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FINAL REPORT

**REFINING OF FOSSIL RESIN FLOTATION CONCENTRATE
FROM WESTERN COAL**

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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: 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

MASTER

February 16, 1995

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EXECUTIVE SUMMARY

Macroscopic fossil resin from the western coal fields is a unique resource in the United States. Such resinous coals are found in the states of Arizona, Colorado, New Mexico, Utah, Washington, and Wyoming. Among these, the Wasatch Plateau coal field in central Utah is particularly significant because of its high content of macroscopic fossil resin. Many seams in this coal field have been reported to contain as much as 5% resin by weight. Fossil resin is friable and easily liberated from other coal macerals. Consequently the resin particles tend to concentrate into the fine sizes during coal preparation and handling. Because of this property, 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.

Fossil resin has been recovered intermittently from the Utah coal field since 1929 by gravity and/or flotation processes. The production, nevertheless, has been on a very small scale and the technologies used have limited the development of a viable fossil resin industry. The resin flotation concentrate thus produced needs to be refined by solvent extraction. Solvent-purified resins, at the present time, have a market value of at least \$1.00/kg as a chemical commodity and can be used in the adhesives, rubber, varnish, paints, coatings, thermoplastics industries, and particularly in the ink industry.

Unfortunately, process technology for the recovery and utilization of fossil resins from coal has not received sufficient attention. Because of the lack of technology and the competition from synthetic resins, the valuable fossil resin resource from western coal has been used inefficiently, being burned together with coal for electric power generation. Based on coal production data from the Utah region, it is estimated that at least 200 million pounds per annum

of fossil resin from the Wasatch Plateau coal field is being used as fuel (\$0.01/lb) for electric power generation rather than being used as a chemical commodity (\$0.50/lb). This practice represents an inappropriate use of a valuable resource. The waste of this unique fossil resin resource is evident.

During the past several years, significant research efforts have been made to develop process technology for the selective flotation of fossil resin from western coals. As a result of these efforts, several new flotation technologies have been developed. Operation of a proof-of-concept continuous flotation circuit showed the selective flotation process to be sufficiently profitable to justify the development of a fossil resin industry. Even with the success of selective resin flotation technologies, there is still a significant amount of research and development required in order to optimize the process technology for a fossil resin industry. In particular, little attention has been given to the refining of the fossil resin flotation concentrate although solvent refining is a critical step for the fossil resin to become a marketable product. In view of this situation, DOE funded the two-year project, "Refining of Fossil Resin Flotation Concentrate from Western Coal," to evaluate the following aspects of the fossil resin refining technology:

- 1) Characterization of the fossil resin flotation concentrate and its refined products.
- 2) Kinetics of fossil resin extraction.
- 3) Effects of operating variables on solvent extraction.
- 4) Extraction solvents.
- 5) Proof-of-concept continuous refining tests.
- 6) Technical and economic analysis.

The results from this research effort have led to the following conclusions:

- Hexane- or heptane-refined fossil resin has a light-yellow color, a melting point of 140 - 142 °C, a density of 1.034 gram/cm³, and good solubility in nonpolar solvents. It is a superior chemical commodity for the ink industry.
- Among the four solvents evaluated (hexane, heptane, toluene and ethyl acetate), hexane is the most appropriate solvent based on overall technical and economic considerations.
- Batch extraction tests and kinetic studies suggest that the main interaction between the resin and the solvent is expected to be the forces associated with solvation phenomena. Temperature has the most significant effect on extraction rate. With hexane as the solvent, a recovery of 90% can be achieved at 50 °C and 10% solids concentration with moderate agitation for 1 hour.
- The proof-of-concept continuous refining circuit with a capacity of 1 lb/hr resulted in almost the same extraction efficiency as was obtained from laboratory bench-scale tests. The results from the continuous tests have demonstrated the success of the solvent refining process.
- A preliminary technical and economic feasibility study shows that for a fossil resin flotation and refining plant with a capacity of approximately 40 million pounds of refined resin per year, capital cost and operating costs are estimated to be \$33.2 million and \$8.9 million/year, respectively. Considering a life time of 20 years, an internal rate of return (IRR) of 23.4% and a 3-year payback period can be expected. Sensitivity analyses on the resin content of the coal fines, the plant size, the total capital cost, the operating cost, the sales volume and the sales price were carried out. The results show that all of these variables have a significant effect on the IRR.

In view of the success of this project, it is recommended that a more detailed feasibility study be conducted to examine in more detail the capital cost and the operating costs, the resource base, and the market for a refined resin product.

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1. INTRODUCTION

Certain bituminous coals of the Western United States are known to contain appreciable quantities of macroscopic fossil resin (resinite). Such resinous coals are found in the states of Arizona, Colorado, New Mexico, Utah, Washington, and Wyoming, etc. The Wasatch Plateau coal field in Utah has a particularly high content of fossil resin. It has been reported that many seams in this field average as much as 5% resin.¹⁻⁴

Macroscopic fossil resins are friable and easily liberated from other coal macerals. Consequently the resin particles tend to concentrate into the fine sizes during coal preparation. Because of this property, 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.⁵

Fossil resins have been recovered intermittently from the Utah coal field since 1929 by gravity and/or flotation processes. A historical review of the Utah fossil resin industry is given in Table 1-1. The production, nevertheless, has been on a very small scale and the technologies used have limited the development of a viable fossil resin industry. Of the four coal preparation plants operating in the Wasatch Plateau coal field (US Fuels, Plateau, Beaver Creek, and Price River) in the 1980's, only one plant, US Fuels, recovered this valuable resource by flotation at a rather low level of production, <1 million pounds per year. In this processing plant, a resin concentrate containing 50% resin at about 50% recovery was obtained after a multistage flotation process. Resin concentrates thus produced were usually refined by solvent extraction prior to marketing. It was reported that the solvent refining step is of equal importance to the selective flotation step in order for a viable fossil resin industry to be developed. At present, however,

fossil resin is not being produced, not even by US Fuels.⁵⁻⁸

Table 1-1. Historical review of Utah fossil resin industry

Year	Company	Concentration process	Extraction process
1930's	Andriaan Nagelvoort	Sink and float	Toluene extraction
1940's	Combined Metals Corp.	Gravity concentration	-----
	I.P.I.	Flotation	Hexane extraction
	U.S. Resin Corp.	Flotation	Hexane extraction
1973	Hercules Powder Corp. (Blackhawk Resin)	Flotation	Hexane extraction
1983	American Resins	Flotation	Hexane extraction
1985	US Fuels, CPS	Flotation	Hexane extraction

Solvent-purified resins have a market value of at least \$1.00/kg as a chemical commodity and can be used in the ink, adhesive, rubber, varnish, enamel, paint and coatings, and thermoplastics industries. Unfortunately, process technology for the recovery and utilization of fossil resins from coal has not received sufficient attention. Research carried out in this field is almost nonexistent when compared to the research effort made for other energy and mineral commodities. Such a situation exists due to the rapid development of the petroleum industry after World War II and the subsequent abundance of petrochemical resins. Because of the lack of technology and the competition from synthetic resins, the valuable fossil resin resource from western coal has been wasted, being burned together with coal for electric power generation.⁹⁻¹¹ The data on coal production from the Wasatch Plateau coal field suggest an annual coal production from this region of about 10 million tons. Assuming the coal contains only 2% resin and the resin has a market value of \$1.00/kg, then the fossil resin burned each year for electric

power generation has a value of \$200 million which is equivalent to the value of the coal itself! Steps must be taken to correct this situation and use the fossil resin resources in a more appropriate manner.

Continual development of other industries in the 80's has gradually brought attention to the unique properties of fossil resins. For example, when solvent-refined fossil resin from the Utah coal field is used as a feed stock in the ink industry, it can provide thermal settling properties superior to any of the synthetic resins available from the petrochemical industry. This feature has become of particular significance today with the development of high speed printing technology. As another example, resins in coal have a higher Btu value than other coal macerals and are the easiest to be liquefied. It has been suggested that these resins could have special value as feed stock for high density jet fuels by proper hydrogenation. In this regard, significant efforts have been made to develop technology for a fossil resin industry in western coal fields. As a result, the surface characteristics of fossil resin from the Wasatch Plateau coal field have been investigated intensely and several new flotation technologies for the recovery of fossil resin from coals have been developed.¹²⁻¹⁶ These flotation technologies provide a highly efficient means to selectively recover fossil resin from coal as shown in Table 1-2. Operation of a proof-of-concept continuous flotation circuit showed the selective flotation process to be sufficiently profitable to justify the development of a fossil resin industry. Even with the above-cited success of selective resin flotation technologies, there is still a significant amount of research and development required in order to optimize the process technology for a fossil resin industry. In particular, little attention has been given to the refining of the fossil resin flotation concentrate although solvent refining is a critical step in order to increase the market value of the fossil resin. Four natural types of fossil resin from the Wasatch Plateau coal field have been classified

Table 1-2. Resin flotation processes

Conventional flotation (minus 28 mesh)

Conditioning -- conventional reagent schedule

Flotation --> Resin concentrate product

Grade 50%

Recovery 50%

Product will have to be solvent-refined prior to utilization

New technology (minus 28 mesh)*

Conditioning -- new reagent schedule combined with high pH

Flotation --> Resin concentrate product

Grade 80%

Recovery 80%

It is expected that the product will have to be solvent-refined prior to utilization

Ozone process (minus 200 mesh)**

Grinding

Conditioning -- Ozonation

Flotation --> Resin concentrate product

Grade 95%

Recovery 85%

Direct use of the product may be possible without further refining

* U.S. Patent No. 4,904,373

** U.S. Patent No. 4,724,071

by color as yellow, amber, light brown, and dark brown. The change in the color of fossil resin represents a change in its physical and chemical properties. It turns out that light colored fossil resin has a higher market value than dark colored resin. The color of the refined resin varies and depends on solvent type, solvent extraction conditions and kinetics.¹⁷ Therefore, additional research was needed to identify appropriate operating conditions for the refining of fossil resin concentrate. The objectives of this project were as follows:

- Evaluate the effects of operating parameters on resin refining in batch experiments;
- Determine appropriate solvents for solvent refining of the fossil resin concentrate;
- Determine the characteristics of solvent refined resins from different refining conditions and/or different solvents;
- Design and install a proof-of-concept continuous refining circuit;
- Carry out continuous tests to evaluate the industrial feasibility of the refining technology;
- Prepare technical and economic analysis for fossil resin refining plant.

2. WORK PLAN

The resin refining research program was administered by the Utah Engineering Experiment Station at the University of Utah. The technical tasks were carried out in the research laboratories of the Department of Metallurgical Engineering, the University of Utah and Advanced Processing Technologies, Inc.(APT), Salt Lake City, Utah.

The major research efforts at the University of Utah were as follows:

- evaluate the effects of kinetic parameters on the refining of the fossil resin concentrate on a batch scale;
- determine the characteristics of the fossil resin concentrate and the solvent-refined resin products in order to coordinate/advise APT personnel on the refining conditions for an appropriate solvent refining strategy in continuous refining tests; and
- provide post-testing support for technical and economical analysis of the results obtained from the continuous refining circuit tests.

The major responsibilities for Advanced Processing Technologies, Inc. included:

- design and construct a continuous refining circuit with a feed rate of 1 lb/hr;
- carry out continuous refining circuit tests and develop an appropriate solvent refining strategy for a commercial resin refining plant based on the test results.

The research program consisted of the following tasks:

Task 1. Project Initiation

The first task was to lay out a detailed project plan including research design, objectives and subtasks to be accomplished.

Task 2. Characterization of Resin Flotation Concentrate and Refined Products

The fossil resin flotation concentrate, which was obtained from a previous DOE-funded project "Selective Flotation of Fossil Resin from Western Coal, DOE Contract #DE-AC22-90PC90178," was the raw material for this project. The preliminary characterization of the fossil resin concentrate included the determination of particle size distribution, petrographic characterization, proximate analysis, elemental analysis, density, melting point, iodine number, acid number, and spectroscopic analysis.

Refined resin products were also characterized by proximate analysis, elemental analysis, spectroscopic examination, and the determination of physical properties.

Task 3. Batch Kinetic Experiments

The batch kinetic experiments for solvent extraction of the resin flotation concentrate by selected solvents were carried out to determine the extraction kinetics and to study the effect of operating conditions. The effects of differential refining, evaporating temperature in product recovery, and recycled solvent on the quality of products were also investigated.

Task 4. Proof-of-Concept Test Circuit Design Engineering

This phase of the project was to provide detailed refining circuit design. The design criteria, the flowsheet/material balance of the circuit, and equipment selection were prepared.

Task 5. Equipment Procurement and Circuit Construction

After DOE approval of the designed test circuit, equipment procurement and construction of the designed refining circuit were completed during this phase of the work.

Task 6. POC Test Plan Formulation

Based on the results of the batch experiments, a detailed proof-of-concept test plan was formed and subsequently approved by DOE.

Task 7. Test Circuit Shake-Down

After equipment procurement and installation, a start-up campaign was conducted to evaluate/modify the circuit prior to the proof-of-concept test.

Task 8. Proof-of-Concept Continuous Testing

The overall purpose of the proof-of-concept test was to provide fundamental data for design and construction of a continuous refining circuit. Three different solvents were used in the tests. The effects of various operating variables on the yield of refining were investigated, including residence time of resin particles, extraction temperature, and resin concentrate/solvent ratio. A spray dryer was used for product drying in the continuous circuit and its performance was evaluated. The proof-of-concept continuous refining test was integrated with the fundamental data obtained from the batch experiments for optimum solvent refining.

Tasks 9 and 10. Economic Analysis and Final Report

After finishing the proof-of-concept test an economic analysis based, in part, on the data obtained from the tests was conducted. The analysis gave capital cost and, particularly, operating costs for a fossil resin refining plant with a capacity to produce approximately 40 million pounds of resin product per annum. The analysis also assessed the viability of the new processing technologies and the potential profitability of a fossil resin industry.

