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REFINING OF FOSSIL RESIN FLOTATION CONCENTRATE FROM WESTERN COAL

Second Quarterly Final Report (April 1, 1993 - June 30, 1993)

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According to the contract schedule, the work conducted during the second quarter of the project "REFINING OF FOSSIL RESIN FLOTATION CONCENTRATE FROM WESTERN COAL" emphasized Task 2 (Characterization of Resin Flotation Concentrate and Refined Products) and Task 3 (Batch Kinetic Experiments). Both tasks were designed to provide fundamental information and process parameter selection for subsequent design and construction of the continuous resin refining circuit. In addition, some technical questions raised by Ms. Patricia A. Rawls, Technical Project Officer, were taken under consideration. The work has been on schedule and the results are presented herein.

1. Physicochemical Characteristics of the Fossil Resin Flotation Concentrate

1.1. Preliminary analysis of the resin concentrate

The proximate analysis of the resin concentrate was conducted and the results are summarized in Table 1. As seen from Table 1, the resin flotation concentrate generally has low ash content (1.23%), low moisture (1.03%), and low density (1.143 g/cc) as compared to other coal macerals. It also found that resin concentrate shows the high melting point (196-198 °C)

Table 1. Proximate Analysis of the Resin Concentrate

Density (gram/cm ³)	1.143
Ash (%)	1.23
Moisture (%)	1.03
Melting point (°C)	196 - 198

1.2. Elementary Composition of the Resin Concentrate

Ultimate analysis was conducted for the fossil resin concentrate and results obtained are given in Table 2. Based on these results and other results from spectroscopic analysis it appears that the fossil resin from the Wasatch Plateau coal field consists mainly of aliphatic components and partially aromatized multicyclic terpenoids with a few oxygen functional groups. As compared with the parent high volatile bituminous coal, the resin has higher hydrogen and carbon content, low oxygen, nitrogen, and sulfur contents, and relatively low aromaticity. The values of the acid number and iodine number indicate that the fossil resins from the Wasatch Plateau coal field contain only a modest amount of oxygen functional groups and unsaturated carbon-carbon double-bonds in their molecular structures.

Table 2. Chemical Composition of the Resin Concentrate

Acid Number	95.8
Iodine Number	75.4
Elemental Composition	
C (%)	84.66
H (%)	9.57
N (%)	0.45
S (%)	0.35
O (%)	4.97
O/C ratio	0.044
H/C ratio	1.36

1.3. Particle Size Distribution of the Resin Concentrate

The particle size distribution of the resin concentrate was determined by wet screening according to ASTM standard procedure (D 4749). The particle size distribution obtained is presented in Table 3.

From Table 3, it is evident that the resin concentrate has a relatively fine particle size distribution with more than 80% (by weight) being less than 200 mesh (74 microns) and about 64% (by weight) less than 38 micron (400 mesh). This tendency to be distributed into the smaller particle sizes is attributed to the fact that fossil resin from Wasatch Plateau coal field is very brittle and is easily broken into fines during materials handling and transportation. For example, it is not unusual to find that the minus 28 mesh coal streams in a coal preparation plant contain more than 10% hexane-soluble resin, even when the run-of-mine coal contains only 3% resin. Such a fine particle size should be favorable for subsequent solvent refining due to the large surface area and kinetic studies of resin extraction for different particle size will be carried out to find out the effect of particle size on resin extraction rate.

