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

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(covering the period October 1 - December 31, 1986)

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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 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 initial period of this project, covered by the present report (October 1, 1986 - December 31, 1986), systematic studies on the low temperature depolymerization and liquefaction of a Burning Star (Illinois no. 6) coal were performed, and parallel studies of a coal from Elkhorn (Kentucky) were initiated. Following is a description of results obtained.

RESULTS

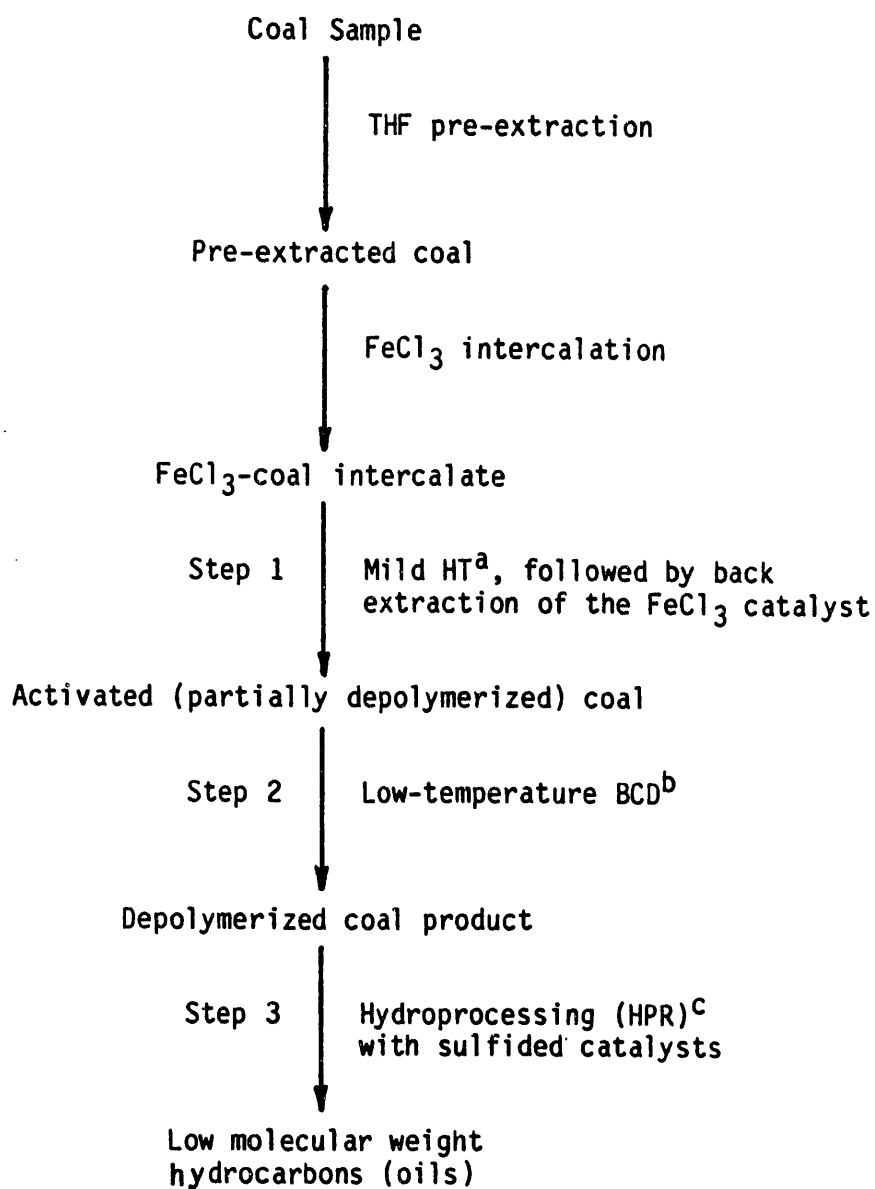
A. Depolymerization-Liquefaction of a Burning Star (Illinois no. 6) Coal

The Burning Star (Illinois no. 6) coal sample, referred below as BS(IL) coal, was characterized by the following ultimate analysis, dry basis, in wt %: C, 69.55; H, 4.72; N, 1.08; Cl, 0.12; S, 3.85; ash 11.83; O (diff.) 8.85. The sample showed a calorific value of 12,533 BTU/lb (dry basis).

