

SOLVENT REFINING OF COAL RESIN CONCENTRATES

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ABSTRACT

Certain bituminous coals of the western United States are known to contain appreciable quantities of macroscopic resinite (fossil resin). Such resinous coals are found in the states of Arizona, Colorado, New Mexico, Utah, Washington, Wyoming, etc. Among these, the Wasatch Plateau coal field in central Utah has a particularly high content of fossil resin. It has been reported that some seams in this field average as much as 5% resin. Fossil resins have been recovered intermittently from the Utah coal field since 1929 by gravity and/or flotation processes. Recently selective flotation procedures have been developed to produce high-grade fossil resin concentrates, and the flotation concentrates thus produced can be refined by solvent extraction. Such solvent-refined resin, at the present time, has a market value of about \$0.50 per lb as a chemical commodity and can be used in the ink, adhesive, rubber, varnish, paints, coatings, and thermoplastics industries.

A detailed study of batch solvent refining of resin concentrates from the Wasatch Plateau coal is in progress at the University of Utah to evaluate the effect of refining conditions on the extraction yield and product quality during various solvent extraction processes. These solvent-refined products are being characterized with respect to their physical/chemical properties. Important extraction variables for differential refining of fossil resin concentrates are examined in order to maximize the commercial value of this unique fossil resin resource.

INTRODUCTION

Macroscopic fossil resin from the western coal fields is a unique resource in the United States.^[1-3] Such resinous coals are found in the states of Arizona, Colorado, New Mexico, Utah, Washington, Wyoming, etc. Among these, the Wasatch Plateau coal field in central Utah is of special significance because of its particularly high content of macroscopic fossil resin.^[4,5] It has been reported that many seams in this field average as much as 5% resin. Fossil resin is derived from terpenoid plant resins that have polymerized in situ and is of predominantly aliphatic character with high hydrogen and carbon content and low oxygen, nitrogen, and sulfur content when compared to the parent bituminous coal.^[6,7] Fossil resin from Utah coal generally exhibits low density, a range of colors, and good solubility in hexane and/or heptane.^[6,7] It has been recovered intermittently on a small scale from the Utah coal field since 1929 by gravity and/or flotation processes. The resin concentrates thus produced are refined by solvent extraction. The resin particles show a basic amber color and contain inclusions of what appear to be fine coal colloids. As the fine coal inclusions increase in the resin matrix, the darker the resin particles appear. Thus solvent refining is required to remove the fine coal inclusions and dark color-inducing compounds (hexane insoluble) from the resin concentrate in order to produce a premium resin product. Solvent-purified resins from the Wasatch Plateau coal typically have a molecular weight of about 1200 and a softening point of about 160°C. This product, at the present time, has a market value of about \$0.40 to \$0.70 per lb as a chemical commodity and can be used in the adhesives, rubber, varnish, paints, coatings, and thermoplastics industries, and particularly in the ink industry.^[6,7]

Because of the lack of technology for the efficient recovery of fossil resins from coal this valuable resource has been wasted, being burned together with coal for electric power generation. It is estimated that the fossil resin from the Wasatch Plateau coal field burned each year for electric power generation has a value of \$100 million - equivalent to the value of the coal itself!! The waste of this valuable resource is evident. In view of these factors, the waste of a valuable resource and the special product quality, significant efforts have been made to develop technology for a fossil resin industry in the western coal fields. As a result of these efforts, several new flotation technologies have been developed and three U. S. patents were granted.^[8,9,10] Nevertheless, the development of a fossil resin industry remains uncertain. The primary reason for this situation is that coal producers who own this valuable resource are not convinced that such a venture to develop a fossil resin industry would be reliable and profitable. In this regard, further research efforts to develop technology for the refining of resin concentrate are needed.

In this paper, the batch solvent refining of coal resin concentrates from the Wasatch Plateau coal is discussed to evaluate the effect of refining conditions on the extraction yield and product quality during various solvent extraction processes. These solvent-refined products are being characterized with respect to their physical/chemical properties. Important extraction variables for differential refining of fossil resin concentrates are examined in order to maximize the commercial value of this unique coal resin resource.

SOLVENT EXTRACTION OF RESIN CONCENTRATE

Fossil Resin Flotation Concentrate

The resin concentrate was obtained by pilot-plant flotation of fossil resin from Wasatch Plateau coal (both UPL and CO-OP coal mines) of south central Utah. About 200 lbs high grade flotation concentrate (approximate 75% resin content) was generated. The resin concentrate was naturally dried, sampled and stored in one-kilogram plastic bags. The ash and moisture contents of the concentrate were found to be 1.23% and 1.03% by weight respectively. Wet-screening of the resin concentrate revealed 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). Such a fine particle size is expected to be favorable for subsequent solvent refining due to the large surface area available for reaction.

