DOE/PC/90537-T8

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

Progress Report no. 8

(covering the period July 1 - September 30, 1988)

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

Principal Investigators

Department of Fuels Engineering

University of Utah

Salt Lake City, UT 84112

Prepared for the United States Department of Energy

under Grant no. DE-FG-22-86PC90537

March, 1989

DISCLAIMER

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

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

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

PERSONNEL

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

Mrs. Y. Zhang, graduate student

Mr. Rick White, graduate student

OBJECTIVES AND SCOPE OF THE RESEARCH PROJECT

One of the main objectives of this project is to investigate the low-temperature ($\leq 300^{\circ}\text{C}$) depolymerization-liquefaction reactions of representative U.S. coals, using a 3-step procedure recently developed in our Laboratory. The procedure involves subjecting the coal first to two consecutive depolymerization steps in which different types of intercluster linkages are subjected to preferential cleavage. The depolymerized products obtained have low molecular weights and consist predominantly of monocluster and bicluster compounds. In the third step of the procedure, these simplified depolymerization products are subjected to hydroprocessing and attendant exhaustive hydrodeoxygenation to yield light liquid hydrocarbon mixtures as main products. It is planned under the research program to adapt and optimize the above indicated procedure for U.S. coals of different rank, and to examine the feasibility of the new processing concept for conversion of these coals into light liquid hydrocarbon fuels.

A second major objective of the research program is to subject the low-temperature depolymerization products (obtained by the first two consecutive steps) to exhaustive structural analysis for the purpose of deriving average structural models for the coals under investigation. Such models are expected to be useful as fingerprints for identification and differentiation of various representative U.S. coals.

PROJECT STATUS

During the July 1 - September 30, 1988 period, covered by the present report, research activities included (a) continuation of the systematic study of the depolymerization-liquefaction reactions of a Beulah Zap (North Dakota) lignite sample (see Progress Report no. 5); and (b) initiation of a systematic study of another Argonne coal, i.e., the Blind Canyon (Utah) coal.

RESULTS

I. Depolymerization-Liquefaction of a Beulah Zap (North Dakota) Lignite

Suitable conditions for high-yield conversion of a Beulah Zap (North Dakota) lignite sample, supplied by the Argonne program and designated below as BZ(ND) coal, were previously developed (see Progress Report no. 5, pp. 3-15). In some recent experiments, the yield of low-boiling hydrocarbon fuel fractions (gasoline, kerosene and gas oil; b.p. up to 325°C) from this coal was found to be in the range of 75-82 wt%.

The main emphasis of the research work during the reporting period was on the structural analysis of the depolymerized BZ(ND) coal, with the ultimate objective of developing an average molecular structure for the predominant (61 - 70 wt%) oil fraction (fr. no. 6, Figure 1) as well as for the small asphaltene and asphaltol fractions (fr. no. 7 and 8, Figure 1) of this depolymerized product.

A. Mass Spectrometric Analysis

The oil and asphaltene fractions of the depolymerized BZ(ND) coal (Figure 1, fractions # 6 and 7, respectively) were analyzed by gas chromatography/mass spectrometry (GC/MS) in collaboration with Dr. H.L.C. Meuzelaar, Center for Microanalysis, University of Utah. A 15 m x 0.25 mm DB-5 (J & D Scientific) capillary column was used, with He as carrier gas. The samples, 2 micrograms, were vaporized using a Curie-point GC inlet. The essentially non-polar column gave simulated distillation chromatograms with linear temperature programming from 40° to 300°C at 15°C/min after an initial hold at 40°C for 1 min. The mass spectrometer was an ion trap detector (ITD-Finnigan MAT) operated with a scan range of 50 to 450 amu at 1 scan/sec.

Figure 2 shows the reconstructed ion chromatogram for the oil fraction of the depolymerized BZ(ND) lignite. As seen, the bulk of the compounds present in this fraction elute in the 125-250°C range as an incompletely resolved hump. It is indicated (see below) that the oil contains a wide

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

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

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

Figure 1. Low-temperature coal depolymerization-liquefaction procedure (including designation numbers of product samples subjected to spectral analysis)

Figure 2. Total ion chromatogram (TIC) for the oil fraction of the depolymerized BZ(ND) lignite: ● - alkanes; o - alicyclics; ▲ - aromatic hydrocarbons; * - phenols; * - possible contaminants

range of compound types including alkylsubstituted benzenes and naphthalenes, mono- and bicyclic phenols, alicyclic and open-chain hydrocarbons, and others, with several of the distinguishable peaks labeled. The earlier eluting compounds are primarily alkylphenols with short (C_1 - C_4) alkyl substituents. The chromatogram also indicates the possible presence of small amounts (< 10%) of contaminants, e.g., phthalates and THF-derived oligomers.

