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REFINING OF FOSSIL RESIN FLOTATION CONCENTRATE FROM WESTERN COAL

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The research work conducted during the third quarter of the project "REFINING OF FOSSIL RESIN FLOTATION CONCENTRATE FROM WESTERN COAL" has been emphasized on Task 3 (Batch Kinetics Experiments). This task was designed to be conducted in such way as to provide a fundamental understanding of the fossil resin refining process and to determine major factors which control the resin extraction. The ultimate objective of the batch extraction study is to provide the basis for subsequent design and construction of a continuous resin refining circuit. This phase of study is divided into two categories:

- . Fundamental study of resin extraction kinetics;
- . Batch experiments on solvent refining of the fossil resin concentrate.

1. Fundamental Study of Resin Extraction Kinetics

1.1 Experimental

A series of experimental tests under different conditions (temperature, particle size and agitation intensity) were designed to study these effects on the resin extraction rate with monosize particles at a low solids concentration. The resin extraction kinetics were determined by analysis of extracted resin solutions taken at certain time intervals during extraction process.

Materials

Technical grade heptane (C_7H_{16}) was used as solvent for the kinetics study. Heptane has a molecule weight of 100.21, density of 0.684 gram/cm³ and boiling point of 98 °C.

The fossil resin sample used in the experiments was the flotation concentrate obtained from the Wasatch Plateau coal. Four monosize samples were prepared from this resin concentrate by wet screening. The heptane-soluble resin contents in all samples were determined

with a TX-6 Soxhlet extraction unit at the boiling point of heptane (98 °C) for about 6 hours and the results are listed in Table 1.

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

Particle Size of Resin Sample (mesh)	Mean Particle Size (μm)	Heptane-Soluble Resin Content %
8×10	2003	95.45
28×35	505	92.92
48×60	274	88.67
100×150	126	90.46

Resin Concentration Analysis

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 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 Fig. 1.

Experimental Apparatus and Procedure

A schematic figure of the experimental apparatus used for the kinetics study is presented in Fig. 2. All resin extraction tests were carried out in a one liter round bottom 3-neck distillation flask. A thermometer, a condenser, and a stainless impeller were placed into the flask

through the three neck openings. The impeller was connected to a motor through a Chesapeake stirrer connection at the center port. The agitation of resin/solvent solution was accomplished with a motor and control system to control the speed of rotation. The flask was submerged in a circulating water bath to control the temperature with an accuracy of ± 0.5 °C.

One liter of pure heptane was taken into the flask together with about 1.1 to 1.5 gram of the monosize sample at a particular temperature for each test. During the extraction process, about 3 ml of 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 a UV/Vis spectroscopy as described previously. All the data presented in the following sections were normalized on the basis of the heptane-soluble resin content in the samples.

1.2 Interpretation of Experimental Results

The effects of resin particle size, extraction temperature and agitation intensity (stirring speed) on the resin extraction rate have been studied and are presented herein.

Effect of Resin Particle Size

The effect of particle size on the resin extraction rate at 20 °C and 500 RPM is presented in Fig. 3. It is evident that the extraction rate decreases with an increase in extraction time, which is to be expected from geometric consideration. As shown in Fig. 3, a strong dependence of resin extraction rate on particle size was found. The initial resin extraction rates are plotted against the inverse of the initial resin particle size in Fig. 4 and the linear relationship suggests that the rate may be limited either by mass transfer or by surface reaction.

Effect of Temperature

Several resin extraction tests at different temperature were performed in order to determine the effect of temperature on the extraction rate and the results are plotted in Fig. 5. The resin extraction rate is found to increase with an increase in extraction temperature. The effect of temperature is very significant. The initial extraction rates at different temperature are plotted according to the Arrhenius equation in Fig.6. As shown in Fig. 6, a good linear relationship between the logarithm of the initial extraction rate and inverse temperature is observed. From Fig. 6, the slope of this linear relationship, an activation energy of 15.5 kcal/mole can be calculated based on the Arrhenius equation ($\ln k = \ln A - E/RT$). The magnitude of the activation energy indicates that the extraction process is mainly controlled by a surface reaction mechanism involving the dissolution of resin molecules into the heptane solution. As such, energetics of the solvation reactions are expected to be related to the observed activation energy.