The BS(IL) coal was subjected to the stepwise depolymerization - liquefaction procedure summarized in Figure 1. A more detailed description of this procedure is provided elsewhere [J. Shabtai, T. Skulthai, and I. Saito, Prepr. Amer. Chem. Soc. Div. Fuel Chem., 31 (4), 15-23 (1986)]. A systematic study was performed with the purpose of adapting the procedure for BS(IL) coal, and determining an optimal range of conditions for the latter in each processing step of the depolymerization - liquefaction sequence. It consists essentially of the following sequential steps: (1) intercalation of the coal sample with catalytic amounts (5 - 20 %) of FeCl_3 , followed by mild hydro-treatment (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.

Mild Hydrotreatment (HT) Step

Figure 2 shows the change in the yield of THF-soluble products from mild HT (at 275°C) of BS(IL)- FeCl_3 intercalates, as a function of the FeCl_3 concentration. As seen, FeCl_3 concentrations in the range of 8 - 20 % by wt lead to low solubilization yields (< 10 %) at a temperature of 275°C. Such low yields in the HT step were previously found to be desirable for several U. S. coals with higher oxygen content. Figure 3 shows the yield of THF-soluble products from HT of a BS(IL)-20 % FeCl_3 intercalate 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.

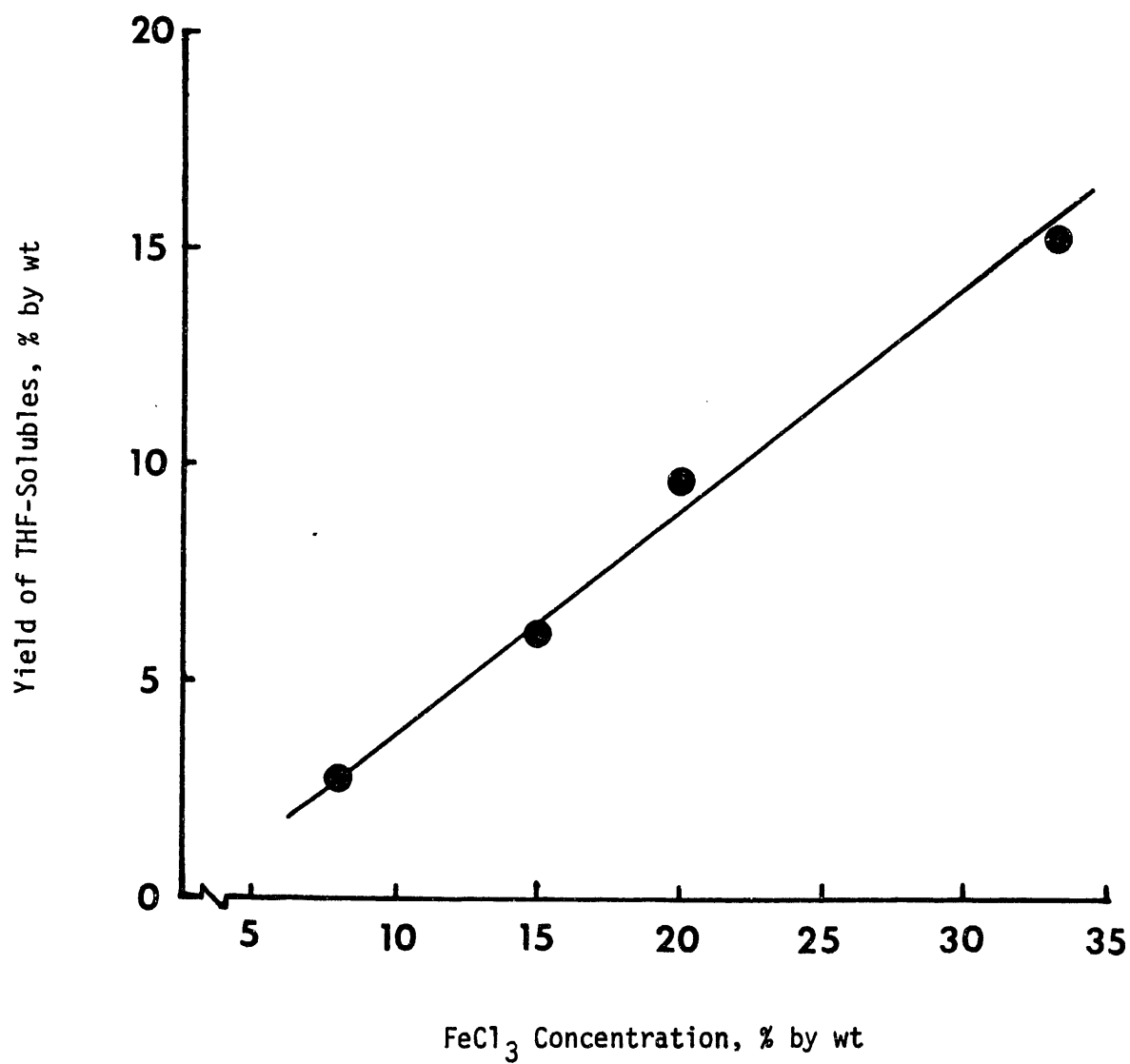


Figure 2. Yield of THF-Soluble Products from mild HT of BS(IL)-FeCl₃ as a Function of FeCl₃ Concentration (275°C; 3 hr).

