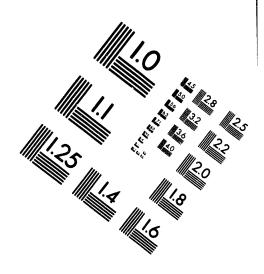
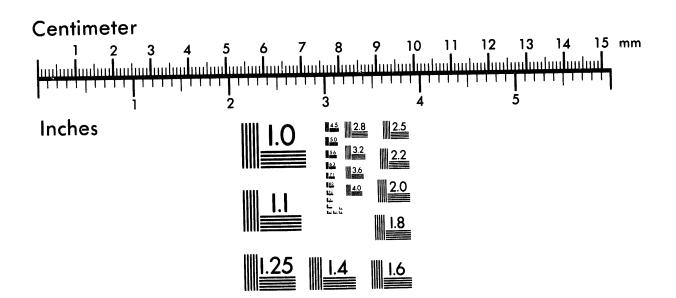


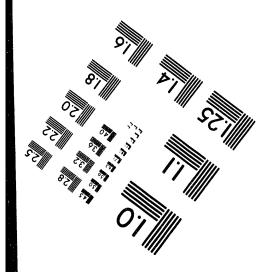


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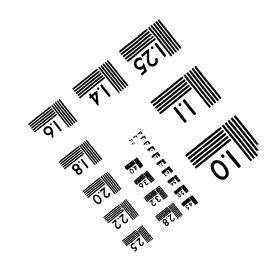
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## REFINING OF FOSSIL RESIN FLOTATION CONCENTRATES FROM WESTERN COAL

Final Fifth Quarterly Report (January 1, 1994 - March 31, 1994)

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Submitted To:

Patricia A. Rawls

Technical Program Manager
US Department of Energy

Pittsburgh Energy Technology Center

P.O. Box 10940, MS 922-H Pittsburgh, PA 15236-0940

(412) 892-5882

Submitted By:

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G. F. Jensen

Director

Utah Engineering Experimental Station

**104 EMRO** 

University of Utah

Salt Lake City, UT 84112

and

J. D. Miller

Department of Metallurgical Engineering

University of Utah

215 WBB

Salt Lake City, UT 84112

(801) 581-5160

May 7, 1994

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As per the contract schedule, the work conducted at the University of Utah during the fifth quarter of the project "REFINING OF FOSSIL RESIN FLOTATION CONCENTRATES FROM WESTERN COAL" continued on Task II (Characterization of Resin Refined Products) and Task III (Batch Kinetic Experiments). Both tasks were designed to provide fundamental information and process parameter selection for subsequent design and construction of the continous resin refining circuit. The work has been on schedule and the results are presented herein.

In the present study, the solvent refined resin products obtained from hexane and toluene extractions were subjected to both GS/MS and FTIR spectroscopic analysis. The purpose of these analysis is to gain further understanding of molecular structure and composition of the solvent-extracted products. The nature of the resinite coloration is also discussed based on the experimental results.

### EXPERIMENTAL PROCEDURE

Curie-Point Evaporation/Pyrolysis Experiment

In this phase of the work, 5 mg of minus 400 mesh powder for both resinite and coal as well as the solvent extracted products from the dark-brown resin were suspended and/or dissolved in 5 ml of spectroscopic grade methanol. About 5 µl of the solution was coated on a ferromagnetic wire for the Curie-Point pyrolysis experiments. The wire then was placed into a borosilicate glass tube after air drying. In all the experiments the sample wire was inserted into the pyrolysis reactor while maintaining a temperature of 290 °C and the volatile component of the sample was subjected to evaporation without activating the pyrolysis coil. After GC/MS

pyrolysis was conducted at 610 °C. The sample was heated at a rate of 1000°/sec and allowed to remain at the set temperature (610 °C) for a period of 4 seconds. Details about the sample preparation techniques and pyrolysis reactor are similar to these reported in the literature.

### GC/EIMS Spectroscopic Study

A 15 meter long and 0.25 mm i.d. fused silica column coated with 0.25 µm DB-5 was used at a helium flow rate of 4 ml/min (15 psi inlet pressure) and a temperature rising rate of 15 °C/min. from 40 to 320 °C. The total analysis was conducted in either 15 or 25 minutes. A Finnigan MAT model 800 Ion Trap detector was used with the low voltage electron (14 ev) impact ionization (EI) method for the generation of both molecular and fragment ions. The mass range scanned was 45-650 amu (m/z) and the scanning rate was 1 spectrum/second. Temperatures for the transfer line and the ion trap manifold were kept at 290 °C and 230 °C, respectively.

