

to know the detailed kinetics of the secondary interactions represented by reaction 1 and CO chemisorption/desorption as a function of experimental conditions. The kinetics of these processes depend upon the nature of the char pore structure in terms of pore size distribution and the locations within this structure where the complexes are formed. This, in turn, depends upon the manner in which porosity is developed by gasification, the rate of gasification, the degree of order of the subject carbon, and the type and amount of inorganic impurities. A fundamental understanding of carbon gasification via oxidizing agents, however, requires the resolution of these issues.

In any case, the most important conclusion to be drawn and the caution that is given here are that secondary interactions can significantly affect TPD spectra of oxidized coal chars and, perhaps, other carbonaceous materials and that such spectra may not necessarily be reflective of the true original state of surface oxygen complexes.

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Registry No. CO₂, 124-38-9; CO, 630-08-0.

Role of Induction Time and Other Properties in the Recovery of Coal from Aqueous Suspensions by Agglomeration with Heptane

C.-W. Fan, Y.-C. Hu, R. Markuszewski, and T. D. Wheelock*

Ames Laboratory and Department of Chemical Engineering, Iowa State University, Ames, Iowa 50011

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The percent recovery of fine coal or graphite particles suspended in water by agglomeration with heptane was highly dependent on the measured induction time, i.e., the gas bubble to particle attachment time of the material. The induction time was found to correlate closely with the heat of immersion of the solids in water, another indicator of the hydrophobic/hydrophilic character of the material. For a series of coals and graphite, the agglomeration recovery decreased exponentially with increasing induction time. For the more oleophilic coal or graphite particles, an increase in salt (NaCl) concentration of the suspending medium caused an increase in agglomeration recovery and a decrease in induction time. For the less oleophilic coal or pyrite particles, an increase in salt concentration caused a decrease in agglomeration recovery and an increase in induction time. Due to the opposing effects of salt concentration on the recoveries of a highly hydrophobic coal and pyrite, it was possible to improve the separation of these materials by an increase in salt concentration. On the other hand, because the recoveries of pyrite and a weakly oleophilic coal were affected similarly by an increase in salt concentration, it was not possible to improve the separation of these materials.

Introduction

The selective agglomeration of ultrafine coal particles suspended in water by bonding the particles with oil or hydrocarbon liquid such as pentane or heptane is the basis for several proposed coal cleaning processes.¹⁻⁴ Following agglomeration, the suspension can be screened to recover the agglomerated coal from unagglomerated mineral particles. The method takes advantage of the greater hydrophobicity and oleophilicity of the coal compared to that of the mineral matter. Generally the competition between oil and water for the particle surfaces favors oil in the case of coal and water in the case of mineral matter. Among

the most commonly occurring minerals in coal, only iron pyrite appears to be sufficiently oleophilic to interfere with separation from coal by this method. However, the oleophilicity of pyrite is quite variable and depends on treatment conditions.

Strongly oleophilic materials respond more favorably to oil agglomeration than weakly oleophilic materials.^{1,5-7} Thus, when heptane was employed as an agglomerant, Drzymala et al.⁷ found that the amount of material recovered per gram of heptane (i.e., the specific recovery) increased with increasing oleophilicity of the material as indicated by the oil receding three-phase contact angle for the heptane-solid-water system. Other work^{8,9} showed

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Table I. Sources and Properties of Coal Samples

	Upper Freeport	Pittsburgh	Illinois No. 6	Iowa
source	Indiana County, PA	Belmont County, OH	St. Clair County, IL	Monroe County, IA
mean diam, ^a μm	34	39	43	42
tot. sulfur, %	2.10	4.03	2.62	3.06
proximate anal., %				
fixed carbon	62.4	48.2	46.5	45.0
volatile matter	26.8	40.6	34.5	39.1
ash	10.4	9.8	9.7	12.4
moisture	0.4	1.4	9.3	3.5
tot.	100.0	100.0	100.0	100.0

^a Mean diameter of particles used for oil agglomeration.

that the specific recovery of a strongly hydrophobic coal was increased by an increase in the salt content or ionic strength of the suspending medium, whereas the specific recovery of pyrite was reduced. While these results were encouraging because increasing the specific recovery of coal and improving the separation of coal and pyrite would improve the economic feasibility of the method, not all coals seemed to respond in the same way to a change in salt concentration. Therefore, the present study was undertaken to obtain a clearer picture of the interaction between coal surface properties and salt concentration.

