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

FINAL REPORT

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Chapter 1

PRINCIPLES OF LOW-TEMPERATURE COAL DEPOLYMERIZATION-LIQUEFACTION AND PROJECT FRAMEWORK

1.1 Low-Temperature Coal Solubilization Reactions

Direct coal liquefaction processes, developed before and after World War II, have been based on the principle of hydrogen addition to coal under severe conditions, i.e., at elevated temperature and pressure. The high temperature leads to initial cleavage reactions of the coal macromolecules by thermally rupturing some weak carbon-to-carbon and carbon-heteroatom linkages. This is followed by various fast secondary chemical reactions. The hydrogen plays an important role in stabilizing the reactive intermediate species to yield the final liquid and gaseous products. Under such rather drastic conditions, the breakdown of the coal framework is non-selective and to a large extent accompanied by retrogressive and resynthesis reactions. As a result, there is predominant production of heavy oils accompanied by high yields of hydrocarbon gases, and the overall process is characterized by low efficiency resulting in high cost of the liquid fuels produced. Therefore, the possibility of developing coal liquefaction processes under less severe processing conditions, leading to higher selectivity for liquid products, lower hydrogen consumption, reduction in the extent of retrogressive reaction and lower operating costs, has recently attracted considerable interest. This has been expressed in developing new approaches to catalytic depolymerization-liquefaction processing of coal under mild temperature and pressure conditions. Low-temperature coal reactions could also be of major value for elucidating the nature of the original building units of coal, and thereby the structure of the latter.

Considerable work has been performed previously on the development of low-temperature coal solubilization procedures which rely to a larger extent on the application of selective chemical-catalytic reactions. Such procedures include reduction with lithium-ethylenediamine, electrochemical reduction, reductive alkylation, transaralkylation with a phenol-BF₃ system, transaralkylation with phenol using p-toluenesulfonic or benzenesulfonic acid as catalysts, Friedel-Crafts alkylation or acylation, base-catalyzed hydrolysis, base-promoted hydrogen donation from isopropanol, treatment with a ZnCl₂-methanol melt, and others. Application of the above procedures leads to coal solubilization in various solvents, e.g., pyridine or benzene, by means of major chemical modification of the coal structure and attendant partial depolymerization.

It has been generally agreed that coal liquefaction involves cleavage of different types of intercluster linkages in the coal structure. For high yields of low molecular weight, monocluster products, selective cleavage reactions of such linkages is essential. The common feature of all the above-mentioned low-temperature procedures is that each one is based on the application of a single type of reaction which affects only a given type of linkages but does not affect or affects to a lesser extent, other types of linking groups. The overall result is only partial depolymerization of the coal and consequent formation of high boiling liquid products.

1.2 Stepwise Low-Temperature Coal Depolymerization-Liquefaction

Intercluster linking groups in coals include alkylene, benzyl etheric, aryl etheric, dibenzofuranic, biaryl, and other groups. Some of these linkages, e.g., alkylene, viz., -(CH₂)_n-, and benzyletheric groups, are easily susceptible at low temperature (250-350°C) to hydrogenolytic cleavage in the presence of mild hydrogenolysis catalysts, e.g., acidic aqua complexes of metal halides. On the

other hand, the important type of diaryl etheric linkages is not susceptible to mild hydrogenolysis, but is easily susceptible to mild hydrolysis. A third type of important linking groups, i.e., dibenzofuranic and direct biaryl, viz., (Ar)C-C(Ar) groups, are not susceptible to either mild hydrogenolysis or hydrolysis, but are susceptible to ring hydrogenation and attendant hydrogenolysis with sulfided Mo-based catalysts. These differences in the reactivity of intercluster linkages have been demonstrated by detailed model compound studies, both in this and other laboratories.

Based on the above described differences in the reactivity of intercluster linkages, an effective new procedure for low-temperature coal depolymerization-liquefaction was proposed and initially examined in our laboratory and then further developed in the framework of this project. It involves the application of three sequential reaction steps in which different types of intercluster linkages in the coal structure are subjected to preferential cleavage.

A scheme of this procedure is given in Figure 1.1.¹⁻⁴. The pre-extraction with THF removes most of the easily extractable material within the coal network, leaving the porous system of the coal more susceptible to catalyst impregnation. During subsequent impregnation, the FeCl₃ catalyst becomes uniformly dispersed in the coal particles as recently demonstrated by electron probe microscopy. The partial depolymerization of the coal during the HT step involves preferential hydrogenolytic cleavage of alkylene (e.g., methylene), benzyl etheric, cycloalkyl etheric, and some activated thioetheric linkages. The following BCD step completes the coal depolymerization by base-catalyzed hydrolysis (or alcoholysis) of diaryl etheric, aryl cycloalkyl etheric, diaryl thioetheric, and other bridging groups. Depolymerized coal samples obtained by the above sequential HT-BCD treatment consist of mixtures of low molecular weight products, composed

Figure 1.1 General scheme of the low - temperature coal depolymerization-liquefaction procedure.

primarily of monocluster compounds. In the final step, the depolymerized product undergoes exhaustive heteroatom removal, partial ring hydrogenation, and some C-C hydrogenolysis to yield a light hydrocarbon oil. As demonstrated in the present work this procedure has the advantages of very high overall coal conversion to low molecular weight hydrocarbon oils. It also provides very valuable structural information on the fundamental building units of the coal structure.

1.3 Framework of the Research Project and of the Present Final Report

One of the main objectives of this research work was to examine in depth the effectiveness of the above three-step low-temperature depolymerization-liquefaction procedure, as applied to U.S. coal samples of varying rank, including lignites, subbituminous, and high volatile bituminous coals. Another objective was to elucidate the complex liquefaction chemistry involved in this procedure by detailed structural analysis of depolymerized coal products. The research work involved the application of advanced analytical techniques and development of theoretical models that allow deeper understanding and prediction of coal liquefaction chemistry. Briefly, the present investigation was performed in the following directions:

1. Determination of the suitable range of specific processing conditions and effective catalysts for each step of the low-temperature depolymerization-liquefaction of Blind Canyon (Utah), Illinois no. 6 (Illinois), Elkhorn (Kentucky), Pittsburgh no. 8 (Pennsylvania), Fruitland (New Mexico), and Wyodak (Wyoming) coals; and Beulah Zap (North Dakota) and Hagel (North Dakota) lignites, using the stepwise procedure indicated in Figure 1.1.
2. Determination of (a) the yield and (b) the solubility distribution

of depolymerized products from the above coals and lignites and examination of their relationship to coal rank and reactivity.

3. Detailed study of the organic-chemical composition of the depolymerized-liquefied products obtained from the above coals and determination of the change in product composition as a function of coal rank and of processing conditions.
4. Determining the distribution of final hydrocarbon products from the above coals and evaluating their quality as potential liquid fuels.
5. Elucidation of the reaction mechanisms involved in the procedure by model compound studies.

The present final report provides detailed information (Chapters 2 and 3) on the depolymerization-liquefaction reactions of five representative coals among those studied (see above, 1). Short summaries of results obtained with the other coals are given in Chapter 4.

CHAPTER 2

LOW-TEMPERATURE DEPOLYMERIZATION-LIQUEFACTION OF (1) BLIND CANYON (UTAH), ILLINOIS NO.6 (ILLINOIS) AND ELKHORN (KENTUCKY) COALS, AND (2) BEULAH ZAP (NORTH DAKOTA) AND HAGEL (NORTH DAKOTA) LIGNITES

2.1 Introduction

Samples of two high volatile bituminous (HVB) coals from Blind Canyon (Utah) and Illinois no. 6 (Illinois) and a sample of Beulah Zap (North Dakota) lignite, referred to hereafter as BC(UT), IL(IL) and BZ(ND), respectively, were supplied by the Argonne National Laboratory premium coal program.

An Elkhorn (Kentucky) HVB coal and a Hagel (North Dakota) lignite, referred to below as EH(KY), and HA(ND), respectively, were supplied by the Pennsylvania State coal bank.

The above samples were first pre-extracted with tetrahydrofuran (THF) and the resulting pre-extracted coals were subjected to a previously mentioned (Chapter 1) stepwise low-temperature depolymerization-liquefaction procedure, which is shown in Figure 1.1.

The objective was to determine the optimal conditions for each step of the process, as a function of coal properties and rank. Products obtained in each step were isolated and characterized. Following is a detailed description of experimental results obtained for the coal and lignite samples studied.

2.2 Low Temperature Depolymerization -Liquefaction Study of a HVB Coal from Blind Canyon, Utah

2.2.1 THF pre-extraction

The BC(UT) coal was first extracted for 48 hr with THF in a Soxhlet apparatus, yielding 16.8 wt% of soluble products. This was the highest yield of THF-soluble pre-extract obtained from representative U.S. Argonne coals of varying rank. Figure 2.1 shows the THF pre-extract yield, as a function of carbon content based on the Argonne coal samples plus other coals investigated in this laboratory. As seen, the yield of THF pre-extract gradually increases with increase in the carbon content of the coal, i.e., from 3.5 wt% for Hagel (ND) lignite (C, 72.20%) to 16.8 wt% for BC(UT) coal (C, 80.69%). The pre-extract yield decreases somewhat for Pittsburgh no. 8 coal (C, 83.20%) and drops sharply to 1.3 wt% for Pocahontas (C, 91.05%), and then further drops to near zero for semi-anthracite and anthracite coals.

Table 2.1 shows the elemental composition (in wt%) of the studied coal samples, whereas Table 2.2 gives the analysis of the corresponding pre-extracts. The significant differences between the extracts and the original coals are that all of the extracts have higher H/C ratios (in wt%) than those of the original coal samples, but lower heteroatom

Figure 2.1 Yield of THF pre-extract from different U.S. coals, as a function of carbon content.

Table 2.1
Elemental composition of coals, % by wt

	C	H	N	S	O	H/C
BC(UT)	80.69	5.76	1.57	0.37	11.58	0.86
EH(KY)	85.36	5.69	1.75	0.72	6.31	0.80
PB(PA)	83.20	5.32	1.64	0.89	8.83	0.77
IL(IL)	77.67	5.0	1.37	2.38	13.51	0.77
BZ(ND)	72.94	4.83	1.15	0.70	20.34	0.79
HA(ND)	72.20	4.44	1.15	0.68	21.53	0.74

Table 2.2
Elemental composition of pre-extracts, % by wt

	C	H	N	S	O	H/C
BC(UT)	83.08	8.66	0.87	0.20	7.19	1.25
EH(KY)	82.5	7.14	1.10	0.43	8.83	1.04
PB(PA)	82.72	6.94	1.24	0.75	8.35	1.01
IL(IL)	81.01	7.08	0.99	1.97	8.95	1.05
BZ(ND)	73.44	8.32	0.45	0.22	17.57	1.36
HA(ND)	79.57	10.06	0.41	0.19	9.77	1.52

content. The two lignites, BZ(ND) and HA(ND), have markedly lower extract yields (< 3.8 wt%) as compared with the HVB coals. Further, the pre-extracts of the lignites have higher H/C values as compared to those of the HVB coal. It should also be noted that the Blind Canyon coal, which shows the highest pre-extraction yield, has a relatively higher H/C value (1.25) in the extract compared to the other high volatile bituminous coals (1.01-1.05).

In view of the unusually high yield of THF-soluble pre-extract from BC(UT) coal, the composition of this extract was studied in some detail. Further fractionation of the pre-extract gave 52.5 wt% of a resin fraction (hexane solubles), which corresponds to a resin content of 9 wt%, calculated on the MAF coal. The distribution of the BC(UT) pre-extract was as follows (in wt%):

Oils (cyclohexane-solubles)	57.0
Asphaltenes (cyclohexane-insolubles, toluene-solubles)	12.2
Asphalts (toluene-insolubles, THF-solubles)	30.8

More details about the pre-extraction product are given later in section 2.1.5.

2.2.2 Dependence of HT-BCD yield upon FeCl₃ catalyst concentration and reaction temperature in the HT step

In order to determine a suitable set of conditions for the HT step of the depolymerization procedure, BC(UT) coal samples were impregnated with FeCl₃ and subjected to mild hydrotreatment. The yields of THF-soluble products were determined as a function of HT temperature

between 250-310°C for two different FeCl₃ concentrations, i.e., 10 and 15 wt%. Results obtained are summarized in Figure 2.2, which shows that as reaction temperature increases, the THF-soluble yield slightly increases at the two FeCl₃ concentrations. Figure 2.3 shows the THF-solubles yield as a function of FeCl₃ concentration both in the HT and BCD step when the HT temperature was kept constant at 275°C and the BCD temperature at 290°C. Even though the THF-solubles yield moderately increases with the increase of FeCl₃ concentration from 5 to 20 wt% in the HT step, the overall yield in the combined HT-BCD treatment decreased with further increase in FeCl₃ concentration above 10 wt%. It is noteworthy that for the BC(UT) coal, a relatively low concentration of 10 wt% of FeCl₃ and a mild reaction temperature of 275°C is sufficient for a solubilization yield of 15.6 wt%. Such solubilization yields in the HT step were higher than those obtained from IL(IL) and BZ(ND) coals under identical conditions (see below).