### FTIR Spectroscopic Examination

FTIR spectra of each resin type and the coal sample were obtained on a Digilab FTS-40 spectrometer equipped with a model 3240-SPC data-processing system. The spectrometer was connected to a liquid nitrogen-cooled, narrow-band MCT detector. The software capability of the instrument included base-line correction, deconvolution, and subtraction of the primary spectra. Transmission spectra of the resin types and coal were obtained in a KBr matrix. An accurately weighed sample was mixed (about 3%) with KBr in a Wig-L-Bug for 5 minutes, and a portion of the mixture (150 mg) was pressed into a disk (13 mm in diameter) under 20,000 psi

(1,400 bar). For the purposes of quantitative comparisons, the accurate compositions of the mixture and the weight of the disk were recorded. Since more than 90% of the sample disk is exposed to the source beam, small differences in the distribution of resin in the KBr matrix were observed to cause an error to the extent of 5% in quantitative comparisons.

Further uncertainties were minimized by the preparation of the disks with equal weights of the components. Primary spectra of the samples were obtained from 256 scans with a nominal resolution of 4 cm<sup>-1</sup> in the range 4000-700 cm<sup>-1</sup>.

### **RESULTS AND DISCUSSION**

## Pyrolysis GC/EIMS Spectra

A composite fossil resin sample (91.2 wt% hexane soluble resin) and coal sample (containing 0.2 wt% hexane soluble resin), both from the Wasatch Plateau coal field, as well as three solvent extraction products from the dark resin extraction were selected for Curie-Point evaporation/pyrolysis GC/MS analysis. The evaporation Py-GC and Py-GC/EIMS profiles for both composite fossil resin and coal are given in Figure 1, and the evaporation and residue pyrolysis Py-GC and Py-GC/EIMS profiles for hexane soluble resin, hexane insoluble but toluene soluble resin and toluene insoluble residue fractions of dark-brown resin are given in Figures 2, 3, and 4. The Py-GC profiles for the composite resin, the extracted fractions and the residue of the dark-brown resin (Figures 1-4) indicate that they all contain three major components. The sequentially eluted major peaks observed in each of the Py-GC profiles have been attributed to sesquiterpenoid monomers, dimers, and trimers, respectively. The Py-GC profile of the coal (see Figure 1), on the other hand, appears altogether different from those of the resin fractions. It is

seen that the pyrolysis of coal takes place continuously with increasing time and temperature. The volatile species are gradually and continuously released from the coal sample as a result of pyrolysis. Those volatiles from coal were identified from the EIMS spectra to be composed mostly of alkyl-substituted benzenes, naphthalenes, and high aromatics as inferred from the molecular ions and their probable fragmentation patterns (M/Z 63, 77, 91, 129, 155, 202, 215, 219, 241, 242, 257, 306, 310, 320, 324, 325). The presence of hydroaromatic and aliphatic compounds in the coal can also be established from the observation of peaks at mass numbers (M/Z) 57, 71 and 85. It is evident that coal contains a large proportion of aromatic compounds. On the other hand, the results from both Py-GC/EIMS and <sup>13</sup>C NMR <sup>[16,28]</sup> studies indicate that fossil resins are mostly aliphatic in nature with a small proportion of aromatic compounds.

Examination of the Py-GC profile yields some useful information regarding the differences among the hexane soluble, hexane insoluble / toluene soluble and finally the toluene insoluble residue of the dark resin. As described earlier, the Py-GC profiles for these samples were obtained at two different temperature settings. In the first setting the samples were rapidly heated to 290 °C and the evaporated portion of each sample was recorded on the Py-GC profile as a function of time. These experimental results are described in Figures 2-4 as evaporation Py-GC profiles. In the second temperature setting the same samples, after removing the relatively volatile portions at 290 °C, were rapidly heated to 610 °C and again the compounds released from the sample were monitored by Py-GC. The Py-GC trace of the latter compounds are referred to as flash residue Py-GC profiles. Of these two different profiles, the first ones (obtained at 290 °C) show more distinct differences for the comparison of chemical composition than the latter profiles (obtained at 610 °C). This is due to the probability that pyrolysis occurring at higher temperature causes extensive fragmentation of the sample and the differences among the resin

fractions may vanish. From this reasoning the evaporation Py-GC profiles of the resin fractions can be compared to derive some additional information about differences in composition.