1.4. Petrographic Characterization of the Resin Concentrate

Since fossil resin or resinite fluoresces under uv and blue light, the petrographic characteristics of fossil resin types and coal components in the resin concentrate can easily be identified and classified by fluorescence microscopy. Under blue light fossil resin grains can be distinguished into four groups: green, green-yellow, yellow-orange and orange-brown which are similar to the hand-sorted resin types of yellow, amber, light-brown and dark-brown resin. The

Table 3. Size Distribution of the Resin Concentrate

Particle Size Range		Weight	Cumulative weight	
(mesh)	(μm)	(%)	+ (%)	- (%)
28-60	600-250	1.79	1.79	100.00
60-100	250-150	4.24	6.03	98.21
100-200	150-75	13.74	19.77	93.97
200-270	75-53	7.71	27.48	80.23
270-400	53-38	8.71	36.19	72.52
-400	-38	63.81	100.00	63.81
Total		100.00		

polished briquettes (pellets), in which the particles of the resin concentrate are accommodated by synthetic resins, were examined using an Axioplan Universal Microscope manufactured by Carl Zeiss, West Germany. Typical microscopic photographs of the four resin types as well as coal are given in Figure 1. For the quantitative petrographic analysis, more than three hundred observations were made and the compositional distribution of various resin types and coal components is presented in Table 4. It is evidenced from the petrographic analysis that resin concentrate consist predominately of green-yellow and yellow-orange resins (63.5%). A considerable amount of green resin (12.6%) and orange-brown resin (11.0%) is also observed. In addition, a significant amount (12.7%) of fine coal particles are also found in the resin concentrate. Very few large coal particles are occasionally observed.

Figure 1. Microscopic photographs of the fossil resin

Figure 1. continued

Table 4. Petrographic Analysis of the Resin Concentrate

Petrographic Type/Component	Count by number (%)
Green Resin	12.62
Green-Yellow Resin	28.64
Yellow-Orange Resin	34.97
Orange-Brown Resin	11.04
Coal	12.72

2. Preliminary Solvent Extraction Tests

Fossil resin is a complex mixture of sesquiterpenoids and the solubility of these resin compounds depends on the type of solvent used. The determination of the extractable resin content in the resin concentrate by different solvents provides an important control variable for selective solvent refining and purification. The data generated during preliminary solvent extraction tests are especially important for process design, control of the refined resin quality and prediction of the refined resin products. In this work, the extractable resin content was determined for each size fraction with four solvents: ethyl acetate (ACS grade), hexanes (ACS grade), heptane (98%, assay grade), and toluene (ACS grade). The extraction tests were conducted in TX-6 Soxhlet extraction units. With about 1 to 2 grams of the resin sample being placed in single-thickness cellulose thimbles and to which about 60 to 70-ml of solvent were added. The extraction was carried out for at least 2 hours at the boiling point of the system followed by rinsing for another 4 hours. Results are given in Table 5.

As can be seen from Table 5 the resin concentrate has the highest solubility in toluene, especially for particles with a large size. Notice for the fine sizes that the extent of extraction is generally reduced. For example, with the exception of ethyl acetate, the percent extracted is reduced from almost 90% for coarse particles to about 70% in the case of fine particles. These results indicate that during preparation of the resin concentrate by flotation fine coal particles were aggregated with resin particles and concentrated into the froth product (resin concentrate).

Table 5. Extraction from Individual Size Fraction of the Resin Concentrate by Different Solvents

Size (mesh)	Extracted weight (%)	Solvent			
		Ethyl Acetate b.p. 77 °C	Hexanes b.p. 70 °C	Heptane b.p. 98 °C	Toluene b.p. 111 °C
28-60	(%)	53.63	89.13	90.98	94.63
60-100	(%)	52.05	90.54	91.72	94.42
100-200	(%)	56.03	87.67	87.94	91.74
200-270	(%)	62.15	82.33	81.92	87.84
270-400	(%)	50.54	78.72	79.17	83.97
-400	(%)	63.44	66.85	66.24	73.92
Total	(%)	60.54	73.34	73.72	79.56

3. Solvent Loading Limits

In this phase of the research a given amount of resin concentrate was placed into 100 ml of solvent and the mixture was shaken with a Junior Orbit shaker at 250 RPM for 24 hours. The resin solution was then separated from the undissolved residue by centrifugation at 10000 RPM for 30 minutes. Finally, the solvent was evaporated and both resin product and residue were weighed and analyzed. Solvent loading limits were thus examined and the results are plotted in Figure 2.