The effect of the reaction temperature used in the HT step upon the yield of THF-soluble products in the subsequent BCD step was also investigated. Runs were performed at hydrotreatment (HT) temperatures in the range of 250-310 °C, keeping a constant BCD temperature of 290°C in each run. The results are summarized in Figure 2.4. As seen, the highest yield of THF-solubles (90.4% by wt) in the BCD step 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 310°C, the THF-solubles yield in the subsequent BCD step (after HT at 310°C) is lower than that after HT at 275°C. Consequently, the total THF-

Figure 2.2 Effect of FeCl_3 concentration and temperature used in the HT step upon the yield of THF-soluble products from BC(UT) coal.

Figure 2.3 Yield of THF-soluble products in the BCD step as a function of FeCl_3 concentration in the preceding HT step of BC(UT) coal.

Figure 2.4 Yield of THF-soluble products in the BCD step as a function of reaction temperature in the preceding HT step.

solubles yield from the combined HT and BCD step is higher (90.4 wt%) for an HT temperature of 275°C compared with that at an HT temperature of 310°C (82.6 wt%).

The optimal HT reaction temperature and FeCl₃ concentration in the HT step are determined by the overall yield of THF solubles obtained in the subsequent BCD step, viz. obtained by the combined HT-BCD treatment. Therefore, on the basis of these results, a FeCl₃ concentration of 10 wt% and a HT temperature of 275°C were selected and used as preferred HT conditions prior to the BCD step in subsequent studies. A reaction time of 3 hr and initial hydrogen pressure of 1500 psig were used in all experiments.

2.2.3 Effect of BCD temperature upon the THF-soluble yield and distribution of products

The effect of the BCD reaction temperature (in the range of 250-310°C) upon the total yield and distribution of THF-soluble products from BC(UT) coal was investigated. The BCD runs were performed subsequent to HT at the optimal temperature of 275°C (see above). The results are shown in Table 2.3 and are also plotted in Figure 2.5. Run no. 10 was performed without preliminary hydrotreatment (HT), for the purpose of comparison. As seen, the total yield of THF-solubles increases with increase in the BCD temperature, i.e., from 78.4 wt% at 250°C to 90.4 wt% at 290°C (pre-extracted MAF coal basis), but then decreases with further increase in temperature to 310°C. Run no. 10 shows that BCD alone, without the preceding HT step results in

significantly lower solubilization (79.9 wt%) as compared to that obtained in run no. 13 (90.4 wt%), even though an identical BCD temperature of 290°C was used.

Table 2.3 also shows the distribution of the THF-soluble products into oils, asphaltenes, and asphaltols, as a function of the BCD temperature. Runs 11-14 show that the concentration of asphaltols and asphaltenes in the products decreases, while that of oils correspondingly increases with increase in BCD temperature from 250°C to 290°C. However, at a higher BCD temperature (310°C), the trend is reversed and the yield of the oil fraction decreases, while those of the asphaltols and asphaltenes increase. The major change in the product composition at a BCD temperature in excess of 300°C is attributed to possible retrograde reactions, e.g., etherification of phenols and condensation of other reactive compounds formed in the initial hydrolysis stage of the BCD reaction (see discussion of reaction mechanisms, Chapter 4). Such resynthesis reactions have been reported in the literature^{153,154} and were confirmed by model compound studies in the present work (see Chapter 4).

The product obtained in the run at 290°C, without the preceding HT step (run no.10) contains 45.2 wt% of asphaltols and 42.5 wt% of oils. In comparison, the corresponding run at 290°C with preceding HT, produces only 23.9 wt% of asphaltols, as the main oil fraction comprises 61.5 wt% of the total product as shown in Figure 2.5. This demonstrates the basic importance of the preliminary mild hydrogenolytic reaction in the HT step.

Table 2.3
Effect of BCD temperature upon the yield and
distribution of products from sequential
HT-BCD of BC(UT) coal

Run No.	10 ^a	11 ^b	12 ^b	13 ^b	14 ^b
HT Temp., °C	--	275	275	275	275
BCD Temp., °C	290	250	275	290	310
Total Yield of THF-Solubles, wt% ^c	79.9	78.4	88.2	90.4	80.1
Distribution of THF-Solubles, wt%					
Oils ^d	42.5	40.8	55.8	61.5	48.3
Asphaltenes	12.3	22.5	18.9	14.6	22.8
Asphaltols	45.2	36.7	25.3	23.9	28.9

^a In this run, the BC(UT) coal was not subjected to mild hydrotreatment (HT) prior to the BCD step.

^b The total yield of THF-solubles from BCD includes 15.7% by wt of the THF-solubles obtained in the preceding HT step.

^c Yields of THF-solubles are calculated on the pre-extracted coal and do not include mechanical losses.

^d Cyclohexane solubles.

Figure 2.5

Effect of BCD temperature upon the yield and distribution of products from sequential HT-BCD of BC(UT) coal.

It must be pointed out that the asphaltol and asphaltene fractions obtained by the HT-BCD low-temperature procedure are in effect partially depolymerized products, susceptible to additional depolymerization. These products are fundamentally different from high molecular weight asphaltenes and asphaltols obtained in high temperature coal liquefaction. By repeating the HT-BCD procedure, i.e., by recycling of the asphaltol and asphaltene fractions, the yield of oil products can be increased by at least 15-20 wt% as found in some runs.

2.2.4 Hydroprocessing of depolymerized products

The predominant oil fraction of the depolymerized BC(UT) coal obtained by the sequential HT-BCD procedure (HT at 275°C, BCD at 290°C) subjected to hydroprocessing under the following conditions: 2700 psig H_2 pressure, sulfided 6%Co8%Mo/ γ - Al_2O_3 catalyst, and a catalyst /feed ratio of 1:5 by wt. A mixture of 2 parts of benzene and 1 part of n-dodecane was used as solvent and the solvent/feed ratio was 3:1 by wt.

The elemental compositions of (a) the original coal; (b) the predominant oil fraction of the depolymerized BC(UT) coal product; and (c) the final hydroprocessed product derived from the depolymerized coal, are summarized in Table 2.4. It is seen that (1) HPR results in the formation of a hydrocarbon product with considerably increased C and H contents and sharply reduced O and N contents as compared with those of the depolymerized BC(UT) coal feed. The oxygen content of the depolymerized oil fraction decreases drastically from 6.53% in the feed to 0.65% in the HPR product, while the nitrogen content decreases from

Table 2.4
Elemental composition of BC(UT) coal and
derived products, wt%

	C	H	N	S	O	H/C
Original Coal ^a	80.69	5.76	1.57	0.37	11.58	0.86
HT-BCD Oil ^b	83.43	8.90	1.0	0.14	6.53	1.28
Asphaltene ^c	83.97	7.14	1.56	0.26	7.07	1.02
Asphaltol ^d	79.75	6.48	1.72	0.23	11.82	0.98
HPR Oil ^e	87.96	11.14	0.21	0.04	0.65	1.52

^a MAF basis.

^b Cyclohexane solubles.

^c Toluene solubles, cyclohexane insolubles.

^d THF solubles, Toluene insolubles.

^e The hydroprocessing (HPR) step was performed at 360°C and 2700 psig H₂ pressure, using a sulfided CoMo catalyst and a mixture of benzene and dodecane (2:1 wt ratio) as a solvent.

1.0% in the feed to a level of 0.21 % in the HPR product, while the sulfur content decreases from 0.14% in the feed to a level of 0.04% in the HPR product. (2) Compared to the original coal, the depolymerized HT-BCD oil fraction has considerably lower heteroatom content, e.g., O, N, S content, while its H/C ratio increased from 0.86 in the original coal to 1.28 in the HT-BCD oil fraction. (3) The asphaltene and asphaltol fractions have a composition intermediate between that of the original coal and the depolymerized HT-BCD oil, e.g., O, N, S content lower than those of original coal, but higher than those of the fully depolymerized HT-BCD oil fraction. (4) The highly aliphatic resin fraction shows an H/C ratio of 1.38 which is higher than that of depolymerized HT-BCD oil fraction. The elemental analysis of this fraction was as follows: C, 86.27; H, 9.92; N, 0.44; S, 0.12; O, 3.25, wt%.

The boiling point distributions of the depolymerized BC(UT) coal (the predominant oil fraction) and of the product derived from it in the HPR step were determined by simulated distillation and are summarized in Table 2.5. The oxygen-rich (O content, 6.53 wt%) depolymerized coal has a relatively low volatility as reflected by a medium vacuum residue of 59.1 wt%, and a lower proportion of gasoline-, kerosene-, and gas oil-range fractions (a total of 16.7 wt% up to 325°C). In contrast, the hydroprocessed product contains almost 100 wt% of total distillables, including 76.5 wt% of low-boiling fractions (gasoline, kerosene, and gas oil; b.p. up to 325°C). These results provide a clear illustration of the high efficiency of the overall HT-BCD-HPR sequential procedure for

Table 2.5

Boiling point distribution of the depolymerized BC(UT)
coal and of the hydrocarbon product derived
from it by hydroprocessing (HPR)*

Fraction, (b.p., °C), wt. %	Depolymerized Coal	Hydroprocessed HPR product
Gasoline (<200 °C)	2.4	14.8
Kerosene (200-275 °C)	8.2	54.7
Gas Oil (275-325 °C)	6.1	7.0
Heavy Gas Oil (325-400 °C)	11.7	9.7
Vacuum Gas Oil (400-538 °C)	12.5	13.8
Total Distillable (<538 °C/760 torr)	40.9	~100
Atmospheric Residue (>350 °C)	79.4	21.1
Vacuum Residue (>538 °C)	59.1	< 0.1

* Boiling point distribution was determined by simulated distillation

converting the BC(UT) coal into light hydrocarbon liquids.

2.2.5 Effect of THF pre-extraction

The solvent extraction of coal has been employed for many years as a means of providing soluble material from coal. Furthermore, solvent extraction under mild conditions is one of the methods to provide useful knowledge about the coal structure through the characterization of its extract and clarification of the extraction mechanism. It was found that extraction can cause coal structure swelling and that this benefits the coal conversion process. The swelling can expand the coal structure thereby enabling faster or more complete penetration of the coal by liquids or by substances dissolved in liquids. In addition, a swollen coal structure allows more complete or more rapid diffusion of reaction products out of the coal structure.¹³⁵

Based on this previous knowledge, pre-extraction was performed on all the coal samples studied in this laboratory, and characterization of pre-extracts was carried out to obtain some insight about their structure. Experimental results indicated that solvents which extract large amounts of soluble material from coals are also good swelling solvents and the best solvents contain a nitrogen or oxygen atom possessing an available unshared pair of electrons. It was reported by many researchers that pyridine extracts contain significant quantities of colloidal material, which can be viewed as being macromolecular rather than molecular in nature. Therefore, THF was chosen for determining the degree of solubilization both in the pre-extraction and

depolymerization steps of the experimental procedure.

A comparative experiment was performed under identical HT-BCD conditions as those of expt.13 (Table 2.3), with the exception that the coal was not pre-extracted with THF. The experimental results are given in Table 2.6, which shows the total THF-solubles yield and product distribution for two comparative runs, viz., with vs without THF pre-extraction. As seen the total THF-solubles yield is somewhat lower and the distribution is inferior (lower yield of oils and higher yield of asphaltenes and asphaltols) as compared with those obtained in experiment 13 (Table 2.3), i.e., with pre-extraction. This result provided evidence to support the previously discussed observation by

Table 2.6

THF-soluble yield from HT-BCD of BC(UT) coal and
product distribution in BCD step
from comparative runs

	With pre-extraction	Without pre-extraction
Total yield of THF-solubles, wt%	90.4	82.3
Distribution of THF-solubles, wt%		
Oils	61.5	53.2
Asphaltenes	14.6	17.4
Asphaltols	23.9	29.4

many researchers, that the pre-extraction step can open the micropore structure of coal by removing some loosely bonded material, thereby improving the penetration of catalysts and reagents, and eventually benefiting the subsequent coal depolymerization and liquefaction. However, from a practical point of view, use of the total coal feed, without pre-extraction is also feasible.

Electron probe microanalysis (EPM) was used in collaboration with Prof. Eyring and coworkers for the purpose of clarifying the observed differences. Figure 2.6 shows the EPM spectrum of FeCl_3 -impregnated BC(UT) coal, when using a coal sample without pre-extraction, while Figure 2.7 shows the EPM spectrum of FeCl_3 -impregnated BC(UT) coal, after preliminary THF extraction of coal sample. It is obvious from this pictures that the FeCl_3 catalyst dispersion in the THF pre-extracted coal sample is considerably more uniform than that in the nonextracted coal. This should result in faster and more efficient hydrogenolysis reactions of the pre-extracted coal feed in the subsequent HT step.

