

## FOSSIL RESIN, A VALUE-ADDED PRODUCT FROM WESTERN COAL

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### ABSTRACT

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, Wyoming, etc. The Wasatch Plateau coal field in Utah (Figure 1) has a particularly high content of fossil resin. It has been reported that many seams in this field average as much as 5% resin. 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. This practice represents an inappropriate use of a valuable resource. Solvent-refined resin, at the present time, has a market value of \$0.50-0.70/lb as a chemical commodity and can be used in the ink, adhesive, rubber, varnish, enamel, paint and coatings, and thermoplastics industries. It is evident that our fossil resin resource is being wasted for electric power generation.

Improved process technology for a viable fossil resin industry is under development and includes selective flotation of fossil resin from fine coal streams, solvent refining of the fossil resin concentrate, and decoloration of the refined product to produce a premium resin product. Recent developments in process technology are discussed with respect to technological limitations. It is clear that the creation of a \$100 million dollar per annum fossil resin industry is not limited by process technology. Nor is it limited by economic considerations. Other peripheral factors appear to account for the reluctance of the Utah coal industry to move forward on this initiative.

### 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, Wyoming, etc. The Wasatch Plateau coal field in Utah (Figure 1) has a particularly high content of fossil resin. It has been reported that some seams in this field average as much as 5% resin [1-5].

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.

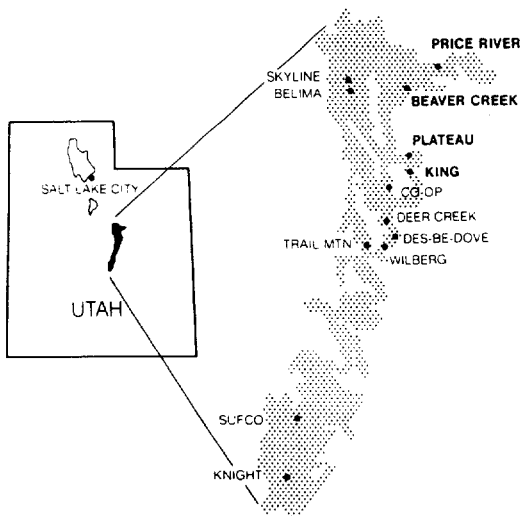


Figure 1. Mine locations in the Wasatch Plateau coal field. Preparation plants located at Price River, Beaver Creek, King and Plateau [6].

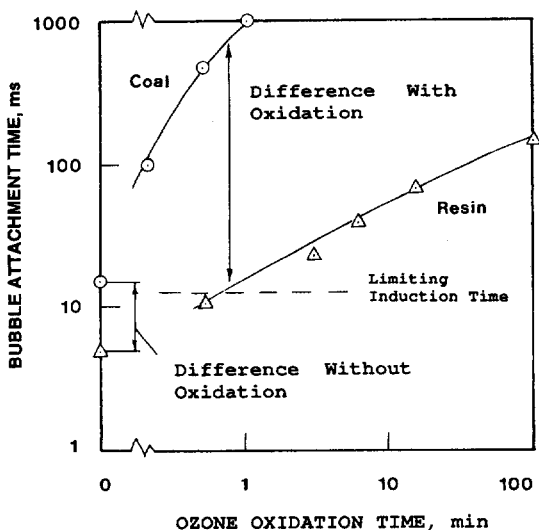


Figure 2. The effect of oxidation time on the hydrophobicity of coal and fossil resin as revealed by changes in bubble attachment time [6].

Fossil resins have 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. Of the four existing coal preparation plants in the Wasatch Plateau coal field (U.S. Fuel, Plateau, Beaver Creek, and Price River), resin has only been recovered intermittently from the U.S. Fuel Plant, where a small amount of this valuable resource (<1 million pounds per year) was recovered by flotation (50% recovery from the fines) as an impure concentrate containing about 50% resin. The chronology of the Utah fossil resin industry is given in Table 1.

Of course the resin flotation concentrates thus produced are purified by solvent refining (such as hexane extraction) and evaporation of the solvent. Solvent-purified resins from the Wasatch Plateau coal field are primarily sesquiterpenoids and typically have a molecular weight of about 1200, a melting point of about 170°C, and an iodine number of about 145. This product, at the present time, has 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. 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 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 — equivalent to the value of the coal itself!! The waste of this valuable resource is evident. Steps must be taken to correct this situation and to use our fossil resin resources in a more appropriate manner. The development of such a fossil resin industry will also allow us to use more of our petroleum resources for liquid fuels and relax the demand for petroleum imports.