The above outlined project involved research tasks at the laboratories of both the University of Utah and Advanced Processing Technologies, Inc. in order to carry out batch refining, characterization, circuit design/construction, and continuous refining of the fossil resin flotation concentrate. The completion of the program provides much-needed proof-of-concept data for fossil resin refining technology and demonstrates the potential for a profitable fossil resin industry.

3. CHARACTERIZATION OF THE RESIN FLOTATION CONCENTRATE

3.1 Sample Preparation

Under a previous DOE-funded program, the University of Utah and APT conducted a series of pilot-plant tests for the selective flotation of fossil resin from Wasatch plateau coal (both UPL coal and CO-OP coal mines) of south central Utah. About 200 lbs of high grade fossil resin flotation concentrate (approximately 75% resin content) was generated from those pilot-plant flotation tests. The resin flotation concentrates were naturally dried and blended. One kilogram samples were stored in plastic bags for future use. The ash and moisture content of the composite resin concentrate were found to be 1.23% and 1.03% by weight respectively.

3.2 Size Analysis

The particle size distribution of the resin concentrate was determined by wet screening according to ASTM standard procedure (D 4749). The particle size distribution which was obtained is presented in Table 3-1.

From Table 3-1, 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 400 mesh (38 microns). 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 material 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 distribution is favorable for subsequent solvent refining due to the large surface area. Kinetic studies of resin extraction for different particle sizes were carried out to determine the effect of particle size on the resin extraction rate and will be presented later.

Table 3-1. Size distribution of the resin concentrate

Particle Size Class		Weight	Cumulative Weight % Passing
(mesh)	(μm)	(%)	(%)
28-60	600-250	1.79	100.00
60-100	250-150	4.24	98.21
100-200	150-75	13.74	93.97
200-270	75-53	7.71	80.23
270-400	53-38	8.71	72.52
-400	-38	63.81	63.81
Total		100.00	

3.3 Microscopic Characterization

Because of the fine particle size it is difficult to sort the resin grains from the flotation concentrate by hand according to their natural color difference. The microscopic characterization of fossil resin concentrate was conducted to classify the fossil resin types in the flotation concentrate. Since fossil resin or resinite fluoresces under UV and blue light, the petrographic characteristics of fossil resin types and the coal component in the resin concentrate can easily be identified and classified by fluorescence microscopy.¹⁸ 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. Polished briquettes (pellets) were used for this examination. About 1-2 g of the fossil resin sample (flotation concentrate) and a suitable amount of epoxy/resin mixture (in the ratio of about four parts resin concentrate to one part epoxy by volume) were thoroughly mixed and poured 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 with a set of successive silicon carbide papers followed by polishing with a 1-micron and a 0.05-micron alumina suspension, according to ASTM Standard D-2013-79.

An Axioplan Universal Microscope manufactured by Carl Zeiss, West Germany, was employed for the analysis of resin type and grain size of the polished samples. The microscope was equipped with a 150-watt xenon arc lamp (model 770), 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).

Microscopic photographs of the samples were taken using a Carl Zeiss Microscopic attachment (MC 100) system with a 35-mm camera and 100° film to produce colored photographs of the polished sections. A 20X dry objective lens and a 10X photo eyepiece were used for all the photography, which gives 200X magnification of the image. Petrographic examination of the fossil resin types was conducted by microscopic counting. Microscopic photographs of the four resin types as well as coal are given in Figure 3-1. For the quantitative petrographic analysis, more than three hundred observations were counted. The distribution of the various resin types and coal is listed in Table 3-2. It is evident from the petrographic analysis that the resin concentrate consists predominately of green-yellow and yellow-orange resins (63.6%) and some

Figure 3-1. Microscopic photographs of the fossil resin concentrate
(continued on next page)

Figure 3-1. Microscopic photographs of the fossil resin concentrate

green resin (12.6%) and orange-brown resin (11.0%). A significant amount (12.7%) of fine coal particles, mostly vitrinite and less than 20 microns (635 mesh), were also found in the resin flotation concentrate. A few large coal particles were observed occasionally. Some fine clay minerals were also occasionally found in the concentrate. All resin types fluoresce under blue light with a greenish yellow color, which gradually diminishes in intensity from green to orange-brown resin. While the microphotograph of green resin indicates that it is homogeneous in appearance, 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 increased in number from green-yellow to orange-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 partly due to the differences in the quantity of finely suspended coal particles.

Table 3-2. Results of petrographic analysis of the resin concentrate

Petrographic Class by Fluorescence	Distribution by Count (%)
Green Resin	12.62
Green-Yellow Resin	28.64
Yellow-Orange Resin	34.97
Orange-Brown Resin	11.04
Coal	12.72

3.4 Preliminary Analysis and Elemental Composition

The proximate analysis of the resin concentrate was conducted and the results are summarized in Table 3-3. The resin flotation concentrate generally has low ash content (1.23%), low moisture (1.03%), and low density (1.143 gram/cm³) as compared to other coal macerals. It was also found that the resin concentrate has a high melting point (196-198 °C)

Table 3-3. Proximate analysis of the fossil resin concentrate

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

Ultimate analysis was conducted for the fossil resin concentrate and the results obtained are given in Table 3-4. 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 modest amounts of oxygen functional groups and unsaturated carbon-carbon double-bonds in their molecular structures.

Table 3-4. Chemical composition of the fossil 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

3.5 Preliminary Solvent Extraction Analysis

Fossil resin is a complex mixture of sesquiterpenoids¹⁹ and the solubility of these resin compounds depends on the solvent used. The determination of the extractable resin content in the resin concentrate by different solvents will provide an important criterion for solvent refining and purification, process design, and prediction of the nature of refined resin products. 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, about 2 grams of the resin sample were placed in a single-thickness cellulose thimble and about 60 to 70-ml of solvent was applied. The extraction was carried out for at least 2 hours in boiling solvent and then rinsed for another 4 hours with the distilled solvent at a rate of 1.2 to 3.6 ml of solvent per minute. The results are given in Table 3-5.

The resin concentrate has the highest solubility in toluene. The larger the particles of the resin concentrate, the higher the resin yield is observed. This is mainly due to the existence of fine coal particles in the resin concentrate. It was observed with microscopic that most coal particles in the resin flotation concentrate are smaller than 635 mesh. It seems that during resin flotation fine coal particles aggregate with resin particles and are recovered in the froth product (resin concentrate).

Table 3-5. Size dependence of extraction yield with different solvents

Size (mesh)	Extraction Yield (%)			
	Ethyl Acetate	Hexane	Heptane	Toluene
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

3.6 Solvent Loading Limit Determination

A solvent loading limit is defined as the maximum ratio of fossil resin concentrate to solvent applied in a extraction experiment at which the resin yield of extraction does not decrease. The solvent loading limit indicates the highest solid/solvent ratio which could be adopted in the

resin refining process. If the loading limit of a solvent is too low, the solvent is usually not suitable because a low solid/solvent ratio will result in high operating costs. On the other hand, the practical solid/solvent ratio in the refining process is not only determined by the solvent loading limit, but also limited by the extraction kinetics and the viscosity of the pregnant solution.

A desired amount of resin concentrate was taken with 100 ml solvent and the mixture was shaken with a Junior Orbit shaker at room temperature and 250 RPM for 24 hours. The resin solution was then separated from the undissolved residue by centrifugation at 10,000 RPM for a half hour. Finally, the solvent was evaporated and both the resin product and coal residue were weighed and analyzed. The results of the solvent loading limit determination are plotted in Figure 3-2.

The plot indicates that no loading limit was found for solvents like heptane, hexane and toluene while ethyl acetate could only load about 18 g of resin per 100 ml solvent. At high resin loading the solutions of toluene, hexane, and heptane became more viscous. Of course, the saturated ethyl acetate solution was less viscous. These results suggest that ethyl acetate is not suitable to be used as a refining solvent. The reason may be that ethyl acetate is a polar solvent while resin is a nonpolar organic material. Since there is no loading limit for heptane, hexane and toluene, the resin concentrate/solvent ratio of resin refining and purification processing by solvent extraction would depend on the extraction kinetics, the viscosity limit of the solution and the separation technologies used to separate the loaded solution from the insoluble residue.

Figure 3-2. Solvent loading limits

4. CHARACTERIZATION OF THE REFINED RESIN PRODUCTS

4.1 Physical Properties

The refined resin products as obtained from solvent extraction tests were characterized in terms of their physicochemical properties.

The melting points of extracted resin products were determined using an 8100 Series Digital Melting Point Apparatus, Electrothermal Engineering Limited. Their densities were measured using an Autopycnometer 1320. The results are shown in Table 4-1. For comparison, Table 4-1 also shows the data for the resin concentrate.

Table 4-1. Melting point and density of solvent-extracted resin products

Resin Sample	Melting Point (°C)	Density (g/cm ³)
Ethyl Acetate Product	141 - 142	1.048
Heptane Product	142 - 143	1.036
Hexane Product	140 - 142	1.034
Toluene Product	175 - 178	1.048
Resin Concentrate	196 - 198	1.143

It can be seen that the melting point of toluene-extracted resin is higher than that of the other solvent-extracted resins. The solubility of the resin concentrate in toluene is also higher than the solubility in the other solvents. This is an indication that some components with higher molecular weight can be extracted by toluene, but can not be extracted by the other solvents.

4.2 Elemental Analysis

The results of elemental analysis for the extracted resin samples are listed in Table 4-2.

Both the acid number and iodine number of the solvent-extracted resins are listed in Table 4-3.

Table 4-2. Elemental analysis of extracted resins

Resin Sample	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
Hexane 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 4-3. Acid number and iodine number of the extracted resins

Solvent	Acid Number	Iodine Number
Ethyl Acetate	138	78.68
Heptane	98.4	78.98
Hexane	90.4	77.67
Toluene	112	79.38
Resin Concentrate	95.8	75.45

It should be noted that the ethyl-acetate-extracted resin is found to contain more oxygen than the oxygen which might be contained in the residual solvent. Both hexane- and heptane-extracted resins contain less oxygen than the toluene-extracted resin. The contents of other

elements are found to be similar for all solvent extracted resins.

The values of both the acid number and iodine number for these various solvent extracted resins are found to be close to the values of the original resin concentrate. This indicates that solvent extraction by these solvents did not change the functional groups and any carbon-carbon double bond during extraction and recovery.

4.3 Py-GC/EIMS Spectra and FTIR Spectra Studies

The solvent-refined resin products obtained from hexane and toluene extractions were subjected to both Py-GC/EIMS (Pyrolysis Gas Chromatography/Impact Ionization Mass Spectrometry) and FTIR (Fourier-Transform Infrared) spectroscopic analysis. The purpose of each analysis was to gain further understanding of the molecular structure and composition of the solvent-extracted products. The nature of the resinite coloration is also discussed based on the experimental results.

4.3.1 Experimental Procedure

Curie-Point Evaporation/Pyrolysis Experiment

In this experiment, 5 mg of minus 400 mesh powder of 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 μ l of the solution was coated on a ferromagnetic wire for the Curie-Point pyrolysis experiments. After air drying the wire was placed into a borosilicate glass tube. 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 scanning of the evaporate, the residue on the wire was then submitted to regular pyrolysis. The 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 literature¹⁹.

GC/EIMS Spectroscopic Study

A 15 meter long and 0.25 mm i.d. fused silica column coated with 0.25 μ m 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 hexane and toluene extracted products, extraction residue 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. A weighed sample, about 3% of the total weight, was mixed 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 disks with equal weights of the components. Primary spectra of the samples were obtained from 256 scans with a nominal resolution of 4 cm^{-1} in the range $4000\text{-}700\text{ cm}^{-1}$.

4.3.2 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 the composite fossil resin and coal are given in Figure 4-1, and the evaporation and residue pyrolysis Py-GC and Py-GC/EIMS profiles for the hexane-soluble resin, hexane-insoluble but toluene-soluble resin and toluene-insoluble residue fractions of the dark-brown resin are given in Figures 4-2, 4-3, and 4-4. The Py-GC profiles for the composite resin, the extracted fractions and the residue of the dark-brown resin (Figures 4-1 to 4-4) indicate that all resin samples contain three major components. The sequentially eluted major peaks observed in each of the Py-GC

Figure 4-1. Evaporation Py-GC/EIMS spectra of the composite resinite and coal samples

Figure 4-2. Evaporation and flash residue Py-GC/EIMS spectra of the hexane-soluble portion of the resin

Figure 4-3. Evaporation and flash residue Py-GC/EIMS spectra of the hexane-insoluble but toluene-soluble portion of the resin

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

profiles have been attributed to sesquiterpenoid monomers, dimers, and trimers, respectively. The Py-GC profile of the coal (see Figure 4-1), 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. The 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 ^{13}C NMR 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 4-2 to 4-4 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 a 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 4-2 to 4-4 shows some interesting differences among the resin fractions. As mentioned before, the first peak in the Py-GC profile is believed to represent the sesquiterpenoid monomer. From Figures 4-2 to 4-4 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 4-3). 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 4-4). These comparisons lead to the conclusion that the less polar sesquiterpenoid monomers are soluble in hexane (at room temperature) and also lighter in color when compared to the dimers and trimers. However when the strength of the solvent is increased, as in 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 of 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 4-2, 4-3 and 4-4) were obtained by summing all spectra with the same background subtraction, which would primarily 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 4-5. It is evident from the intensity of the aromatic band at $\sim 1600\text{ cm}^{-1}$ that the hexane purified resin contains the lowest amount of aromatic components and oxygen functional groups (-OH, -COOH, $>\text{C}=\text{O}$). 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^{-1}) 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 regard, 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 4-5, 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

Figure 4-5. FTIR spectra of the hexane- and toluene-extracted products from the resin

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.

4.3.3 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, $>\text{C}=\text{O}$, -C-O) and few aliphatic chains. The color difference observed among the four resin types is explained by the presence of chromophores (aromatized polyterpenoids) 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 compared to the hexane-insoluble but toluene-soluble resin fraction. The results suggest that a non-polar solvent such as hexane is preferred because it can produce light color, higher value product.