2.3 Low-Temperature Coal Depolymerization-Liquefaction of Illinois No.6 High Volatile Bituminous Coal

A preliminary study of the low temperature depolymerization-liquefaction of Illinois no. 6 coal was previously initiated in this laboratory. In the present work, a systematic study of the reactions of this coal was performed, and the products obtained were subjected to detailed structural analysis (Chapter 3). Following is a description

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Figure 2.6

Electron probe microanalysis of FeCl_3 -impregnated BC(UT) coal, performed on coal sample directly.

of results obtained:

2.3.1. Determination of suitable processing conditions for the HT step

The change in the yield of THF-soluble products from mild HT (at 275°C) of FeCl₃-impregnated IL(IL) coal as a function of the FeCl₃ concentration was investigated and the result is shown in Figure 2.8. As seen, low solubilization yields (<10%) were obtained in the range of 5-20% by wt of FeCl₃ concentration. As indicated in the previous section, such low yields in the HT step are desirable from the point of view of maximal solubilization in the subsequent BCD step. As the FeCl₃ concentration is further increased from 20% to 35%, there is an additional increase in the THF soluble yields but this increase is slower. Figure 2.9 shows the yield of THF-soluble products from HT of an IL(IL) sample impregnated with 10% by wt of FeCl₃ as a function of hydrotreatment temperature and reaction time. As seen, the solubilization yield increases with an increase in HT temperature and/or reaction time. At 275°C and a reaction time of 2-3 hr, or at 290°C and 1 hr, the yield of THF-soluble products is 7-10 wt% which was found to be suitable from the point of view of the efficiency of the overall sequential depolymerization procedure (see below).

2.3.2. Determination of suitable conditions for the BCD step

The effect of the reaction temperature used in the HT step upon the yield of THF-soluble products in the subsequent BCD step was also investigated. It was found that the maximal yield of THF-solubles (89

Figure 2.8

Yield of THF-solubles from hydrotreatment (HT) of FeCl₃-intercalated IL(IL) coal as a function of FeCl₃ concentration.

Figure 2.9 Yield of THF-solubles from hydrotreatment (HT) of FeCl₃-intercalated IL(IL) coal as a function of HT time, FeCl₃ concentration 10% by wt.

wt%) in the BCD step (performed at 290°C with a sample impregnated with 10 wt% of FeCl_3) was obtained when the temperature in the preceding HT step was 275°C.

2.3.3 Dependence of product yields and composition
from base-catalyzed depolymerization (BCD) of
IL(IL) coal upon reaction temperature

Table 2.7 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. As seen from experiments no. 54 to 56, the total yield of THF solubles from the sequential HT-BCD steps increases markedly with an increase in BCD temperature, viz from 62.1 wt% at 250°C to 88.7 wt% at 290°C (MAF coal basis, excluding the THF pre-extract). Experiments no. 52 and 53 show that BCD alone, without the preceding HT step, results in markedly lower solubilization (30.8% at 250°C and 45.9% at 275°C) of the IL(IL) coal.

Table 2.7 shows also the distribution of the THF-soluble products from IL(IL) coal into oils, asphaltenes, and asphaltols, as a function of the BCD temperature. As seen (experiment no. 54 to 56), the proportion of asphaltols and asphaltenes in the products decreases, while that of oils (cyclohexane-solubles) correspondingly increases with an increase in BCD temperature from 250° to 290°C. Products obtained by BCD alone (expt. 52 and 53) consist mostly of asphaltols. Relevant data in Table 2.7 are also plotted in Figure 2.10.

Table 2.7

Effect of BCD temperature upon the yield and
distribution of products from sequential
HT-BCD of IL(IL) coal

Run No.	52 ^a	53 ^b	54 ^b	55 ^b	56 ^b
HT Temp., °C	--	--	275	275	275
BCD Temp., °C	250	275	250	275	290
Total Yield of THF- Solubles, wt% ^c	30.8	45.9	62.1	73.1	88.7
Distribution of THF- Solubles, 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

^a In this run, the IL(IL) coal was not subjected to mild hydrotreatment (HT) prior to the BCD step.

^b The total yield of THF-solubles from BCD includes 9.8% by wt of the THF-solubles obtained in the preceding HT step.

^c Yields of THF-solubles are calculated on the pre-extracted MAF coal, viz. they do not include mechanical losses.

^d Cyclohexane solubles.

Figure 2.10

Effect of BCD temperature upon the yield and distribution of products from sequential HT-BCD treatment of IL(IL) coal.

2.3.4. Hydroprocessing of the depolymerized
products derived by sequential
HT-BCD of IL(IL) coal

The predominant depolymerized coal product from IL(IL) coal was further hydroprocessed into light hydrocarbon oils at 350-370°C and a hydrogen pressure of 2500-3000 psig, using a sulfided 6Co8Mo catalyst.

Table 2.8 compares the elemental compositions of the original IL(IL) coal, depolymerized coal products obtained by the sequential HT-BCD steps (oil fraction), and hydroprocessed (HPR) product. As seen in Table 2.8, the high sulfur content (2.38%) of the Illinois no.6 coal is reduced to a much lower level (0.91%) in the BCD step. The depolymerized IL(IL) coal product (oil fraction) obtained by the combined HT-BCD procedure, retains a relatively high oxygen content (10.5%). On the other hand, the final HPR of the depolymerized IL(IL) coal results in exhaustive HDO, HDS and HDN reactions, which are reflected in the lower heteroatom content of final HPR oil fraction, yielding a light hydrocarbon oil product.

Table 2.9 summarizes the boiling point distribution of the depolymerized IL(IL) coal and of the hydrocarbon product derived from it in the HPR step. As seen, the oxygen-rich (O content, 10.5 wt%), depolymerized IL(IL) coal product has a lower volatility as reflected in a total distillable portion (<538°C) of 78.8% by wt, including 20.5% of low boiling fractions (gasoline, kerosene, and gas oil; b.p. up to 325°C). In comparison the HPR hydrocarbon product is almost fully distillable (93.9 wt%) and contains 72.6 wt% of low boiling fraction. In a blank experiment, a sample of IL(IL) coal was subjected directly

Table 2.8
Elemental composition of IL(IL) coal and
derived products, wt%

	C	H	N	S	O	H/C
Original Coal ^a	77.67	5.0	1.37	2.38	13.51	0.77
HT-BCD Oil ^b	79.87	7.83	0.89	0.91	10.5	1.18
HPR Oil ^c	87.01	11.55	0.07	0.08	1.29	1.59

^a MAF basis.

^b The depolymerized IL(IL) coal sample was obtained by HT at 275°C, followed by BCD at 290°C. The oil (cyclohexane solubles) fraction represents about 69 wt.% of the total product (see Table 2.7).

^c The hydroprocessing (HPR) step was performed at 360°C and 2700 psig H₂ pressure, using a sulfided CoMo catalyst and a mixture of benzene and dodecane (2:1 wt ratio) as a solvent.

Table 2.9

Boiling point distribution of the depolymerized IL(IL)
coal and of the hydrocarbon product derived
from it by hydroprocessing (HPR)^a

Fraction, (b.p., °C), wt. %	Depolymerized Coal	Hydroprocessed HPR product
Gasoline (<200 °C)	3.4	19.2
Kerosene (200-275 °C)	10.8	37.9
Gas Oil (275-325 °C)	6.3	15.5
Heavy Gas Oil (325-400 °C)	9.7	4.4
Vacuum Gas Oil (400-538 °C)	7.8	16.0
Total Distillable (<538 °C/760 torr)	38.0	93.9
Atmospheric Residue (>350 °C)	73.0	19.1
Vacuum Residue (>538 °C)	62.0	6.1

^a Boiling point distribution was determined by simulated distillation

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.

2.4 Low Temperature Depolymerization-Liquefaction of an Elkhorn (Kentucky) High Volatile Bituminous Coal

2.4.1 Introduction

It was shown above that the three-step coal depolymerization--liquefaction procedure (HT-BCD-HPR) is very effective for converting an HVB-B and HVB-C coal into a light hydrocarbon oil. The overall efficiency of the procedure was reflected in the high volatility of final products (after the HPR step), which contained almost fully distillable fractions (b.p < 538°C). This chapter summarizes results obtained in the application of the same depolymerization-liquefaction procedure to a HVB-A rank coal, e.g., Elkhorn (Kentucky) coal, designated below as EH(KY) coal.

A systematic study of EH(KY) as feed was performed with the purpose of determining the optimal conditions for each of the steps of the sequential depolymerization procedure indicated in Figure 1.6. Following is a description of the results obtained.

2.4.2 Mild hydrotreatment (HT) step

The yield of THF-solubles in the HT step of the depolymerizing treatment of EH(KY) coal was first determined as a function of HT temperature and FeCl₃ concentration. The change in the yield of THF-soluble products from mild hydrotreatment of EH(KY) coal-FeCl₃

intercalates as a function of reaction temperature at three different FeCl_3 concentration (5, 10, and 15 wt%) is shown in Figure 2.11. As seen, the solubilization yield increases moderately with increases 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, see discussion later) in comparison with the previously studied coal samples from Wyodak and Beulah Zap it was anticipated that this coal will have a higher concentration of methylene (and other hydrocarbon) intercluster linkages and lower concentration of etheric linkages. Consequently, a somewhat higher level of solubilization in the HT step, e.g., 15-20% by wt, was expected to be preferable, in comparison with the previously indicated optimal HT solubilization level of 8-10 wt% for lower rank coals. Figure 2.12 shows that such higher solubilization level for EH(KY) coal is attained at HT temperatures of 275-310°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 2.13. 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% therefore were selected as suitable conditions for the purpose of the study. It should be noted that this temperature and metal halide catalyst concentration are higher than those indicated as optimal for

Figure 2.11

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

Figure 2.12

Yield of THF-soluble products from hydrotreatment (HT) of EH(KY) coals, as a function of FeCl₃ concentration and HT temperature.

lower rank coals (from the point of view of the overall yield of THF-solubilization by the HT-BCD depolymerization procedure).

2.4.3 Base-catalyzed depolymerization (BCD) step

The effect of reaction temperature used in the HT step upon the yield of THF-soluble products in the subsequent BCD step was investigated and the results are summarized in Figure 2.13. As seen, the yield of THF-solubles in the BCD step (performed at a selected constant 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 (63 wt%).

Table 2.10 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. An experiment (run 39) was performed without preliminary hydrotreatment (HT) of the EH(KY) coal for the purpose of comparison. As seen from runs 31 to 34, the total yield of THF-solubles from the sequential HT-BCD steps increases markedly with an increase in BCD temperature from 250 to 290°C but then decreases sharply with a further increase in temperature to 305°C. Run 39 shows that BCD alone,

Figure 2.13

Effect of temperature used in the HT step upon the yield of THF-soluble products in the subsequent BCD step at 275°C.

Table 2.10

Effect of BCD temperature upon the yield and
distribution of products from sequential
HT-BCD of 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	64.6	71.7	45.7
Distribution of THF-Solubles, wt%					
Oils ^d	29.0	39.4	51.2	56.9	37.6
Asphaltenes	27.5	9.8	21.8	27.4	22.4
Asphalts	43.5	50.9	27.0	15.7	40.0

^a In this run, the EH(KY) coal was not subjected to mild hydrotreatment (HT) prior to the BCD step.

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

^c Yields of THF-solubles are calculated on the pre-extracted coal and do not include mechanical losses. The yield of THF-soluble pre-extract for EH(KY) coal is 12.8 wt%.

^d Cyclohexane solubles.

without the preceding HT step, results in a very low extent of solubilization (27.5 wt% at 275°C).

Table 2.10 also shows 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 fraction gradually increases, while that of the asphaltol fraction correspondingly decreases with an 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 behavior can be ascribed to the occurrence of retrograde reaction at temperatures > 300°C (see chapter IV). The relevant data in Table 2.10 are also plotted in Figure 2.14.

2.4.4 Hydroprocessing (HPR) step

A sample of depolymerized EH(KY) coal obtained by sequential HT-BCD treatment under the conditions of expt. 33 (Table 2.10) was subjected to hydroprocessing (HPR) at 370°C and a hydrogen pressure of 2700 psig, using sulfided 6Co8Mo as catalyst and a mixture of benzene and dodecane (2:1 wt ratio).

Table 2.11 shows the elemental composition of original coal, pre-extract, depolymerized product (HT-BCD oil) and final HPR product. As seen, HPR results in the formation of a hydrocarbon product with considerably increased C and H contents and sharply reduced O and N contents as compared with those of the depolymerized EH(KY) coal feed. The oxygen content of liquid products decreases drastically from 9.89%

Figure 2.14

Effect of BCD temperature upon the yield and distribution of products from sequential HT-BCD of EH(KY) coal.