hydrotreatment temperature and reaction time (in an autoclave system). As seen, the solubilization yield increases with increase in HT temperature and reaction time. At 275°C and a reaction time of 2-3 hr, or at 290°C and 1 hr, the yield is ca 7 - 10 % which could be considered suitable from the point of view of the efficiency of the overall sequential depolymerization procedure. Specifically, the optimal conditions for the HT step were previously defined as those under which the extent of overall solubilization after the subsequent base-catalyzed depolymerization (BCD) step is maximal (J. Shabtai, I. Saito, and T. Skulthai, Proc. 1985 Internat. Confer. Coal Science, Sydney, Australia, Pergamon Press, 1985, pp. 223 - 226).

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 very low BCD temperature of 230°C was used in these runs in order to determine more clearly the solubilization tendencies of the BS(IL) coal. As seen, highest yield of THF-solubles (30.0 % by wt) in the BCD step (at 230°C) is obtained in the run using a temperature of 275°C in the preceding HT step. Although the yield of THF-solubles in the HT step is higher at 290°C, the THF-solubles yield in the subsequent BCD step is markedly lower (21.8 %) as compared with that obtained in the run with an HT temperature of 275°C. Consequently, the total THF-solubles yield from the combined HT and BCD is higher for a HT temperature of 275°C as compared with 290°C.

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 275°C in the preceding HT step. Two experiments (nos. 81 and 82) were performed without preliminary hydrotreatment (HT) of the BS(IL) coal for the purpose of

