**COAL CLEANING VIA LIQUID-FLUIDIZED CLASSIFICATION (LFBC)
WITH SELECTIVE SOLVENT SWELLING**

FINAL REPORT

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ABSTRACT

The concept of coal beneficiation due to particle segregation in water-fluidized beds, and its improvement *via* selective solvent-swelling of organic material-rich coal particles, was investigated in this study. Particle size distributions and their behavior were determined using image analysis techniques, and beneficiation effects were explored *via* measurements of the ash content of segregated particle samples collected from different height locations in a 5 cm diameter liquid-fluidized bed column (LFBC).

Both acetone and phenol were found to be effective swelling agents for both Kentucky #9 and Illinois #6 coals, considerably increasing mean particle diameters, and shifting particle size distributions to larger sizes. Acetone was a somewhat more effective swelling solvent than phenol. The use of phenol was investigated, however, to demonstrate that low cost, waste solvents can be effective as well.

For unswollen coal particles, the trend of increasing particle size from top to bottom in the LFBC was observed in all cases. Since the organic matter in the coal tends to concentrate in the smaller particles, the larger particles are typically denser. Consequently, the LFBC naturally tends to separate coal particles according to mineral matter content, both due to density and size.

The data for small (40-100 μm), solvent-swollen particles clearly showed improved beneficiation with respect to segregation in the water-fluidized bed than was achieved with the corresponding unswollen particles. This size range is quite similar to that used in pulverized coal combustion.

The original process concept was amply demonstrated in this project. Additional work remains to be done, however, in order to develop this concept into a full-scale process.

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EXECUTIVE SUMMARY

The concept of coal beneficiation due to particle segregation in water-fluidized beds, and its improvement *via* selective solvent-swelling of organic material-rich coal particles, was investigated in this study. Particle size distributions and their behavior were determined using image analysis techniques, and beneficiation effects were explored *via* measurements of the ash content of segregated particle samples collected from different height locations in a 5 cm diameter liquid-fluidized bed column (LFBC).

Both acetone and phenol were found to be effective swelling agents for both Kentucky #9 and Illinois #6 coals, considerably increasing mean particle diameters, and shifting particle size distributions to larger sizes. Illinois #6 was swollen somewhat more by these solvents than Kentucky #9. Acetone was a somewhat more effective swelling solvent than phenol. Leaching of solvent out of the coal particles into water was observed to occur. This was found to be more rapid for phenol than for acetone. Phenol-swollen particles were observed to return to their original size in about an hour. However, this process is still slow enough to allow sufficient time for segregation and separation of solvent-swollen coal particles in a water-fluidized bed.

For unswollen coal particles, the trend of increasing particle size from top to bottom in the LFBC was observed in all cases. Since the organic matter in the coal tends to concentrate in the smaller particles, the larger particles are typically denser. Consequently, the LFBC naturally tends to separate coal particles according to mineral matter content, both due to density and size.

For the larger coal particle sizes investigated in the current study (355-500 μm (C) and 840-1000 μm (D) samples), it was found that solvent-swelling did not have a significant effect on improving beneficiation over that obtained for the unswollen coal particles. This was attributed to the larger particles being relatively homogeneous with respect to their organic/inorganic composition.

For the smaller coal particle samples however, a significant improvement in beneficiation due to solvent-swelling was observed. In fact, in the case of A" (40-100 μm) particles swollen with acetone, the *larger* particles appeared in the *top* fraction of the bed and the *smaller* particles in the *bottom* fraction after swelling. This, of course, is the opposite of what was always observed for the unswollen samples. This is because the original smaller and lighter particles, containing a higher proportion of organic matter than the larger particles, swelled more than larger particles, thereby reducing their density and causing them to accumulate preferentially at the top of the water-fluidized bed. The data for the small, solvent-swollen particles clearly showed improved beneficiation with respect to segregation in the water-fluidized bed than was achieved with the corresponding unswollen particles.

The size range of the smaller particles investigated here is quite similar to that used in pulverized coal combustion. Therefore, additional grinding is unnecessary in order to implement improved beneficiation *via* selective solvent-swelling in LFBC. Moreover, as demonstrated, the process can utilize waste solvents, such as phenol, in order to swell the particles, while minimizing costs.

In summary, the original hypothesized concept was amply demonstrated in this project. Additional work remains to be done, however, in order to develop this concept into a full-scale process.

1.0. INTRODUCTION

1.1. Background.

One of the most critical aspects of coal preparation involves cleaning and beneficiation. These processes are fundamental to reducing the environmental impact of coal utilization, the most important of which involve ash formation and sulfur emissions.

There are generally four types of approaches to coal cleaning: (1) conventional physical methods; (2) advanced physical methods; (3) chemical coal cleaning; and biological coal cleaning (Yürüm, 1992). However, currently only physical coal cleaning is commercially important. It is based on achieving physical separation by exploiting density differences between particles that are composed primarily of organic material from those that are principally inorganic mineral matter, as well as by differences in surface properties. Consequently, physical coal cleaning is focused primarily on the removal of pyritic sulfur and other ash-forming mineral matter impurities. Commercially available methods remove about 25% of the sulfur and 50% of the mineral matter (Gibbs and Hill, 1978), on average, depending of course, on the particular coal and the manner in which the mineral matter is distributed in the coal.