One widely used method of surface characterization is to measure the three-phase contact angle for either the air–solid–water system or the oil–solid–water system. The former is regarded as a measure of hydrophobicity whereas the latter is regarded as a measure of oleophilicity. Unfortunately, this method generally requires a flat, polished surface, and it is not very sensitive when determining the equilibrium contact angle. Also it is questionable whether the wettability of a polished surface is the same as that of the small granular particles treated by oil agglomeration. Therefore, other methods of surface characterization were sought, and two other methods were found subsequently to correlate well with oil agglomeration recovery. One of these methods involved measuring the so-called induction time and the other method involved measuring the heat of immersion of fine particles in water.

The induction time was taken to be the time required for attachment of one or more particles to a small air bubble when the bubble is brought into sudden contact with a layer of particles submerged in water.¹⁰ The attachment time is believed to be a combination of the time required to thin the water film between a particle surface and the air bubble to the point of rupture (considered true induction time) and the time required to displace the film.^{11,12} Since the attachment time or induction time is based on a dynamic measurement, it depends on the kinetics and hydrodynamics as well as the thermodynamic properties of the system.^{10–14} Thus, particle attachment time has been found to depend on both particle size and density as well as on interfacial properties. Consequently, particle size and density must be controlled while the interfacial properties of different materials are compared by this method.

Provided certain conditions are satisfied, the heat of immersion ($-\Delta H$) of a fine powder in water per unit surface

area has been shown to be proportional to $\cos \theta$, where θ is the three-phase contact angle measured through the water phase for the air–solid–water system.¹⁵ Therefore, the heat of immersion is another measure of hydrophobicity, and it has been used by various workers^{16,17} to compare the relative hydrophobicity of different types of coal and mineral matter.

In the present study, the surface of coal and graphite particles was characterized by measuring the bubble–particle attachment time and the heat of immersion of the materials in water. The response of these materials to agglomeration with heptane was determined by measuring the percent recovery of each material with a given amount of heptane. Different types of coal were utilized, which ranged from weakly hydrophobic to strongly hydrophobic. In addition, the effect of salt (NaCl) concentration on coal recovery and induction time was determined for the various coals, graphite, and mineral pyrite.

Materials and Experimental Methods

Samples of coal were obtained from various sources as indicated in Table I. The Upper Freeport coal is a medium-volatile bituminous coal whereas the other coals are high-volatile bituminous coals. Relatively pure samples of graphite from Sri Lanka and mineral pyrite from Huanzala, Peru, were obtained through Ward's Natural Science Establishment. These materials were ground in the dry state with a high-speed impact mill and then screened. Since no special measures were taken to prevent oxidation of the pyrite surface, the surface was oxidized to some extent by the time it was used. For the agglomeration experiments the materials were suspended in deionized water having a resistivity of 17.9 M Ω cm and agglomerated with heptane from Eastman Kodak Co. The specified normal boiling point of this material was 98 °C.