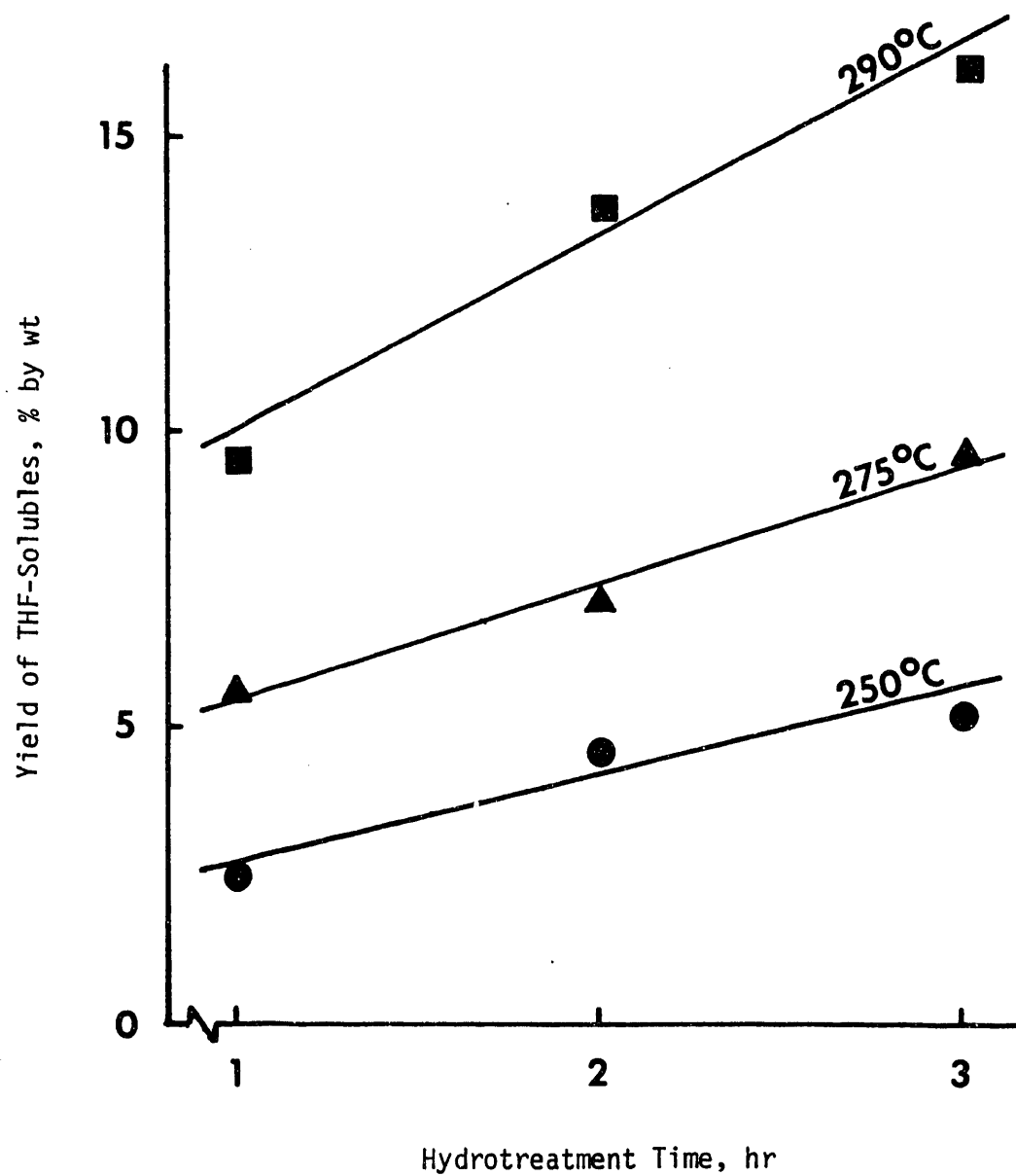


Figure 3. Yield of THF-Soluble Products from Mild HT of BS(IL)-20 % FeCl₃ Intercalate as a Function of HT Temperature and Reaction Time.

