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REFINING OF FOSSIL RESIN FLOTATION CONCENTRATE FROM WESTERN COAL

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The research work conducted during the past quarter of the project “REFINING OF FOSSIL RESIN FLOTATION CONCENTRATE FROM WESTERN COAL” has emphasized laboratory solvent extraction studies for different resin types and the continuous refining circuit design (APT's Task II , Test Circuit Engineering).

1. Laboratory Solvent Extraction Studies for Different Resin Types

In the present study, the macroscopic fossil resins (10x28 mesh) were first classified by hand sorting into four different color types. These resin types were subjected to physical/chemical characterization, petrographic examination, and hexane/toluene extraction. The purpose of this study is to gain further understanding with respect to the physical/chemical and petrographic properties of these four resin types and the solvent-extracted products. The nature of the resinite coloration is discussed based on the experimental results.

1.1 EXPERIMENTAL

1.1.1 Sample Preparation

A composite resinite sample containing 90.6% hexane soluble resin (-10 mesh) was obtained by gravity separation from the Wasatch Plateau coal (Hiawatha seam). The particle size of the sample used for classification was 10x28 mesh, with an average size of approximately 1 mm. These resinite particles were then fractionated on the basis of their natural color by hand-sorting. Four different resin groups with gradual variation in color,

viz., yellow, amber, light brown, and dark brown, thus obtained, were weighed, and analyzed. A dark resin sample (-28 mesh) was obtained by dense medium separation with sodium chloride solution (1.06 g/cc) from the composite resinite sample (-28 mesh). After separation the float and sink portions were collected, washed with deionized water, and dried in a vacuum oven at 70 °C for 24 hours.

The coal sample was also from the Wasatch Plateau coal field (Hiawatha seam), and was found to contain about 7% fossil resin. Most of the resin in the coal sample was removed by froth flotation with MIBC. The final coal sample was found to contain about 0.21% by weight hexane-soluble resin and was used in subsequent studies and analyses.

1.1.2 Microscopic Analysis

Since resinite fluoresces under UV and blue light, the optical characteristics of these four fossil resin types can be analyzed by a fluorescence microscopy. Polished briquettes (pellets) were prepared and used for such analysis. The polished briquettes were prepared by cutting the sample with an IsometTM Low Speed Saw made by BUEHLER and then polishing on a plate with Buehler #600 sand paper followed by a 1-micron and then a 0.05-micron alumina suspension. In each case about 2-3 grams of this 28x65-mesh sample and a suitable amount of epoxy/resin mixture (in the ratio of about four parts of the sample to one part epoxy by volume) were thoroughly mixed and filled into a cylindrical rubber mold (1.5 cm in height and 2.4 cm in diameter). The briquette was then dried and hardened in the mold overnight. After removal from the mold, the briquette was ground and polished according to ASTM D-2013-79 method.

An Axioplan Universal Microscope (Carl Zeiss, West Germany) was employed for the

analysis of the polished samples. The microscope was equipped with a 150-watt xenon arc lamp and a blue-light excitation set (450-490 SB) with an exciter filter (BP 450-490), a chromatic beam splitter (FT 510), and a barrier filter (LP 520).

In each case, color photographs of the polished section were taken using a Carl Zeiss Microscopic attachment (MC 100) system with a 35-mm camera and Kodak 100 film. A 20X dry objective lens and a 10X photo eyepiece were used for all the photography, which gave a 200X magnification of the image.

1.1.3 Solvent Extraction

One gram of each resin type, obtained by hand-sorting (10x28 mesh), was placed into a flask with 200 ml of spectroscopic grade hexane or toluene and the flask was agitated on a Junior Debit shaker at room temperature. The extraction lasted for 4 hours in the case of hexane extraction and for only 1 hour in the case of toluene. The extraction was kinetically monitored by withdrawing a 5 ml of loaded solution into a beaker at desired time intervals and drying in a vacuum oven at 90 °C for 24 hours. The resin which remained after drying was weighed to determine the mass balance. Only yellow resin was completely dissolved after four hours of hexane extraction while a portion of the other resin types remained undissolved. Most of the insoluble residue from hexane extraction was found to be light to dark brown resin, which was soluble in toluene.