The agglomeration experiments were carried out with a specially designed closed system so that the operation was conducted without air present.¹⁸ The system utilized the motor and agitator from a 14-speed kitchen blender, but the open container furnished with the blender was replaced by a 500-mL glass jar that was nearly square in cross section. A small hole had been drilled in the bottom of the jar, which was plugged with a rubber septum. During operation the jar was inverted, and heptane was introduced through the septum with a hypodermic syringe. For each experiment, the jar was completely filled with an aqueous suspension containing either 10 g of coal or graphite or 3 g of pyrite. In some experiments a suspension containing a mixture of coal and pyrite was employed. The suspension at its natural pH was conditioned for 3 min at high speed (about 18 000 rpm), and then a predetermined amount of heptane was introduced. Agitation was continued at high speed for 3 min to produce agglomerates. The

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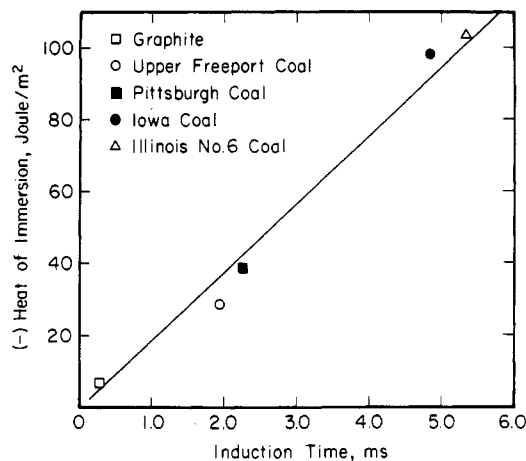


Figure 1. Correlation between heat of immersion and induction time.

agglomerates were recovered on a 100-mesh screen (U.S. Standard), dried in an oven for several hours at 100–110 °C, and weighed. When a mixture of coal and pyrite was treated, the total sulfur and ash contents of the product were determined, and sulfur and ash balances were used to calculate the recovery of the coal and pyrite, respectively.

The so-called induction time of the various materials was measured with a special apparatus¹⁹ using the procedure described previously.^{10–12} For this measurement, –100/+140-mesh coal or graphite particles and –200/+325-mesh pyrite particles were employed. The particles were spread in a thin layer under water and a 2-mm-diameter air bubble was formed on the end of a capillary just above the layer of particles. The initial gap between the captive bubble and the surface of the particles was set at approximately 0.1 mm. The bubble was subsequently brought into contact with the particles for successively longer contact times, and the number of particles that adhered to the bubble was noted. The induction time was taken to be the minimum contact time that resulted in particle attachment in 5 out of 10 trials.

For the heat of immersion measurement the materials were prepared by grinding and screening them in air to provide –200/+400-mesh particles. The particles were stored over Drierite in a desiccator, which was outgassed with a rotary vacuum pump. The moisture content of the stored materials, determined by drying samples at 140 °C for several hours, was about 1.5% for most of the samples of coal and graphite. The exception was Illinois No. 6 coal, which had a moisture content of 0.8%. The heat of immersion of the different materials in deionized water at 25 °C was determined by the isoperibol method (an essentially adiabatic method) using a Tronac Model 450 microcalorimeter. In addition, the particle size distribution and external surface area of the particles were determined with a Microtrac particle size analyzer (Leeds and Northrup Model 7991-01). The heat of immersion was divided by the surface area to obtain the reported value in J/m².

To determine the uptake of sodium cations by coal, different portions of –200-mesh coal were suspended in sodium chloride solutions of different concentrations and mixed for 6 min. For each 5-g portion of coal, 500 mL of solution was employed. The coal was recovered by filtration and washed thoroughly with deionized water. The coal was subsequently leached with 100 mL of boiling 1:4 hydrochloric acid for 1 h and separated by filtration. The filter cake was washed with an additional 100 mL of 1:4 hydrochloric acid and then with 100 mL of deionized water. The acidic filtrate was recovered and analyzed by atomic absorption spectrophotometry to determine the sodium content.