Figure 3 shows the integrated spectrum of the oil fraction compounds eluting between 100° to 250°C. The electron ionization spectrum includes both molecular peaks and large mass fragmentations with three homologous ion series connected and indicated as examples. The series 77, 91, 105, and 119 is typical of alkylbenzene fragments, while the higher series 147, 161, 175, 189, and 203 probably represents alkylsubstituted hydroxytetralins and hydroxyindanes (with the OH group as a phenolic group, *viz.*, as substituent in the aromatic moiety). The ions 115, 129, and 143 are probably rearrangement ions of hydroxyindans. The spectrum also shows some higher molecular weight compounds in the 200-270 amu range, possibly representing small amounts of saturated or partially saturated polycyclic structures. Further investigation of specific compounds and structural types in the depolymerized BZ(ND) coal products is presently in progress.

The mass spectral data obtained so far indicate that most of the compounds present in the predominant oil fraction (comprising 65-71 wt% of the total depolymerized Beulah Zap lignite) have molecular peaks below 260 (Figure 3). These indicated low molecular weights are consistent with the expectation that the two consecutive depolymerization steps 1 and 2 (Figure 1) cause extensive cleavage of intercluster linkages in the lignite, ultimately leading to a product consisting mostly of monocluster compounds (see below, derivation of average molecular structures for the Beulah Zap lignite and Pittsburgh #8 coal).

Figure 3. Integrated spectrum of compounds eluting between 100-250°C in the GC/MS analysis (see Fig. 2) of the oil fraction of depolymerized Beulah Zap lignite.

B. NMR Analysis

PMR spectra of the oil and asphaltene fractions (fractions #6 and 7, Figure 1) of the depolymerized BZ(ND) lignite were obtained using dioxane- d_8 as a solvent. Appropriate compensation for resonance lines of the solvent was applied.

The PMR spectra of the oil and asphaltene fractions are shown in Figure 4, and the distribution of hydrogens into various types is summarized in Table 1.

As seen, the ratio of aliphatic/aromatic hydrogens is higher for the oil fraction (78:15) as compared with that for the asphaltene fraction (74:21). This may be due to a higher population of alkyl substituents per aromatic ring and to a higher concentration of hydroaromatic rings in the oil as compared with the asphaltene fraction. Further, it is found that the asphaltene fraction contains a higher proportion of α -hydrogens (58%) and a lower proportion of β - and γ -hydrogens (42%) as compared with the corresponding hydrogens in the oil fraction (47% and 53%, respectively). This would indicate a longer chain length of the alkyl substituents in the oil as compared with the asphaltene fraction. These differences are consistent also with the ^{13}C NMR analysis of the same fractions.

The estimated distribution of aromatic hydrogens in 1-ring, 2-ring, and 3-ring compounds in the same fractions (Table 1) indicates that in the oil fraction such hydrogens are found predominantly (80%) in 1-ring and 2-ring systems [particularly in 1-ring systems (56%)]. This result, when coupled with the indicated low molecular weights of products present in the oil fraction (see above) points out to the probable predominance of monocluster compounds in this main fraction of the depolymerized coal.

The NMR analysis of depolymerized coals is being pursued in collaboration with Dr. R.J. Pugmire of our Department. The ^{13}C NMR spectra of the oil and asphaltene fractions of depolymerized BZ(ND) lignite and of depolymerized Pittsburgh no. 8 coal were measured and will be included in Progress Report no. 9. These and other analytical data were used in deriving average molecular structures for the above fractions of the two depolymerized coals (see below).

(A)

9

(B)

Figure 4. Proton NMR spectra of the oil (A) and asphaltene (B) fractions of depolymerized Beulah Zap (ND) lignite.