1.1.4 Density Measurement

The densities of each of the separated resin types, solvent extracted products, and coal sample were measured by a Micromeritics 1320 Autopycnometer. Prior to these measurements, the samples were dried in a vacuum oven at 60 °C for 24 hours. The pycnometer was calibrated with a standard steel ball and was found to be capable of yielding reproducible density values to the third decimal place.

1.1.5 Proximate and Ultimate Analysis

Proximate analysis including determination of the moisture, ash, fixed carbon and volatile matter content for each of the hand-sorted resin types, solvent extracted resins, and coal were carried out using the same standard procedures that are used for coal analyses. Moisture and ash contents were determined at 110 °C for 2 hours and 750 °C for 5 hours respectively in the Model 450 Fisher Ash Analyzer.

Elemental analysis for carbon, hydrogen, nitrogen, sulfur, and oxygen (by difference) along with the determination of calorific values constituted the ultimate analysis. Carbon, hydrogen, and nitrogen analyses were made with a LECO-600 and the analysis for sulfur with a LECO-SC 132 analyzer. Calorific values were measured with a LECO AC-300 automatic calorimeter.

1.1.6 Molecular Weight Determination

Molecular weights of the four resin types as well as the solvent extracted products were determined by Vapor Pressure Osmometry. These measurements were carried out using a Wescan Model 233 Vapor Phase Osmometer with toluene as solvent at an operating temperature of 47 °C. A standard solution of sucrose octaacetate (MW = 678.6 g/mol) was used to obtain the instrument calibration factor. The concentration of resin in toluene was varied over an order of magnitude. The results have shown that the molecular weight determined in each case was independent of the resin concentration.

1.2 RESULTS AND DISCUSSION

1.2.1 Proximate Analysis of Resin Types

Some physical and chemical properties of the four fossil resin types and coal sample from the Wasatch Plateau coal field are presented in Tables 1 and 2. It is seen from the tables that the densities of the four resin types gradually increase from yellow (1.037 g/cm³) to dark-brown (1.054 g/cm³) and finally to coal (1.290 g/cm³). This increase in density is accompanied by an increase in molecular weight, and ash content. These resins are considered to be mostly aliphatic compounds and are completely volatile (>96.9%) with a higher BTU value (>18,194 BTU/lb) when compared to the parent coal.

1.2.2 Macroscopic Resin Types

Four macroscopic resin types, based on their natural color, as obtained by hand-sorting the particles (10x28 mesh) from a gravity concentrate, change gradually in color from yellow, to amber, to light-brown, and finally to dark-brown.

As seen from Table 1 the distribution of these resin types in Wasatch Plateau coal was found to increase gradually from yellow resin (8.2%) to dark-brown resin (51.6%). A major portion of the composite resin (resinite) is of the dark-brown type, while the light colored resin constitutes a smaller proportion. Although the light colored resins are of greater economic value, the dark colored resins are also used in the industry.

1.2.3 Microscopic Examination

Fluorescent microscopic examination was carried out for all resin types and the results show that all resin types fluoresce under blue light with a greenish yellow color, which gradually diminishes in intensity from yellow to dark brown resin. While the microphotograph of yellow resin indicates that it is homogeneous, the other resin types show inclusions of what appear to be fine coal particles. These colloidal coal particles were found to be 1 to 20 microns in diameter and gradually increase in number from amber to dark brown resin. These observations lead to the conclusion that the differences among the four resin types, particularly their color in the natural state may be due to the differences in the quantity of finely suspended coal particles.