A comparison of the evaporation Py-GC profiles presented in Figures 2 to 4 shows some interesting differences among the resin fractions. As mentioned before, the first peak in Py-GC profile is believed to represent the sesquiterpenoid monomer. From Figures 2 to 4 it is clear that this monomer is present almost exclusively in the hexane soluble portion of the dark resin. Further the second peak, which was attributed to the sesquiterpenoid dimer, appears to dominate in the hexane insoluble / toluene soluble portion of the dark resin (Figure 3). Finally in the toluene insoluble residue, the relative intensity of the dimer peak in relation to a third peak, which presumably represents the sesquiterpenoid trimer, is substantially reduced (Figure 4). These comparisons lead to the conclusion that less polar sesquiterpenoid monomers are soluble in hexane (at room temperature) and also lighter in color when compared to the dimers and trimers as is evident from their number average molecular weights. However when the polarity of solvent is increased, as is the case with toluene, relatively more dimers and trimers go into solution thus rendering a darker color to the solution containing the dissolved resin fraction. It is assumed that the toluene insoluble residue consists mainly trimers and some dimers, which are highly polar and even toluene is incapable of dissolving them. It must be emphasized, however, that even though one can distinguish several polymeric forms of sesquiterpenoid compounds from Py-GC profiles, their effective separation and isolation is rather difficult to achieve.

It should be noted that the Py-GC/EIMS spectra (see Figures 2, 3 and 4) were obtained by summing all spectra with the same background subtraction, which would mostly represent the sum of the mass spectra of molecular ions and fragment ions in all of the Py-GC spectra range.

## FTIR Spectra

FTIR spectra of hexane soluble, hexane insoluble but toluene soluble, and toluene insoluble products from dark resin as well as the parent coal sample are given in Figure 5. It is evident from the intensity of the aromatic band at ~ 1600 cm<sup>-1</sup> (Figure 5) that the hexane purified resin contains the lowest amount of aromatic components and oxygen functional groups (-OH, -COOH, >C=O). These components are found to increase gradually from hexane soluble through hexane insoluble / toluene soluble to toluene insoluble fractions of the resin. However, in the latter fraction the characteristic bands (at around 1700 cm<sup>-1</sup>) of the oxygen functional groups are buried under the overwhelming band for the aromatic C=C group. The spectrum of the toluene insoluble fraction shows a relatively far smaller amount of aliphatic compounds and quite a significant amount of aromatics making it somewhat similar to the spectrum of coal. In this way, it is speculated that the toluene insoluble portion of the dark-brown resin might be simply the spectrum of fine/colloidal coal particles dispersed in the resin matrix.

As observed from Figure 5, a gradual increase in color from the hexane soluble portion, to the hexane insoluble but toluene soluble portion, to the toluene insoluble portion of dark resin and a parallel increase in the fixed carbon content and aromaticity of these fractions in the same order may be due to both aromatized polyterpenoids, and the presence of colloidal coal inclusions in the resinite matrix. From the standpoint of the industrial utilization of fossil resins, particularly in printing inks, colorless or slightly colored resins are preferred and hence are of greater economic value. To this end, it is important to note that the hexane-extracted portion of the composite resin closely resembles the hand-sorted yellow resin.

### **SUMMARY AND CONCLUSIONS**

Fossil resins occurring in the Wasatch Plateau coal field are mainly composed of aliphatic components, partially aromatized multi-cyclic terpenoids and a few oxygen functional groups (such as -OH and -COOH). The solvent extracted resins show the presence of a relatively large number of methyl groups when compared to the methylene groups, and this indicates the presence of extensive tertiary carbon and/or highly branching chains. In contrast coal consists primarily of aromatic ring structures, various oxygen functional groups (-OH, >C=O, -C-O) and few aliphatic chains. The color difference observed among the four resin types is explained by the presence of chromophores (aromatized polyterpenoid) and also by the presence of finely dispersed coal particle inclusions in the resin matrix. The hexane soluble resin fraction has few aromatic compounds when comapred to the hexane insoluble but toluene soluble resin fraction.