Table 1

Distribution of Hydrogens in the Oil and Asphaltene Fractions
of Depolymerized Beulah-Zap Lignite^a

Hydrogens, type	Chemical Shift region, ppm	Oil fr. hydrogens, %	Asphaltene fr. hydrogens, %
<u>Aliphatic</u> (total)	0.5 - 4.0	78^b	74^b
alpha (total)	1.9 - 4.0	37 (47) ^c	43 (58) ^c
α -CH ₂	2.3 - 4.0	25 (32)	31 (41)
α -CH ₃	1.9 - 2.3	12 (15)	12 (16)
beta + gamma (total)	0.5 - 1.9	41 (53)	31 (42)
β - and γ -CH ₂	1.0 - 1.9	33 (42)	26 (36)
β -CH ₃	0.5 - 1.0	8 (11)	5 (7)
<u>Olefinic</u> (total)	4.0 - 6.0	7	6
<u>Aromatic</u> (total)	6.0 - 9.0	15	21
1-ring	6.0 - 7.3	8 (56) ^d	8 (37) ^d
2-ring	7.3 - 7.8	4 (24)	5 (26)
3-ring	7.8 - 9.0	3 (20)	8 (37)

^a As determined by proton NMR analysis, using dioxane-d₈ as solvent.

^b Bold numbers in this column represent the percentage of total aliphatic, total olefinic, and total aromatic hydrogens in the oil or asphaltene fractions.

^c Numbers in parentheses in this column represent % of hydrogens of a given type out of the total aliphatic hydrogens.

^d Numbers in parentheses in this column represent % of hydrogens in 1-ring, 2-ring, or 3-ring compounds out of the total non-substituted aromatic hydrogens.

C. FTIR Analysis

The depolymerized BZ(ND) lignite products were also subjected to infrared analysis. Liquid samples and solutions were analyzed in a CIRCLE cell, whereas the diffuse reflectance infrared Fourier transform (DRIFT) technique was used to analyze solid samples. Spectra were recorded on a Digilab FTS-40 spectrometer. For all spectra given as examples in the present report, a 64-scan data accumulation was obtained at a resolution of 4 cm^{-1} . These spectra provide considerable information on the types of functional groups present in components of depolymerized coal or lignite products. Figures 5-8 give the FTIR spectra of the oil and asphaltene fractions of the depolymerized BZ(ND) lignite.

Figures 5 and 6 indicate the presence of several types of functional groups in components of the oil fraction, as follows: phenolic groups (O-H stretching bands in the $3200\text{-}3650\text{ cm}^{-1}$ region); CH_3 , CH_2 and CH groups and hydroaromatic rings (C-H stretching bands in the $2860\text{-}2970\text{ cm}^{-1}$ range); carbonyl groups (C=O stretching band at 1709); CH_2 and CH_3 groups (C-H bending bands at 1377 , 1454 , and 1465 cm^{-1}); phenols and/or aryl ethers (C-O stretching bands in the $1200\text{-}1280\text{ cm}^{-1}$ range); tetra- and pentasubstituted aromatic rings, viz. 1 or 2 adjacent non-substituted aromatic hydrogens (C-H out-of-plane bending band at 864 cm^{-1}); tetra- and trisubstituted aromatic rings, viz. 2 or 3 adjacent non-substituted aromatic rings (C-H out-of-plane bending band at 814 cm^{-1}); and disubstituted aromatic rings, viz. 4 adjacent non-substituted aromatic hydrogens (C-H out-of-plane bending band at 750 cm^{-1}).

A comparison of the FTIR spectra in Figures 5 and 6 with those of the corresponding oil fraction of depolymerized Pittsburgh #8 coal (see Progress Report no. 7, Figure 5 and 6) reveals some important differences which reflect anticipated structural differences between the depolymerized BZ(ND) lignite and the HVB Pittsburgh no. 8 coal, i.e., (1) the O-H stretching bands in the depolymerized BZ(ND) oil fraction are stronger compared to the corresponding bands in the oil fraction of

depolymerized PB(PA) coal, indicating a higher concentration of phenolic, alcoholic and carboxylic acid groups in the lignite product; (2) the C=O stretching bands in the $1690\text{--}1775\text{ cm}^{-1}$ range of the lignite-derived oil are markedly stronger (and more diverse) as compared with the single band at 1709 cm^{-1} shown by the PB(PA) coal-derived oil, indicating a higher concentration and larger variety of carbonyl-containing compounds, e.g., various types of carboxylic acids and esters, ketones, etc., in the lignite-derived oil; and (3) the relative intensities of the aromatic C-H out-of-plane bands near 752 , 816 , 868 , and 920 cm^{-1} when compared with corresponding bands shown by the PB(PA) coal reveal that the degree of aromatic ring condensation in the coal-derived oil is higher than that in the lignite-derived oil.

The FTIR spectra of the small asphaltene (Figures 7 and 8) and asphaltol fractions from BZ(ND) lignite show similarities but also some major differences in comparison with the oil fraction (Figures 5 and 6). The absorption maxima of these fractions are less effectively resolved, apparently due to their higher compositional complexity.