1.2.4 Solvent Extraction

Solvent extraction has been used extensively to isolate and purify the resinite maceral and has also been used as a commercial extraction process for the solvent refining of fossil resin. With respect to solvent extraction, Figures 1 and 2 give the extraction kinetics of the four fossil resins in hexane and toluene, respectively. The extraction rate for these fossil resins in both solvents follows the order (from fast to slow): yellow resin > amber resin > light-brown > dark-brown resin. This sequence in solvent extraction rate may be more or less related to the molecular weight of the resin types and the presence of finely dispersed coal inclusions which are insoluble in hexane and slightly soluble in toluene. The number average molecular weight of the four resin types in toluene as determined by vapor pressure osmometry is given in Table 2. These values, which may vary with the experimental method used, increase from a molecular weight of 1140 g/mol. for yellow resin to 1500 g/mol. for dark brown resin. The higher the molecular weight, the more difficult and slower the extraction by the solvent. On the other hand, the finely dispersed coal inclusions which gradually increase in number from amber to dark-brown resin may account for the decrease in extraction rate from yellow resin to dark-brown resin as revealed in Figures 1 and 2.

It can also be seen from the Figures 1 and 2 that toluene is a stronger solvent for fossil resin extraction than hexane, and that toluene gives a higher extraction percentage for light-brown and dark-brown resins. Such a finding might be expected due to the fact that hexane (solubility parameter = 7.3) is a non-polar solvent while toluene (solubility parameter = 8.9) is weakly polar with a permanent dipole and p-electron system that provides for stronger interaction with or penetration into resinite. The photographs of extracted hexane and toluene solutions with different resin types at the same concentration (20 mg/ml) are

presented in Figure 3. It is clear from the photographs in Figure 3 that hexane extracted products from all resin types have a light yellow color. On the other hand toluene, being a more polar solvent, can extract extraneous matter from all resin types and the color of the extracted solution changes gradually from light yellow for yellow resin to brown for the dark-brown resin.

It is evident from Figures 1 and 2, that a significant portion of both light-brown and dark-brown resins is hexane insoluble but toluene soluble. To evaluate the properties of this portion of the resin, 20 grams of dark resin (-28 mesh) was placed into a 500 ml flask with 300 ml of spectroscopic grade hexane and extracted for 2.5 hours. After hexane extraction, the hexane insoluble portion was filtered and subjected to toluene extraction (300 ml of spectroscopic grade toluene). The hexane insoluble but toluene soluble portion of dark resin was isolated, and its physical properties and chemical constitution were determined. A photograph of the hexane soluble, hexane insoluble / toluene soluble, and finally toluene insoluble portion of the dark resin is presented in Figure 4. Tables 3 and 4 list the measured density, molecular weight, proximate and ultimate analysis of the two soluble resin fractions as well as the toluene insoluble residue from the dark resin.

It is evident from the Tables 3 and 4 that most of the dark brown resin (61.3%) is hexane soluble after 2.5 hours extraction. The hexane soluble portion has a yellow color, low density, high volatile matter, and low molecular weight while the hexane insoluble but toluene soluble portion (31.8%) appears dark in color, has a slightly lower volatile matter, and higher density and molecular weight. The toluene insoluble residue from the dark brown resin resembles coal and has a relatively high density, (1.205 g/cc), ash (3.1%), and very low volatile matter (58.9%). The proximate and ultimate analysis of the toluene insoluble residue

of the dark brown resin indicates that it mostly consists of very highly dispersed coal particles as well as polymerized and aromatized terpenoids with higher oxygen content as will be discussed later. Further it should be noted that the hexane soluble portion has a higher carbon and hydrogen content, higher H/C atomic ratio and low oxygen content. In contrast, the hexane insoluble but toluene soluble portion has a significantly higher oxygen content. Finally, as was noticed previously, the hexane soluble portion from either the light-brown or dark-brown resin has a light color similar to the natural yellow resin sample.