Preliminary Solvent Extraction Tests

Fossil resin is a complex mixture of sesquiterpenoids and the solubility of these resin compounds depends on the solvent used. Determination of the extractable resin content in the concentrate by different solvents will provide an important criterion for the design of a solvent refining and purification process and to establish the quality of the refined resin products that might be produced. The extractable resin content was determined with four solvents: ethyl acetate, hexane, heptane, and toluene. The extraction tests were conducted in a TX-6 Soxhlet extraction unit. In the tests, approximately 1-2 grams of the resin sample of a specific size fraction were placed in a single-thickness cellulose thimble with 60 to 70-ml of solvent. The extraction was carried out for at least 2 hours at the boiling point of the solvent and then rinsed for another 4 hours. The results are given in Table 1.

It can be seen from Table 1 that among the four solvents tested the resin concentrate has the highest solubility in toluene and the lowest solubility in ethyl acetate. It was also found that the hexane-, heptane-, and ethyl acetate-extracted resins appear light-yellow in color while the toluene-extracted resin exhibits a significantly darker color. In most cases,

the larger particles in the resin concentrate exhibit greater solubility. This is due to the fact that the fine coal contamination is found in the smaller size fractions of the resin concentrate.

It is evident from Table 1 that, of the four solvents, toluene is the strongest solvent for resin extraction and that a higher percentage of the resin can be recovered. Such a high extraction is expected due to the fact that toluene is weakly polar with a permanent dipole and π -electron system that provides for a stronger interaction with resin. On the other hand toluene, being a more polar solvent, also extracts extraneous polar molecules, such as alkyl-substituted benzenes, naphthalenes and other aromatic compounds, imparting a darker coloration to the extracted resins as evidenced from FTIR and pyrolysis GC/EIMS analysis.^[7]

Table 1. Resin extraction results for various size fraction with four solvents.

Size (mesh)	Extracted weight (%)	Solvent			
		Ethyl Acetate	Hexane	Heptane	Toluene
28x60	(%)	53.63	89.13	90.98	94.63
60x100	(%)	52.05	90.54	91.72	94.42
100x200	(%)	56.03	87.67	87.94	91.74
200x270	(%)	62.15	82.33	81.92	87.84
270x400	(%)	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

Characteristics of the Extracted Resin Products

The extracted resin products as obtained from preliminary solvent extraction tests on the composite resin concentrate were characterized in terms of their melting point, density, and chemical composition. The melting points of the extracted resin products were determined using the 8100 Series Digital Melting Point Apparatus manufactured by Electrothermal Engineering Limited. Density measurements were carried out using the Autopycnometer 1320 manufactured by Micromeritics. The results for the composite concentrate are shown in Table 2.

Table 2. Characteristics of solvent extracted resin products from the composite concentrate.

Solvent used for extracting resins	Melting point of extracted resin products (°C)	Density of extracted resin products (g/cm ³)
Ethyl acetate	141 - 142	1.048
Heptane	178 - 180	1.036
Hexane	140 - 142	1.034
Toluene	175 - 178	1.048
Resin concentrate	196 - 198	1.143

Kinetics of Resin Extraction by Heptane

This research was designed to be conducted in such a way as to provide a fundamental understanding of the fossil resin refining process and to determine major factors which control resin extraction such as temperature and particle size. Of course, the ultimate objective of the batch extraction study is to provide the basis for subsequent design of a continuous resin refining circuit. A series of experimental tests were undertaken to determine the effect of temperature and particle size on resin extraction at low solids concentration. Resin extraction kinetics were determined by analysis of extracted resin solutions taken at periodic time intervals during the extraction process. Technical grade heptane (C₇H₁₆) was used as solvent for the kinetic study. Four size fractions were prepared by wet screening of the resin concentrate. The heptane-soluble resin contents in all samples were determined with a TX-6 Soxhlet extraction unit at the boiling point of heptane (98 °C) for about 6 hours and the results are presented in Table 3. As shown in Figure 1, all resin extraction tests were carried out in a one liter round bottom 3-neck distillation flask. A thermometer, a condenser, and a stainless impeller were placed into the flask through the three neck openings. The impeller was connected to a motor through a Chesapeake stirrer connection at the center port. The agitation of resin/solvent suspension was accomplished using an impeller/motor with a control system to set the speed of rotation. The flask was submerged in a circulating water bath to control the extraction temperature with an accuracy of ±0.5 °C.

Table 3. Heptane-soluble resin content of selected size fractions

Size Fraction (mesh)	8x10	28x35	48x60	100x150
Heptane-soluble resin (wt.%)	95.45	92.92	88.67	90.46