5. BATCH EXPERIMENTS

5.1 Fundamental Study of Resin Extraction Kinetics

The kinetics of fossil resin extraction from a flotation concentrate by heptane were investigated as a function of process variables using monosize particles. Experimental results provide for a better understanding of the refining process and the basis for subsequent design and construction of a continuous resin refining circuit. Based on the effect of process variables (particle size, stirring speed, and temperature) the resin extraction rate appears to be controlled by surface solvation phenomena. The initial extraction rate was found to be inversely proportional to the initial particle size.

5.1.1 Characterization of Resin Concentrate

As described in Section 3, the fossil resin flotation concentrate is a heterogenous material. Even at the molecular level fossil resin is known to be a complicated organic polymer. Fossil resin from the Wasatch Plateau coal field is believed to be derived from diterpenoic acid rich precursors. Based on the results of Py-GC/MS analysis, the bulk component of the Utah resin appears to be a polymer consisting of sesquiterpenoid ($C_{15}H_{24}$) repeat units. It has been reported that approximately 10% of the resin consists of a mixture of cyclic terpenoids.¹⁹ In view of the foregoing, it is evident that the composition and structure of the Utah resin are not uniform. However, based on present results an approximate description can be made. The average elemental composition of heptane extracted resin is as follows:

C	H	N	S	O
86.88%	10.85%	0.17%	0.30%	1.80%

Only small amounts (2.3%) of heteroatoms (N, S and O) are found in the heptane extracted resin, which implies that the polar functional groups are rare. By adsorption chromatography with silica gel as the static phase and heptane as the elution solvent, a distinct component (7.7%) was separated from the heptane extracted resin. The IR spectra of this component and the remaining more-polar fraction are shown in Figures 5-1a and 5-1b, respectively. Figure 5-1a has typical alkane features. For the more-polar fraction in Figure 5-1b, the peaks of the CH stretching vibrations (2850 to 2960 cm^{-1}) and CH bending vibrations (1462 and 1382 cm^{-1}) obviously predominate. However, there is a signal which shows significant carbonyl (C=O bond) stretching vibrations at 1711 cm^{-1} for the more-polar fraction. In conclusion, the fossil resin from the Wasatch coal field is heterogenous and nonuniform in its chemical composition. It mainly consists of hydrocarbons with small amounts of functional groups containing heteroatoms.

5.1.2 Experimental

A series of experiments for resin extraction by heptane were designed to study the effect of process variables on the rate of the resin extraction from monosize particles at a low solids concentration. Process variables studied included temperature, particle size and agitation intensity. The resin extraction kinetics were determined by analysis of the resin in heptane solutions taken at certain time intervals during extraction process.

Technical grade normal heptane (C_7H_{16}) was used as the solvent for the kinetics study.

Figure 5-1a. IR spectrum of the component separated by elution chromatography from the heptane-extracted resin

Figure 5-1b. IR spectrum of the remaining more-polar fraction separated by elution chromatography from the heptane-extracted resin.

Heptane has a molecule weight of 100.21, density of 0.684 gram/cm³ and boiling point of 98 °C. Four monosize samples (8×10, 28×35, 48×60, and 100×150 mesh) were prepared by wet screening from the flotation concentrate. The heptane-soluble resin content in all samples was determined with a TX-6 Soxhlet extraction unit operating at the boiling point of heptane (98 °C) for 6 hours. The results are presented in Table 5-1.

Table 5-1. Heptane-soluble resin content of monosize resin samples

Particle Size of Resin Sample (mesh)	Heptane-Soluble Resin Content (%)
8×10	95.5
28×35	92.9
48×60	88.7
100×150	90.5

The resin concentration in heptane was determined by a UV/Vis spectrophotometer (Beckman DU-7) at room temperature. It was found that a good linear relationship between UV absorbance at 300 nm and resin concentration in the heptane solution exists as long as the resin concentration is below 500 ppm. The calibration curve used for analysis of dissolved resin in heptane is given in Figure 5-2.

A schematic drawing of the experimental apparatus used for the kinetics study is presented in Figure 5-3. The reactor is a one liter round bottom three-neck distillation flask. One liter of heptane was taken into the flask and heated to the desired temperature at which time 1.5 grams of resin sample was added to initiate the reaction. During the extraction process, about 3 ml of

Figure 5-2. UV/Vis calibration curve for dissolved resin in heptane

1. Bath temperature controller	2. Extraction flask
3. Agitation impeller	4. Water bath
5. Chesapeake Connector	6. Solvent condenser
7. Thermometer	

Figure 5-3. Schematic drawing of resin extraction apparatus

resin solution was taken from the suspension by a syringe with a prefilter at each desired time interval. 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 in the samples.

5.1.3 Experimental Results and Discussion

Effect of Resin Particle Size

The effect of particle size on heptane extraction of resin at 20 °C and 500 RPM is presented in Figure 5-4. It is evident that the extraction rate decreases with an increase in extraction time, which is to be expected from geometric considerations and from the heterogeneity of the fossil resin. As shown in Figure 5-4, a strong dependence of resin extraction rate on particle size was found. The initial resin extraction rates ($d\alpha/dt$) are plotted against the inverse of the initial resin particle size in Figure 5-5 and the linear relationship suggests that the initial rate may be limited either by mass transfer or by surface reaction.

Effect of Temperature

Several tests on heptane extraction of resin were performed at different temperatures in order to determine the effect of temperature on the extraction rate and the results are presented in Figure 5-6. As expected, the resin extraction rate was found to increase with an increase in extraction temperature. The effect of temperature is very significant. The initial extraction rates at different temperatures are plotted according to the Arrhenius equation in Figure 5-7 and a good linear relationship between the logarithm of the initial extraction rate and inverse

Figure 5-4. Effect of particle size on heptane extraction of resin at 25 °C and 500 rpm

Figure 5-5. Initial extraction rates vs. the inverse of the particle size from data presented in Figure 5-4.

Figure 5-6. Effect of temperature on heptane extraction of 48×60 mesh resin particles and 500 rpm

Figure 5-7. Arrhenius plot for heptane extraction of 48×60 mesh resin particles from data presented in Figure 5-6

temperature was found. From the slope of this linear relationship, an activation energy of 12.3 kcal/mole can be calculated. The magnitude of the activation energy indicates that the initial extraction process is controlled by a surface reaction mechanism involving the dissolution of resin molecules into the heptane solution. In this regard, the energetics of such solvation reactions are expected to be related to the observed activation energy.

Effect of Agitation Intensity

The effect of agitation intensity on heptane extraction of resin is presented in Figure 5-8 in terms of stirring speed (RPM). It was found that the agitation intensity has hardly any effect on the resin extraction rate, again providing evidence that the extraction process is not under diffusion or mass transfer control for these experimental conditions (room temperature, low solids concentration, and moderate stirring speed).

Solvent extraction and purification of fossil resin from a resin flotation concentrate is accomplished by dissolving the resin compounds into an organic solvent in which other coal macerals will not be dissolved. It should be possible to describe the resin extraction reaction by a typical kinetic analysis for shrinking core geometry. However, it must be noted that the resin extraction reaction has special features. As mentioned before, the fossil resin particles are heterogeneous in terms of their structure (both macroscopic and molecular) and their chemical composition. They are complex polymers and copolymers of varied molecular weight. Different components of the fossil resin, even components with the same structural characteristics but different in their molecular weight, are expected to have different dissolution rates in organic solvents such as heptane.

Figure 5-8. Effect of stirring speed on heptane extraction of 48×60 mesh resin particles at 25 °C and 500 rpm

For nonporous uniform particles of spherical shape, the relationship between the extent of extraction (α) and the extraction time (t) for a batch reaction under surface reaction control can be described by the following equation,²⁰

$$1 - (1 - \alpha)^{\frac{1}{3}} = kt$$

where k is the overall rate constant which includes reactant concentration and many other factors such as surface area, intrinsic rate constant, initial particle size, shape factor, reactive sites on the particle surfaces, et cetera. The constant, k, should be inversely proportional to the initial particle size. However, this traditional shrinking core model does not fit the data shown in Figure 5-4. It is evident that the rate constant varies with time and thus the kinetic analysis must be considered in more detail.

From characterization studies, it was found that the fossil resin particles are heterogeneous and not of uniform composition based on microscopic examination and chemical analysis. During extraction, it is expected that the resin components with high solubility will be extracted more rapidly than those with low solubility. Therefore, the composition of the extracted resin will change as a function of time and the rate will decrease more than might be expected as the extraction reaction proceeds. A sequential extraction test was conducted to examine this hypothesis. Sequential extraction of the concentrate was carried out for different time intervals and heptane extraction temperatures. One hundred and eighty grams of the concentrate and 1800 ml of heptane were taken into the reactor for the first stage of extraction. After the first extraction, the pregnant resin solution was filtered and the first resin product was obtained by evaporation. The residual resin concentrate was processed with fresh heptane using the same

extraction procedure as the first extraction for desired times and temperatures. A stirring speed of 700 RPM was used throughout all experiments. Products from these sequential tests were recovered and the conditions with the analytical results are summarized in Table 5-2. A Klett-Summerson Photoelectric Colorimeter manufactured by Klett Manufacturing Co., Inc. was used to analyze the resin products obtained. The light beam of the colorimeter has a visible spectral range, from approximately 400 to 465 nm. Toluene was used as the solvent for these transmittance measurements, and the concentration of the resins in the toluene was fixed at 0.1 gram per 50 ml of toluene. The analytical results obtained from the transmittance measurements show that the extracted resin composition changes with an increase in extraction time.

Thus it can be imagined that the resin extraction kinetics must take into consideration the fact that the resin is nonuniform, and also that the composition of the unreacted resin particle changes with time during extraction.

Table 5-2. Sequential extraction results and analysis of products

Extracted Resin Product	Extraction Temperature (°C)	Extraction Time (min)	Transmittance (%)	Extracted Product	
				Wt. (%)	Cumulative Wt. (%)
Product 1	27	10	53.75	48.97	48.97
Product 2	27	20	46.78	12.76	61.73
Product 3	27	90	37.00	7.28	69.01
Product 4	60	20	23.44	3.67	72.68
Final Residue			<1	27.32	100.00

5.1.4 Brief Summary of Resin Extraction Kinetics

Although fossil resin is heterogeneous in terms of its macroscopic character and its chemical composition, it is mainly composed of non-polar hydrocarbon compounds with a small number of functional groups containing heteroatoms. The non-polar solvent, heptane which was used in the kinetics study instead of hexane because of its higher boiling point has almost the same chemical properties as hexane. It is expected that no chemical reactions occur in such an extraction process at low temperature (0-90 °C). The main interaction between resin and heptane is expected to be the van der Waals forces of interaction associated with solvation phenomena. In this regard, the resin extraction rate was found to be largely independent of agitation intensity at room temperature, low solids concentration and moderate agitation. Further the initial extraction rate was found to be inversely proportional to the initial particle diameter. Temperature has a significant effect on extraction rate and the activation energy for initial resin extraction by heptane was found to be 12.3 kcal/mole. On this basis it is expected that the extraction rate is controlled by surface solvation phenomena. Additional research is in progress to develop a kinetic model for the fossil resin extraction reaction.

5.2 Batch Experiments on Solvent Refining of the Fossil Resin Concentrate

The kinetics and extraction mechanism experiments were discussed in Section 5.1. However, the experiments described in Section 5.1 were carried out at very low solids concentration to ensure that the solvent would be in excess. In order to provide the necessary information for design of a continuous solvent refining circuit, batch solvent refining of the resin concentrate was carried out at high solids concentrations (50-200 g/l). The results are presented below.

5.2.1 Experimental

The sample used in these batch experiments was the resin flotation concentrate which has a maximum size of 28 mesh and contains about 80% by weight minus 200 mesh particles. Technical grade heptane was again used as the solvent for the batch experiments.

The extraction apparatus used for the batch tests was similar to that shown in Figure 5-2 except the round-bottom flask was replaced by a one-liter baffled glass reaction kettle with a clamp-held lid containing four fitted openings for agitation, condensate collection, temperature measurement, sampling and feeding. For batch extraction tests, the composite resin concentrate was first put in the kettle. Then 1000 ml of heptane at the desired temperature was poured into the reactor to initiate the extraction. Agitation was started simultaneously. During extraction, 5 ml of resin/solution suspension was taken from the reactor at each desired time interval and the sample was filtered immediately to obtain the resin content of the heptane solution. The dissolved resin fraction was calculated on the basis of the heptane-soluble resin content in the

samples, which was determined with the TX-6 Soxhlet extraction unit at the boiling point of heptane (98 °C) for about 6 hours. The experiments were performed to investigate the effect of four major extraction factors, agitation intensity, particle size, temperature and solids concentration.

5.2.2 Results and Discussion

Effect of Particle Size

The effect of particle size on the extraction process is shown in Figure 5-9. The tests were carried out at 700 RPM and 20 °C with 100 grams of different sized resin particles per liter of solvent. It can be seen that resin particle size has a significant effect on the extraction rate. For example, after 20 minutes of extraction, the fraction of dissolved resin particles was approximately 57% for 100×200 mesh resin particles while it reached about 73% for minus 400 mesh resin particles. After 90 minutes of extraction, all three different sized resin samples had reached their maximum extent of extraction of 77%.

Effect of Agitation

The effect of agitation (RPM) on the resin extraction rate is given in Figure 5-10. The experiments were carried out for the resin concentrate at 100 grams of solids per liter of solvent and 20 °C. As shown in Figure 5-10, variation in the agitation (500-1200 RPM) seems to have no effect on the extraction rate and yield under these conditions. In practice, it should be possible to reduce agitation to a low level and still achieve satisfactory extraction rate.