Results and Discussion

The particle–bubble attachment time of graphite and four types of bituminous coal was found to correlate closely

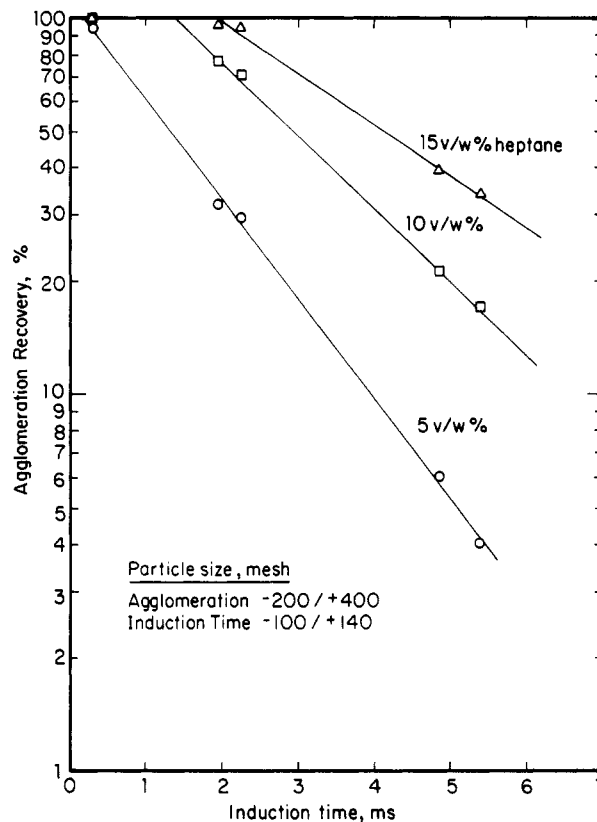


Figure 2. Effect of induction time on the recovery of various carbonaceous materials.

with the heat of immersion of these materials in water (see Figure 1). While some degree of correlation was anticipated because both quantities are known indicators of hydrophobicity, the high degree of correlation was surprising. The materials ranged from highly hydrophobic graphite with an attachment time of 0.3 ms to weakly hydrophobic Illinois No. 6 coal with an attachment time of 5.4 ms. The correlation of results suggests that both surface characterization methods can be used to account for differences in hydrophobicity among the materials. Although particle size was controlled carefully within each series of measurements, it was found necessary to use somewhat coarser particles for the induction time measurements than for the heat of immersion measurements. Thus, to measure induction time, –100/+140-mesh particles were required to avoid disturbing the layer of particles in the measuring cell when the particles were contacted rapidly with a gas bubble, whereas –200/+400-mesh particles were used for measuring the heat of immersion.

For a meaningful comparison of the induction time of different materials, the particle density of the materials should be similar. This requirement was satisfied by the coals used in this study since the particle density of each coal was close to 1.4 g/cm³. While the density of graphite at 2.2 g/cm³ was somewhat greater, the induction time of graphite was so much smaller than that of coal due to a difference in surface properties that any difference due to density was probably not significant.

The influence of particle surface characteristics and heptane dosage on agglomeration recovery is illustrated by the results presented in Figure 2. To obtain these results, the materials listed in Figure 1 were agglomerated individually with heptane, and for a given amount of heptane, there was an excellent correlation between the percent recovery of the material and the induction time. It can be seen that the recovery decreased exponentially as the induction time increased. Moreover, for a given

(19) Electronic induction timer, Virginia Coal and Mineral Services, Inc., Blacksburg, VA.

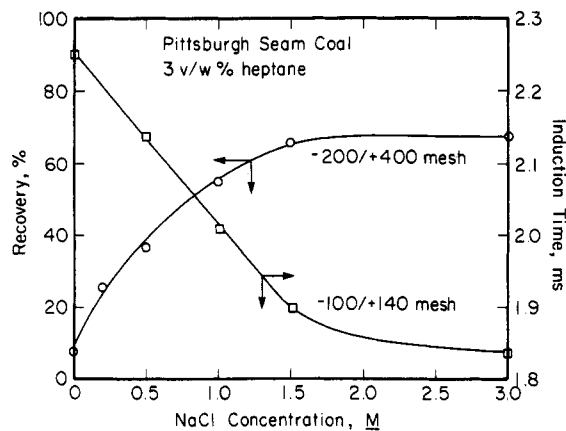


Figure 3. Effect of salt concentration on recovery and induction time of Pittsburgh coal.