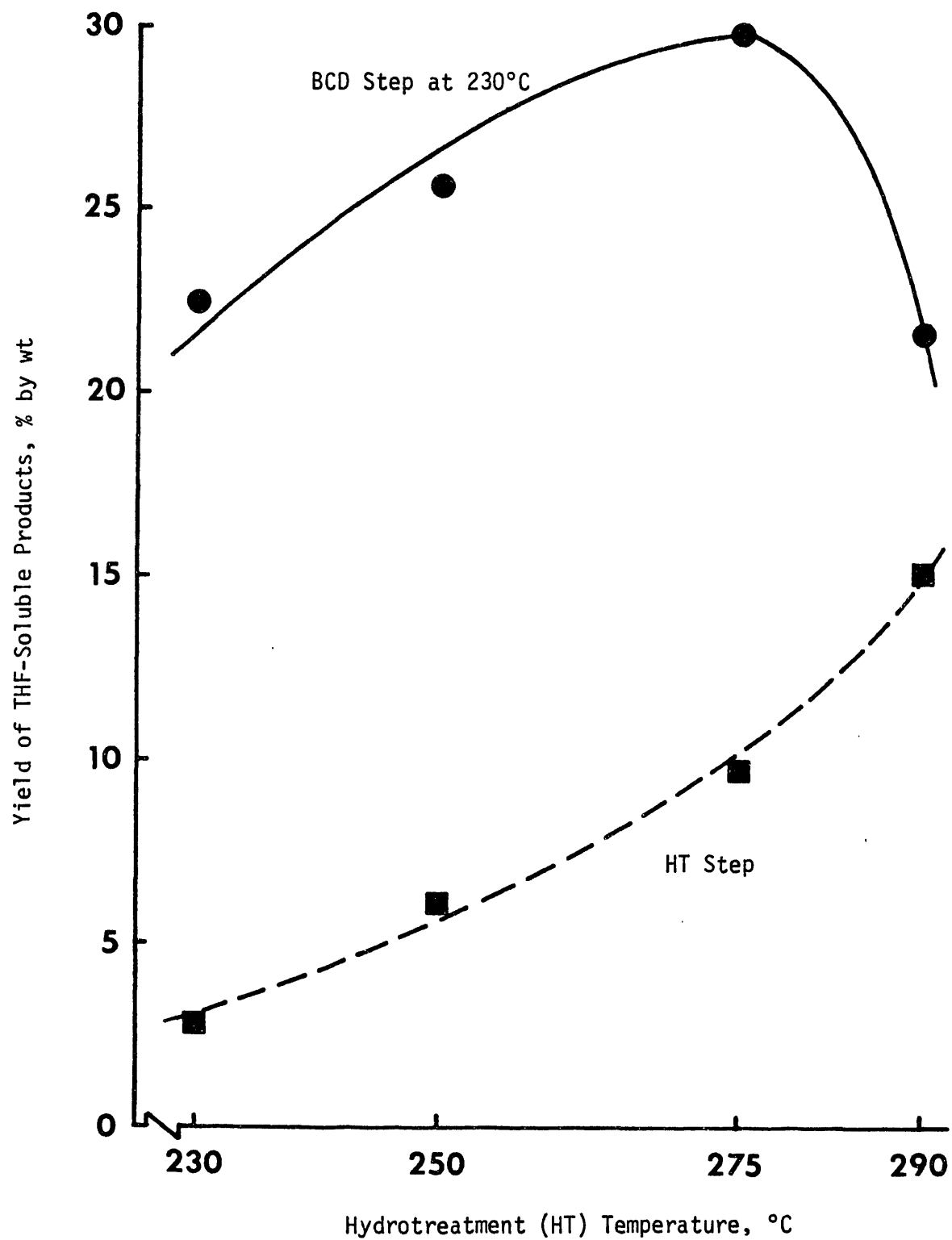


Figure 4. Effect of Reaction Temperature, used in the HT Step, upon the Yield of THF-Soluble Products in the Subsequent BCD Step.

comparison. As seen from experiments no. 83 to 85, the total yield of THF solubles from the sequential HT-BCD steps increases markedly with increase in BCD temperature, viz from 62.1 % at 250°C to 88.7 % at 290°C. Solubilization can be brought essentially to completion at 290°C by extension of the reaction time. Experiments no. 81 and 82 show that BCD alone, without the HT step, results in markedly lower solubilization (30.8 % at 250°C, and 45.9 % at 275°C) of the BS(IL) coal.

Table 1 shows also the distribution of the THF-soluble products from BS(IL) coal into oils, asphaltenes, and asphaltols, as a function of the BCD temperature. As seen (experiment no. 83 to 85), the proportion of asphaltols and asphaltenes in the products decreases, while that of oils (cyclohexane-solubles) correspondingly increases with increase in BCD temperature from 250°C to 290°C. Products obtained by BCD alone (expts. 81 and 82) consist mostly of asphaltols. Relevant data in Table 1 are also plotted in Figure 5.

Hydroprocessing (HPR) Step

It was found in previous studies that a depolymerized Wyodak coal product is effectively converted into a light hydrocarbon oil by hydroprocessing at 350 - 370°C and a hydrogen pressure of 2500 - 3000 psig, using a sulfided 6Co8Mo catalyst (Y. Shukla, Ph.D. thesis, University of Utah, 1985). A similar set of hydroprocessing conditions was applied in the present study of the depolymerized BS(IL) coal products.

Table 2 summarizes the elemental compositions of the original BS(IL) coal, the coal derived from it by pre-extraction with THF, and the mildly hydrotreated coal obtained in the HT step, while Table 3 provides the elemental compositions of the depolymerized coal product (THF-solubles) obtained by the sequential HT-BCD steps, and of the final, hydroprocessed (HPR) product. As seen in Table 2, the mild hydrotreatment (HT) step results

Table 1
Effect of Temperature on the Yield and Distribution
of Products from BCD of Mildly Hydrotreated BS(IL) Coal

Experiment No.	81 ^a	82 ^a	83 ^b	84 ^b	85 ^b
HT temperature, °C	-	-	275	275	275
BCD temperature, °C	250	275	250	275	290
Total yield of THF-solubles, % by wt. ^c	30.8	45.9	62.1	73.1	88.7
Distribution of THF solubles, % by wt.					
Oils	9.6	39.0	39.9	52.9	65.7
Asphaltenes	8.1	4.8	24.0	19.1	9.8
Asphalts	82.4	56.2	36.1	28.0	24.5

^aThe BS(IL) coal was not subjected to mild hydrotreatment (HT) in these runs.

^bThe total yield in these experiments includes 9.8 % 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 7.9 % by wt of THF-soluble pre-extract.