1.3 SUMMARY AND CONCLUSIONS

Four resinite types, namely yellow, amber, light-brown, and dark-brown in color, occurring in the Wasatch Plateau coal field, are mainly composed of aliphatic components. 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 hand-sorted resin types is explained by the presence of chromophores (O, S, and N atoms and C=C double bonds) and also by the presence of finely dispersed coal particle inclusions in the resin matrix. The extraction rate for these resin types follows the order yellow > amber > light-brown > dark-brown. Hexane purified resin from all resin types closely resembles the properties of the physically separated yellow resin. Resinites are distinct from other coal macerals, which show a high heat value and high volatile matter content. The four resin types also show distinct differences among certain physical and chemical properties such as density, and softening point. All these properties were noted to change gradually from yellow to dark-brown resin.

1.4 FUTURE RESEARCH WORK

- 1) Test other solvents such as toluene, hexane in batch experiments.
- 2) Further characterize and evaluate the solvent refined resin products.
- 3) Examine the effect of solute loading on the extraction kinetics.

Table 1. The distribution of four fossil resin types (10x28 mesh)

<u>Resin Type</u>	<u>Weight Distribution (%)</u>
Yellow	8.2
Amber	11.4
Light Brown	28.8
Dark Brown	51.6

Table 2. Proximate analysis and calorific value of the four hand-sorted resin types and coal

<u>Resin Type</u>	<u>Density</u>	<u>Ash</u>	<u>Volatile Matter*</u>	<u>Calorific Value</u>	<u>Molecular</u>
	<u>(g/cm³)</u>	<u>(Wt.%)</u>	<u>(Wt.%)</u>	<u>(Btu/lb)</u>	<u>Weight</u>
Yellow	1.037	0.0	100.0	18,667	1140
Amber	1.042	0.0	99.1	18,329	1170
Light brown	1.049	0.0	97.9	18,453	1350
Dark brown	1.054	0.2	96.9	18,194	1500
Coal	1.293	4.5	44.4	15,538	-----

* Dry, ash free basis;

Table 3. Proximate analysis of hexane/toluene extracted fractions from dark-brown resin and its residue

<u>Extracted Fraction</u>	<u>Wt.(%)</u>	<u>Ash (%)</u>	<u>Volatile Matter (%)</u>	<u>Density (g/cm³)</u>
Hexane soluble 150 minutes at 25 °C	61.3	0.0	100.0	1.023
Hexane insoluble Toluene soluble 60 minutes at 25 °C	31.8	0.0	98.7	1.068
Toluene insoluble	6.9	3.1	58.9	1.205

Table 4. The elemental composition, H/C and O/C ratios, and the molecular weights of hexane/toluene extracted fractions from the dark-brown resin and its residue

<u>Extracted Product</u>	<u>Elemental Composition (%)</u>					<u>Atomic Ratio</u>		<u>Molecular Weight</u>
	C	H	O	N	S	H/C	O/C	
Hexane soluble 150 minutes at 25 °C	87.05	11.08	1.48	0.26	0.13	1.53	0.01	1270
Hexane insoluble Toluene soluble 60 minutes at 25 °C	85.09	10.29	3.83	0.41	0.38	1.45	0.03	1700
Toluene insoluble	82.27	7.76	8.45	1.07	0.45	1.13	0.08	n.d

n.d --- not determined

Caption of Figures

1. **Hexane extraction kinetics for different resin types.**
2. **Toluene extraction kinetics for different resin types.**
3. **Color photographs of solvent solutions of the four resin types (20 mg/ml). A - -- Hexane extracted solutions (4 hours at 25 °C); B --- Toluene extracted solutions (1 hour at 25°C);**
4. **Photograph of hexane/toluene extracted products from dark resin. A --- Hexane soluble portion (150 minutes at 25 °C); B --- Hexane insoluble but toluene soluble portion (60 minutes at 25 °C); C --- Toluene insoluble residu**

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