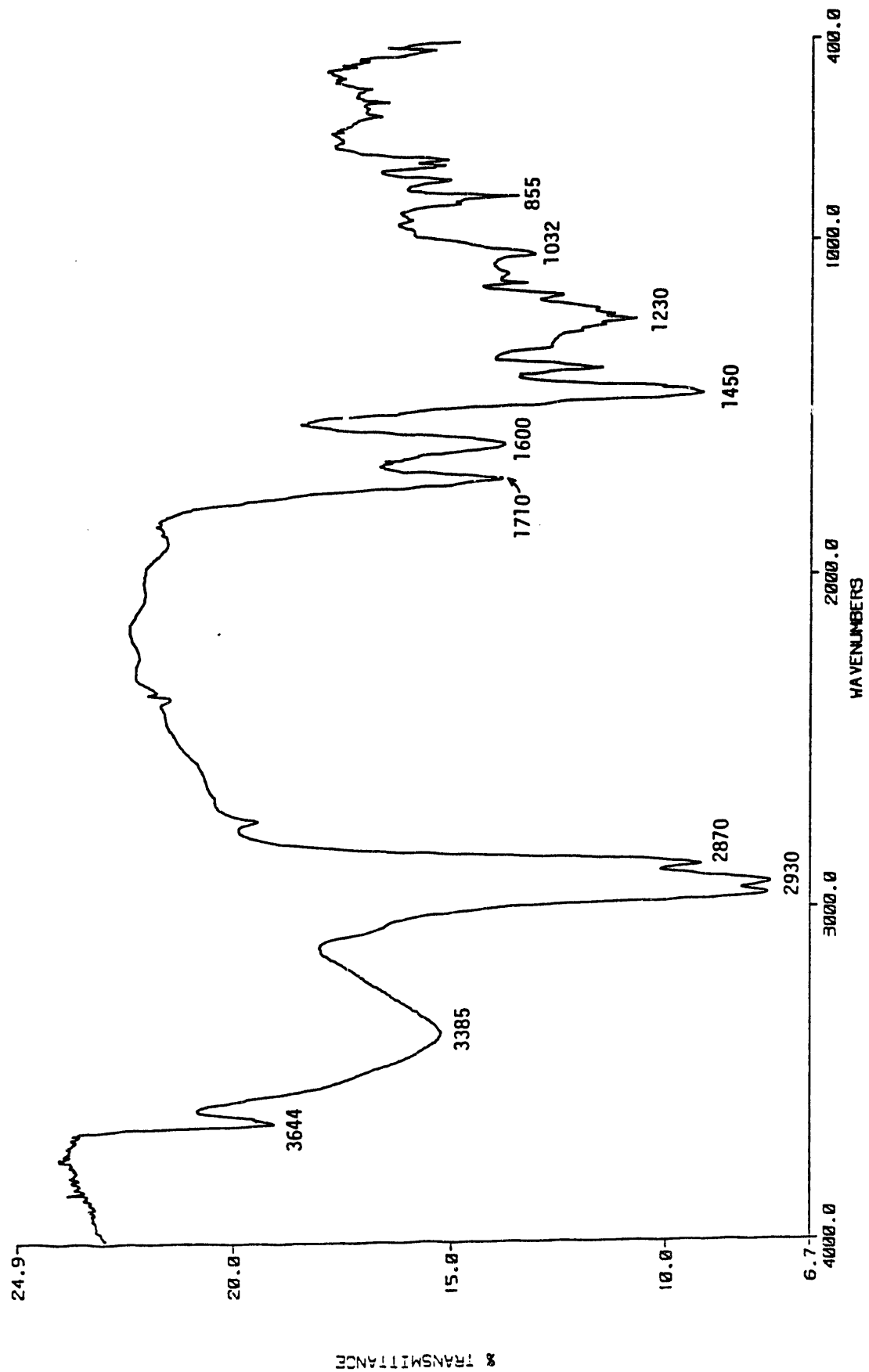


Figure 8. FTIR spectrum of the oil fraction obtained from HT-BCD of BS(IL) coal.

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