TABLE 1.  
Historical Review of the Utah Fossil Resin Industry

Year	Company	Concentration Process	Refining Process
1930s	Andriaan Nagelvoort	Sink/Float	Toluene Extraction
1940s	Combined Metals Corp. I.P.I.	Gravity Flotation	Hexane Extraction
	U.S. Resin Corp	Flotation	Hexane Extraction
1973	Hercules Powder Co. (Blackhawk Resin)	Flotation	Hexane Extraction
1983	American Resins	Flotation	Hexane Extraction
1985	US Fuel, CPS	Flotation	Hexane Extraction

In view of these factors, the waste of a valuable resource and the special characteristics of the fossil resin product, researchers at the University of Utah have made significant efforts to develop improved technology for a fossil resin industry in the western coal fields. These efforts include selective flotation, solvent refining, and decoloration of the refined product.

### SELECTIVE FLOTATION OF FOSSIL RESIN

Based on the limited difference in hydrophobicity between fossil resin and other coal macerals conventional flotation for efficient fossil resin recovery is unsatisfactory [6]. Even with traditional polymeric depressants, resin recovery is limited to 50% at a concentrate grade of 50% resin. In this regard, several selective flotation procedures have been developed during the past decade [7-9].

#### Surface Oxidation

One approach is based on the discovery that controlled surface oxidation can be used to accentuate the difference in hydrophobicity [6, 7, 10]. For example, in the case of ozone oxidation the surfaces of all coal macerals except resinite react rapidly to significantly increase the hydrophilic state of the coal surface as shown by the bubble attachment time data presented in Figure 2. Resinite particles react slowly and retain their hydrophobicity so that selective flotation can be achieved. Using the ozone technology it has been possible to produce resin concentrates containing 95% resin at a recovery of 80% [6].

#### Dispersion by pH Control

Another approach is based on the findings that the heterocoagulation between resin and coal particles, which also contributes to the inefficiency of the flotation separation, can be controlled by pH adjustment. In this regard, the state of dispersion and coal hydrophobicity can be controlled for selective resin flotation if the pH is adjusted to an appropriate level, between pH 8 and 12, depending on the resinous coal type and previous treatment [8, 9].

As is evident from the data presented in Figure 3, excellent fossil resin concentrates (80% resin) can be produced at a high level of recovery (80%) if the pH is maintained in the alkaline pH region. The exact pH necessary for the selective separation of course depends on the resinous coal sample.

As a result of these research efforts, a proof-of-concept test program was supported by DOE to evaluate the selective resin flotation technology in a 0.1 tph pilot plant, operated by Advanced Processing Technologies, Inc. under subcontract from the University of Utah.

The results from the POC program have been very successful. In summary, the test program has demonstrated that:

- (1) technically, the new flotation technology provides a highly efficient means to selectively recover fossil resin from coal. The proof-of-concept continuous flotation circuit resulted in fossil resin recovery with the same separation efficiency as was obtained from the laboratory bench-scale testing (more than 80% recovery at about 80% concentrate grade); and
- (2) economically, the selective resin flotation process has been evaluated and found to be sufficiently profitable to justify the development of a fossil resin industry based on this new flotation process [11].

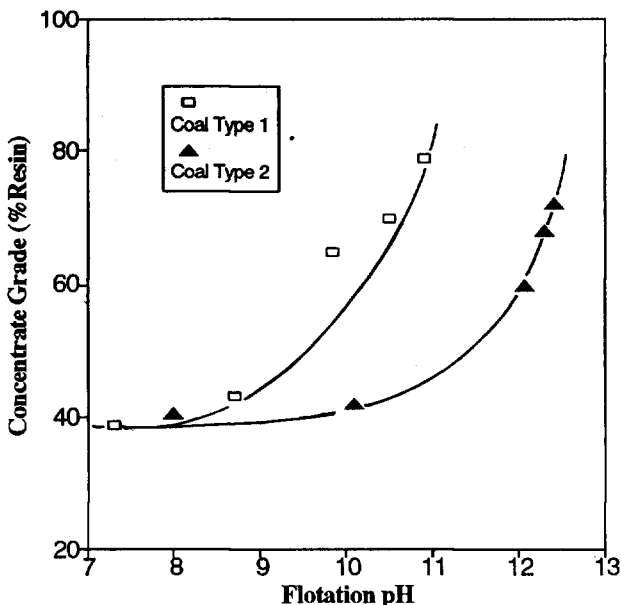


Figure 3. The significance of pH control for the selective flotation of fossil resin [9].