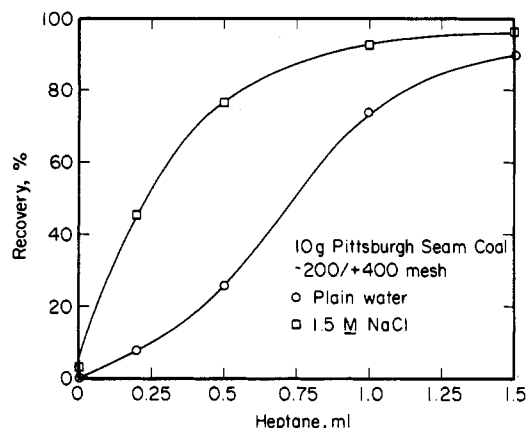


Figure 4. Effect of heptane level on the recovery of Pittsburgh coal from different suspensions.

induction time the recovery increased in proportion to the heptane level. Furthermore, for any given heptane level there was a critical induction time below which the recovery approached 100%. Thus, for a heptane level of 15% (v/w) (i.e., 1.5 mL of heptane/10 g of solids) the recovery was nearly 100% for any material having an induction time less than 2 ms. Of course, the recovery achieved in these and subsequent agglomeration experiments was dependent on the design of the mixing system, intensity of agitation, time of mixing, size of screen used for agglomerate recovery, and other factors.

The surface characteristics of the various materials and, therefore, the response of these materials to agglomeration were affected greatly by the salt concentration of the suspending medium. For the more oleophilic materials such as graphite, Upper Freeport coal, and Pittsburgh coal, an increase in salt concentration reduced the induction time and increased the agglomeration recovery with a given amount of heptane as indicated in Figure 3. While the agglomeration recovery curve in this diagram appeared to be a mirror image of the induction time curve, the effect of salt concentration on recovery was much greater in proportion than was the effect of salt concentration on induction time. Therefore, when the salt concentration was varied, the relationship between recovery and induction time was more complex than is indicated by Figure 2.

By suspension of a more oleophilic material in a salt solution, the quantity of heptane required for a high recovery of the material was greatly reduced (see Figure 4). This finding has the potential for reducing one of the major costs of an oil agglomeration process, namely, the cost of oil.

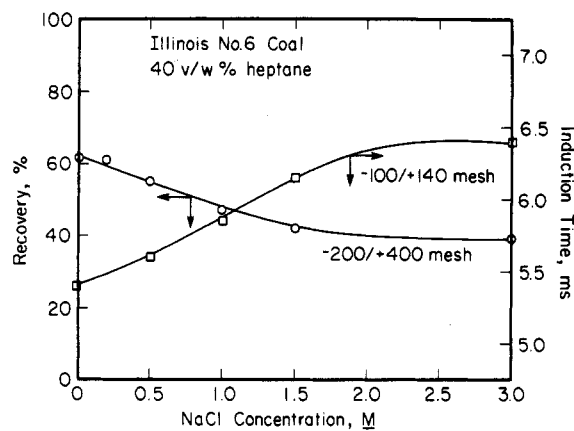


Figure 5. Effect of salt concentration on recovery and induction time of Illinois No. 6 coal.

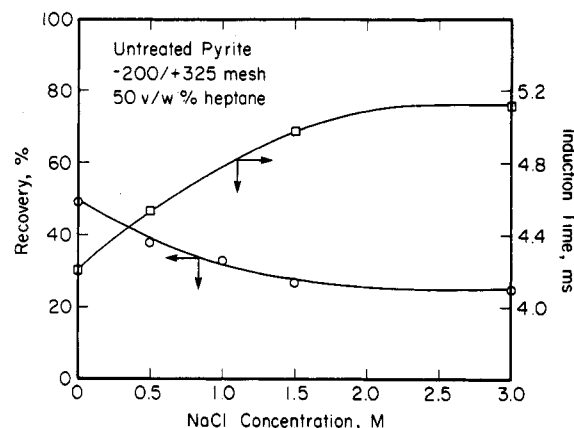


Figure 6. Effect of salt concentration on recovery and induction time of mineral pyrite.