Table 2.11
Elemental composition of EH(KY) coal
and derived products, wt%

	C	H	N	S	O	H/C
Original coal ^a	85.36	5.69	1.75	0.72	6.31	0.80
HT-BCD Oil ^b	80.40	8.50	0.81	0.42	9.89	1.29
HPR Oil ^c	88.17	9.96	0.06	0.07	1.74	1.37

^a MAF basis.

^b The depolymerized EH(KY) coal sample was obtained by HT at 290°C, followed by BCD at 290°C. The oil (cyclohexane solubles) fraction represents about 64 wt.% of the total product.

^c The hydroprocessing (HPR) step was performed at 360°C and 2700 psig H₂ pressure, using a sulfided CoMo catalyst and a mixture of benzene and dodecane (2:1 wt ratio) as a solvent.

in the feed to 1.74% in the HPR product. While the nitrogen content decreases from 0.81% in the feed to a level of 0.06% in the HPR product. Sulfur content decreases from 0.42% in the feed to a level of 0.07% in the HPR product. Further, the HPR oil fraction shows a slightly higher H/C value of 1.37 compared to that of 1.29 for HT-BCD oil fraction.

Table 2.12 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 90.2 % of distillables (b.p. < 538°C) including 72.2 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 a 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 primarily of simple, mostly monocluster compounds, and oxygen is in the form of nonbonding functional groups, e.g. phenolic groups, which are easily susceptible to exhaustive hydrodeoxygenation in the hydroprocessing (HPR) step to yield a hydrocarbon oil product.

Table 2.12

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

Fraction, (b.p., °C), wt. %	Depolymerized Coal	Hydroprocessed HPR product
Gasoline (<200 °C)	8.04	24.9
Kerosene (200-275 °C)	6.9	36.0
Gas Oil (275-325 °C)	7.3	11.3
Heavy Gas Oil (325-400 °C)	10.3	6.9
Vacuum Gas Oil (400-538 °C)	12.7	11.2
Total Distillable (<538 °C/760 torr)	45.2	90.2
Atmospheric Residue (>350 °C)	69.5	24.8
Vacuum Residue (>538 °C)	54.8	9.8

* Boiling point distribution was determined by simulated distillation

2.5 Low Temperature Depolymerization-Liquefaction Study of BZ(ND) Lignite

The BZ(ND) lignite was subjected to a detailed study using the same stepwise depolymerization-liquefaction procedure. This feed was of considerable interest in view of its higher oxygen content (20.3%) and different functionality - reactivity as compared to the above HVB coals. A systematic investigation of processing variables was performed with the objective of examining the response to adapting the low temperature depolymerization-liquefaction of representative U.S. lignites, e.g., BZ(ND), as feeds. Following are the results obtained in processing the BZ(ND) lignite according to the above procedure.

2.5.1. THF pre-extraction

Samples of BZ(ND) lignite were pre-extracted for 48 hr 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. The elemental composition analysis shows that the pre-extract of BZ(ND) has a very high H/C value (1.36 compared to 0.79 for the original lignite). This might be due to the special properties of lignite.

2.5.2 Mild hydrotreatment (HT) step

FeCl₃-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 FeCl₃ concentration in the range of 5-20 wt%. Results obtained are summarized in Table 2.13. 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.

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. Results obtained are summarized in Table 2.14 and Figure 2.15. As seen, the yield of THF-soluble products from the BCD reaction increases from 64.0% to 84.5 wt% with an increase in HT temperature from 250° to 290°C . However, a further increase in the HT temperature to 310°C causes a marked decrease in the yield of THF-soluble products in the subsequent BCD step (65.0%). 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).

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.

Table 2.13

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 2.14

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% ^c	64.0	78.9	84.8	65.0

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

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

^c This is the total yield obtained by the sequential HT-BCD.

Figure 2.15

Effect of temperature used in the HT step upon the yield of THF-soluble products in the subsequent BCD step at 275°C of BZ(ND) coal.

2.5.3. Base-catalyzed depolymerization (BCD) step

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 the mildly hydrotreated BZ(ND) lignite product as feed 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. As seen in Table 2.15 and Figure 2.16, the total THF solubles yield (MAF is) is very high (> 81 wt%) in the entire temperature range studied. It increases only slightly with an 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 wt% at 275°C) and in an undesirable product distribution (about 50% asphaltols) as compared with runs 11, which was performed also at a BCD temperature of 275°C, but with a preceding HT step.

Table 2.15 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 an increase in BCD temperature from 250° to 290°C. The asphaltene fraction remains almost at the same level. The product from run 9 (BCD alone, without

Table 2.15

Effect of BCD temperature upon the yield and
distribution of products from sequential
HT-BCD of BZ(ND) lignite

Run No.	9 ^a	10 ^b	11 ^b	12 ^b	13 ^b
HT Temp., °C	--	290	290	290	290
BCD Temp., °C	275	250	275	290	310
Total Yield of THF-Solubles, wt% ^c	59.1	81.0	84.8	86.0	78.1
Distribution of THF-Solubles, wt%					
Oils	31.8	30.2	52.5	63.0	44.1
Asphaltenes	19.0	13.5	16.9	17.8	12.3
Asphalts	49.2	56.3	30.6	19.2	43.6

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

^b The total yield of THF-solubles from BCD includes 7.9% by wt of the THF-solubles obtained in the preceding HT step.

^c Yields of THF-solubles are calculated on the pre-extracted coal and do not include mechanical losses. The yield of THF-soluble pre-extract for BZ(ND) coal is 3.8 wt%.

^d Cyclohexane solubles.

Figure 2.16

Effect of BCD temperature upon the yield and distribution of products from sequential HT-BCD treatment of BZ(ND) coal.

HT) consists mostly of asphaltols, clearly demonstrating the need for 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 2.15 and Figure 2.16), is similar to that observed previously with an Elkhorn (KY) 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.

2.5.4 Hydroprocessing of the depolymerized products of sequential HT-BCD of BZ (ND) lignite

The predominant depolymerized coal product from BZ (ND) lignite was further hydroprocessed into light hydrocarbon oils at 350⁰-370⁰C and a hydrogen pressure of 2500-3000 PSig, using a sulfided 6Co8Mo catalyst. Table 2.16 summarizes the elemental compositions of (a) the starting Beulah Zap lignite and pre-extract; (b) the depolymerized products obtained by sequential HT-BCD treatment; and (c) of the final hydroprocessed (HPR) product, as obtained in a typical experiment. As seen, the depolymerized HT-BCD oil fraction is accompanied by a considerable reduction of heteroatom content, i.e., O, from 20.3 to 12.7 wt%; N, from 1.15 to 0.62 wt%; and S, from 0.7 to 0.23 wt%. The decrease in oxygen is attributable primarily to decarboxylation reactions of the depolymerized lignite in the presence of the base catalyst. Hydroprocessing (HPR) of the depolymerized product yields a hydrocarbon oil having sharply reduced O, N, and S contents and

Table 2.16
Elemental composition of BZ(ND) coal
and derived products, wt%

	C	H	N	S	O	H/C
Original lignite ^a	72.94	4.83	1.15	0.70	20.34	0.79
HT-BCD Oil ^b	78.57	7.88	0.62	0.25	12.68	1.21
Asphaltene ^c	80.44	7.06	0.86	0.33	11.31	1.05
Asphatol ^d	79.14	6.40	0.98	0.38	13.10	0.97
HPR Oil ^e	88.73	10.14	0.08	0.03	1.02	1.38

^a MAF basis.

^b Cyclohexane solubles.

^c Toluene solubles, cyclohexane insolubles.

^d THF solubles, Toluene insolubles.

^e The hydroprocessing (HPR) step was performed at 360°C and 2700 psig H₂ pressure, using a sulfided CoMo catalyst and a mixture of benzene and dodecane (2:1 wt ratio) as a solvent.

correspondingly increased C and H contents.

Table 2.17 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 fully distillable and contains 77.4 wt% of gasoline, kerosene, and gas oil fractions. This demonstrates the high efficiency of the overall HT-BCD-HPR procedure for converting a representative U.S. lignite into a low-boiling hydrocarbon fuel.

The high 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.

2.6 Low Temperature Depolymerization-Liquefaction Study of Hagel (North Dakota) Lignite

The HA(ND) lignite was subjected to the same stepwise depolymerization-liquefaction procedure. Experiments were performed under identical conditions as those found suitable for BZ(ND) lignite, i.e., 20% FeCl₃ and 290°C in the HT step, 290°C and 310°C in the BCD step. Following is a brief summary of experimental results.

The pre-extract yield was 3.5 wt% (MAF basis) which is very close to 3.8 wt% for the BZ(ND) sample.

Table 2.17

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		Hydroprocessed HPR product	
Gasoline (<200 °C)	8.6	] 24.6	35.9	] 77.4
Kerosene (200-275 °C)	3.8		35.2	
Gas Oil (275-325 °C)	12.2		6.3	
Heavy Gas Oil (325-400 °C)	25.0		10.9	
Vacuum Gas Oil (400-538 °C)	23.4		12.7	
Total Distillable (<538 °C/760 torr)	73.0		~100	
Atmospheric Residue (>350 °C)	66.2		19.7	
Vacuum Residue (>538 °C)	27.0		< 0.1	

^a Boiling point distribution was determined by simulated distillation

The total THF-soluble yield in the HT step is 9.2 wt%, which is slightly higher than that of the BZ(ND) sample (7.9 wt%).

The total yield of THF-solubles and the product distribution from the HT-BCD treatment, using BCD temperatures of 290° and 310°C, are summarized in Table 2.18.

From Table 2.18, it can be seen that, in comparison with BZ(ND), HA(ND) lignite shows a slightly higher yield of total THF-solubles, but lower yield of oil fraction. The trend toward the decrease of both total THF-solubles and oil yield at higher temperature is the same as that found for BZ(ND). The results indicate that the depolymerization-liquefaction behavior of the two lignites is similar.

Table 2.18

Total THF-soluble yield and product distribution
of HA(ND) lignite

BCD temperature, °C	290	310
Total THF solubles(wt%)	88.6	79.2
Product distribution		
Oils	64.7	46.0
Asphaltenes	13.2	9.4
Asphalts	22.1	44.6

2.7 Comparison of the Depolymerization-Liquefaction Behavior of the Coals Studied as a Function of Rank

As discussed before, one of the objectives of the present work was to determine the range of suitable processing variables for depolymerization-liquefaction of representative U.S. coals and to examine the possibility that the depolymerization-liquefaction behavior of the latter is dependent on coal rank. Following are several relevant comparisons.

2.7.1 Pre-extract yield and elemental composition

The five coals studied in the present work, their ranks, pre-extract yields, and the elemental compositions of the pre-extracts, are given in Table 2.19. As seen from the Table 2.19, the three HVB coals show similar pre-extract yields in the range of 12.8 to 16.8 wt%. These yields are markedly higher than those of the two lignites (3.5-3.8 wt%). On the other hand, the elemental composition data clearly show that the H/C ratios for the two lignites are sharply higher (1.36 and 1.52) as compared with those of the three HVB coals (1.05 to 1.25). Among the latter the HVB-B coal from Blind Canyon, Utah, shows the highest H/C value (1.25).

2.7.2 Total yield of depolymerization products

Table 2.20 shows the total yields of depolymerized products, viz., total THF-soluble products, obtained in the HT step for a hydrotreatment

Table 2.19

Pre-extract yields, elemental composition and H/C ratios as a function of coal rank

	EH(KY)	BC(UT)	IL(IL)	BZ(DN)	HA(ND)
Rank	HVB-A	HVB-B	HVB-C	Lignite	Lignite
Pre-extract yield, wt%	12.8	16.8	14.6	3.8	3.5
C	82.5	83.08	81.01	73.44	79.57
H	7.14	8.66	7.08	8.32	10.1
N	1.10	0.87	0.99	0.45	0.41
S	0.43	0.20	1.97	0.22	0.19
O	8.83	7.19	8.95	17.6	9.77
H/C	1.04	1.25	1.05	1.36	1.52

Table 2.20

Total THF-soluble products in the HT step as a function of coal rank

Coal	Total THF-solubles
EH(KY)	15.8
BC(UT)	15.6
IL(IL)	8.6
BZ(ND)	7.3
HA(ND)	7.1

temperature kept constant at 275°C. As seen, the EH(KY) and BC(UT) coals show almost the same yield of total THF-soluble product which are twice as high as those from the BZ(ND) and HA(ND) lignites. These indicates concentration of hydrogenolyzable, indicating that the concentration of alkylene linkages in the HVB EH(KY) and BC(UT) coals is considerably higher than that in the oxygen-rich lignites (which characteristically are expected to have a higher concentration of non-hydrogenizable diaryl etheric linkages; see Chapter 3).