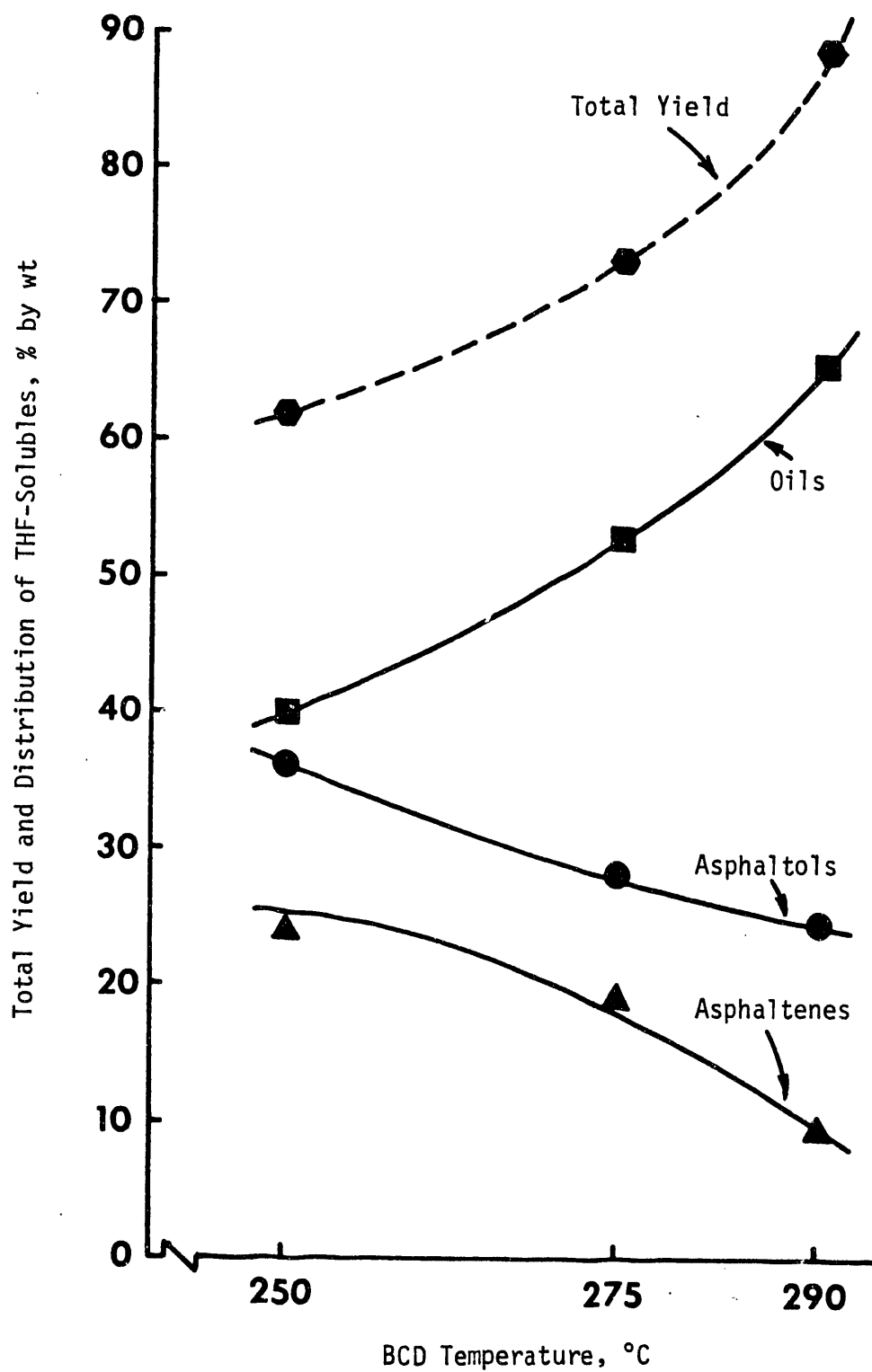


Figure 5. Change in Total Yield and Distribution of THF-Soluble Products from Sequential HT (at 275°C) and BCD of BS(IL) Coal, as a Function of BCD Temperature.