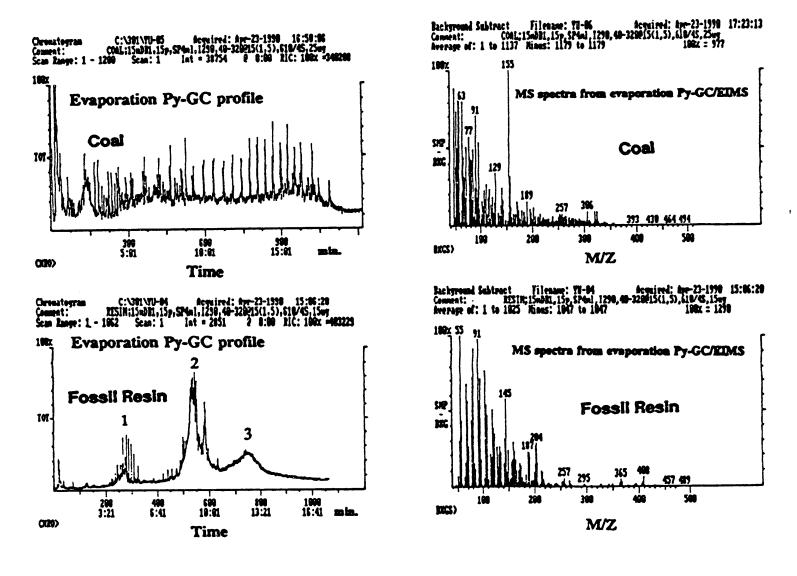
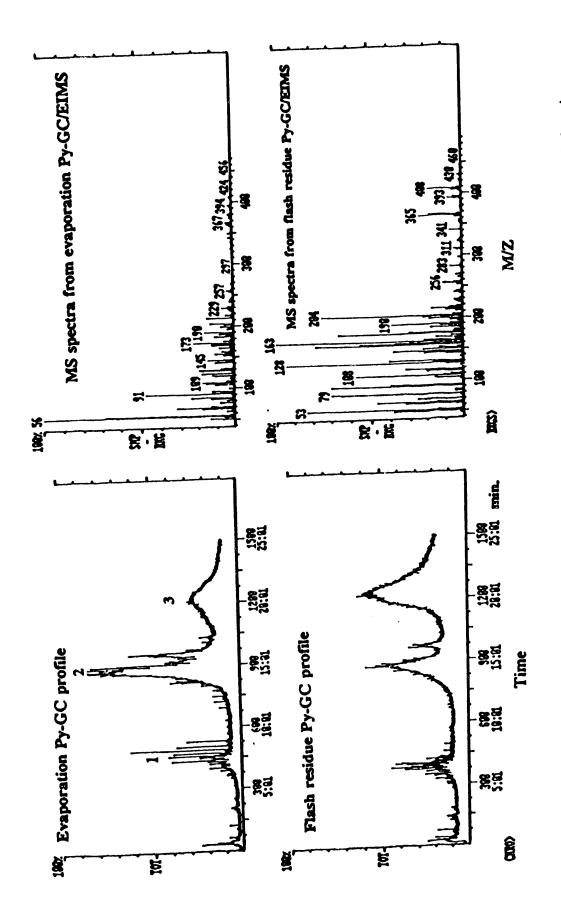


Figure 1. Evaporation Py-GC/EIMS spectra of the composite resinite and coal samples from the Wasatch Plateau coal field.



Evaporation and flash residue Py-GC/EIMS spectra of the hexane soluble portion of the dark resin. Figure 2.