For the more oleophilic materials, it appears that the underlying effect of increasing salt concentration or ionic strength of the suspending medium is to compress the electrical double layer surrounding the individual particles.^{8,9} This in turn destabilizes the water film in contact with the solid, according to Laskowski and Iskra.¹³ Consequently, the water film is more easily ruptured between colliding particles and oil droplets or between oil-coated particles. In a similar way the induction time is reduced because the water film between any given particle in contact with a gas bubble also is more easily ruptured.

For the less oleophilic materials such as Illinois No. 6 coal and pyrite, the effects of salt concentration on particle recovery and induction time were opposite to those noted above for the more oleophilic solids (see Figures 5 and 6). Thus, for the less oleophilic solids the recovery decreased and the induction time increased as the salt concentration rose. But again the recovery curve and induction time curve were virtually mirror images of each other for any given material, which further confirmed the inverse relationship between agglomeration recovery and induction time.

While the induction time curve for pyrite was similar to that for Illinois No. 6 coal, the induction time of pyrite is not directly comparable to that of the coal because of differences in particle size and density of the materials. Since pyrite is much denser than coal, smaller particles had to be used for measuring induction time than were used for coal.

The effects of salt concentration on the agglomeration recovery and induction time of Illinois No. 6 coal and pyrite suggest that these materials were made more hydrophilic and, therefore, less oleophilic through adsorption

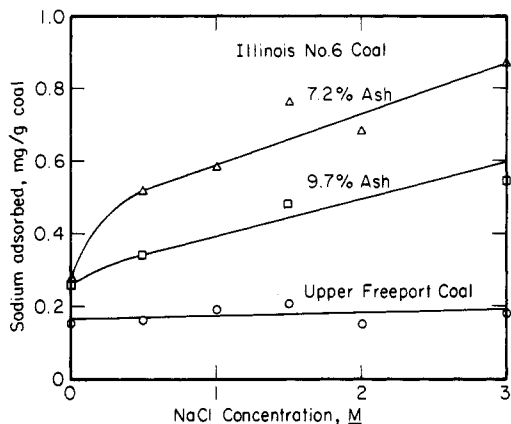


Figure 7. Sodium adsorbed from salt solutions and recovered by acid leaching.

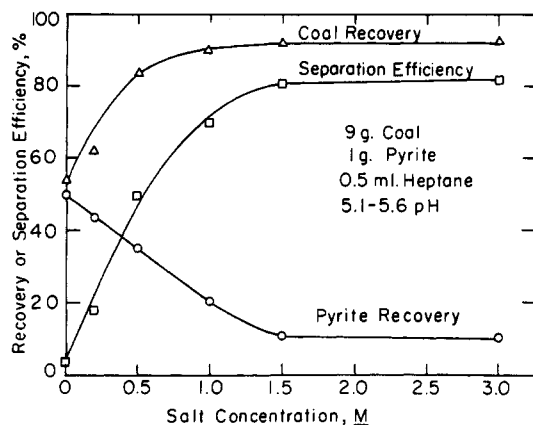


Figure 8. Results of agglomerating a mixture of Upper Freeport coal and mineral pyrite.⁹

of hydrated sodium ions. Pyrite is known to adsorb sodium ions, with the quantity adsorbed being proportional to their concentration in solution.²⁰ Moreover, it was found that Illinois No. 6 coal adsorbed sodium ions by an apparent ion-exchange process. Figure 7 shows the quantity of sodium that was adsorbed per gram of coal from salt solutions of various concentrations and subsequently recovered from the coal by acid leaching. Not included were sodium ions that were removed by water washing. Clearly, Illinois No. 6 coal adsorbed a significant amount of sodium. It is interesting to note that the amount adsorbed was greater for the coal having the lower ash content. Also the amount adsorbed increased as the salt concentration of the solution was raised. On the other hand, Upper Freeport coal did not adsorb a significant amount of sodium that could only be recovered by acid leaching. The difference in the behavior of these two coals is probably due to the difference in the concentration of oxygen functional groups on their surfaces. It is well-known that Illinois No. 6 coal has a higher oxygen content than the more hydrophobic coals such as Upper Freeport coal.