Figure 5-9. Effect of resin particle size on the rate and extent of extraction

Figure 5-10. Effect of stirring speed on the rate and extent of extraction

Effect of Extraction Temperature

The effect of extraction temperature was found to be very significant for the batch extraction experiments. The results are presented in Figure 5-11 where it is evident that the extraction rate rose significantly and the extraction yield increased at least 20% at 60 °C as compared to that at 20 °C. Therefore, a higher temperature should be considered for the continuous extraction circuit in order to obtain a high extraction yield for a short extraction time.

Effect of Solids Concentration

The effect of solids concentration on the extraction process is shown in Figure 5-12. The tests were conducted at 900 RPM and 20 °C for the composite resin concentrate. It can be seen that solids concentration has only a moderate effect on the extraction rate. It may be possible to use a higher solids concentration in the continuous extraction process as long as the solution viscosity does not become a problem. Thus, an appropriate solids concentrate can be set based on the subsequent behavior of the solid/liquid separation process.

5.2.3 Summary of Batch Extraction Experiments

- 1) Resin extraction rate is not significantly affected by agitation intensity and low agitation should be suitable for the continuous extraction process.
- 2) The effect of resin particle size on the extraction rate and yield should be taken into consideration. Because of the fine size of the composite resin concentrate (80% minus 200 mesh), the extraction reaction occurs in a reasonable amount of time therefore process design conditions can be established accordingly.
- 3) The effect of temperature on the rate and yield of the extraction process is found to be very significant. Higher temperatures (about 60 °C) should be considered for the continuous extraction circuit.
- 4) The effect of solids concentration on the extraction rate is moderate.

Figure 5-11. Effect of temperature on the rate and extent of extraction

Figure 5-12. Effect of solids concentration on the rate and extent of extraction

5.3 Differential Refining of Fossil Resin Concentrate

Differential refining tests were conducted in a 2-liter reactor as shown in Figure 5-3. In order to obtain and examine different resin products, the differential refining of resin flotation concentrate was carried out in a series of extraction tests for different time intervals and extraction temperatures with both heptane and toluene. A sample of resin concentrate (180 g) and 1800 ml of heptane were taken into the reactor for the first stage of extraction. Extraction was carried out for 10 minutes at room temperature. After the first extraction, the pregnant resin solution was filtered and the first resin product was obtained by evaporation at 60 °C using a vacuum rotary evaporator. The remaining undissolved resin concentrate was transferred from the filter paper back to the reactor with the addition of another 1800 ml of fresh heptane for the second extraction at room temperature for 20 minutes. The resulting pregnant resin solution was filtered and the second resin product was recovered. The same procedure was repeated for the third extraction with heptane under room temperature for 90 minutes. The fourth extraction was carried out with heptane at 60 °C for 20 minutes. The last extraction was carried out with toluene first at room temperature for 30 minutes, then at 80 °C for 48 hours. A stirring speed of 700 RPM was applied throughout all experiments. The results are summarized in Table 5-3.

Both color and melting point of the resin products are important criteria to determine resin quality and suitability for industrial applications, particularly in the ink industry in which a high melting point of resin and light resin color are desired. A Klett-Summerson Photoelectric Colorimeter manufactured by Klett Manufacturing Co., Inc. was used to investigate the transmittance of the resin products obtained from the differential refining of resin flotation concentrate. A Digital Melting Point Apparatus 8100 made by Electrothermal Engineering

Limited was used to measure the melting points of these resin products. The light beam of the colorimeter has a visible spectral range of approximately 400 to 465 nm. Toluene was used as the solvent for the transmittance measurements, and the concentration of the resins in the toluene was 0.1 gram per 50 ml of toluene. The results obtained from both the melting point measurements and the transmittance measurements are presented in Table 5-4.

Table 5-3. Extraction results for differentially refined products

Extracted Product	Extraction Solvent	Extraction Temperature (°C)	Extraction Time (min)	Extracted Product	
				Wt. (%)	Cumulative Wt. (%)
Product 1	Heptane	27	10	48.97	48.97
Product 2		27	20	12.76	61.73
Product 3		27	90	7.28	69.01
Product 4		60	20	3.67	72.68
Product 5	Toluene	27	30	5.56	78.24
Product 6		80	48 hr.	2.72	80.96
Remaining Residue				19.04	100.00

As seen from Tables 5-3 and 5-4 it is evident that the quality of the resin products with respect to the melting point and light transmittance can be controlled by extraction time, extraction temperature, and solvent type.

Using heptane as the solvent for resin refining, a superior resin product can be obtained with an average transmittance of 48.12% and a melting point of 145 to 155 °C. If toluene is used for resin extraction, a significant amount of dark brown resin (>5%) can be extracted from

Table 5-4. Characteristics of the differentially refined resin products

Extracted Product	Color by visual Observation	Transmittance (%)	Melting Point (°C)
Product 1	Light Yellow	53.75	145 - 148
Product 2	Light Yellow	46.78	149 - 150
Product 3	Yellow	37.00	147 - 150
Product 4	Brown Yellow	23.44	152 - 155
Product 5	Dark Brown	<1	230 - 235
Product 6	Black	<1	No Melting until 400

the flotation concentrate even at room temperature. This dark-brown resin fraction will definitely deteriorate the quality of refined resin products in terms of color or light transmittance. Therefore, stronger solvents such as toluene should not be considered for the production of premium resin products.

5.4 Effect of Evaporating Temperature on the Quality of the Products

The effect of evaporation or crystallization temperature on the quality of refined resin products was investigated with respect to their color and melting point. In this study, the pregnant heptane solution, which was obtained from an extraction experiment with 100 g of resin concentrate in 1000 ml of heptane at 50 °C for 2 hours, was evaporated with a rotary evaporator at the desired temperature. Three different evaporation temperatures were examined and the results are given in Table 5-5.

Table 5-5. Effect of evaporation or crystallization temperature on the quality of refined resin product

Evaporating Temp. (°C)	Transmittance* (%)	Melting Point (°C)	Density (g/cm ³)
25	44.7	146 - 148	1.021
60	44.9	147 - 149	1.028
93(B.P. of Heptane)	43.7	146 - 149	1.025

* Transmittance measurement was described in Section 5.3.

From Table 5-5, it can be seen that in terms of light transmittance, melting point, and density no significant differences were found between these products recovered at different temperatures. Therefore, an appropriate evaporation temperature can be set based on processing capacity, convenience, and cost considerations.

5.5 Effect of Recycled Solvent on Product Quality and Yield

In order to examine the effect of the recycled solvent (resulting from the solvent evaporation and resin precipitation processes) on the quality of the refined resin product and the resin yield, three different heptanes were characterized by UV/Vis and FTIR spectroscopy. Fresh heptane (technical grade), twice recycled heptane, and heptane which was recycled more than 5 times were used. The UV/Vis absorption spectra for these heptanes obtained with a Beckman DU-7 Spectrophotometer are shown in Figure 5-13. The UV/Vis absorption spectra for these three heptanes have a similar shape but the absorption intensity or absorbance increases with an increase in the number of times the solvent has been recycled. These results might indicate that

Figure 5-13. UV/Vis spectra of heptane solvents

a small amount of resin or impurity builds up in the recycled heptane. It is believed that some non polar and low-molecular-weight resin compounds are transported into the recycled heptane during solvent evaporation and resin precipitation.

The FTIR spectra of these three heptanes were obtained by the liquid transmission method with a FTS-40 Spectrometer manufactured by Bio-Rad. A liquid cell with two germanium windows was used to hold the heptane sample at a thickness of 0.5 mm. Carbon tetrachloride (CTTC) was used as the background solvent. The concentration of heptane in the CTTC was 1% by volume. The spectra of these three heptanes are shown in Figures 5-14, 5-15, and 5-16. As seen from these figures, the IR spectra of all three heptanes represent a typical alkane structure and all three heptanes have very similar IR spectra except that a minor variation occurs at the wavenumber 1549.3 cm^{-1} , which might suggest that contamination occurs during the recycling. With the increase in the number of heptane recycling times, the peak intensity at 1549.3 cm^{-1} seems to increase slightly, which may indicate an increase in the level of contamination. However, it should be noticed that all the major vibrational bands of the three heptanes are found to be predominant and unchanged even after the heptane was recycled for more than 5 times.

To examine the effect of the recycled solvent on the resin refining process, several extraction tests were carried out with the resin flotation concentrate at different temperatures with fresh heptane and recycled heptanes. The extraction yields and the quality of the refined resins are presented in Table 5-6 and Table 5-7, respectively.

It is shown clearly in Table 5-6 that the yield with recycled heptane is lower than that with fresh heptane. However, the difference is not large. Also, it seems that an increase in extraction recycle does not lead to a significant decrease in extraction yield. An increase in extraction time will, of course, increase the yield with recycled heptane. It can be estimated from

Figure 5-14. FTIR spectra of heptane

Figure 5-15. FTIR spectra of heptane (wavenumber 2700 to 3100)

Figure 5-16. FTIR spectra of heptane (wavenumber 1200 to 1600)

Figure 5-10 that even doubling the extraction time (from one hour to two hours) the fraction extracted increases only approximately 2.5% (or the recovery increases 3.5%). However, as shown in Table 5-6, increasing the temperature is a more effective means to improve both recovery and decrease extraction time. At 50 °C, the recycled heptane almost achieves the same extraction as fresh heptane in only 20 minutes. These results indicate that temperature control can be used to achieve the desired level of extraction.

Table 5-6. Comparison tests of fresh heptane vs. recycled heptane on resin yield

No.	Solvent Type	Extraction Temperature (°C)	Extraction Time (min)	Fraction Extracted (%)
1	Fresh Heptane	24 ± 0.6	60	58.54
2	Fresh Heptane	24 ± 0.6	60	58.80
3	Fresh Heptane	23 ± 0.6	60	57.38
4	Recycled Heptane (1 time)	24 ± 0.6	60	57.40
5	Recycled Heptane (2 times)	24 ± 0.6	60	57.40
6	Recycled Heptane (3 times)	24 ± 0.6	60	57.20
7	Recycled Heptane (many times)	23 ± 0.6	60	53.85
8	Fresh Heptane	50 ± 0.6	20	64.80
9	Recycled Heptane (many times)	50 ± 0.6	20	64.40

Table 5-7. Comparison tests of fresh heptane vs. recycled heptane on resin quality

Product	Melting Point (°C)	Transmittance* (%)
Produced with Fresh Heptane	146 - 151	51.0
Produced with Recycled Heptane	146 - 151	51.0

* Transmittance measurement was described in Section 5.3.

The results in Table 5-7 show that the properties of the resin products recovered from the resin concentrate are essentially the same for both fresh and recycled heptanes. It can be concluded that the change in quality and composition of the heptane during recycle is small and that it has no notable effect on the resin refining process.

5.6 Solvent Extraction Study for Different Resin Types

In this study, a macroscopic fossil resin sample (10×28 mesh) was 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 was to gain further understanding of 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.

5.6.1 Experimental

Sample Preparation

A resinite sample containing 90.6% hexane soluble resin (-10 mesh) was obtained by gravity separation from 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, were obtained, weighed, and analyzed. A dark resin sample (-28 mesh) was obtained by

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.

Microscopic Analysis

Since resinite fluoresces under UV and blue light, the optical characteristics of these four fossil resin types can be analyzed by fluorescence microscopy. Polished briquettes (pellets) were prepared and used for such analyses. The polished briquettes were prepared by the procedure described in Section 3.3.

An Axioplan Universal Microscope (Carl Zeiss, West Germany) was employed for the analysis of the polished samples. The analysis method is also described in Section 3.3.

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 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.

Density Measurement

The densities of each of the hand-sorted resin types, solvent extracted resins, 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.

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 a 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.

Molecular Weight Determination

Molecular weights of the four hand-sorted resin types as well as of 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 the 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.

5.6.2 Results and Discussion

Proximate Analysis of Resin Types

Some physical and chemical properties of the four hand-sorted resin types and coal sample from the Wasatch Plateau coal field are presented in Tables 5-8 and 5-9. 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) as compared to the parent coal (15,538 Btu/lb).

Macroscopic Resin Types

As seen from Table 5-8 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 resin is of the dark-brown type, while the light colored resin constitutes a smaller portion.

Table 5-8. 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 5-9. Proximate analysis and calorific value of the resin types and coal

Resin Type	Density (g/cm ³)	Ash (Wt. %)	Volatile Matter* (Wt. %)	Calorific Value (Btu/lb)	Molecular Weight
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.

Microscopic Examination

Fluorescent microscopic examination was carried out for all resin types. It turns out 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.

Solvent Extraction

Solvent extraction has been used extensively to isolate and purify resinite macerals and has also been used as a commercial extraction process for the solvent refining of fossil resin. With respect to solvent extraction, Figures 5-17 and 5-18 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 each of the four hand-sorted resin types in toluene, as determined by vapor pressure osmometry, is given in Table 5-9. 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 5-17 and 5-18.

Figure 5-17. Extraction results for four types of resin with hexane

Figure 5-18. Extraction results for four types of resin with toluene

It can also be seen from the Figures 5-17 and 5-18 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 π -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 5-19. It is clear from the photographs in Figure 5-19 that hexane extracted products from all hand-sorted resin types have a light yellow color. On the other hand toluene, being a more powerful solvent, can extract extraneous matter from all hand-sorted 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 5-17 and 5-18, 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) were 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. Tables 5-10 and 5-11 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.