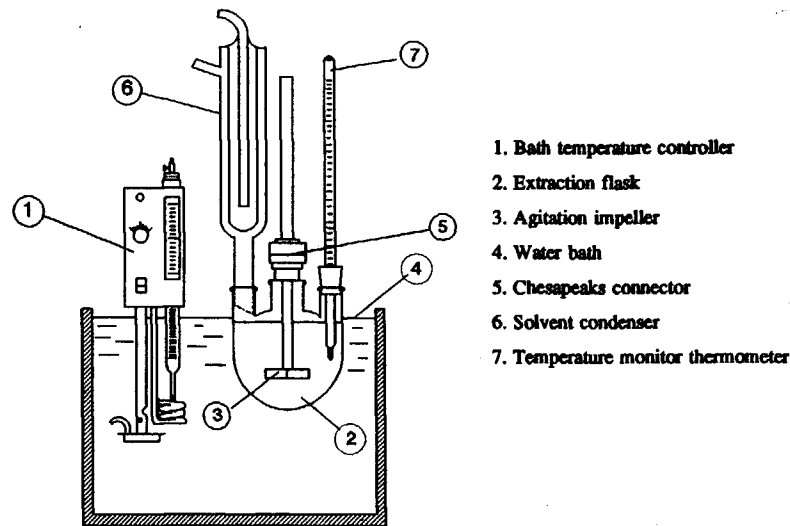


Figure 1. Schematic drawing of the resin extraction apparatus

One liter of pure heptane was placed into the flask with about 1.1 to 1.5 grams of the resin sample at a desired temperature for each test. During the extraction process, approximately 3 ml of resin solution was taken from the suspension at pre-set time intervals by a syringe equipped with a prefilter. The heptane solution was analyzed for resin concentration by UV/Vis spectroscopy. All the data presented in the following sections were normalized on the basis of the heptane-soluble resin content of each size fraction as previously reported in Table 3.

The effect of particle size on the resin extraction rate at 20 °C and 500 RPM is presented in Figure 2. It is evident that the extraction rate decreases with an increase in extraction time and that there is a strong dependence of resin extraction rate on particle size. The extraction rate was found to decrease dramatically with an increase in particle size. For example, after 40 minutes of extraction, the percent dissolved was approximately 20% for the 8x10 mesh resin particles while about 80% dissolved for the 100x150 mesh resin particles. After 2 hours of extraction, the 100x150 mesh sample had reached 92% of its ultimate extraction whereas only 40% had been extracted from the 8x10 mesh sample. The rate shows an inverse 1st-order dependence on particle size typical of diffusion or surface reaction controlled kinetics.

A number of resin extraction tests were performed at different temperatures in order to determine the effect of temperature on the extraction rate. The resin extraction rate was found to increase with an increase in extraction temperature. The effect of temperature is very significant. The results are presented in Figure 3 for the 48x60 mesh sample where it is evident that the extraction rate does rise significantly with temperature. Almost complete extraction was observed in 20 minutes at 60 °C while only 25% extraction was observed at 0 °C. As expected higher temperatures should be considered for the continuous extraction circuit in order to maximize yield and minimize extraction time. An activation energy of 15.5 kJ/mole can be calculated based on the initial extraction rates. The magnitude of the activation energy indicates that the extraction process is mainly controlled by a surface reaction mechanism involving the solvation of resin molecules by the heptane solution. As such, energetics of associated solvation reactions are expected to account for the observed activation energy.

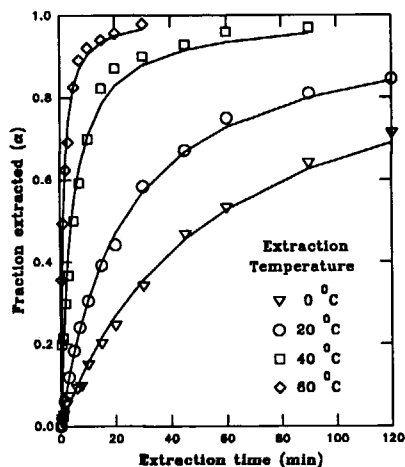


Figure 2. Effect of resin particle size on the rate of extraction with heptane at 20 °C.

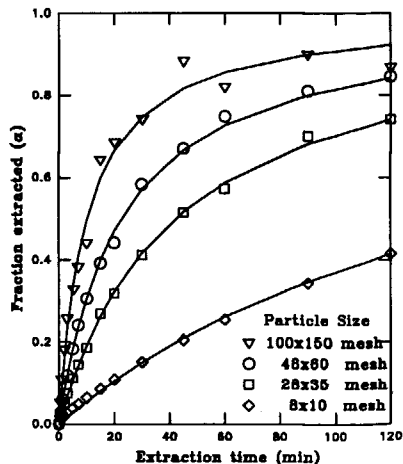


Figure 3. Effect of temperature on the rate of extraction with heptane for the 48x60 mesh sample.

SUMMARY AND CONCLUSIONS

Solvent extraction studies indicate that two major factors contribute to the natural color variation of the fossil resin: (1) relative abundance of chromophores (mostly polar and unsaturated compounds); and (2) finely dispersed inclusions of coal colloids (<100 μm).

The hexane-, heptane-, and ethyl acetate-extracted resins appear light-yellow in color while the toluene-extracted resin exhibits a significantly darker color. Of the four solvents, the resin concentrate has the highest solubility in toluene and the lowest solubility in ethyl acetate.

The rate of resin extraction from the resin concentrate is significantly affected by both particle size and extraction temperature. The finer the particle size the higher the extraction rate. The rate for heptane extraction significantly increases with an increase in extraction temperature (from 0 °C to 60 °C). Therefore a moderate extraction temperature (about 60 °C) should be considered for the continuous extraction circuit in order to maximize yield and minimize extraction time.

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