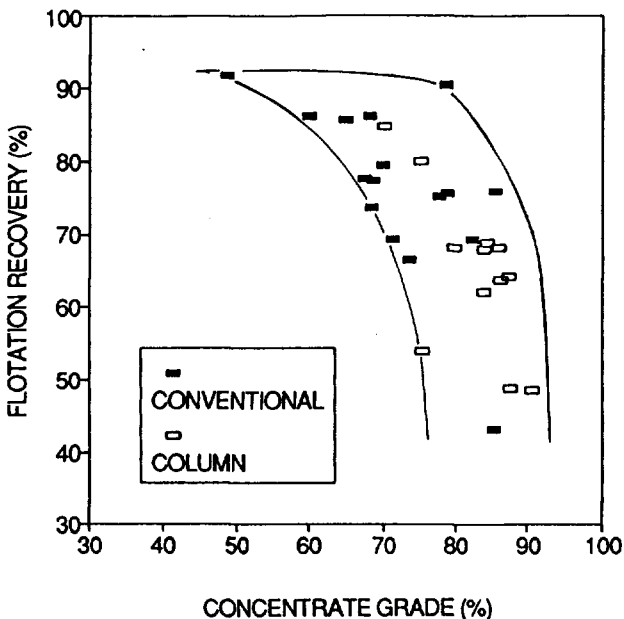


Figure 4. Pilot-plant comparison of conventional two-stage flotation with single-stage column flotation (wash water chemistry control) for selective fossil resin recovery [9].

## Column Flotation with Wash Water Chemistry Control

Finally the selective fossil resin flotation can be accomplished either with a multistage conventional flotation circuit or by column flotation. Of particular interest in column flotation is the opportunity to operate the system by control of the wash water chemistry, and under these conditions excellent separation efficiencies can be achieved as shown in Figure 4 [9].\*

### **SOLVENT REFINING OF FOSSIL RESIN CONCENTRATES**

For some time, hexane and other solvents have been known to dissolve resinite from resinous coals and based on this property hexane extraction for solvent refining of fossil resin concentrate has been practiced industrially beginning in the 1940's. Since that time, several companies have been involved in the fossil resin industry (Table 1), but none of them has successfully produced large quantities of fossil resin for the market. Actually, the last company to produce and sell Utah-refined fossil resin was Hercules, Inc. This production of about 1-2 million pounds per year continued until a fire destroyed the solvent refining plant in the mid 1970s. At present, a fossil resin product is not being produced from Utah coal. Although it has many outstanding properties and a significant market potential exists (200 million pounds per year), fossil resin has never been available in large quantities. It has been in and out of the market five or six times. The quality of the refined fossil resin product has varied considerably depending on refining practice, and the future remains uncertain. For these reasons, a research and development effort on fossil resin refining is now in progress.

Of particular concern in the solvent refining of fossil resin concentrates is the color of the refined resin product. The light-colored resins demand a premium price in the marketplace. In this regard, molecular characterization of fossil resin is an important consideration and analysis of the resin components has helped to identify the color inducing compounds that are present in resins [5]. Since the dark color of the resin diminishes its market value, these results should help develop refining techniques to enhance the economic value of the resin resource.

It has been found from the characterization studies that four resin types, namely yellow, amber, light-brown, and dark-brown in color, occurring in the Wasatch Plateau coal field, are mainly composed of aliphatic components, with a low content of partially aromatized multi-cyclic terpenoids, and a few oxygen functional groups (such as -OH and -COOH). Their molecular weight and aromaticity were shown to increase in the following order yellow < amber < light-brown < dark-brown resin [5]. All resin types show the presence of a relatively large number of methyl groups when compared to the number of methylene groups, and this indicates the presence of extensive branching in the carbon chains. In contrast coal consists primarily of aromatic ring structures, various oxygen functional groups (-OH, >C=O, -C-O) and few aliphatic chains. The color difference observed among the four hand-sorted resin types is explained in part by the presence of finely dispersed coal particle inclusions in the resin matrix. In addition, however, the presence of chromophores accounts for some coloration at the molecular level which may remain after solvent refining. It is evident that the solvent refining of fossil resin is a necessary step to purify and control the quality of final resin product as a chemical commodity. Both extraction kinetics and solvent type have significant impact on the final resin product's characteristics, including recovery, color, melting point, molecular weight, and so on. It has been found that the extraction rate follows the order yellow > amber > light-brown > dark-brown. Hexane-extracted resin from all four resin types closely

resembles the properties of the physically separated yellow resin.