Figure 5-19. 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)

Table 5-10. Proximate analysis of hexane/toluene extracted fractions from dark-brown resin and its residue

Fraction Extracted	Wt. (%)	Ash (%)	Volatile Matter (%)	Density (g/cm ³)
Hexane Soluble (150 min. at 25 °C)	61.3	0.0	100.0	1.023
Hexane Insoluble but Toluene Soluble (60 min. at 25 °C)	31.8	0.0	98.7	1.068
Toluene Insoluble	6.9	3.1	58.9	1.205

Table 5-11. Elemental composition and the molecular weights of hexane/toluene extracted fractions from the dark-brown resin and its residue

Fraction Extracted	Elemental Composition (%)					Atomic Ratio		Molecular Weight
	C	H	O	N	S	H/C	O/C	
Hexane Soluble (150 min. at 25 °C)	87.05	11.08	1.48	0.26	0.13	1.53	0.01	1270
Hexane Insoluble but Toluene Soluble (60 min. 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	---

It is evident from the Tables 5-10 and 5-11 that most of the dark brown resin (61.3%) is hexane soluble after 2.5 hours of extraction. The hexane soluble portion has a yellow color, low density, high percentage of volatile matter, and low molecular weight while the hexane insoluble but toluene soluble portion (31.8%) appears dark in color, has a slightly lower percentage of 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

a very low percentage of volatile matter (58.9%). The proximate and ultimate analysis of the toluene insoluble residue of the dark brown resin indicates that it consists primarily of very highly dispersed coal particles as well as polymerized and aromatized terpenoids with higher oxygen content.^{17,19} 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, the hexane soluble portion from either the light-brown or dark-brown resin has a light color similar to the natural yellow resin sample.

5.6.3 Summary and Conclusions

Four resinite types, yellow, amber, light-brown, and dark-brown in color, occurring in the Wasatch Plateau coal field, are composed mainly of aliphatic components.¹⁷ 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 in 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.

6. PROOF-OF-CONCEPT TEST CIRCUIT DESIGN ENGINEERING AND INSTALLATION

6.1 Design Considerations

Based on kinetic studies and batch scale experimental work as well as environmental requirements the continuous fossil resin refining circuit was designed with the following considerations:

- Environmental suitability
- High efficiency
- Compact size
- Ease of operation

Due to the complexity of the refining system, the circuit was divided into eight unit operations, i.e., fossil resin concentrate feeder, solvent feeder and circulation system, extraction equipment, residue separation, resin product drying and receiving, compressed nitrogen heater used for dryer and solvent recovery.

6.2 Flowsheet and Layout of the Circuit

The continuous refining circuit was built as a mobile unit except the spray dryer. A conceptual diagram of the circuit is shown in Figure 6-1. The fossil resin concentrate was charged to a screw feeder where the concentrate was introduced into the solvent extractor at a pre-calibrated feed rate. Solvent was continuously added to the extractor to sustain a certain liquid to solid ratio. When the mixture in the extractor approached the desired residence time,

Figure 6-1. Conceptual diagram of the refining circuit

the mixture began to be discharged at a controlled rate to the separation step. Two filters were employed here to separate pregnant liquor from the mixture. The liquid flowed into the pregnant liquor tanks and then was ready to be pumped into the spray dryer to evaporate the solvent. Resin product was collected at the bottom of the dryer.

In order to be an energy efficient system, multi-level lay out of the equipment was used for the circuit. A detailed layout sketch is shown in Figure 6-2.

6.3 Equipment Selection/Design

6.3.1 Solid Resin Concentrate Feeder

The western fossil resin concentrate has a density of 1.14 gram/cm^3 and more than 75% of the particles are finer than $75 \text{ }\mu\text{m}$. To feed this kind of fine powder quantitatively into an extraction system normally will be troublesome if the feeder is not properly chosen. The main problem for the fossil resin concentrate feeder is bridging before discharge due to surface properties of the system. Bridging will make it impossible to have an accurate quantitative feed rate which is very critical to the operating of the entire circuit. In order to solve these common dry material feeding problems, an AccuRate feeder with a state-of-the-art agitation system (Model 104) was chosen to feed the fossil resin concentrate into the refining system.

The AccuRate feeder utilizes a Tuf-Flex vinyl hopper with rounded corners and contoured shape to promote mass flow of dry materials. The hopper is massaged (at variable speeds and amplitudes) from the outside by two paddles gently pressing against the side of the hopper. As the hopper walls distort, they create fault lines in the stored material. This feeder is further

Figure 6-2. Sketch of layout of the refining circuit

enhanced by a wide variety of helixes and nozzle adapters, therefore, it has a variable feed rate from 0.000017 to 0.5 cu ft/hr. This equipment has been used successfully to feed more than 50 different kinds of dry materials, including phenolic resin and other powders. The main specifications of the feeder are:

MODEL: AccuRate 104

FEED RATE: 0.000017 - 0.5 cu ft/hr

HELIX SIZES: 0.125", 0.25", 0.38", 0.50", 0.75"

ELECTRICAL REQUIREMENTS: 110 VAC, 50/60 Hz, single phase, 1 A

HOPPER CAPACITY: 0.1 cu ft

WEIGHT: 15 lb.

A photograph of the feeder is shown in Figure 6-3.

6.3.2 Solvent Extraction System

The solvent used for fossil resin extraction was pumped into the extractor. Both recycled and fresh solvent were used according to the basic study. In the beginning, fresh solvent was fed into the solvent tank and condenser to the desired level, then the pump was started. The pump took two streams, one from the condenser and the other from the extractor, in a ratio of approximately 1:30 at its inlet, to enhance the circulation in the extractor. The solvent flow rate was kept at a 6 : 1 to 8 : 1 (wt) ratio to the fossil resin concentrate to ensure good mass transfer.

A detailed sketch of the extractor is shown in Figure 6-4. A T-shaped tube with spray heads at its ends divides the main stream into two branches of the feed/circulation stream. The mixture of solvent and solid comes out of the spray head at a desired pressure and acts as an

Figure 6-3. AccuRate screw feeder

Figure 6-4. Sketch of the solvent extractor

agitator that will enhance the mass transfer between the solid fossil resin and the solvent. Coiled copper tubing containing hot water was used to maintain the operating temperature at the bottom of the extractor. The heating rate is controlled by adjusting the hot water flow rate inside the tubing. A thermocouple located at the center of the extractor was used to monitor the temperature.

When the solid/liquid mixture approached the desired residence time in the extractor, the solid and pregnant liquor flowed out from the extractor to the separator. To monitor the liquid level in the extractor, a fluid-level gauge was linked from the top to bottom of the extractor.

Aluminum was used to make the extractor body and Chem-Fluor tubing and fittings were used for connections between the different pieces of equipment.

6.3.3 Residue Separation

This step of the operation was designed to separate the suspended residue particles from the fluid stream by passing the solution through a porous medium. As the fluid is forced through the pores of the medium the solid particles are retained on the surface of the medium and a "cake" forms.

To account for the parameters governing filtration and to select the filtration equipment best suited for this particular application, two important parameters were considered:

- (1) the method used for forcing the liquid through the medium, and
- (2) the material that constitutes the filter medium.

When the resistance opposing the fluid flow is small, gravity force will transport the fluid through the filter. As the cake gradually forms, the force of gravity is insufficient to maintain

the flow, therefore positive pressure in the form of compressed nitrogen is necessary to accomplish filtration. This operation is a hydrodynamic process in which the fluid's volumetric rate is directly proportional to the existing pressure gradient across the filter medium, and inversely proportional to the flow resistance imposed by the connectivity, tortuosity and size of the medium's pores, generated by the filter cake. The pressure gradient constitutes the driving force responsible for the flow of the fluid. The structure of the cake formed and, consequently, its resistance to liquid flow depend on the properties of the solid particles and the liquid phase suspension, as well as on the conditions of filtration. The cake structure is first established by hydrodynamic factors such as cake porosity, mean particle size, size distribution, particle specific surface area and sphericity, etc. It also will be influenced strongly by some factors that can conditionally be denoted as physicochemical such as the rate of coagulation of solid particles, the presence of tar and colloidal impurities clogging the pores, etc. The influence of physicochemical factors is closely related to surface phenomena at the solid-liquid boundary. It is especially manifested by the presence of small particles in suspension. Large particle sizes result in increase in the relative influence of hydrodynamic factors, while smaller sizes contribute to a more dramatic influence from physicochemical factors.

Based on the above considerations and the results from kinetic studies, a cylindrical shaped pressurized filter was chosen to perform the filtration operation of the circuit as shown in Figure 6-5.

Aluminum was used to build the filters. Two layers of Whatman Filtration paper were used as the filtration medium supported by porous material. All connections were sealed to prevent solvent leakage.

The fluid from the extractor was introduced to the filter by gravity. The volume of the

Figure 6-5. Solid/liquid filter

filter chamber was designed to handle 25 liters of liquid/solid mixture, therefore, after the liquid level in the filter approached 4/5 of the capacity, the mixture was switched to another filter. The feed line valve for the occupied filter was then closed and compressed nitrogen was introduced to the chamber to force the separation process. When the pressure above the cake dropped below 2 psi, the nitrogen was turned off.

6.3.4 Refined Fossil Resin Collection

This step included evaporation of the solvent and collection of the refined fossil resin product. Pregnant liquor was pumped under pressure to a spray nozzle and atomized into the spray chamber. A hot nitrogen stream was used to evacuate any vapor solvent and the dried resin product was concentrated by centrifugal force at the bottom of the chamber cone.

A schematic diagram of the spray dryer is shown in Figure 6-6.

6.3.5 Solvent Recovery and Recycle

The fossil resin refining circuit was designed so that the whole system was closed to the environment to prevent solvent pollution and minimize the possibility for fire or explosion. In addition, to reduce the operating cost of the process, the solvent was recycled and blended with new solvent during the extraction phase. In this regard, a solvent condenser, as shown in Figure 6-7, was designed to recover as much solvent vapor as possible.

Figure 6-6. Diagram of a spray dryer

Figure 6-7. Solvent condenser

6.4 Equipment Construction and Performance Testing

All equipment was put into place and assembled immediately after the equipment procurement phase. A photograph of the complete circuit is shown in Figure 6-8. Figures 6-9 through 6-12 are photographs of the AccuRate screw feeder, solvent extractor, filter, and spray dryer, respectively. Chem-fluor Teflon tubing was used to connect equipment in order to observe the fluidity of the material at different stages in the circuit.

The solvent extractor was custom designed and manufactured. Both solvent and fossil resin concentrate were introduced into the extractor where extraction took place. In order to enhance the mass transfer rate, an air operated circulation pump was used for stirring. When the solvent/resin-concentrate mixture approached the desired residence time, a discharge valve was opened to discharge the product mixture for the solid/liquid separation step. The extractor was equipped with a hot water heater which was used to supply energy to the mixture in case a higher extraction temperature was required. A thermocouple was used to monitor the extraction temperature.

There were two custom designed filters which were fabricated for the system. Individually each of them worked in a batch mode but together they allowed for continuous operation. The filtration operation started as soon as the suspension was discharged into one of the two filters. The suspension was diverted to the second filter when $2/3$ of the mixture tank was filled. After separation, pregnant liquor flowed, via gravity, into a holding tank and was ready for drying.

When the pregnant liquor in the holding tanks reached $2/3$ of the tank capacity, the heating system of the spray dryer was turned on and prepared for the drying process. Then

Figure 6-8. Photograph of fossil resin refining circuit

Figure 6-9. AccuRate dry material screw feeder (model AccuRate 104)

Figure 6-10. Photograph of solvent extractor

Figure 6-11. Photograph of cylindrical filter

Figure 6-12. Photograph of spray dryer

nitrogen gas was introduced through a regulator followed by pumping the pregnant liquor into a spray nozzle. Evaporated solvent went through a pipe line to a solvent condenser where it was cooled, condensed and recovered as liquid for recycle.

After the equipment had been assembled and appeared to be operational, all equipment was tested for performance and the results are given as follows.

a) AccuRate Screw Feeder

The AccuRate feeder is one of the key pieces of equipment used in the proof-of-concept test circuit. A series of performance tests were conducted using fossil resin concentrate sample and typical results are shown in Figure 6-13.

It was clear that this equipment is satisfactory to feed the resin concentrate into the extractor without problems. During the test it was noticed that the resin flow rate was relatively stable if the resin in the feed hopper was stirred every ten minutes during the process.

b) Solvent Extractor

The solvent extractor is the core equipment of the entire process. It was carefully tested and evaluated during the performance test period. A series of preliminary extractions were carried out using different extraction conditions. The extraction rate/yield using this equipment easily approached batch test level. It was observed that good circulation of the mixture within the extractor was necessary in order to prevent sedimentation of suspended particles.

c) Filtration

Two custom filters were used for this project. Cake accumulation and cake thickness during and after filtration were examined and found to be satisfactory.

6.5 Improved Solvent Extractor

Due to special characteristics of the fossil resin concentrate, it was found that good circulation of the solid/solvent suspension was necessary to prevent sedimentation and plugging of the system. Accordingly the solvent extractor was modified as shown in Figure 6-14. Note

AccuRate feeder performance chart

Figure 6-13. Performance chart of AccuRate screw feeder

Figure 6-14. Schematic diagram of the modified solvent extractor

that the overflow line was moved to the bottom of the extractor. Instead of using 1/4" tubing, 3/8" pipe was used for both the circulating pump inlet and the discharge line. An on-line ball valve was used to control the discharge rate. With this design the residence time of the solid could be adjusted thereby minimizing the plugging problem.

7. PROOF-OF-CONCEPT CONTINUOUS REFINING TESTS

7.1 Test Conditions

Basic variables for this continuous refining operation included temperature, solvent type, extraction time, solid loading rate, etc. The following matrix of process variables was designed for the initial refining test. Only one variable was changed per individual test; all other variables were kept constant.

Temp. °C	Solvent	Residence time min. (approximately)	Load rate (approximately) wt% to slvt.
20	hexane	5	5
40		10	10
60	heptane	20	

Two to three liters of solvent were taken into the solvent extractor to start the test. When the desired temperature was reached inside the extractor, fossil resin concentrate was charged into the system using an AccuRate dry material feeder operated at a certain pre-calibrated rate. After a period of time (determined by the feeding rate and solid/liquid ratio) fresh solvent was introduced into solvent extractor at a rate to sustain the desired solid/liquid ratio. After the desired residence time was established, the mixture was discharged to filtration through the discharge valve. A temperature accuracy of ± 2 °C was controlled by adjusting the hot water flow in the heating coil.