2.7.3 Depth of depolymerization (total yield of THF-solubles from HT-BCD treatment)

Table 2.21 shows the total THF-soluble yields obtained by the sequential HT-BCD steps, using two different BCD temperatures of 275 and 290°C (HT step performed under identical conditions). As seen from Table 2.21, the highest rank EH(KY) coal gives the lowest total THF-soluble products yield at both temperatures studied. On the other hand, the HVB-B and HVB-C coals, as well as the BZ(ND) lignite show very similar total THF-soluble yields at a temperature of 290°C. These results indicate that except for high rank coals, there is no major effect of coal rank upon the total yield of depolymerized products from the combined HT-BCD treatment.

2.7.4 Boiling point distribution of the final HPR products

Table 2.22 shows a comparison of the boiling point distributions of final HPR products for the coals studied. As seen, the higher rank HVB-A coal, viz., EH(KY), gives the lowest yield of total distillable

Table 2.21

Total THF-soluble products from sequential HT-BCD treatment as a function of coal rank^a

	BCD temp. 275°C	Total THF-solubles BCD temp. 290°C
EH(KY)	64.6	71.7
BC(UT)	88.2	90.4
IL(IL)	73.1	88.7
BZ(ND)	84.8	86.0
HA(ND)	--	88.6

^a HT conditions: temperature 275°C, H₂ pressure, 1500-2500 psig, reaction time, 2-3 hr.

Table 2.22

Comparison of boiling point distribution of final HPR products^a

Coal	EH(KY)	BC(UT)	IL(IL)	BZ(ND)
Low b.p. fraction ^b	72.2	76.5	72.6	73.6
Total distillable	90.2	-100	93.9	-100
Atmospheric residue	24.8	21.1	19.1	19.7
Vaccum residue	9.8	< 0.1	6.1	< 0.1

^a Determined by simulated distillation.

^b Low boiling point fractions including gasoline, kerosene and gas oil, b.p. up to 325°C/760 torr.

products and the highest yield of vacuum residue. On the other hand, the BC(UT) coal shows the highest yield of total distillable products and the lowest yield of vacuum residue. It should be generally noted that within the range of coals studied (C contents between 72.2 to 85.36 wt%), the coal rank does not have a major effect upon the boiling point distribution of the final hydrocarbon products obtained in the HPR step. This is consistent with the indication (see Chapter 3) that the size and nature of aromatic-hydroaromatic clusters in depolymerized coal products is similar (mostly 1-to 3-ring compounds). Although the depolymerized products from coals of different rank differ in the relative concentrations of functional groups, e.g., phenolic, thiophenolic, carboxylic acid, alkyl, and other groups, this functionality difference is essentially eliminated in the HPR step through exhaustive HDO (and other heteroatom-removal reactions) as well as partial ring hydrogenation and C-C hydrogenolysis. This ultimately results in similar hydrocarbon products from coals of different rank (within the rank range studied).

2.8 Summary and Conclusions

The main results obtained from the systematic study of low-temperature depolymerization-liquefaction of the EH(KY), IL(IL), and BC(UT) HVB coals, and BZ(ND) and HA(ND) lignites, can be summarized as follows:

- (1) Suitable mild hydrotreatment conditions for the HT step of the sequential HT-BCD-HPR procedure were determined to be as

follows, FeCl_3 concentration: 5-10% for BC(UT) and IL(IL) coals, 10-15% for EH(KY) coal, and 10-20% for BZ(ND) lignite; 1500 psig initial hydrogen pressure and 3 hr reaction time.

- (2). Suitable base-catalyzed depolymerization (BCD) conditions were determined for all the coals to be: BCD temperature, 290°C; 10% methanolic KOH solution as base-catalyst-solvent system; feed to catalyst weight ratio 1:1, 1000 psig initial nitrogen pressure, and 1 hr reaction time.
- (3). Under the above optimal processing conditions the sequential HT-BCD treatment yields between 72 to 91 wt% of depolymerized, THF-soluble products. The predominant part of these products (57-63 wt%) consists of an oil (cyclohexane-soluble) fraction. The small asphaltene (benzene-soluble) and asphaltol (THF-soluble) fractions are partially convertible to oils by recycling through the HT-BCD treatment.
- (4). The final, hydroprocessing (HPR) step of the procedure causes exhaustive hydrodeoxygenation, hydrodenitrogenation, and hydrodesulfurization of the depolymerized product (obtained by the preceding HT-BCD steps) as evidenced by very low oxygen, nitrogen and sulfur contents of the HPR product. The final HPR product is essentially a light hydrocarbon oil characterized by high volatility and a very high content of low-boiling fractions (gasoline, kerosene, and gas oil, b.p. up to 325°C/760 torr).

- (5). On the basis of the above results it is concluded that the low temperature sequential MT-BCD-HPR procedure is very effective in converting high volatile bituminous coals and lignites into a high quality hydrocarbon oil.

CHAPTER 3

STRUCTURAL ANALYSIS OF DEPOLYMERIZED COAL PRODUCTS

3.1. Introduction

As shown in Chapter 2, HVB coals and lignites can be effectively converted into light hydrocarbon products by low-temperature depolymerization (HT-BCD treatment), followed by hydroprocessing (HPR). The structural analysis of products obtained in the depolymerization stage of the procedure is of particular interest since the mild HT-BCD treatment employed is expected to proceed with preservation of the original aromatic-hydroaromatic building units of the polymeric coal network and to cause only predictable changes in the intercluster linkages resulting from hydrogenolytic and hydrolytic cleavage reactions (see Chapter 4).

The purpose of this part of the work was, therefore, to analyze in detail the depolymerized, THF-soluble products obtained by the sequential HT-BCD treatment of selected HVB coals and liquids. The products were analyzed by a combination of simulated distillation, molecular weight determination, GC/MS, GC/CIMS, FTIR, ^{13}C and ^1H NMR, and other methods. Results obtained are described below.

3.2 Thermogravimetric (TG) Analysis of HT-BCD Products

Thermogravimetric analysis (TG) experiments were performed on the predominant (57-63 wt%) oil fraction of the depolymerized HT-BCD products obtained from BZ(ND), BC(UT) and IL(IL) coal samples. The TG results in Figures 3.1, 3.2 and 3.3 (obtained in the laboratory of Prof. Meuzelaar) show that about 90-95% of each oil fraction can be distilled below 350°C under vacuum (10^{-2} torr) and that about 80% of the oil fraction is distillable below 500°C under a nitrogen atmosphere at ambient pressure. These results are consistent with the results obtained by simulated distillation (see Chapter 2) and imply that the oil fractions consist of relatively low molecular weight, volatile compounds. Therefore, such products are suitable for direct analysis by high resolution gas chromatography and combined gas chromatography/mass spectrometry (GC/MS) methods.

3.3 Molecular Weights of Depolymerized products

An important breakthrough was achieved by Prof. Meuzelaar and Dr. Huai in the development of MS techniques for molecular weight profiling of depolymerized coal products (in the MW 100-650 range), prepared in the framework of this dissertation. The above mentioned MW range corresponds to the typical range of an Ion Trap Detector or other small bench-top sized MS systems. Use of GC/MS techniques offers several advantages over direct MS methods for MW profiling, i.e., positive identification of components (if desired); generation of simulated

Figure 3.1 Thermogravimetric analysis of HT-BCD oil fraction of Beulah Zap lignite, performed under vacuum and under nitrogen at ambient pressure.

Figure 3.2 Thermogravimetric analysis of HT-BCD oil fraction of Illinois no. 6 coal, performed under vacuum and under nitrogen at ambient pressure.

Figure 3.3 Thermogravimetric analysis of HT-BCD oil fraction of Blind canyon coal, performed under vacuum and under nitrogen at ambient pressure.

distillation profiles; and ease of sample injection. Routine GC/MS methods, however, are less useful for obtaining MW distribution information because of (a) limited MW range of compounds that can elute through the GC column and (b) loss of molecular weight information by electron ionization (extensive fragmentation of molecular ions).

A very short (4m) capillary column, known to allow for rapid elution of relatively large and polar molecules was used in the experiment. Such a short column provides not only short analysis times, but also the ability to observe the distribution profile of the eluting oil components as a function of column temperature. This concept is similar to that of simulated distillation that was utilized in the preceding Chapter 2 for determination of the b.p. distribution of depolymerized coal products.

The summed mass spectra of three depolymerized HT-BCD oil fractions are shown in Figures 3.4, 3.5 and 3.6. As seen, the components elute between M/z 50-480, with most components between M/z 200-350. The average molecular weight found for BZ(ND) lignite was 242, for BC(UT) coal, 247, and for IL(IL) coal, 253.

3.4 Gas Chromatography/Mass Spectrometry of Depolymerized Products

Positive structural identification of the various types of components present in the above oil fractions could not be carried out by MS techniques alone but required the use of GC/MS techniques, which have an upper limiting molecular weight limit of ~500.

Figures 3.7 and 3.8 show the total ion chromatogram (TIC) profiles

Figure 3.4 Summed mass spectrum of depolymerized HT-BCD oil fraction of Beulah Zap lignite by GC/CIMS.

Figure 3.5 Summed mass spectrum of depolymerized HT-BCD oil fraction of Illinois no. 6 coal by GC/CIMS.

Figure 3.6 Summed mass spectrum of depolymerized HT-BCD oil fraction of Blind Canyon coal by GC/CIMS.

Figure 3.7 Total ion chromatogram (TIC) profiles for HT-BCD oil fractions of (a) BZ(ND) sample, (b) IL(IL) sample.

Figure 3.8 Total ion chromatogram (TIC) profile for HT-BCD oil fraction of BC(UT) sample.

of the oil fraction from the depolymerized Beulah Zap lignite, Illinois no.6 and Blind Canyon coals. As seen, all the oils contain various compound types including three prominent classes of compounds: alkylsubstitutedhydroxyaromatics (e.g., alkylphenols), alkylsubstituted aromatic hydrocarbons (e.g., alkylnaphthalenes) and long chain n-alkanes, with several of the distinguishable peaks labelled.

Figure 3.9 shows the integrated spectrum of the compounds eluting from 125 to 250°C for the Beulah Zap oil sample. The electron ionization spectra are dominated by odd mass fragment ions with three homologous ion series (connected as example). The m/z 77, 91, 105, and 119 series is typical of alkylbenzene fragments, while the higher series members at m/z 147, 161, 175, 189 and 203 probably represent hydroxytetralins and hydroxyindans (with the OH group more likely as substituent in the aromatic moiety). The ions at m/z 115, 129, and 143 are also possible rearrangement ions from the hydroxyindans.

A comparison of single ion fragmentograms of alkanes at M/z 71, alkylphenols at M/z 107, and alkylnaphthalenes at M/z 141 for the three HT-BCD oil fractions is presented in Figures 3.10-3.12 respectively. From the plotted characteristic ion summation chromatograms, it is clear that the examined HT-BCD oil fractions from the three coals show different concentrations and distributions of the three major compound groups. The n-alkanes (C_{12} - C_{31} range) were found to increase in relative abundance in the following order: Illinois no.6 < Beulah Zap < Blind Canyon. This trend is partially shown in Figure 3.10. The Blind Canyon oil sample also showed a very different alkylphenol and alkylnaphthalene

Figure 3.9 Integrated mass spectrum for compounds eluting between 150-250°C in GC/MS of the BZ(ND) oil fraction.

Figure 3.10 Comparison of single ion fragmentogram of alkanes at M/Z 71 of HT-BCD oil fractions.

Figure 3.11 Comparison of single ion fragmentograms of alkylphenols at M/Z 107 of HT-BCD oil fractions.

Figure 3.12 Comparison of single ion chromatograms of alkyl naphthalenes at M/Z 141 for HT-BCD oil fractions.

pattern while the other two samples show similar patterns.

Figure 3.13 shows the total ion chromatogram profiles of the pre-extract and of the HT-BCD total THF-soluble product (referred below as HT-BCD TS) obtained from the BC(UT) coal. The comparison between the two products is of some interest because both consist of THF-soluble products, but one is extracted from the original coal, whereas the other represents the total depolymerized coal. There are several significant differences in the spectra of the two products. The HT-BCD TS product shows a more abundant presence of alkylphenols than that of pre-extract. This much higher concentration of phenolic compounds in the HT-BCD TS product is obviously the result of hydrolysis reactions in the BCD step (see Chapter 4). Further, the TIC of the pre-extract shows considerable concentration of alkylated aromatic-hydroaromatic compounds, e.g., alkyltetralins, whereas the HT-BCD TS product contains appreciable amounts of alkylarenes. Finally, there is an abundance of biomarkers in the pre-extract sample, whereas such compounds are practically absent in the HT-BCD TS product. The comparison of single ion fragmentograms of alkanes at M/z 71, alkylphenols at M/z 107 and alkyl-naphthalenes at M/z 141 is shown in Figure 3.14.