Table 2
Elemental Composition of Products Derived from
BS(IL) in the Extraction and HT Steps

Element, % by Wt	Original Coal	Pre-Extracted Coal	Mildly Hydrotreated (HT) Coal
Carbon	78.89	76.06	74.33
Hydrogen	5.35	5.83	8.17
Nitrogen	1.22	1.38	0.59
Sulfur	4.37	3.28	1.03
Chlorine	0.14	n.d	n.d
Oxygen (by difference)	10.04	13.45	15.88

^aBS(IL) coal after removal of 7.9 % by wt of THF-solubles (resins) in the pre-extraction step.

Table 3
Elemental Composition of Depolymerized BS(IL) Coal
and of HPR Products Derived from it in the HPR Step

Element, % by wt.	Depolymerized Coal ^a	Hydroprocessed (HPR) Product ^b
Carbon	77.85	87.09
Hydrogen	7.36	11.55
Nitrogen	0.89	0.07
Sulfur	0.01	< 0.01
Oxygen (by difference)	13.89	1.29

^aThe THF-soluble, depolymerized BS(IL) coal product was obtained by HT at 275°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.

in some decrease in C content and a considerable increase in H content. Further, the high sulfur content (4.37 %), typical of the Illinois no. 6 coal is reduced to a much lower level (1.03 %) in the HT step.

As seen in Table 3, the depolymerized BS(IL) coal product (THF-solubles), obtained by the combined HT-BCD procedure, retains a high oxygen content, viz., the depolymerizing HT and BCD steps do not cause any appreciable extent of hydrodeoxygenation. In contrast, the final HPR of the depolymerized BS(IL) coal results in exhaustive hydrodeoxygenation, hydrodesulfurization and hydrodenitrogenation, yielding a light hydrocarbon oil product (see below).

Table 4 summarizes the boiling point distribution of the depolymerized BS(IL) coal and of the hydrocarbon product derived from it in the HPR step. As seen, the oxygen-rich, depolymerized BS(IL) coal product has a rather low volatility as reflected in a total distillable portion (< 538°C) of 38.0 % by wt, including 20.5 % of low boiling fractions (gasoline, kerosene and gas oil; b.p. up to 325°C). In contrast, the hydrocarbon product obtained by hydroprocessing of the depolymerized BS(IL) coal is a volatile, light oil, containing 73.9 % by wt of components boiling < 538°C. The distillate includes 57.1 % by wt of low-boiling fractions (gasoline, kerosene, and gas oil, b.p. up to 325°C). In a blank experiment, a sample of BS(IL) coal was subjected directly to hydroprocessing (HPR), without prior depolymerization by the combined HT-BCD procedure. The product obtained in this run contained < 5 % by wt of components boiling up to 325°C.

Results obtained in the studies with BS(IL) coal as feed can be summarized as follows:

- (1) The low-temperature depolymerization - liquefaction procedure, summarized in Figure 1, is easily adaptable and applicable to a high-sulfur, Burning Star (Illinois no. 6) coal sample. The final product obtained consists

Table 4
Boiling Point Distribution of Depolymerized BS(IL) Coal
and of Hydrocarbon Products Derived From it by HPR^a

Fraction (b.p., °C) wt %	Depolymerized Coal ^b	Hydroprocessed (HPR) ^c Product
Gasoline (< 200°)	3.4	15.1
Kerosene (200-275°)	10.8	29.8
Gas Oil (275-325°)	6.3	12.2
Heavy Gas Oil (325-400°)	9.7	3.5
Vacuum Gas Oil (400-538°)	7.8	13.3
Total Distillable (< 538°)	38.0	73.9
Atmospheric Residue (> 350°)	73.0	41.4
Vacuum Residue (> 538°)	62.0	26.1

^aBoiling point distributions were determined by simulated distillation.

^bThe depolymerized coal was obtained by HT at 275°C, followed by BCD at 290°C.

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

of a fully desulfurized, light hydrocarbon oil.

- (2) Suitable processing conditions for each step of the stepwise depolymerization - liquefaction of the above coal were determined.
- (3) Direct hydroprocessing of the Burning Star (Illinois no. 6) coal with sulfided catalysts is ineffective for its conversion into a light hydrocarbon product.

In accordance with the research program the depolymerized, THF-soluble coal products will be subjected to detailed analysis for the purpose of deriving average molecular structures for the oil, asphaltene and asphaltol fractions. The data obtained will be used to develop a structural model for the BS(IL) coal.

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

A systematic study of the low-temperature stepwise depolymerization - liquefaction of a high-volatile bituminous coal from Elkhorn (Kentucky) is presently being performed. Results obtained will be provided in Progress Report no. 2.

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