7.2 Material Characteristics

Technical grade hexane (C_6H_{14}) and heptane (C_7H_{16}) with the following physical properties were used as solvents for these experiments.

	<u>Molecular Weight</u>	<u>Density, g/cm³</u>	<u>Boiling Point, °C</u>
Hexane	86.18	0.659	68
Heptane	100.12	0.684	98

Toluene was not used as a refining solvent for the following reasons:

As shown by the differential refining tests presented in the Sixth Quarterly Report, the melting point of the heptane-extracted resin is less than 155 °C while the melting point of the toluene-extracted residue (taken from the residue of heptane extraction) is higher than 230 °C. The difference is obviously due to the fact that the toluene-extracted material has a much higher molecular weight or a much larger molecular size. These large molecules remain insoluble during hexane or heptane extraction and bridge other insoluble residue particles (eg. coal) which are very fine and thus a porous structure is created for the insoluble residue particles. With heptane as the solvent, the integrity of the porous structure is preserved and with the relatively large porous particles filtration after extraction is facilitated. However, with toluene as the solvent, the porous structure is destroyed and the very fine insoluble residue particles (eg. coal with an estimated size of 0.5 to 20 μm) are released. These fine residual particles inhibit filtration. Finally, as expected, the color of the toluene extracted products is much darker than the color of the heptane or hexane extracted products and thus the toluene extracted products would be of significantly lower economic value.

Feed material for the test was fossil resin concentrate obtained from the Wasatch Plateau

coal (see Section 3). The relevant properties of the concentrate were:

Density (gram/cm ³)	1.143
Ash content (%)	1.23
Moisture (%)	1.03
Hexane-soluble (%)	73.34

The particle size distribution of the resin concentrate was determined by wet screening according to ASTM standard procedure (D 4749) and the particle size distribution was found to be as follows:

Particle Size (mesh)	Weight %	Cumulative Weight % Passing
28-60	1.79	100
60-100	4.24	98.21
100-200	13.74	93.97
200-270	7.71	80.23
270-400	8.71	72.52
-400	63.81	63.81
Total	100.00	

7.3 Proof-of-Concept Continuous Test Procedure

7.3.1 General Start-Up Procedure for the Circuit

- 1) Load AccuRate screw feeder with certain amount of fossil resin concentrate (approximately 1 kg);

- 2) Charge solvent into solvent tank as well as into solvent condenser (to a level of approximately 25 liters);
- 3) Start feed pump and pump the solvent from solvent condenser to extractor.
- 4) Adjust ratio of recycle to fresh feed rate at about 30:1 (based on solvent feed rate of 0.5 l/min.);
- 5) Start resin concentrate feeder when solvent level in the extractor (monitored by observation gauge) approaches 3 inches from the bottom of the extractor.

7.3.2 Steady-State Operation

Approximately 15 minutes from start-up, the system can be assumed to approach steady-state operation. Before the mixture in the extractor reaches the desired residence time, prepare for the following tasks:

- 1) Open one of the valves which transfers the mixture onto one of the filters;
- 2) Switch the mixture to the other filter when the mixture level in the first filter approaches the top line of the observation gauge;
- 3) Apply nitrogen (about 30 psi. pressure) to the first filter and initiate the filtration process;
- 4) Turn off the nitrogen when the mixture level reaches the bottom line of the observation gauge;
- 5) Open the filter when its pressure gauge shows zero back-up pressure and take out the filter cake, prepare for next cycle;
- 6) Repeat the same procedure for the second filter;
- 7) Turn on nitrogen heater, prepare spray dryer when pregnant liquor tanks are 4/5 filled;
- 8) Open coolant-in valve in the solvent condenser, open nitrogen supply valve, start

spray dryer feed pump when temperature in the nitrogen heater reaches a pre-set point.

- 9) Collect refined resin product.

7.3.3 Shut Down

Normal shut down:

- 1) Turn off resin concentrate feeder;
- 2) Close solvent feeding valve;
- 3) Keep feed pump running to circulate for about 10 minutes;
- 4) Turn off the feed pump;
- 5) Open discharge valve, empty the extractor;
- 6) Turn off spray dryer feed pump when pregnant liquor tanks are almost empty;
- 7) Clean up filter medium, replace it with new one.

Emergency shut down:

In case of an emergency situation, turn off all electrical equipment and air supply to the pump followed by appropriate action to minimize damage.

7.4 Results and Discussion

Immediately after test circuit shake-down, continuous fossil resin refining tests were carried out. During this phase of the program, a series of tests were performed based on the results from batch scale experiments and the designed experimental protocol. These test results, as discussed later, tends similar to those of the bath experiments.

7.4.1 Continuous Refining Tests Using Hexane as Solvent

Test results for the experiments using technical grade hexane are discussed below.

Effect of Extraction Temperature

The effect of extraction temperature on resin extraction is presented in Figure 7-1, where yield is simply the weight percent of the feed dissolved and recovery is the weight percent of resin in the feed that has been dissolved (resin in the feed is based on solvent extraction result using Soxhlet solvent extractor for 12 hours). The feed rate of the resin concentrate was 5 grams per minute and the solid residence time was 10 minutes.

It is obvious that the effect of temperature is very significant. Extraction of the resin product increases dramatically with an increase in extraction temperature when other conditions are held constant. As indicated in previous sections, the extraction process is controlled mainly by a surface reaction mechanism involving the solvation of resin molecules at the surface, followed by subsequent release of the molecules into solution. Therefore, the kinetics of the extraction reaction were expected to be significantly dependent upon the operating temperature.

Effect of Average Solid Residence Time

As mentioned in the sixth quarterly report, the solid residence time for a continuous extractor is an important parameter that needs to be considered in both design and operation. First of all, continuous resin extraction could be considered as ideal backmixing or well mixed reactor, the residence time distribution of the liquid is defined as:

Figure 7-1. Effect of hexane extraction temperature on resin recovery and yield at a feed rate of 5 gram/min. and a residence time of 10 min. (concentrate/solvent ratio = 0.10)

$$E(t) = \frac{Q}{V} \exp \left(-\frac{Q}{V} * t \right)$$

where: V is the volume of the reactor (extractor);

Q is the volumetric flow rate;

V/Q is defined as average residence time.

In the original plans for the test circuit, the average residence time of the resin concentrate was designed to be varied from 1.3 to 2.7 hours . However, during the shake-down testing it was found that the continuous circuit extractor approached the batch extraction level in a much shorter residence time, therefore such long residence times were not needed. Hence, the extractor was modified so that the residence time could be adjusted as desired. The effect of the average residence time on resin extraction is presented in Figure 7-2. As can be seen, for a given temperature and concentrate feed rate, the yield of the resin product increases with an increase in the average residence time.

Effect of Resin Concentrate to Solvent Ratio

The effect of the resin concentrate to solvent ratio (by weight) on resin recovery was investigated in this continuous refining study. As presented in Figure 7-3, the resin recovery begins to drop when the resin concentrate to solvent ratio is greater than about 0.15 by weight for the given conditions (temperature 50 °C, residence time 10 minutes). However, it was observed that this drop could be offset to a certain extent if the average residence time is increased.

Figure 7-2. Effect of average residence time on resin yield and recovery with hexane at a feed rate of 5 gram/min. (concentrate/solvent ratio = 0.10)

Figure 7-3. Effect of resin concentrate to solvent ratio (by weight) on resin yield and recovery with hexane at 50 °C for 10 min. at a feed rate of 5 gram/min.

7.4.2 Continuous Refining Test Using Heptane as Solvent

During this phase of the research program technical grade heptane was used as the refining solvent. The effects of extraction temperature, average residence time, and resin concentrate/solvent ratio were investigated under conditions similar to those in which hexane was used as the solvent. Test results using heptane as the solvent are presented in Figures 7-4 to 7-6. The heptane results are similar to the results obtained with hexane in all aspects and the conclusions are similar to those reached when hexane was used as the solvent.

7.4.3 Heptane vs. Hexane

In order to evaluate the solvents used, a simple comparison was carried out from both a technical and economical viewpoint.

Technical Evaluation

Heptane showed a consistently higher extraction yield than hexane even though heptane contains only one more methylene group in its molecular structure. Figures 7-7 to 7-9 compare the extraction yields for these two solvents under the same extraction conditions. It is clear that heptane extracts a little more resin than hexane and is a slightly more effective solvent for fossil resin than hexane. With heptane as the solvent, both the extraction rate and the resin yield are enhanced. The reason for improved extraction with heptane appears to be due to kinetic considerations (laboratory Soxhlet extraction for 6 hours results in the same extraction for both mixed hexanes and normal heptane). Thus it seems that molecular structure has a significant

Figure 7-4. Effect of heptane extraction temperature on resin yield at a feed rate of 5 gram/min. and a residence time of 10 min. (concentrate/solvent ratio = 0.07)

Figure 7-5. Effect of average residence time on resin yield with heptane at a feed rate of 5 gram/min. and 49 °C (concentrate/solvent ratio=0.07)

Figure 7-6. Effect of the resin concentrate to solvent ratio (by weight) on resin yield with heptane at a feed rate of 5 gram/min. and 49 °C

Figure 7-7. Comparison of resin yields with two different solvents as a function of temperature at a feed rate of 5 gram/min. and a residence time of 10 min. (concentrate/solvent ratio = 0.07)

Figure 7-8. Comparison of resin yields with two different solvents as a function of residence time at a feed rate of 5 gram/min. and 49 °C (concentrate/solvent ratio = 0.07)

Figure 7-9. Comparison of resin yields with two different solvents as a function of concentrate to solvent ratio at 49 °C and a residence time of 10 min.

effect on the rate of extraction. Additional laboratory experiments are planned to examine this hypothesis further. In any event, based on the results from the continuous testing normal heptane would be the preferred solvent.

Economic Evaluation

As mentioned previously, from a technical perspective, heptane is the better solvent to be used in the resin refining process. However economic factors must also be considered in the overall evaluation of the process. In this regard a simple economic evaluation was carried out taking into consideration the operating costs for the resin concentrate refining process.

First of all, the price of industrial grade heptane is about the same as hexane. Because the process operates in a recycle mode, the initial cost would be about the same for both solvents. But in order to obtain the final resin product, the extracted resin has to be recovered from solution using evaporation techniques, which consume energy. Due to the significant difference in boiling points between the two solvents, approximately 25 - 35% more energy will be required for resin recovery by evaporation if heptane is used as the solvent for extraction. This represents a very significant increase in the operating cost.

Secondly, based on bench scale tests the same yield can be achieved with hexane if the average residence time is increased. Such an increase in retention time only requires an increase in the capacity (or volume) of the extractors in a resin refining plant, which subsequently increases the capital cost by a small amount.

It appears then from an economic perspective that hexane is the most appropriate solvent.

8. TECHNICAL AND ECONOMIC ANALYSIS

A preliminary technical and economic feasibility study was completed for fossil resin flotation and refining plants with a capacity of approximately 40 million pounds of refined resin per year. The specific aims of this analysis were to achieve the following:

- develop conceptual flowsheets for industrial resin flotation and refining plants based on estimated reserves and present technologies;
- determine the performance of these plants based on the results of pilot plant tests and/or laboratory experiments;
- outline important features of the facilities;
- estimate the capital and operating costs;
- evaluate the feasibility by determination of the discounted cash flow rate of return (DCFROR).

8.1 Design Criteria

The proposed project consists of a resin flotation plant and a resin refining plant. The feed stock would be minus 100 mesh coal fines with a 10% resin content as might be produced from a present coal preparation plant on the Wasatch Plateau coal field. It is assumed that the resin flotation and refining plants would be built 2000 feet from an existing coal preparation plant having a capacity of 1400 tons/hr and processing 4 million tons per year. The reserve is sufficient for 50 years of production at the current annual rate.

In the coal preparation plant, the 6-in $\times$ 0 raw coal is screened on 0.5-in wet screens. The 6-in $\times$ 0.5-in oversize from the screens is processed with jigs. The 0.5-in $\times$ 0 undersize from the

screens is deslimed on 100-mesh screens. The 0.5-in $\times$ 100 mesh material is cleaned by heavy medium cyclones in the coal preparation plant and the minus 100-mesh material, which is 7.43% by weight of the raw coal, would be transported to the resin flotation plant through a 12-in pipe line. The percent solids in the pulp is assumed to be 20% by weight.

The coal preparation plant operates two 8-hour shifts per day, 200 days per year.

The resin flotation plant is designed to have the same operating schedule and minus 100 mesh capacity as the coal preparation plant. The lifetime of the resin flotation plant is considered to be 20 years.

The design criteria are summarized as the followings:

<u>Item</u>	<u>Unit</u>	<u>Quantity</u>
Plant feed	tpa	300,000
Days per year		200
Shift per day		2
Hours per shift		8
Operating hours per year		3200
Tons per hour		104 ($1.1 \times 300,000/3200$)
Tons per day		1664
Size	mesh	-100
Solid concentration	%	20
Density of coal	g/cm ³	1.4
Density of resin concentrate	g/cm ³	1.15
Density of refined resin	g/cm ³	1.04
Density of hexane	g/cm ³	0.67
Bulk density of dry concentrate	g/cm ³	0.43
Ash content of raw coal	%	20
Resin content of raw coal	%	10

8.2 Resin Flotation Plant

8.2.1 Conceptual Flowsheet

The conceptual flowsheet of the resin flotation complex is shown in Figure 8-1.

Pulp from the coal preparation plant is pumped into a buffer thickener at a rate of 1980 gpm and a concentration of 20% by weight. The resin is recovered by a rougher-cleaner flotation circuit, a process which was developed at the University of Utah. Resin concentrate is dewatered by filters before it is conveyed to the resin refining complex. After the resin is recovered, a coal flotation circuit which directly follows the resin flotation circuit is used to recover coal fines and to reject mineral matter. The concentrate from coal flotation is dewatered by filtration and then is thermally dried. The dry clean coal is delivered back to the coal preparation plant by trucks. The final tailings stream is sluiced to a thickener. The underflow of the thickener is pumped to a refuse disposal dam.