Figure 3.15 shows the TIC profile of HPR the final hydrocarbon oil product from hydroprocessing (HPR) of BC(UT) coal. Compared to Figure 3.8, the significant difference is that the HPR oil product is free of oxygen-containing functional groups, due to the effective hydrodeoxygenation reaction. The product consists entirely of hydrocarbons, i.e., naphthenes, naphthenoaromatics, arenes and alkanes.

Figure 3.13 Total ion chromatogram profiles for (a) pre-extract; (b) HT-BCD TS from BC(UT) coal

● Alkylphenols
 ◆ Alkylbenzenes
 C Alkanes
 ▽ Alkyl naphthalenes
 ■ Alkyl tetralins
 * Biomarkers

Figure 3.14

Comparison of single ion fragmentograms of (a) Alkanes at M/Z 71, (b) Alkylphenols at M/Z 107, and (c) Alkyl-naphthalenes at M/Z 141 in the pre-extract and the HT-BCD TS product obtained from BC(UT) coal.

Figure 3.15 Total ion chromatogram profile of the final hydroprocessed (HPR) oil product from Blind Canyon, Utah coal.

- ▼ Monocyclic naphthenes
- Decalins(or Indanes)
- ▽ Higher naphthenes and naphthenoaromatics
- Naphthenoaromatics
- ⊙ Alkanes
- ◆ Bicyclohexyls

The concentration of alkylarenes is decreased because some of these components were converted into naphthenoaromatics and naphthenes, due to ring hydrogenation reactions during the HPR step.

3.5 Separation of Depolymerized Coal Products into Compound Classes. Followed by GC-MS Analysis

In order to obtain more accurate information on the composition of depolymerized coal products, work was performed (in collaboration with Prof. M. Lee, Brigham Young University) on the separation of such products into compound classes by elution chromatography. The fractions were analyzed using gas chromatography/mass spectrometry. Structural identifications were based on a combination of chromatographic retention and mass spectral fragmentation data.

In addition to the BZ(ND), BC(UT) and IL(IL) samples studied before, a sample of Pocahontas no. 3, which is low volatile bituminous coal, was added in this study for the purpose of comparison.

The predominant (65-70%) oil fractions of the depolymerized (HT-BCD) products of the above coals were first separated into four fractions by elution chromatography with solvents of gradually increasing polarity. The fractions consisted of the following compound classes:

- Fraction 1: Aliphatic compounds (paraffins and naphthanes).
- Fraction 2: Alkylarenes.
- Fraction 3: Phenols (plus some N-containing compounds).
- Fraction 4: Phenols (plus some carboxylic acid).

The distribution of products into the above fractions for the four coals studied is given in Table 3.1. As seen, the table points out that

Table 3.1
Alumina column fractionation HT-BCD products^a

Wt % of Coal, MAF basis				
Fraction	Beulah Zap	Illinois no. 6	Blind Canyon	Pocahontas no. 3
Aliphatic ^b	3.2	2.7	8.3	2.2
Neutral ^c	9.5	11.0	16.2	17.5
Polar-1 ^d	30.6	2.5	3.4	24.0
Polar-2 ^e	28.1	53.9	44.6	8.1
Total wt% of Coal	71.4	70.1	72.5	51.8

^a The feeds consisted of the predominant (65-70%) oil fraction of the product.

^b Paraffins + naphthenes.

^c Alkyl-substituted aromatic hydrocarbons.

^d Phenolic fraction.

^e Phenols + N-containing compounds.

as rank increases, the amount of polar components (i.e., Polar-1 and Polar-2 fractions) decreases. Also, as expected, fewer fatty acids are present in the low volatile bituminous samples than in the BZ(ND) lignite. In fact, Snape et al.¹⁵⁶ reported the absence of (i.e. < 0.1 wt%) fatty acids in a bituminous coal. The long chain aliphatic compounds may be the reduction products of straight chain fatty alcohols, acids and their esters in the coal structure such as reported by Snape et al.,¹⁵⁷ and Mudamburi and Given.¹⁵⁸ Similar aliphatic products have been observed by other researchers.¹⁵⁹⁻¹⁶¹ Further, it is possible that the majority of the n-alkanes reported in the Pocahontas no.3 coal are present in a difficult to extract mobile phase or, more likely as substituents or linking groups within the macromolecular network, which are released during the HT-BCD process. Nelson¹⁵⁹ has shown the importance of such aliphatic structures in coal pyrolysis, and Narayan¹⁶² concluded that longer alkylene ($-(CH_2)_n-$) groups are major aliphatic components of the coal and are part of the macromolecular network.

The chromatographic results of the aliphatic fractions obtained from the HT-BCD products of the four coals studied are shown in Figures 3.16 and 3.17. As seen, the HT-BCD product consists predominantly of stable compounds, e.g., alkanes, alkylarenes, phenols and N-heterocyclics. The aliphatic fractions of the four HT-BCD products (Figures 3.16 and 3.17) show a normal hydrocarbon distribution from C_{12} to C_{40} , accompanied by branched alkanes and naphthenes. The Pocahontas no.3 HT-BCD product shows a slight odd over even preference

Figure 3.16 Gas chromatograms of the aliphatic fractions (HT-BCD products) of (A) Beulah Zap and (B) Illinois no.6 coals

Figure 3.17 Gas chromatograms of the aliphatic fractions (HT-BCD products) of (C) Blind Canyon, and (D) Pocahontas no.3 coals.

for $n\text{-C}_{27}$ to $n\text{-C}_{31}$. Likewise, the aliphatic fractions of the Illinois no.6 and Blind Canyon HT-BCD products exhibit an odd over even carbon number preference for n -alkanes in the same range. A similar odd over even hydrocarbon preference has been observed in soils, living plants, and other coal products, and it is also apparent in the pre-extraction products. On the other hand, the distribution of n -alkanes in the HT-BCD Beulah Zap product appears to be smooth, having no preference of odd over even carbon number hydrocarbon.

The chromatograms of the HT-BCD products of the alkyl-substituted aromatic hydrocarbon fractions are shown in Figures 3.18 and 3.19. Table 3.2 lists the compounds which correspond to the peak numbers in Figures 3.18 and 3.19. Analysis of the HT-BCD fractions resulted in the detection of alkylbenzenes, alkylnaphthalenes, and biphenyl compounds in addition to alkylated fluorenes, benzofluorenes, phenanthrenes, and other two-and three-ring aromatic compounds. The types of alkylarenes in the HT-BCD products remain quite similar. For example, each sample contains the same classes of compounds, such as the C_1 to C_4 alkylbenzenes, alkylnaphthalenes, alkylfluorenes, and alkylphenanthrenes. However, as rank increases, a noticeable shift to higher boiling products is apparent. Comparison of the Beulah Zap HT-BCD product to the Pocahontas no.3 HT-BCD product indicates that as maturation proceeds, the number and size of condensed aromatic rings increases and the product distribution favors the more thermally stable compounds. Also of interest is the very low concentration of methoxy and phenolic compounds in the Pocahontas no.3 product. This is not

Figure 3.18 Gas chromatograms of aromatic hydrocarbons fractions (HT-BCD products) of (A) Beulah-Zap, (B) Illinois no.6 coals.

Figure 3.19 Gas chromatograms of aromatic hydrocarbons fractions (HT-BCD products) of (C) Blind Canyon, and (D) Pocahontas no.3 coals.

Table 3.2

Compounds identified in the aromatic hydrocarbon
fractions of depolymerized (HT-BCD)
coal products.

Peak No.	Compounds identified ^a
1	C ₂ -Benzenes
2	C ₃ -Benzenes
3	2-Methylnaphthalene
4	1-Methylnaphthalene
5	C ₄ -Anisoles
6	Biphenyls
7	C ₁ -Biphenyls
8	C ₃ -Naphthalenes
9	C ₄ -Naphthalenes
10	C ₂ -Biphenyls
11	C ₁ -Fluorenes
12	C ₂ -Fluorenes
13	C ₃ -Biphenyls
14	C ₃ -Fluorenes
15	C ₁ -Phenanthrenes
16	Phenylnaphthalene
17	C ₄ -Fluorenes
18	Benzofluorene
19	C ₁ -Benzofluorenes
20	C ₂ -Benzofluorenes
21	C ₁ -Phenylnaphthalenes
22	Benzopyrene

^a Identification based on relative chromatographic retention
volumes and GC-MS fragmentation patterns.

surprising since the amount of oxygen-containing compounds decreases as maturation proceeds; however, it is interesting that such a pattern is found in the HT-BCD products, and clearly indicates the mild nature of the depolymerization method applied. Furthermore, it was found that as coal rank increases, the molecular profiles of the pre-extracts begin to resemble the molecular profiles of the HT-BCD products.

Figures 3.20 and 3.21 show an example of the chromatographic results of the predominantly phenolic Polar-1 fraction of BC(UT) and BZ(ND) coals respectively, obtained by the alumina fractionation of the depolymerized coals. These fractions are more polar than the polycyclic aromatic hydrocarbon fractions and are important in the complete characterization of depolymerized coals. Chloroform and tetrahydrofuran/ethanol (9:1 v/v) were used to elute these fractions, which consist mostly of phenols, accompanied by some nitrogen-containing polycyclic aromatic compounds (N-PAC) and higher molecular weight PAC. As seen from Figures 3.20 and 3.21, BZ(ND) sample shows much simpler components, mainly alkylated mono- and bi-cluster phenols, whereas BC(UT) sample shows higher concentration of higher molecular weight PAC and sulfur-containing compounds, also some carboxylic acid.

Figure 3.20 Gas chromatograms of Polar-1 fraction of the HT-BCD oil of Beulah Zap lignite

Peak no: 1=C₂-phenols; 2=C₃-phenols; 3=C₄-phenols

Figure 3.21 Gas chromatograms of Polar-1 fraction of the HT-BCD oil of Blind Canyon coal

Peak no: 1=C₂-phenols; 2=C₃-phenols; 3=C₄-phenols; 4=C₅-phenols

3.6 Nuclear Magnetic Resonance Analysis of Depolymerized HT-BCD Products

3.6.1 ^{13}C NMR study

The ^{13}C NMR spectra of the predominant (65-70 wt%), cyclohexane-soluble (oil) fractions from BZ(ND), BC(UT) and IL(IL) coals are given in Figures 3.22-3.24 respectively. These spectra show a large number of well-resolved peaks both in the aliphatic C and aromatic C (plus oxygenated C) ranges, indicating the presence of monocluster compounds as predominant components of the oil fractions. The spectra indicate the presence of a variety of aromatic carbons in the 110-165 ppm region, including oxygenated aromatic carbons. Types of compounds indicated include phenols and benzofurans (bands in the 110-120 ppm region) alkylated arenes and phenols (120-140 ppm), aromatic ethers and 2-alkylbenzofurans (140-155 ppm), esters (around 160 ppm) and carboxylic acids (174-177 ppm). In addition to aliphatic carbons due to paraffins and hydroaromatic rings (10-50 ppm), the spectra show an interesting group of signals between 55-70 ppm (partially overlapped by the solvent signal near 67 ppm), which are indicative of alcohols and cycloalkanols. Such compounds are expected products of hydrolytic reactions of some alkyl or cycloalkyl esters and alkyl (or cycloalkyl) aryl ethers. Also, observed is a group of signals between 98-105 ppm due to terminal olefinic carbons in $\text{CH}=\overset{*}{\text{CH}}_2$ groups (the C-2 carbons in such groups viz. $\overset{*}{\text{CH}}=\text{CH}_2$ carbons, overlap with aromatic carbons in the 110-140 ppm region and, therefore cannot be easily determined). Alcohols (δ = 55-90 ppm) are clearly present in the spectrum of the depolymerized lignite, but

Figure 3.22 ^{13}C NMR spectrum of depolymerized HT-BCD oil fraction of BZ(ND) sample.

Figure 3.23 ^{13}C NMR spectrum of depolymerized HT-BCD oil fraction of BC(UT) sample.

Figure 3.24 ^{13}C NMR spectrum of depolymerized HT-BCD oil fraction of IL(IL) sample.

the spectra of the higher rank Blind Canyon and Illinois no.6 coals indicate that their concentration decreases with increase in coal rank. The assignments for the observed signals are included in the three Figures. Table 3.3 shows the quantitative results, regarding the carbon and proton aromaticities of HT-BCD oils obtained from the BZ(ND), BC(UT) and IL(IL) coals.

As seen from the Table 3.3, for the Beulah Zap(ND) lignite, the depolymerized HT-BCD oil has an aromaticity which is only slightly lower than that of starting coal. On the other hand the higher rank IL(IL) coal shows a considerable decrease in aromaticity, while the Blind Canyon coal, which has the highest C content among the three samples, shows the greatest decrease in aromaticity after depolymerization. It is noteworthy that among the three depolymerized HT-BCD products, the total C aromaticity of the BC(UT) oil is markedly lower than that of the other two samples. This may be due to a higher extent of hydrogen transfer (from the MeOH solvent) in the BCD depolymerization step with BC(UT) coal, possibly indicating a structure-depending higher reactivity of the BC(UT) coal in comparison with that of the IL(IL) and BZ(ND) coal samples.