Effect of Agitation Intensity

The effect of agitation intensity on extraction rate is presented in Fig. 7 in terms of stirring speed (RPM). It is found that the agitation 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).

1.3 Kinetic Model for Resin Extraction

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 typical kinetics analysis for a shrinking core geometry. The principal methodology used in describing mineral particle leaching processes may be applied to study resin extraction kinetics. However, it should be noted that resin extraction has special features. For example, the composition of fossil resin particles is known to be heterogeneous in terms of its macro and microstructure as well as its chemical composition. It has been found that fossil resins from the Wasatch Plateau coal field have four different macroscopic resin types classified according to color -- yellow, amber, light-brown and dark-brown. These fossil resins consist of polymers and copolymers of a large number of different monomers such as terpenoids, sesquiterpenoid dimers and some trimers with an average molecule weight of 1000-1700. Different components of the fossil resin are expected to have different dissolution rates in an organic solvent. Some of these compounds are so highly polar that even toluene is incapable of dissolving them.

To describe the resin extraction process, a simplified mathematic model can be obtained for isometric particles. Assuming that the extraction rate is controlled by a surface reaction, the relationship between the extent of extraction (α) and the extraction time (t) has been well established for a shrinking core model in a batch system and for a constant reactant (heptane) concentration,

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

where k is the overall rate constant which includes reactant concentration and many other factors such as surface area, rate constant, initial particle size, shape factor, fraction of resin sites on the

particle surfaces et cetera. The constant, k , is inversely proportional to the initial particle size. However, this shrinking core model can not fit the data shown in Fig. 3. It is expected that some of these other factors vary with time and thus the kinetics analysis must be considered in more detail.

To begin with, the resin extraction rate can be expressed by shrinking core model with surface reaction control

$$\text{Extraction rate} = - \frac{dn}{dt} = A C k_0 k' \quad (2)$$

where,

n is the unreacted number of moles of the soluble resin in a solid;

t is extraction time (minute);

A is the surface area of the resin particles (cm^2);

C is the solvent concentration on the surface (mole/cm^2);

k_0 is the fraction of solvent-soluble resin sites on the surface;

k' is the rate constant (minute^{-1}).

Assuming the resin particles to be spherical shape, the following equation can be derived

$$\frac{d\alpha}{dt} = \frac{6VCk_0k'}{d_0} (1 - \alpha)^{\frac{2}{3}} \quad (3)$$

where,

α is the particle fraction of the resin dissolved in solution;

V is the molar volume of the solvent-soluble resin (cm^3/mole);

d_0 is the initial diameter of the resin particles (cm).

Since the solvent (heptane) is excessive, C can be considered as a constant. From previous characterization studies, it was found that the fossil resin particles are heterogenous in the microscopic and chemical composition, particularly for light-brown and dark brown resin particles which constitute a major fraction of the resin concentrate. The results as obtained from fluorescent microscopy indicated that only yellow resin is homogenous in appearance and all other resin types show inclusion of what appear to be various fine coal particles which are insoluble in hexane or heptane. These carbonaceous particles were found to vary in particle size ($\sim 200 \mu\text{m}$) and gradually increase in number from amber to dark brown resin. These fine coal particles and insoluble inclusions existing in the resin matrix will decrease the exposure of resin compounds during the extraction process and only those resin molecules exposed at the surface of the resin particles can be readily extracted into solution. Thus, only the resin exposed on the resin particle surface will significantly contribute to the extraction rate. As the extraction process progresses, the exposed soluble resin at the particle surface decreases or k_0 becomes smaller. Generally, the following relationship may be established:

$$k_0 = f\left(\frac{d}{d_0}\right) \quad (4)$$

For simplicity, k_0 can be expressed as an exponential function of d/d_0 , that is

$$k_0 = B\left(\frac{d}{d_0}\right)^n \quad (5)$$

where,

d is the diameter of particles at time t ;

B and n are constants.