8.2.2 Mass Balance

Based on the results of continuous proof-of-concept tests of resin flotation (a project funded by DOE Contract #DE-AC22-90PC90178), the following assumptions were made in mass balance calculation:

1. The recovery and grade of the resin concentrate are assumed to be 80% and 60%, respectively.
2. The ash content of the resin concentrate is 2%.
3. The ash contents of the clean coal and tailings are 10% and 60%, respectively.

The mass balance of the resin flotation complex is given in Table 8-1.

Table 8-1. Mass balance for the resin flotation plant

Stream	Solid (ton/hr)	Water (gal/hr)	Resin (Wt.%)	Ash (Wt.%)	Solids (Wt.%)	Pulp (gal/hr)	Yield (%)	Recovery (%)
1	104.00	99,708	10.00	20.00	20.00	118,107		
2		369,543				369,543		
3	52.00	70,627	19.00		15.00	80,093		
4	104.00	473,614	10.00	20.00	5.00	492,012		
5		6,232				6,232		
6	52.00	49,854	19.00		20.00	59,320	50.00	95.00
7	52.00	423,759			2.86	432,692		
8	13.87	4,985	60.00	2.00	40.00	7,834	26.67	84.21
9	38.13	65,641				72,259		
10	13.87	1,424	60.00	2.00	70.00	4,273		
11		3,561				3,561		
12	90.13	489,401	2.31	22.77	4.23	504,950		
13	67.11	48,259	3.10	10.00	25.00	59,868	74.46	
14	23.02	441,142	0.00	60.00	1.24	445,083		
15	23.02	5,517	0.00	60.00	50.00	9,458		
16		480,550				480,550		
17		388,446				388,446		
18	67.11	6,894	3.10	10.00	70.00	18,503		
19		41,365				41,365		
20	67.11	1,787	3.10	10.00	90.00	13,396		
21		5,107				5,107		
22	23.02	486,068				490,008		
23		18,903				18,903		
24		4,362				4,362		
25		1,870				1,870		
26		92,104				92,104		

8.2.3 Equipment

Equipment is listed in Table 8-2. The design criteria were obtained from the mass balance calculations. A safety factor of 1.2 was selected for all the equipment except the feed pump in the coal preparation plant which has a safety factor of 1.3. In fact, because the design capacity is 1.1 times the actual capacity, the safety factor is $1.1 \times 1.2 = 1.32$. All the equipment and prices were obtained from Reference 21. The prices of a few items of equipment were estimated by the 0.6 size exponent method.

8.2.4 Capital Costs

The capital cost estimation was made on the basis of the cost models listed in Reference 21. The items in the cost model were converted to fractions of the total equipment cost. The converted factors in turn were applied to estimate the capital cost of the resin flotation plant. Some factors which are not included in the cost model of Reference 21 were determined based on Reference 22. All prices are in 1994 dollars. The capital costs are given in Table 8-3.

8.2.5 Operating Costs

The operating cost estimation was also made on the basis of the cost models listed in Reference 21. Although the designed capacity of the flotation plant is 300,000 ton per year, the feed tonnage in Table 8-4 is the actual number from the present coal preparation plant which is 297,143 ton per year (or 269,568 metric ton per year). However, the administration fee and

Table 8-2. Equipment list for the resin flotation plant

Item	Unit	Design Criteria	Specifi- cations	Number of Units	HP (kw)	Unit Price (\$)	Price (\$)
Feed Supply							
Pump	gal/min	2,559	3,000	3	3 × 70	46,301	138,903
Polyurethane Pipe	ft		12 inches	2020		112.13	226,503
Elbow				6		452.45	2,715
Coupler				101		280.01	28,281
Buffer Thickener	ft	200	200	1		284,820	284,820
Rougher Flotation							
Conditioner	gal	19,680	5,000	4		3,500	14,000
Mixer	hp	4	5	4	4 × 5	47,591	190,364
Feed Pump	gal/min	9,840	5,000	2	2 × 70	46,301	92,602
Flotation Cell	cu. ft	9,313	1,000	10		52,020	520,200
Motor	hp			5	5 × 60	16,220	81,100
Cleaner Flotation							
Conditioner	gal	3,204	5,000	1		3,500	3,500
Mixer	hp	4	5	1	5	47,591	47,591
Flotation Cell	cu. ft	1,516	1,000	2		52,020	104,040
Motor	hp			1	60	16,220	16,220
Resin Concentrate							
Rotary Disk Filter	sq. ft	555	600	1	30	138,940	138,940
Feed Tank	gal		2,000	1		1,800	1,800
Feed Pump	gal/min	157	180	1	5	1,030	1,030
Filtrate Pump	gal/min	71	80	1	3	888	888
Belt Conveyor	ton/hr	24	50	1	5	37,997	37,997

To be continued

Table 8-2. Equipment list for the resin flotation plant

Item	Unit	Design Criteria	Specifi- cations	Number of Units	HP (kw)	Unit Price (\$)	Price (\$)
Coal Flotation							
Conditioner	gal	20,198	5,000	4		3,500	14,000
Mixer	hp	4	5	4	4 × 20	47,591	190,364
Feed Pump	gal/min	10,099	6,000	2	2 × 70	46,301	92,602
Flotation Cell	cu. ft	5,575	1,000	6		52,020	312,120
Motor	hp			3	5 × 60	16,220	48,660
Coal Concentrate							
Rotary Disk Filter	sq. ft	2,685	1,500	2	2 × 60	251,600	503,200
Feed Tank	gal		2,000	1		1,800	1,800
Feed Pump	gal/min	1,197	1,200	1	55	14,869	14,869
Filtrate Pump	gal/min	827	1,000	1	55	14,869	14,869
Belt Conveyor	ton/hr	90.0	120	1	5	34,829	34,829
Rotary Dryer	lb/hr	51,138	73,000	1		508,000	508,000
Tailings							
Tailing Pump	gal/min	8,902	5,000	2	2 × 70	46,301	92,602
Thickener	ft		150	1	10	199,879	199,879
Pump	gal/min	9,600	5,000	2	2 × 70	46,301	92,602
Pump	gal/min	189	200	1	8	2,086	2,086

Table 8-3. Capital cost of the resin flotation plant

Item	Factor	Cost
Equipment	1.00	\$4,053,975
Installation Labor	0.60	\$2,432,385
Concrete	0.10	\$405,398
Piping	0.20	\$810,795
Structural	0.10	\$405,398
Instrumentation	0.08	\$324,318
Insulation	0.03	\$121,619
Electrical	0.12	\$486,477
Coating & Sealants	0.02	\$81,080
Site Improvements	0.10	\$405,398
Mill Building	0.20	\$810,795
Tailings Embankment	0.10	\$405,398
Engineering / Management	0.30	\$1,216,193
Environmental	0.10	\$405,398
Contractors Fee	0.10	\$405,398
Contingency	0.30	\$1,216,193
Land	0.10	\$405,398
Subtotal	3.55	\$14,391,612
Subtotal	100%	\$14,391,612
Off-Site Facilities	1%	\$143,916
Plant Start-Up	5%	\$719,581
Working Capital	10%	\$1,439,161
Total Capital Cost		\$16,694,270

sundry items are not listed here and will be estimated later as overhead of sales. Two items are added:

1. Coal (raw material). The resin flotation plant receives minus 100 mesh feed with 20% ash content from the coal preparation plant. Since a coal product is priced and paid on the basis of 10% ash content in this region, the tonnage of the raw coal which will be paid is determined by converting the raw coal to coal with 10% ash content. After recovery of the resin, a clean coal product with 10% ash content is produced and returned to the coal preparation plant. Losses occur because resin is recovered from the coal and because a small amount of coal is removed together with mineral matter during coal flotation. The refining plant will pay the difference at the average price of Utah raw coal (\$21.83/ton).²³

2. Transportation fee. It is assumed that the refining plant would pay \$0.90/ton of the transportation fee to send the clean coal (10% ash content) back to the coal preparation plant. The refining plant should pay the fee because the fee occurs due to resin recovery.

The operating costs are given in Table 8-4.

Table 8-4. Operating cost estimation of the resin flotation plant

Item	Unit Cost (\$/metric ton feed)	Cost	Feed Tonnage (metric ton/year)
Supplies & Material	4.2	\$1,132,186	269,568
Labor	2.895	\$780,399	
Coal		\$1,156,641	
Transportation of Coal		\$191,743	
Total		\$3,260,969	

8.3 Resin Refining Plant

8.3.1 Conceptual Flowsheet

The conceptual flowsheet of the resin refining plant is shown in Figure 8-2. Based on the analysis in Section 7 of this report, hexane is selected as the solvent for resin refining. According to the results of laboratory experiments and proof-of-concept tests, raising the temperature enhances the extraction. Therefore, the extraction temperature is designed to be 50 °C. Because a spray dryer has very high operating costs especially when nitrogen is used as the heat transfer media, an agitated thin-film evaporator (wiped-film evaporator) is selected to recover dry solid resin from the resin-hexane solution. The agitated thin-film evaporator is suitable to dry very viscous and heat sensitive material according to its specifications.²⁶ It should be noted that a spray dryer was used in the proof-of-concept tests because of cost considerations and budget limitations on this project.

The resin flotation concentrate from the resin flotation complex is fed to a dryer in which the moisture of the concentrate is decreased to <1.5%. The dry concentrate and preheated hexane (50 °C) are added into a group of jacketed extractors connected in series. The pregnant hexane solution is first filtered. Then, the filtrate is polished by a cartridge. Finally, the solvent is evaporated by a two stage evaporation system. A powder resin product is produced in the wiped-film evaporator. The filter cake (residue) is dried in a steam tube dryer. The dried cake which has a low ash content and a high Btu value is mixed with clean coal from coal flotation and is sent back to the coal preparation plant. All the equipment should be operated under reduced pressure or be completely sealed in order to meet environmental requirements and to recover the expensive solvent. The solvent is recovered in two condensers.

Figure 8-2. Flowsheet of the resin refining plant

8.3.2 Mass Balance

Based on the results of laboratory experiments on resin extraction, the following assumptions were made in the mass balance calculations:

1. The amount of solvent used in extraction is 1 liter per 200 gram of the resin concentrate which has a grade of 70% (The grade of the resin concentrate used in laboratory experiments and continuous refining circuit tests is 73%. For safety factor consideration, the resin grade of the concentrate is assumed to be 70%).
2. The retention time for extraction is 60 minutes.
3. The hexane loss is 1% of the flowrate of hexane.
4. The recovery of the resin is 85% (laboratory results gave a recovery of 90%).

The mass balance of the resin refining plant is presented in Table 8-5.

8.3.3 Equipment

Equipment is listed in Table 8-6. The design criteria were obtained from the mass and heat balances. A safety factor of 1.2 was selected for all equipment. All the prices of equipment were obtained from References 21, 22, and 24 and were adjusted by the CE Index of Nov. 1994. The prices of a few pieces of equipment were estimated by 0.6 size exponent method.

8.3.4 Capital Costs

The capital cost estimation shown in Table 8-7 was made by a multiplying factor method.²²

Table 8-5. Mass balance for the resin refining plant

Stream	Solid (ton/hr)	Water (gal/hr)	Resin (Wt.%)	Hexane (gal/hr)	Solids (Wt.%)	Pulp (gal/hr)	Yield (%)	Recovery (%)
0	13.87	1,424	60.00		70.00	4,273		
1	13.87	51	60.00		98.50	2,899		
2	13.87	51	60.00	18,517		21,417		
3	6.79	51	18.37			21,417	51.00	85.00
4	6.79	51	18.37	966	70.00	2,251		
5	7.07		100.00	13,278		14,892		
6	6.79		18.37		100.00	1,234		
7	0.00	51		966		1,017		
8	7.07		100.00	12,820		14,434		
9	7.07		100.00	6,410		8,024		
10	7.07		100.00			1,614		
11				12,820		12,820		
12				6,410		6,410		
13				2,849		2,849		
14				14,244		14,244		
15				14,244		14,244		
16				14,244		14,244		
17				18,517		18,517		
18				2,849		2,849		
19		1,374				1,374		
20	Hexane loss			142		142		

Table 8-6. Equipment list for the resin refining plant

Item	Unit	Design Criteria	Specifi- cations	Number of Units	HP (kw)	Unit Price (\$)	Price (\$)
Feed							
Steam-Tube Dryer	Btu/hr	13.3 M		2	40	212,741	425,482
Screw Feeder	ton/hr	17	14 in	1	3	4,913	4,913
Concentrate Bin	gal	9,262	10,000	1		6,477	6,477
Hexane Supply							
Fresh Hexane Tank	gal	37,867	38,000	1		20,818	20,818
Pump	gal/min	3	10	1	1	775	775
Hexane Tank	gal	34,186	35,000	1		19,662	19,662
Pump	gal/min	285	300	1	10	5,320	5,320
Heat Exchanger	Btu/hr	3.18 M	3.18 M	1		6,014	6,014
Extraction							
Extractor	gal	25,700	3,700	7	7 × 10	46,263	323,841
Filtration							
Pump	gal/min	428	500	1	30	6,940	6,940
Filter	sq. ft	272	300	1	20	130,000	130,000
Filtrate Tank	gal	17,870	20,000	1		24,288	24,288
Pump	gal/min	400	500	1	30	6,940	6,940
Screw Conveyor	ton/hr	8	10 in	1	7	11,550	11,550
Cartridge				2		2,000	4,000
Residue Drying							
Stream-Tube Dryer	Btu/hr	2.00 M		1	15	187,493	187,493
Belt Conveyor	ton/hr	8	20	1	3.5	30,677	30,677