The opposing influences of salt concentration on the agglomeration recovery of pyrite and Upper Freeport coal suggested a series of experiments in which a mixture of these materials was agglomerated with heptane. The preliminary results that were presented in an earlier publication⁹ show that coal recovery increased and pyrite recovery decreased as the salt concentration was raised (see Figure 8). Thus the results achieved with the mixtures corresponded well with the results of agglomerating the

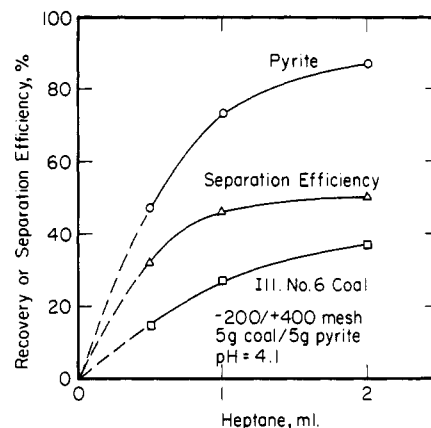


Figure 9. Results of agglomerating a mixture of Illinois No. 6 coal and mineral pyrite suspended in water.

materials separately. Also shown in Figure 8 is the separation efficiency as defined below.

$$\text{separation efficiency (\%)} = \frac{\text{coal recovery (\%)} - \text{pyrite recovery (\%)}}{\text{coal recovery (\%)}}$$

It can be seen that the separation efficiency increased with salt concentration until the concentration reached 1.5 M and then remained constant.

While attempts to separate a mixture of Illinois No. 6 coal and mineral pyrite were less successful, the results of agglomerating a mixture suspended in water at the natural pH of the system were surprising because the recovery of pyrite exceeded the recovery of coal by a wide margin (see Figure 9). Absolute values of the separation efficiency are shown in Figure 9 in order to avoid a negative efficiency. The relatively greater recovery of pyrite was unexpected since the recovery of pyrite was less than the recovery of coal when the materials were agglomerated separately under similar conditions (see Figures 5 and 6). Although this result was unexpected, the surface properties of pyrite are quite variable and easily affected by the state of oxidation of the surface.

Further experiments in which a mixture of Illinois No. 6 coal and mineral pyrite was suspended in 1.5 M sodium chloride and agglomerated with different amounts of heptane produced inferior results. As expected the recovery of both coal and pyrite was reduced in the presence of the salt solution, but in addition the separation efficiency also suffered. Thus, when 5 g of coal and 5 g of pyrite were suspended in 1.5 M sodium chloride and agglomerated with 2.0 mL of heptane, the recovery of coal was only 23% and the recovery of pyrite was 43%, providing a separation efficiency of only 20%.

In the future additional consideration will be given to the effect of pyrite surface properties on the agglomeration and separation characteristics of the material. Pyrite derived from coal as well as mineral pyrite will be utilized.

Conclusions

When aqueous particle suspensions of graphite or various types of coal were agglomerated individually with heptane, the percent recovery correlated very well with the measured induction time of the solids, which in turn correlated closely with the heat of immersion. A close correspondence between agglomeration recovery and induction time was also observed in other experiments in which the carbonaceous materials or mineral pyrite were suspended separately in salt solutions of various concentrations. In these experiments, increasing salt concentrations enhanced the recovery and shortened the induction time of the more oleophilic solids but reduced the

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recovery and lengthened the induction time of the less oleophilic solids. The effect of salt concentration on the more oleophilic solids appeared to be due to compression of the electrical double layer surrounding individual particles, whereas the effect on the less oleophilic particles seemed to be due to adsorption of hydrated cations. Because of these differing effects, it was possible to improve the separation of highly oleophilic Upper Freeport coal and mineral pyrite by increasing the salt concentration of the agglomeration system, whereas it was not possible to improve the separation of weakly oleophilic Illinois No. 6 coal and mineral pyrite. Surprisingly, a larger recovery of pyrite

than coal was achieved when mixtures of mineral pyrite and Illinois No. 6 coal were agglomerated with heptane, which indicates that pyrite may be more oleophilic than coal under some conditions.