Figure 7 indicates a higher concentration of phenolic, alcoholic, and carboxylic acid groups (O-H stretching bands in the $3200\text{--}3650\text{ cm}^{-1}$ region) in the asphaltene fraction as compared with that in the oil fraction (Figure 5). Further, comparison of Figures 6 and 8 (C-H out-of-plane bending bands of the oil and asphaltene fractions, respectively; $600\text{--}1000\text{ cm}^{-1}$ range) indicates a considerably higher level of ring condensation in the asphaltene as compared with that in the oil fraction. This is reflected in a higher relative concentration of tetra- and pentasubstituted aromatic rings versus mono-, di-, and trisubstituted rings in the asphaltene as compared with the oil fraction.

FTIR studies are being performed in collaboration with Professor E.M. Eyring, Department of Chemistry, University of Utah.

Figure 5. Infrared absorption maxima of the oil fraction of depolymerized Beulah Zap lignite, cm⁻¹.

Figure 6. Infrared absorption maxima of the oil fraction of depolymerized Beulah Zap lignite, 600-1000 cm^{-1} range.

Figure 7. Infrared absorption maxima of the asphaltene fraction of depolymerized Beulah Zap lignite, cm⁻¹.

Figure 8. Infrared absorption maxima of the asphaltene fraction of depolymerized Beulah Zap lignite, 600-1000 cm⁻¹ range.

II. Derivation of Average Molecular Structures for Depolymerized BZ(ND)
and PB(PA) Coal Products

The quantitative ^{13}C NMR, PMR, GC/MS, and FTIR data, as well as elemental composition data for the depolymerized products obtained from Beulah Zap and Pittsburgh no. 8 coals, (Progress Reports no. 5 and 7; and present report) were input into a structural analysis computer program, based on a modified Brown-Ladner method, to derive average structural parameters and, thereby, average molecular structures for the above-mentioned depolymerized coal products (for a description of the method see T. Skulthai, Ph.D. Dissertation, University of Utah, 1987; and Progress Report no. 4). The emphasis was on the structural analysis of the predominant, 65-80 wt%, oil fractions (cyclohexane-solubles) of the depolymerized products.

Examples of average molecular structures derived for the oil fractions of depolymerized Pittsburgh no. 8 coal and Beulah Zap lignite are given in Figure 9. These monocluster structures indicate some features which are typical for some of the components comprising the above oil fractions. However, based on (a) the molecular weight distribution of the fractions as determined by mass spectral analysis; and (b) FTIR data indicating the type and relative concentration of oxygen-containing functional groups in the fractions, it is possible to design molecular structures for probable components in the above two oil fractions, including mostly monocluster* (mono-, bi-, and tricyclic) compounds, accompanied by small amounts of bicluster components. Some examples of probable components in the oil fractions of depolymerized Pittsburgh no. 8 coal and Beulah Zap lignite are indicated in Figure 10.

* Monocluster compounds are defined as containing a single condensed aromatic-hydroaromatic ring system in their molecular structure. Bicluster compounds are defined as containing two condensed ring systems interconnected by a linking group susceptible to hydrogenolytic or hydrolytic cleavage.

Figure 9. Derived average molecular structures for the oil fractions of depolymerized Pittsburgh #8 coal (A, average M.W. = 176; B, average M.W. = 200) and depolymerized Beulah Zap Lignite (C, average M.W. = 204; D, average M.W. = 192).

Figure 10. Examples of probable components of (A) Depolymerized Pittsburgh #8 coal, and (B) Depolymerized Beulah Zap lignite (R = H or alkyl; n = number of alkyl groups).

As seen in Figure 3, the average molecular structures for the oil fractions of the depolymerized Pittsburgh no. 8 coal and Beulah Zap lignite show some significant differences, i.e., (a) there are two O atoms per molecule for the BZ(ND) lignite-derived oil, whereas there is only one O atom per molecule (HVB) Pittsburgh no. 8 coal; and (b) structure (B) for the PB(PA) coal-derived oil may indicate a somewhat higher degree of condensation in components of the coal-derived as compared with the lignite-derived oil product.

In the framework of the project, we are presently trying to correlate the average structures of depolymerized U.S. coals with the rank and maceral composition of the starting coals. This should allow for structural differentiation of representative U.S. coals. Additional results and a more detailed discussion concerning this important point will be included in subsequent progress reports.

END

**DATE
FILMED**

7 / 13 / 93