To be continued

Table 8-6. Equipment list for the resin refining complex

Item	Unit	Design Criteria	Specifi- cations	Number of Units	HP (kw)	Unit Price (\$)	Price (\$)
Resin Product							
F.C. Evaporator	Btu/hr	12.75 M	Forced	1	20	259,070	259,070
A.F. Evaporator	Btu/hr	3.12 M	Wiped	1	20	740,200	740,200
Condenser	gal/min	2,000	2,000	1		17,055	17,055
Pump	gal/min	2,000	2,000	1	50	36,302	36,302
Steam Jet Ejector				1		30,071	30,071
Hexane Recycle							
Decanter	cu. ft	22,336		1		26,647	26,647
Condenser	gal/min	445	500	1		7,752	7,752
Pump	gal/min	445	500	1	20	14,869	14,869
Steam Jet Ejector				1		30,071	30,071
Product Packing							
Packing Machine	bag/min		10	2	10	43,000	86,000
Bag Placing Mach.				2	1	43,000	86,000
Product Storage	O.D. m		4	1		9,831	9,831
Screw Feeder	ton/hr	24	30	1	3	4,913	4,913
Belt Conveyor	ton/hr	24	30	1		30,677	30,677
Steam Ceneration							
Furnace	Btu/hr	34.4 M		1		309,959	309,959
Pump	gal/min	1,000	1,000	1	50	31,227	31,227

Table 8-7. Capital cost of the resin refining plant

Item	Factor	Cost
Equipment	1.00	\$2,935,834
Piping	0.43	\$1,262,409
Electrical	0.12	\$352,300
Instrumentation	0.23	\$675,242
Utilities	0.52	\$1,526,634
Foundations	0.10	\$293,583
Insulation	0.05	\$146,792
Painting, Fireproofing & Safety	0.06	\$176,150
Yard Improvements	0.10	\$293,583
Environmental	0.15	\$440,375
Buildings	0.52	\$1,526,634
Construction & Engineering	0.53	\$1,555,992
Contractors Fee	0.20	\$587,167
Contingency	0.43	\$1,262,409
Land	0.05	\$146,792
Subtotal	4.49	\$13,181,895
Subtotal	100%	\$13,181,895
Off-Site Facilities	1%	\$131,819
Plant Start-Up	5%	\$659,095
Working Capital	10%	\$1,318,189
Total Capital Cost		\$15,290,998

8.3.5 Operating Costs

The operating cost estimation was also made by the factoring method. The operating cost estimation is shown in Tables 8-8 and 8-9.

Table 8-8. Estimation of operating cost items for the resin refining plant

Item	Unit	Quantity	Total/Year	Unit Cost	Cost
Raw Material					
Hexane	gal/hr	142	454,400.00	1.01	\$458,944
Utilities					
Electricity	kw/hr	391.16	1,251,702.00	0.08	\$100,136
Recycled Water	1000 gal/hr	190.71	610,272.00	0.25	\$152,568
Steam	M Btu/hr	34.4	110,080.00	12.00	\$1,320,960
Operating Labor					
Control Room	worker/day	2			
Dryer	worker/day	2			
Extractor	worker/day	2			
Evaporator	worker/day	2			
Sampler	worker/day	2			
Laborer	worker/day	4			
Mechanician	worker/day	4			
Electrician	worker/day	2			
Sum	worker/day	20	4,000.00	\$160	\$640,000

Table 8-9. Operating costs of the resin refining plant

Item	Factor	Cost
Raw Material		\$458,944
Utilities		\$1,573,664
Operating Labor		\$640,000
Labor Related Costs		\$320,000
Operating Labor	100.00%	
Payroll Overhead	30.00%	\$192,000
Supervisory and Miscellaneous	20.00%	\$128,000
Capital Related Costs		\$1,257,553
Plant Cost	100.00%	
Maintenance	4.00%	\$558,912
Operating Supplies	1.00%	\$139,728
Environmental	3.00%	\$419,184
Plant Overhead Cost	1.00%	\$139,728
Total		\$4,250,161

8.4 Economic Evaluation

The costs for the resin flotation and refining plants are summarized in Table 8-10. All the costs are given in 1994 dollars. The discounted (or after tax) cash flow rate of return (DCFROR) is shown in Table 8-11. The property tax rate was determined by Utah tax laws. The federal tax rate is 34% of taxable income. The depreciation is made by the straight line method. Since the fossil resin is recovered from coal resources, the 10% percent depletion rate

of the coal industry was applied. The following assumptions were made:

- One percent of royalties is needed to cover the resin flotation and resin refining patents.
- The plant will be built within 2 years and the regular operation will be started at the beginning of the third year.
- Fifty percent of the fixed capital will be spent at the beginning of the project (time zero) and fifty percent of the fixed capital will be spent at the end of the first year (year 1). The start-up fee and working capital will be put in at the end of the second year (year 2). There is a 5% escalation of these costs.
- Operating costs and product value escalate at the same rate.

As shown in Table 8-11, the DCFROR is 23.636% and the payback period is approximately 3 years. These figures are quite encouraging and suggest that an economical fossil resin industry is viable. However, further study is warranted to evaluate assumptions and undertake more detailed analysis.

Table 8-10. Summary of cost estimation for the resin flotation and resin refining plants

Item	Amount	Assumption
Sale Income	\$24,240,012	Resin price \$0.60/lb
Total Capital	\$31,985,268	
Fixed Capital	\$27,849,242	
Plant Costs	\$27,573,507	
Off-Site Facilities	\$275,735	
Start-Up Fee	\$1,378,675	
Working Capital	\$2,757,351	
Operating Costs	\$9,790,997	
Operating Costs	\$7,511,130	
Overhead and Sales	\$1,454,401	6% of sales
Mining Severance Tax	\$188,682	Based on Utah tax laws
Insurance	\$278,492	1% of property value
Property Taxes	\$358,292	1.28654 of property value
Patents and Royalties		1% of sales
Salvage Value	\$3,309,541	
Working Capital	\$2,757,351	
Land	\$552,190	
Depreciation		
Year	Depreciation	Value to be depreciated
3 to 22	\$1,364,853	\$27,297,052

Table 8-11. Cash flow for the resin flotation and resin refining plants

Year	0	1	2	3	4 to 22	Salvage
Sales				\$24,240,012	\$24,240,012	
Patents and Royalties				\$242,400	\$242,400	
Start-Up Fee				\$1,519,990		
Operating Costs				\$9,790,997	\$9,790,997	
Depreciation				\$1,364,853	\$1,364,853	
Taxable Income before Depletion				\$11,321,772	\$12,841,762	
% Depletion				\$2,399,761	\$2,399,761	
50 % Limit				\$5,660,886	\$6,420,881	
Taxable Income				\$8,922,011	\$10,442,001	
State Income Tax				\$446,101	\$522,100	
Federal Income Tax				\$3,033,484	\$3,550,280	
Net Profit				\$5,442,427	\$6,369,620	
Depreciation				\$1,364,853	\$1,364,853	
Depletion				\$2,399,761	\$2,399,761	
Cash Flow	\$-13,924,621	\$-14,620,852	\$-3,039,979	\$9,207,041	\$10,134,235	\$3,309,541
Present Value	\$-13,924,621	\$-11,825,693	\$-1,988,742	\$4,871,715	-----	\$583,275
DCFROR	23.636					

8.5 Summary of Technical and Economic Analysis

From this technical and economic analysis, the following points should be noted:

1. The DCFROR (23.636%) of the resin refining plant project is high enough to warrant further study of this project.
2. Improvements in the economics could be made in the following areas:
 - The solids concentration for resin flotation is quite low (5%). If the solids concentration could be raised to 10%, the load of both resin flotation (including rougher and cleaner) and coal flotation would be reduced at least 50%. Consequently, the load on the tailing thickener would be decreased, too. As a result, the capital cost of the resin flotation plant would be reduced.
 - The ratio of solvent to solid in the resin refining complex was determined to be 1 liter per 200 gram of the resin concentrate having a grade of 70%. If this ratio could be increased by 50% or even 100%, both capital cost and operating cost of the resin refining complex would be reduced significantly.
 - As one can see from Tables 8-8 and 8-9, the utility costs for the refining plant comprise more than 1/3 of the operating costs and 84% of the utility costs is for steam. In order to decrease the steam cost, a process option is to extract the wet feed directly without predrying. In this way, the capital cost will also be reduced because the number of expensive steam-tube dryers will be reduced. According to laboratory results, a mixture of the resin-loaded hexane solution with water is very difficult to filter. On the other hand, the water contained in the extraction residue seems to act as an agglomerating reagent and to facilitate the settling of the fine residue particles from the pregnant hexane solution. Consequently, a centrifuge could be a suitable alternative to separate the fluids from the residue. However, only a few experiments were done. Further study is needed.
 - The schedule at the resin flotation and refining plants was set at two shifts per day which is the same as the existing coal preparation plant. If the recovery plant operated on a three-shift per day schedule, the capital cost might be reduced.
3. As expected from the estimation method used, this preliminary economic analysis is believed to have an accuracy of ± 50 .

9. CONCLUSIONS AND RECOMMENDATIONS

The research carried out on this project, "Refining of Fossil Resin Flotation Concentrate from Western Coal", covers several aspects of the fossil resin refining technology, namely, characterization of fossil resin flotation concentrate and its refined products, fossil resin extraction kinetics, effect of operating parameters, extraction solvents, proof-of-concept continuous refining tests, and technical and economic analysis. This research effort has led to the following findings and conclusions:

- 1) The fossil resin flotation concentrate from the Wasatch coal field has a relatively fine particle size distribution with more than 80% being less than 200 mesh (74 μm) and approximately 73% hexane-soluble resin content. Petrographic analysis shows that there is 12.7% coal fines in the concentrate. The hexane-refined product appears light-yellow in color, has a melting point of 140 - 142 $^{\circ}\text{C}$, density of 1.034 g/cm^3 , and good solubility in nonpolar solvents. These properties together with thermal setting and solvent release properties account for the fact that it is a superior chemical commodity for the ink industry.
- 2) Four solvents, hexane, heptane, toluene and ethyl acetate were used to evaluate the loading limit of the fossil resin in the solvent. Loading was only limited in the case of the polar solvent, ethyl acetate, in which case the solvent was saturated at 18 grams per 100 ml at 25 $^{\circ}\text{C}$.
- 3) Based on the analyses of Py-GC/EIMS spectra and FTIR spectra, it was found that the fossil resin is composed mainly of aliphatic components, partially aromatized multi-cyclic terpenoids and a few oxygen functional groups. The solvent-extracted resins show the presence of a relatively large number of methyl groups when compared to the number of methylene groups.
- 4) Heptane was used as the solvent in the extraction kinetic studies. Since heptane is an inert solvent, the main interaction between resin and heptane is expected to be the van-der-Waals forces of interaction associated with solvation phenomena. It was found that the extraction rate is independent of agitation intensity at room temperature, low solids concentration and moderate agitation. The initial extraction rate was found to be inversely proportional to the initial particle diameter. The temperature has a significant effect on the extraction rate and the activation energy for resin extraction by heptane was found to be 12.3 kcal/mole .

- 5) Batch extraction tests were carried out with an one liter reactor. Heptane was used as the solvent. The effects of several operating parameters on extraction were investigated, including the particle size (100 × 200 mesh, 270 × 400 mesh and minus 400 mesh), the stirring speed (500 to 1200 RPM), the temperature (20 to 60 °C) and the solids concentration (50 g/liter to 200 g/liter). It was found that:
- the resin extraction rate is not significantly affected by the agitation intensity and low agitation should be suitable for the extraction process;
 - the effect of resin particle size on the extraction rate and yield is obvious;
 - the effect of solids concentration on the extraction rate is moderate;
 - the effect of temperature on the rate and yield of extraction is very significant. In order to increase the productivity and yield of the resin extraction, a higher temperature should be considered for an industrial process.
- 6) Differential refining tests show that the extent of coloration of the refined resin, which is an undesired feature, increases as the extent of extraction increases. Using heptane or hexane as the solvent, a quality resin product can always be produced. If a strong solvent, such as toluene, is used for resin extraction, a significant amount of dark resin (>5%) can be extracted, which decreases the quality of the refined resin product.
- 7) Heptane was used in batch extraction tests to investigate the effect of recycled solvent. It was found that the resin yield in the recycled solvent is only about 1% lower than in the fresh solvent at room temperature for 1 hour extraction time. Increasing the extraction temperature to 50 °C reduced the difference to 0.4%.
- 8) A continuous refining test circuit with a capacity of 1 lb/hr was designed and built. The proof-of-concept continuous refining circuit resulted in almost same extraction efficiency as obtained from the laboratory bench-scale tests. The results from the continuous tests have demonstrated the success of the solvent refining process. It was also found that:
- raising the temperature could significantly increase the resin recovery and extraction rate;
 - after 10 minutes of extraction, the effect of average residence time on resin recovery is moderate;
 - for resin concentrate/solvent ratios of more than 0.15 by weight extraction is diminished but can be offset by longer residence times.
- 9) Based on the continuous tests, heptane increases the extent of resin recovery compared to hexane. However, heptane has a much higher boiling point than hexane, consequently, more energy is needed when separating the refined resin from the heptane solution. It appears then, from an economic perspective, that hexane is a more appropriate solvent

than heptane. On the other hand, when toluene is used as the solvent, it is almost impossible to separate the pregnant resin solution from the solid residue by filtration probably because the toluene solvent releases more very fine insoluble residue particles. Toluene also extracts some undesired dark resin which would result in a product of significantly lower value.

- 10) A preliminary technical and economic feasibility study was completed for a fossil resin flotation and refining plant with a capacity of approximately 40 million pounds of refined resin per year. A 20 year life time was considered for the plant. It was estimated that an internal rate of return (IRR) of 23.4% and a 3-year payback period can be achieved.

Based on the results of this study, it is recommended that a more detailed feasibility study be conducted with emphasis on estimation of capital cost and the operating costs, fossil resin resource evaluation, and further investigation of the market for the refined resin product. Sensitivity analyses on economic sensitive variables, such as the resin content of the coal fines, the plant size, the total capital cost, the operating cost, the sales volume and the sales price, are also needed.

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