The ^{13}C NMR data obtained are fully consistent with the GC/MS analysis of the HT-BCD oils, viz., they confirm the findings that these depolymerized products consist predominantly of simple, monocluster component, i.e., alkylphenols, alkylarenes, naphthenes and naphthenoaromatics, accompanied by some paraffins.

Table 3.3

Carbon and proton aromaticities of HT-BCD oil obtained from
BZ(ND), BC(UT) and IL(IL) coals

Coal Sample	HT-BCD Oil		Starting Coal $f_a(\text{carbon})$
	$F_a(\text{proton})$	$f_a(\text{carbon})$	
Beulah Zap	0.16	0.53	0.54
Blind Canyon	0.13	0.44	0.64
Illinois No.6	0.22	0.57	0.72

3.6.2 ^1H NMR study

Proton NMR spectra of the predominant oil fractions of the depolymerized BC(UT), IL(IL), and BZ(ND) coal (HT-BCD oil fractions) show good agreement with the above ^{13}C NMR data. The ^1H NMR spectra of these oil fractions are shown in Figures 3.25, 3.26 and 3.27 respectively. The distributions of hydrogens into various types were calculated and summarized in Table 3.4. The total concentrations of α -hydrogens (H_a) viz., those attached to a saturated carbon in an α -position relative to an aromatic ring, are found to be almost the same in the three samples (0.31-0.33%). However, the total concentration of β -hydrogens (H_β), those incorporated in paraffinic CH_2 , and naphthenic CH_2 groups, as well as in CH_2 and CH_3 groups in a β -, or γ - of farther position relative to an aromatic ring is found to be quite different for the three depolymerized coal samples. This high value for β -, γ -, and

Figure 3.25 Proton NMR spectrum of depolymerized HT-BCD oil fraction from BZ(ND) coal.

Figure 3.26 Proton NMR spectrum of depolymerized HT-BCD oil fraction from BC(UT) coal.

Figure 3.27 Proton NMR spectrum of depolymerized HT-BCD oil fraction from IL(IL) coal.

Table 3.4
Distribution of hydrogens in the depolymerized
HT-BCD products (oil fractions)^a

Hydrogens, type	Chemical shift region, ppm	BZ(ND)	BC(UT)	IL(IL)
<u>Aliphatic</u> (total)	0.5-4.0	83^b	85^b	78^b
alpha (total)	1.9-4.0	33(40) ^c	31(36) ^c	33(42) ^c
α-CH ₂	2.3-4.0	20(24) ^d	19(22) ^d	19(24) ^d
α-CH ₃	1.9-2.3	13(16) ^d	12(14) ^d	14(18) ^d
bata+Gamma (total)	0.5-1.9	50(60) ^c	54(64) ^c	45(58) ^c
β-H	1.0-1.9	33(40) ^d	45(53) ^d	32(41) ^d
γ-H	0.5-1.0	17(20) ^d	9(11) ^d	13(17) ^d
<u>Olefinic</u> (total)	4.0-6.0	3	1	2
<u>Aromatic</u> (total)	6.0-9.0	14	14	20
1-ring	6.0-7.3	8(57) ^e	5(36) ^e	9(45) ^e
2-ring	7.3-7.8	4(29)	4(28)	6(30)
3-ring	7.8-9.0	2(14)	5(36)	5(25)

a As determined by proton NMR analysis, using dioxane-d₆ as solvent.

b Bold numbers represents the percentages of total aliphatic, total olefinic, and total aromatic hydrogens in the oil fractions.

c Numbers in parenthesis represent percent of hydrogens of a given type out of the total aliphatic hydrogens.

d These numbers in parenthesis give the distribution of hydrogens within a given type.

e Numbers in parenthesis in this column represent percent of hydrogens in 1-ring, 2-ring, or 3-ring compounds out of the total non-substituted aromatic hydrogens.

farther removed CH_2 groups in the BZ(ND) oil is consistent with the presence of long alkyl chains (or free paraffins) in this sample, whereas the particularly high concentration of β -hydrogens in the BC(UT) oil are consistent with the presence of a high concentration of hydroaromatic rings in this product. The values of H_γ , which are due to the protons of paraffinic methyls or methyls γ , or farther, removed from an aromatic ring varies between 9 to 17% for the three samples, as the highest value obtained was for BZ(ND) and the lowest value for BC(UT). This is consistent with the previously discussed results, by GC/MS, indicating the presence of long alkyl chain components in the lignite.

Table 3.4 also shows the distribution of aromatic hydrogens into 1-, 2-, and 3-ring components. The major differences is that BZ(ND) sample showed the predominance of 1- and 2-ring compounds. This is not surprising since the structure of original lignite is relatively simpler than the HVB coals and also it is relatively active during the depolymerization-liquefaction.

3.7 Fourier Transform Infrared Spectroscopic Analysis of Coals and Their Derived Products

Infrared spectroscopy is an important and extensively used analytical tool for the characterization of coal and coal derived products. In this part of the analytical study, the FTIR spectra of depolymerized products were measured in order to provide further corroboration of the data obtained by GC/MS and NMR. The assignment of the most characteristic bands in the infrared spectra of coals can be considered

well established. These assignments are listed in Table 3.5 for hydrocarbon groups and in Table 3.6 for oxygen-containing functional groups.¹⁶³⁻¹⁶⁵

3.7.1 FTIR spectra of depolymerized HT-BCD products

Figure 3.28 shows the FTIR spectra of the predominant oil fractions of the depolymerized BZ(ND), BC(UT) and IL(IL) coals. The spectra indicate the presence of several types of functional groups and characteristic substitution patterns in components of these depolymerized products, as follows:

- (a) Phenolic, alcoholic, and carboxylic acid groups (O-H stretching bands in the 3200-3650 cm^{-1} region);
- (b) CH_3 , CH_2 , and CH groups in paraffins, and CH_2 and CH groups in hydroaromatic rings (C-H stretching bands in the 2840-2970 cm^{-1} region);
- (c) Carbonyl groups (C=O stretching bands near 1725 and 1700 cm^{-1}); hydroaromatic rings (C-C stretching bands between 1350-1470 cm^{-1});
- (d) Aromatic rings (breathing band between 1600-1616 cm^{-1});
- (e) CH_3 , CH_2 and CH groups in alkylsubstitutents or CH_2 and CH groups in hydroaromatic rings (C-C stretching bands between 1350-1470 cm^{-1});
- (f) aryl ethers (C-O stretching bands in the 1170-1320 cm^{-1} region);
- (g) aromatic out-of-plane bending, e.g., pentasubstituted aromatic rings, viz., a single nonsubstituted aromatic hydrogen (C-H out-of-plane bending at 861 cm^{-1}); tri- and tetrasubstituted aromatic rings, viz., two or three adjacent nonsubstituted aromatic hydrogens (C-H out-of-plane bending at 813 cm^{-1}); and orthodisubstituted aromatic rings, viz. four

Table 3.5

Band assignments for maxima in the FTIR spectra
of coal and coal-derived products:
Aliphatic and aromatic groups

Wave Number, cm^{-1}	Assignment
3030	Aromatic C-H stretching
2964	Asymmetric C-H stretching in CH_3
2956	Symmetric C-H stretching in CH_3 and in hydroaromatic CH_2
2923	Asymmetric C-H stretching in CH_2
2864	Symmetric C-H stretching in CH_3
2850	Symmetric C-H stretching in CH_2
1620-1600	Aromatic ring breathing mode, which can be enhanced by OH substitution
1456	Symmetric C-H bending in CH_3 and CH bending in CH_2
1380	Symmetric C-H bending in CH_3
900-700	Aromatic C-H out-of-plane bending modes
860	Isolated aromatic hydrogens
833(weak)	1,4 substitute aromatic groups
815	2 or 3 adjacent aromatic hydrogens
750	1,2 substituted, i.e., 4 neighboring hydrogens
730	Skeletal vibration of linear $-(\text{CH}_2)_n-$, where $n > 25$
720	Skeletal vibration of linear $-(\text{CH}_2)_n-$, where $n > 4$

Table 3.6

Band assignments for maxima in the FTIR spectra
of coal and coal-derived products:
Oxygen-containing functional groups

Wave Number, cm^{-1}	Assignment
3600	Free phenolic O-H stretching
3600-3200	Hydrogen bonded phenolic O-H stretching
1740	C=O stretching in saturated esters
1735-1700	C=O stretching (esters, ketones)
1690	C=O stretching in Ph-C=O, hydrogen bonding will lower this frequency to 1648 cm^{-1}
1340-1150	C-O stretching (aryl ethers, dibensofurans), O-H deformation in phenols
1150-1040	C-O stretching of aliphatic ethers

Figure 3.28 FTIR spectra of depolymerized HT-BCD oil samples

adjacent non-substituted aromatic hydrogens (C-H out-of-plane bending band between 750-770 cm^{-1}).

The three oil samples show considerable differences in the intensity of some adsorption peaks indicating the presence of different concentrations of the above described functional groups. For example, the HT-BCD oil from the BC(UT) coal shows a medium intensity band at 1725 cm^{-1} due to carbonyl-containing groups, whereas such a band is practically absent in the spectrum of the IL(IL) oil product. Further, the combination of the bands near 1700 cm^{-1} and 3624 cm^{-1} in the spectrum of the BZ(ND) lignite oil indicates a relatively higher concentration of carboxylic acid groups in this product.

3.7.2 FTIR spectra of hydroprocessed light oil products

Figures 3.29 and 3.30 show the FTIR spectra of the final, hydroprocessed (HPR) oil products from BZ(ND) and BC(UT) coals. As seen, the spectra are very different from the spectra of the corresponding HT-BCD oil precursors. Both of the HPR oil samples show a very strong aliphatic absorption bands at the 2950, 2920, 2850, 1450 and 1370 cm^{-1} region, while the aromatic absorption bands near 1600 cm^{-1} are rather weak. This is due to the high aliphatic and hydroaromatic content of the final HPR products. As expected, the HPR step causes partial ring hydrogenation of aromatic to naphthenic and naphthenoaromatic compounds. The elemental analysis of HPR oil fraction also confirmed this result. Another remarkable difference is the practical disappearance of OH absorption bands in the 3200-3650 cm^{-1}

Figure 3.29 FTIR spectra of hydroprocessed (HPR) light oil of BZ(ND) sample.

Figure 3.30 FTIR spectrum of hydroprocessed (HPR) light oil of BC(UT) sample.

region and of etheric absorption bands in the 1100-1300 cm^{-1} , indicating the occurrence of exhaustive hydrodeoxygenation of the HT-BCD oil during the HPR step. As seen, both samples show the final HPR product is a hydrocarbon mixture with only traces of carbonyl-containing compounds remaining in the product from the BZ(ND) lignite (band at 1739 cm^{-1}).

3.7.3. FTIR spectra of coal pre-extracts

The FTIR spectra of the pre-extracts of three coals are shown in Figure 3.31, while the FTIR spectra of the pre-extracts of two lignites are shown in Figure 3.32. In general sharp, well resolved peaks are obtained for these relatively minor (5-17 wt%) extracts. Moreover almost all the peaks can be easily assigned to various functional groups.

One very noticeable difference between the FTIR spectra of coals and their extracts is the absence of absorptions due to the minerals in the coal extracts. This is logical since minerals consist of non-extractable inorganic compounds while the extracts are organic in nature. Thus, the absorptions at 3695 and 3645 cm^{-1} which are due to OH group in kaolinite are not observed in the coal THF pre-extracts. As seen in Figure 3.31 and 3.32, there are broad and strong absorptions due to OH group stretching near 3430 cm^{-1} in all of the extracts. Since these extracts have been dried under vacuum overnight, the peaks are indicative of the presence of phenols and carboxylic acids. Further, the distinct peaks near 2920 and 2850 cm^{-1} can be assigned to aliphatic CH_3 , CH_2 , & CH stretching vibrations. These peaks are much stronger than

Figure 3.31 FTIR spectra of THF pre-extracts of three coals.

Figure 3.32 FTIR spectra of THF pre-extracts of two lignites.

those observed in the parent coals. Another feature of the spectra of the extracts is an absorption band near 1700 cm^{-1} , which is due to carbonyl-containing groups. EH(KY) and IL(IL) extracts show only a weak shoulder peak near 1700 cm^{-1} , the BC(UT) pre-extract shows a medium intensity peak at 1700 cm^{-1} , whereas the two lignites show a strong peak at this frequency, indicating the presence of higher concentrations of carbonyl-containing compounds. Further, a sharp peak near 720 cm^{-1} is typical for the spectra of the two lignites, and is apparently due to skeletal vibrations of linear $-(\text{CH}_2)_n-$ (where $n > 4$). This confirms the presence of some long aliphatic chain components in lignites.