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Registry No. NaCl, 7647-14-5; graphite, 7782-42-5; heptane, 142-82-5; pyrite, 1309-36-0.

Additive Effects of Solvent-Refined Coal Fractions and Aromatic Compounds on the Hydrogenolysis of Diarylmethanes

Shigeru Futamura,* Seiya Koyanagi, and Yoshio Kamiya

Department of Reaction Chemistry, Faculty of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo, 113 Japan

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The solvent system promoting hydroliquefaction of coal and the additive effect of some aromatic compounds on the hydrogenolysis of diarylmethanes in hydrocarbon solvents were investigated. Solvent-refined coal (SRC) promoted this latter reaction in tetralin, but no additive effect of SRC was observed in the thermal decomposition of bibenzyl under the same conditions. It was shown that SRC acted not only as a hydrogen donor but also as a hydrogen shuttler. The additive effect of recovered SRC was greatly affected by the hydrogen donatability of solvent. The hydrogen-shuttling effects of some quinones and azaaromatics were investigated on the basis of the structural analysis of SRC. Phenanthridine was shown to be the most effective hydrogen shuttler. The optimum molar mixing ratio of hydrogen shuttler to tetralin was determined to be 1:5.

Introduction

It has been established that coal fragmentation proceeds successively in processes of coal liquefaction. In relation to its mechanism, Whitehurst and co-workers have discussed the role of asphaltols.¹ Kleinpeter and co-workers have noted that light solvent-refined coal (SRC) is an excellent hydrogen-transfer agent.² The authors have also reported that SRC promotes the hydrogenation of aromatic compounds in tetralin.³ Further investigation has revealed that SRC not only donates its inherent hydrogen but also mediates the hydrogen transfer from tetralin to the diarylmethane.⁴ The structural analysis of raw and recovered SRC's was carried out, and some imino linkages in SRC were suggested as the possible moiety shuttling hydrogen.

This paper clarifies the action mechanism of SRC in hydrogen-transfer reactions and presents the SRC-mimetic hydrogenolysis of diarylmethanes, using aromatic compounds as the hydrogen shuttler.

Table I. Elemental Analyses of the Fractionated Miike SRC's

	SRC raw	SRC-1	SRC-2	SRC-3
eluent		ether-methanol	THF	pyridine
wt % eluent		54	38	8
anal., %				
C	86.9	87.2	87.0	78.3
H	5.7	5.9	6.0	5.6
N	1.2	1.1	1.1	1.9
O (diff)	6.0	5.8	5.9	11.4
ash	0.2			2.8
H/C	0.80	0.82	0.83	0.86

Experimental Section

Materials. The diarylmethanes were synthesized according to the method described in a previous paper.⁵ The additives and the solvents were commercially purchased and purified if necessary by conventional methods. The SRC's were prepared from Miike (C, 84.5%; H, 6.1%), Akabira (C, 83.4%; H, 6.2%), and Yallourn (C, 67.4%; H, 5.9%) coals as follows: each coal (20 g) was reacted in tetralin (60 ml) at 400 °C at 9.0 MPa of hydrogen for 30 min. The reaction mixtures were subjected to Soxhlet extraction for 15 h using tetrahydrofuran (THF) as the solvent. The residues obtained in the vacuum distillation (3 mmHg, at 250 °C, for 1 h) of the THF extracts were used as SRC (raw SRC) in the hydrogenolysis of the diarylmethanes. Column chromatographic separation of the SRC derived from Miike coal, which will be

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