It is believed that fossil resins consist generally of three major components: (1) sesqui- and tri-terpenoid (monomers, dimers and trimers); (2) some content of alcohols, ketones, and acids; and (3) a small amount of aromatized hydrocarbons. The four resin types also show distinct differences among certain physical and chemical properties such as density, and softening point [5]. All these properties were noted to change gradually from yellow to dark-brown resin.

Of course toluene is a stronger solvent for fossil resin extraction than hexane, and a higher percentage of the fossil resin can be recovered. Such a high extraction is expected due to the fact that hexane is a non-polar solvent while toluene is weakly polar with a permanent dipole and  $\pi$ -electron system that provide for a stronger interaction with or penetration into the resin grains. On the other hand toluene, being a more polar solvent, also extracts extraneous polar molecules imparting a darker coloration to the refined resin product.

Although the light-colored resins are of greater value in the ink industry, the dark-colored resins also have other industrial applications. It has been found that in some cases a significant amount of the fossil resin flotation concentrate is dark resin (more than 60% by weight). Therefore, the identification of color inducing compounds in fossil resins and their characterization are of great commercial interest.

### DECOLORATION OF REFINED PRODUCT

As mentioned previously, colorless or nearly colorless resins demand a premium price in the marketplace. The economic value of fossil resins can be dramatically enhanced if they are decolorized without affecting their other properties. The color of the resins can be attributed, in part, to the presence of various chromophores that are present even in refined resins. Among these chromophores are the conjugated olefinic linkages in association with such functional groups as carbonyl, amine, and thionyl groups. The oxygen and nitrogen content of fossil resin is significant, and the presence of carbonyl and amine groups has been verified by infrared characterization studies [5]. In addition, the  $^{13}\text{C}$ -NMR and GC-MS analyses of these resins have indicated the presence of aromatic moieties.

Decoloration of refined resins by chemical methods involves deliberate chemical reactions. These chemical reactions would have to be broad in scope, as the exact nature of the compounds present in resins is at best guess-work. As stated earlier, the color of the resins is most likely due to the presence of some chromophoric functionalities; therefore, a chemical reaction to engage these functional groups is envisioned. Catalytic hydrogenation is a powerful means of achieving controlled transformations of organic compounds. The effectiveness of a hydrogenation reaction is well documented in the petroleum-refining processes. Hydrogenation not only diminishes the unsaturated character of the resins by the addition of hydrogen across the olefinic linkages, but with a proper choice of catalysts it is also capable of reducing the partially aromatized multi-cyclic compounds, aromatic compounds, compounds containing functional groups involving nitrogen, oxygen and sulfur atoms, and finally heterocyclic compounds.

Hydrogenation has the potential to diminish the presence of chromophores in the resins and bring about decolorization, but it also could affect the desirable properties of resins. However, a controlled hydrogenation can be accomplished with selection of a suitable catalyst and other process variables so that it is possible to determine the thresholds of improving the color of the resins but not radically altering their properties in the process.

The resin hydrogenation reaction can be carried out in the liquid phase in an autoclave using a suitable solvent. The temperature and the choice of solvent constitute important variables. Perhaps the most important variable is the choice of a catalyst. Generally, there are three types of catalysts used in hydrogenation reactions. These consist of single metal, combination of metals, and dispersed metallic sites on support materials such as graphite, alumina, and silica. Supported metal catalysts such as Ni-Mo and Ni-W are most frequently used. The choice of a catalyst also depends on the feed material. Since there is no literature on hydrogenation of fossil resins, the initial choice of the catalyst and other variables will have to be conducted on a trial-and-error basis. The literature survey of similar hydrogenation reactions applied to petroleum-refining processes indicates that the temperature can be varied in the 150–400°C region.

## ACKNOWLEDGMENTS

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