3.7.4 FTIR spectra of products from pre-extract

The yield of THF-soluble pre-extract from BC(UT) coal was found to be 16.8 wt%, which is the highest yield among all Argonne coal samples. The pre-extract was fractionated into n-hexane soluble resinite and an n-hexane-insoluble fraction and their FTIR spectra are given in Figures 3.33 and 3.34 respectively. As seen from Figure 3.33, the resinite fraction is a highly aliphatic material (C-H stretching bands between $2850\text{--}2970\text{ cm}^{-1}$, due to CH_3 , CH_2 , and CH groups; C-H bending bands at 1457 and 1379 cm^{-1} , due to the same groups). The resinite apparently contains only minor amounts of aromatic rings, or more likely double bonds, as evidenced by the presence of some very weak absorption bands at 1616 cm^{-1} . The resinite contains also components with at least two types of carbonyl and/or carboxylic acid groups (C=O stretching bands at 1705 and 1741 cm^{-1}). The free OH group at 3646 cm^{-1} is also observed.

Figure 3.33 Infrared absorption maximum of resinite (n-hexane soluble fraction of THF pre-extract) from Blind Canyon, Utah coal.

Figure 3.34 Infrared absorption maximum of n-hexane-insoluble fraction from THF pre-extract of Blind Canyon, Utah coal.

In contrast to the resinite, the n-hexane-insoluble fraction of the THF pre-extract apparently has a high content of aromatic rings and/or olefinic bonds, as indicated by the absorption peak at 3030 cm^{-1} and a strong absorption band near 1616 cm^{-1} . The FTIR spectrum of this fraction of the pre-extract also shows strong O-H stretching bands between $3200\text{--}3650\text{ cm}^{-1}$ and strong (Ar)C-O stretching bands between $1180\text{--}1300\text{ cm}^{-1}$ (Figure 3.34).

Figure 3.35 shows the comparison of FTIR spectra of the oil fractions from the pre-extract (referred to below as PE oil) and from the HT-BCD product (referred to below as HT-BCD oil). As can be seen, the two spectra show certain similarities. However, the two spectra also show some significant differences. The PE oil shows a free OH group stretching near 3644 cm^{-1} , whereas the HT-BCD oil shows a strong band at 3350 cm^{-1} , due to H-bonded phenolic groups resulting from hydrolytic reactions in the BCD step. The aryl etheric peak in the PE oil (at 1234 cm^{-1}) is not shown by the HT-BCD oil, but the HT-BCD oil shows moderate peaks at 1056 , 1093 and 1186 cm^{-1} which are absent in the PE oil spectrum. Further, the HT-BCD oil sample shows three well resolved bands in the $600\text{--}900\text{ cm}^{-1}$ aromatic C-H (out of plane) bending region, indicating the efficiency of the depolymerization reaction in the BCD step.

3.8 Average Molecular Structures of Depolymerized HT-BCD Oil Fractions

The oil fractions obtained under optimal HT-BCD conditions were analyzed by a combination of GC/MS, PMR, ^{13}NMR , FTIR, and elemental

Figure 3.35 FTIR spectra of oil fractions from pre-extract and from depolymerized HT-BCD product.
—— HT-BCD oil ---- PE oil

analysis. The data allowed to derive average molecular structures for this fractions, using a modified Brown-Ladner structural analysis; and (b) NMR and FTIR data indicating the type and relative concentrations of oxygen-containing functional groups, it was also possible to design molecular structures for probable components in the above oil fractions of the depolymerized coal products, including mostly monoccluster (mono-, bi- and tricyclic) components. An example of two alternative average molecular structures for the oxygen-rich HT-BCD oil obtained from the BZ(ND) lignite is given in Figure 3.36. Probable oxygen-containing components in this products are indicated in Figure 3.37. Average molecular structures with markedly lower oxygen content were indicated for depolymerized products of the HVB coals.

The detailed structural analysis of depolymerized coal products described in this chapter allows for several important conclusions:

1. The cyclohexane soluble "oil" fractions obtained by HT-BCD depolymerization represented 65-70% (MAF basis) of the pre-extracted coal and were almost completely vacuum distillable(~98 wt%).
2. The above indicated, predominant oil fractions are primarily composed of low molecular weight monoccluster compounds. Comparison of the HT-BCD oils obtained from Blind Canyon and Illinois no.6 coals with that from Beulah Zap lignite revealed much higher concentration of oxygen-containing functional groups in component of in the latter, viz. carbonyl-containing groups (NMR, FTIR), secondary and/or tertiary alcohols (NMR), phenols (NMR, FTIR, GC/MS) and methoxy groups (NMR, GC/MS). Illinois no.6 oil was characterized by a major

Figure 3.36 Derived average molecular structure for the oil fractions of depolymerized BZ(ND) lignite.

R = alkyl

n = no. of alkyl groups

Figure 3.37 Examples of probable O-containing components in the HT-BCD oil fraction of depolymerized BZ(ND) lignite.

sulfur (S_8 +) peak (GC/MS), indicating the beneficial effect of low-temperature elimination of sulfur from S-containing compounds during the HT-BCD stage of the process.

3. Compound class separation of the HT-BCD oils by elution chromatography, followed by GC/MS analysis showed the depolymerized products consisted mainly of the following classes of compounds: (a) mono-, bi-, and tricyclic alkylarenes; (b) mono-, bi- and tricyclic phenols; (c) mono-, bi-, and tricyclic naphthenoaromatics; (d) aliphatic components, i.e., paraffins and naphthenes; and (e) some N-containing compounds.
4. FTIR, NMR and GC/MS techniques showed the aromatic rings of the oil fractions to be highly substituted (di-, tri-, tetra-, and pentasubstituted).
5. The relative abundance of n-alkanes as determined by GC/MS increased in the following order:

Blind Canyon > Beulah Zap > Illinois no.6.

In general, it was established that low-temperature coal depolymerization by the HT-BCD procedure yields a mixture of simple, low-molecular weight products. Due to their simplified^{structure, these} products are easily converted by hydroprocessing (HPR) into a highly desirable, light hydrocarbon oil as final product.

CHAPTER 4
DEPOLYMERIZATION - LIQUEFACTION STUDIES
OF WYODAK (WY), FRUITLAND (NM), AND
PITTSBURGH NO. 8 (PA) COALS

The optimal conditions for each step of the HT-BCD-HPR procedure for the above coal feeds were determined. Products obtained were analyzed by a combination of FTIR, ^{13}C NMR, PMR, elemental analysis, and simulated distillation.

With the subbituminous Wyodak coal as feed, suitable processing conditions were found to be as follows: (a) HT step, FeCl_3 catalyst concentration, 15-20% wt.%; 275°C, 1500 psig H_2 pressure, and 2-3 hr reaction time. (b) BCD step, 275°C, 10% methanolic KOH solution, 1:1 feed to catalyst weight ratio, 1000 psig N_2 pressure, and 1 hr reaction time. Use of these conditions, resulted in nearly complete solubilization of the product in THF (90.2% by wt on a MAF basis). In the HPR step, hydroprocessing of the solubilized (depolymerized) coal with a sulfided 6Co8Mo catalyst for 8 hr at 370°C, using 5:1 feed to catalyst weight ratio, and 2700 psig H_2 pressure, yielded a light hydrocarbon oil (C, 87.57; H, 11.60; O, 0.59; and N, 0.24% by wt), which contained 71.3% by wt of low-boiling fractions. Somewhat different results were obtained with the higher rank (HVB) Fruitland (NM) coal as feed, i.e., the optimal FeCl_3 catalyst concentration in the HT step was lower (8-12 wt%), the total yield of depolymerized coal products was slightly higher, and the proportion of final low-boiling products (b.p. up to 325°C/760 torr) was somewhat lower (61.6 vs 71.3 wt%) as compared with the Wyodak coal.

With Pittsburgh no. 8 (PA) coal as feed, the optimal conditions for the HT-BCD depolymerization sequence were as follows: for the HT step: FeCl_3 concentration, 5 wt %; H_2 pressure, 1500 psig; reaction temperature, 290°C; and

reaction time, 3 hrs; and for the BCD step: 10% methanolic KOH solution, coal feed/alkali solution weight ratio, 1:10; initial N₂ pressure, 1000 psig; reaction temperature, 290°C; and reaction time, 1 hr. The consecutive HT-BCD steps yielded 71.5% of depolymerized, THF-soluble products (MAF basis) in addition to 14.1 wt% of preextract. The predominant oil fraction (cyclohexane-solubles) of the depolymerized coal product had the following composition: C, 82.24; H, 8.20; O, 8.01; N, 1.06; and S, 0.39% by wt. Structural analysis of this fraction showed that it consists mostly of monocluster compounds having molecular weights in the 125-250 amu range. Suitable conditions determined for the HPR step (hydroprocessing the depolymerized coal product); sulfided 6Co8Mo/ γ -Al₂O₃ catalyst, reaction time 4-8 hr, temperature, 370°C and 2700 psig H₂ pressure. Hydroprocessing yielded a light hydrocarbon oil with the following composition: C, 88.51; H, 10.81; O, 0.60; N, 0.08; and S, <0.01% wt. This final hydrocarbon product contained 70.8 wt% of low-boiling fractions (gasoline, kerosene, and gas oil; b.p. up to 325°C).

The above results, together with the detailed data reported in Chapters 2 and 3, clearly demonstrate that the HT-BCD-HPR procedure can be easily adapted for high-yield conversion of coals of various rank (lignites, subbituminous coals, and HVB coals) into low-boiling hydrocarbon fuels. With all of the coal feeds studied, the depolymerization (HT-BCD) stage can be effectively performed under very mild temperature conditions (<300°C). Furthermore, the final hydroprocessing (HPR) of the depolymerized coal can be performed at essentially quantitative conversions, using milder conditions than those employed in direct hydroprocessing of coals.

Table 5.1.
Intercluster linkages and their specific reactivity

<u>Type</u>	<u>Specific reactivity</u>
(1) Alkylene ($-(\text{CH}_2)-$), e.g., CH_2- , $-\text{CH}_2-\text{CH}_2-$, etc.	Susceptible to hydrogenolytic cleavage with weak-moderate hydrogenolysis catalysts, e.g., aquo complexes of metal halides.
(2) Reactive etheric linkages e.g., benzyl etheric, thioetheric, cycloalkyl aryl etheric, etc.	Susceptible to hydrogenolytic cleavage as above for type 1.
(3) Diaryl etheric ($\text{Ar}-\text{O}-\text{Ar}$)	Not susceptible to mild hydrogenolysis, but easily susceptible to base-catalyzed hydrolysis or alcoholysis
(4) Debenzofuranic, i.e.,	Not susceptible to either mild hydrogenolysis or hydrolysis, but susceptible to hydrogenolysis with sulfided MMo catalyst (M = group VI-VIII transition metal promoter).
(5) Direct biaryl, i.e., $(\text{Ar})\text{C}-\text{C}(\text{Ar})$	Same as above for linkages of type 4.

depolymerizing catalyst - solvent system; $<300^{\circ}\text{C}$). Compounds of types (4) and (5) were subjected to hydroprocessing under conditions simulating the final (HPR) step of the liquefaction process.

Based on the above model compound studies and the detailed structural analysis of coal depolymerization products (see Chapter 3) it was possible to elucidate the mechanisms of the main types of reactions involved in the HT, BCD, and HPR steps of the coal liquefaction process, as outlined in Figure 5.1, 5.2 and 5.3, respectively.

Figure 5.1 Indicated mechanisms of hydrogenolytic cleavage reactions in the HT step of coal depolymerization.

Figure 5.2 Indicated mechanisms of hydrolytic reactions in the BCD step of coal depolymerization.

Figure 5.3 Indicated mechanisms of some hydrogenolytic cleavage reactions in the HPR step of the HT-BCD-HPR coal liquefaction procedure.

EDUCATIONAL ACHIEVEMENTS

The following three students graduated in the framework of this project:

Ricky R. White, M.S. Thesis, University of Utah, 1989

Yuan (Joan) Zhang, Ph.D. Dissertation, University of Utah, 1991,

T. Skulthai, Ph.D. Dissertation, University of Utah, 1987

The Ph.D. studies of Y. Zhang and T. Skulthai were funded in part through other DOE-sponsored projects.

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Conclusions and Recommendations

This research project has demonstrated the validity of a new coal processing concept. The latter consists of subjecting the coal feed to low-temperature depolymerization prior to hydroprocessing. The depolymerization stage of the newly developed procedure results in a mixture of low-molecular weight, monocluster products which are smoothly converted to light liquid fuels in the final hydroprocessing stage of the procedure.

Some additional work on the development of a two-stage process based on the above principle is presently being pursued by the P.I., with very modest funding in the framework of the CFFLS (Consortium for Fossil Fuel Liquefaction Science). It is strongly recommended that the U.S. Department of Energy examines very carefully the implications of the above development and finds the way of supporting at a proper level this highly promising line of research and coal conversion technology.

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