Substitution of Eq. (5) into Eq. (3) results in

$$\frac{d\alpha}{dt} = K(1 - \alpha)^{\frac{1}{3}} \left(\frac{d}{d_0}\right)^n \quad (6)$$

where

$$K = \frac{6VCBk'}{d_0} \quad (7)$$

For spherical particles,

$$\frac{d}{d_0} = (1 - \alpha)^{\frac{1}{3}} \quad (8)$$

By integration of Eq. (6),

$$(1 - \alpha)^{-\frac{n-2}{3}} = K't + 1 \quad (9)$$

where

$$K' = \frac{3}{n-2}K \quad (10)$$

Using a curve fitting technique, n was found to be 5. Therefore,

$$\frac{1}{1 - \alpha} = K't + 1 \quad (11)$$

According to Eq. (11) a plot of $1/(1-\alpha)$ vs extraction time, t should give a straight line from which the slope K' can be determined. Such plot is shown in Fig. 8 which reveals the linear relationship expected. According to Eq. (11), it can be derived

$$\frac{d\alpha}{dt} = K' \quad \text{at } t=0 \quad (12)$$

Eq. (12) shows that the initial rate of the extraction process should be equal in numerical value to K' . The K' values obtained from curve fitting are plotted in Fig. 4. In comparison with experimental data which were measured from Fig.3, the results are satisfactory.

1.4 Brief Summary of Resin Extraction Process

As concluded from our characterization study, it is known that fossil resin is mainly composed of aliphatic components, partially aromatized multicyclic compounds with a small number of oxygen functional groups. The solvent, heptane, is also a nonpolar aliphatic compound. It is expected that no chemical reaction will 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 should be largely 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 significant effect on extraction rate and the activation energy for resin extraction by heptane was found to be 15.5 kcal/mole. The resin extraction kinetics can be expressed by the following equation

$$\frac{1}{1 - \alpha} = K't + 1$$

2. Batch Experiments on Solvent Refining of the Fossil Resin Concentrate

In order to provide the necessary information to describe a continuous solvent refining process, some batch solvent refining experiments have been carried out at high solids concentrations (50-200 g/l). The results are presented herein.

2.1 Experimental

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

The extraction apparatus used for the batch tests is similar to that as shown in Fig. 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, condensation, thermometer, and sampling & feeding. For batch extraction tests, the composite resin concentrate was first taken into the kettle. Then 1000 ml of heptane at desired temperature was poured into the reactor. Agitation and extraction time were 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. The experiments were performed to investigate the effect of four major extraction factors, agitation intensity, particle size, temperature and solids concentration.

2.2 Results and Discussion

Effect of Particle Size

The effect of particle size on the extraction process is shown in Fig. 9. The tests were carried out at 700 RPM and 20 °C with a 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 -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 Fig. 10. The experiments were carried out for the composite resin concentrate at 100 grams of solids per liter of solvent and 20 °C. As shown in Fig. 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 very low level and still achieve satisfactory extraction rate.

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 Fig. 11 where it is evident that the extraction rate rose largely 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 in solution on the extraction process is shown in Fig. 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 impact the subsequent filtration and solid/liquid separation process.

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 is obvious. Because of the fine size of the composite resin concentrate (80% minus 200 mesh), the extraction reaction occurs in reasonable times and 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.

3. Further Work for More Batch Extraction Tests

1) Determine optimum solvent extraction conditions such as temperature and percentage solids.

2) Develop a predictive model for solvent extraction of the resin concentrate.

3) Test other solvents such as toluene, hexane in batch experiments.

4) Characterize and evaluate the solvent refined resin products.

5) Examine the effect of solute loading on the extraction kinetics.

Fig. 1 UV/Vis calibration curve
for dissolved resin in heptane

Fig. 3 Effect of resin particle size on extraction rate

Fig. 4 Initial extraction rate vs. the inverse of the resin particle size

Fig. 5 Effect of temperature on extraction rate

Fig. 6 Arrhenius plot for heptane extraction of 48x60 mesh resin particles

Fig. 7 Effect of stirring speed on extraction rate

Fig. 8 Kinetic model of resin extraction

Fig. 9 Effect of resin particle size on the rate and extent of extraction

Fig. 10 Effect of stirring speed on the rate and extent of extraction

Fig. 11 Effect of temperature on the rate and extent of extraction

Fig. 12 Effect of solids concentration on the rate and extent of extraction

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