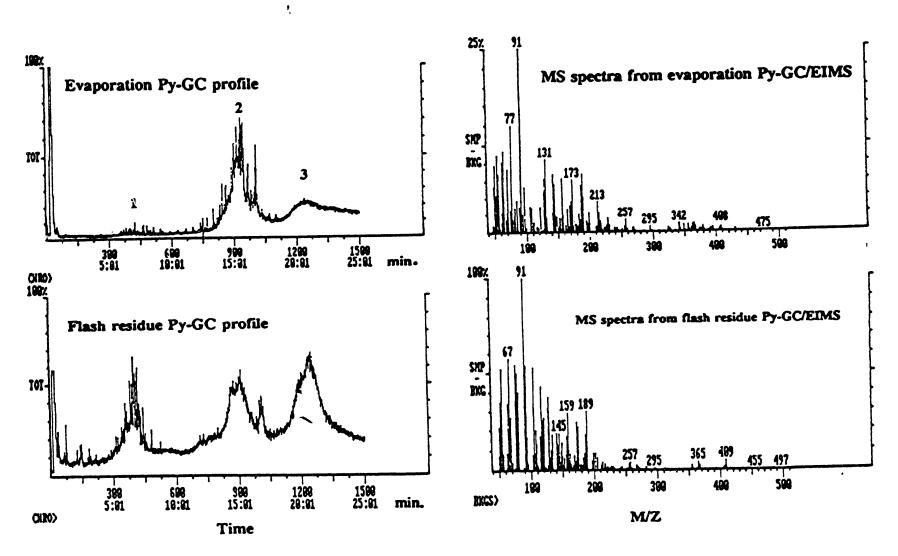


Figure 3. Evaporation and flash residue Py-GC/EIMS spectra of the hexane insoluble but toluene soluble portion of the dark resin.

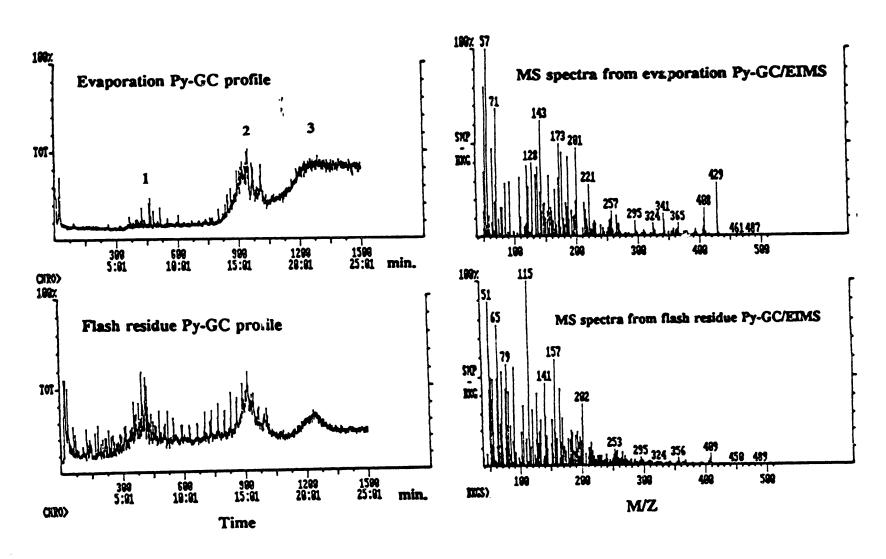


Figure 4. Evaporation and flash residue Py-GC/EIMS spectra of the toluene insoluble residue of the dark resin.

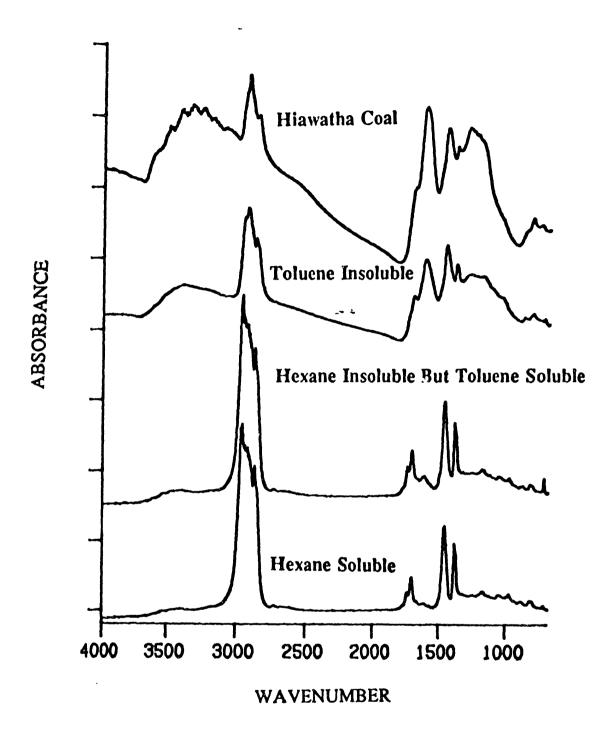


Figure 5. Transmission FTIR spectra of the hexane and toluene extracted products from the dark resin.

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