The data suggest that the loading limits were not reached for heptane, hexanes and toluene under the range of compositions examined. On the other hand, ethyl acetate was found to load only about 18 g of resin per 100 ml solvent. In fact, at high concentration the resin solutions in toluene, hexane, and heptane become more viscous and dark in color while the resin solution in ethyl acetate seems more clear and less viscous. These indicate that the nature of dissolution of fossil resin in ethyl acetate may be different from that in other solvents. Since no loading limits for heptane, hexanes and toluene were observed, the resin refining & purification processing by the solvent extraction totally may depend on the viscosity of the solution and the separation technologies to be used to separate loaded solvent and insoluble residue. Nevertheless future confirmation is required and it is interested that the solubility of the resin will be examined at higher concentrations and different temperatures for a selected solvent to establish the rudiments of a phase diagram.

Figure 2. Solvent loading limits

4. Characteristics of Extracted Resin Products

The solvent extracted resin products obtained from the work were then characterized in terms of their physicochemical properties.

4.1. Physical Properties

Melting points of the extracted resin products were determined using the 8100 Series Digital Melting Point Apparatus of Electrothermal Engineering Limited. Their densities were measured using Micromeritics Autopycnometer 1320. Experimental results are presented in Table 6. For comparison Table 6 also lists the data obtained for the feed, the fossil resin concentrate.

Table 6. Melting Point and Density of Solvent Extracted Resin Products

Solvent refined Product	Temperature of extraction (°C)	Melting point of extracted product (°C)	Density of extracted product (g/cm ³)
Ethyl acetate-product	79	141 - 142	1.048
Heptane-product	100	178 - 180	1.036
Hexanes-product	74	140 - 142	1.034
Toluene-product	113	175 - 178	1.048
Resin concentrate-feed		196 - 198	1.143

It should be noted that the melting point of heptane-extracted resin is higher than that of hexanes-extracted resin. It appears that the increase in the carbon chain length of solvent results in an rising in the melting point of the refined resin products. Therefore, some long chain solvents such as octane, nonane or decane might be considered as optional solvents for resin refining.

4.2. Elemental Analysis

Results of element analysis for the extracted resin samples are listed in Table 7. Both the acid number and iodine number of the solvent extracted resin products are listed in Table 8.

Table 7. Elemental analysis of extracted resins

Solvent refined product	Element content %					Atomic ratio	
	C	H	N	S	O	O/C	H/C
Ethyl acetate-product	85.79	10.57	0.19	0.29	3.16	0.0276	1.48
Heptane-product	86.88	10.85	0.17	0.30	1.80	0.0155	1.50
Hexanes-product	86.79	10.84	0.16	0.40	1.81	0.0156	1.50
Toluene-product	86.49	10.63	0.20	0.30	2.38	0.0206	1.47
Resin concentrate	84.66	9.57	0.45	0.35	4.97	0.0440	1.36

Table 8. Acid number and iodine number of the extracted resins

Solvent refined product	Acid number	Iodine number
Ethyl acetate-product	138	78.68
Heptane-product	98.4	78.98
Hexanes-product	90.4	77.67
Toluene-product	112	79.38
Resin concentrate feed	95.8	75.45

It is evident that the ethyl acetate-product was found to contain more oxygen than the toluene product while both hexane- and heptane-products were found to contain less oxygen content than the toluene-product. Other elemental composition features were found to be quite constant for all solvent refined resin products.

The values for both acid number and iodine number for these various solvent refined resin products were found to be close to the values of the original resin concentrate. This indicates that the solvent extraction by these solvents will not change the functional groups and carbon-carbon double bond in the resin composition. Only slight variations in the iodine numbers were found for the solvent refined products. On the other hand some variation in the acid numbers were found and these must be taken into consideration in future selection of an appropriate solvent.

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