Current physical coal cleaning equipment includes jigs, dense media vessels, dense media cyclones, hydroclones, and froth flotation (Tsai, 1982; Yürüm, 1992). Perhaps the most common category of commercial equipment is jigs. These devices rely on stratification of particles in a *fixed bed* according to density as a result of pulsations of water in alternating directions, producing expansion and contraction of the bed. The pulsating action causes the lighter coal particles to gradually migrate to the top of the fixed bed, while the heavier particles, containing most of the mineral matter impurities, gradually move to the bottom. These devices work best for larger particles (*ca.* 1" or greater) with densities significantly greater than water.

Dense media vessels comprise perhaps the next most popular category of commercial equipment. These devices are typically used to separate finer coal particles, and provide much better recovery and sharpness of separation than jigs. The density of the flotation medium is controlled by varying the concentration of finely ground magnetite in a water slurry, such that coal particles of a specific density and lighter will "float" and be removed. However, efficient recovery of the magnetite is very important for the economics of these systems. Generally, the

amount of magnetite used increases with the amount of coal cleaned and the smaller the size of the coal particles.

Dense media cyclones also operate on density differences with the aid of both dense media and centrifugal force; and hydroclones simply employ water and centrifugal force. These devices are primarily used for finer coal particles and generally produce two fractions -- “lights” and “heavies.”

Froth flotation is used primarily to clean “ultrafine” coal particles from 48 to 150 mesh, down to 325 mesh. It relies on hydrophobic surface properties of coal particles, which serve to attach small air bubbles, introduced into a water bath and thus concentrate fine coal particles in the surface froth. The heavier, non-hydrophobic particles sink and settle to the bottom of the tank (Gibbs and Hill, 1978).

Increasing demands on commercial coal require continually finer separations in the most economical fashion. The current project is directed at a fundamental investigation of an innovative technique for coal cleaning -- liquid-fluidized bed classification (LFBC) with selective particle modification using “solvent swelling.”

1.2. Coal Cleaning With Liquid-Fluidized Bed Classification (LFBC).

Liquid-fluidized bed classification (LFBC) has been used for a number of applications, ranging from industrial crystallizers to expanded bed absorbers for biopharmaceutical applications, for waste plastics separations in our laboratory (Calo *et al.*, 1996), and now for coal cleaning in the current work.

Under liquid-fluidized conditions, particles segregate vertically in height in the bed according to their density and size. For particles denser than the fluidizing medium (for example, coal particles in water), the lighter/smaller particles accumulate near the top of the bed, and the heavier/larger particles populate the bottom of the bed (Al-Dibouni and Garside, 1979). Particle classification is related to the Archimedes or Galileo number, $Ga = g(\rho_p - \rho_f)d_p^3/\mu^2$, where ρ_p and ρ_f are the densities of the particle and the liquid, respectively, d_p is the equivalent particle diameter, and μ is the kinematic viscosity of the liquid. Ga is a measure of the relative importance of the buoyant and viscous forces on an individual particle. Since the terminal particle settling velocity is roughly proportional to Ga (the exact dependence is a function of

particle shape, flow regime, etc.) for “upflow” fluidization, the larger the value of Ga , the more likely the particle will assume a steady-state location at a low height in the bed. Consequently, everything else being equal, denser, larger, particles will populate the bottom of the bed., and lighter, smaller particles will be located at the top.

This behavior is somewhat related to the principles upon which coal cleaning jigs are based. Unlike in jigs, however, in LFBC the bed expansion caused by fluidization is *continuous*, and particles achieve a *unique location in height* in the column due to their density and size as a result of a balance of both *drag* and buoyancy forces. Essentially, the void fraction of the bed adjusts itself so that the local interstitial liquid velocity exerts enough drag on the particles to completely cancel their settling velocities. In addition, recovery and sharpness of separation can be considerably enhanced when auxiliary, selective particle modification techniques, such as “solvent-swelling,” in conjunction with LFBC.

The mechanisms of solvent-swelling are discussed below. For the current discussion, however, solvent-swelling will generally tend to decrease the particle density, but increase the particle size. Although these are counteracting tendencies (as discussed above), in general particle segregation in a LFBC is more sensitive to density. This can be shown with a simple analysis. The sensitivity of the Galileo number at *constant particle size* to ρ_p is $[\ln(Ga)] / [\ln(\rho_p)] = \rho_p / (\rho_p - \rho_f)$. Thus, for example, for coal particles of specific gravity 1.6 in water, a 30% increase in particle volume due to swelling with methanol (0.79 S.G.), causes a 12.5% decrease in density, which will cause about a 33.3% *decrease* in Ga . On the other hand, the sensitivity of the Galileo number to d_p at *constant density* is $[\ln(Ga)] / [\ln(d_p)] = 3$. Consequently, a 30% increase in volume, or a 3.1% increase in d_p will cause a 9.3% *increase* in Ga . This represents a net 24% *decrease* in Ga , controlled by the density change. This change has a considerable effect on the location of the particle in the bed; and in this case solvent swelling will cause the particle to migrate *upwards* in the bed.

The preceding characteristics suggest a number of reasons why LFBC can be used to significantly improve coal cleaning. First of all, LFBC works best on particles in the “fine” particle range that is desirable for improved physical coal cleaning (Tsai, 1982; Yürüm, 1992). LFBC also operates extremely well on “near gravity” material (e.g., 1.05 - 1.6 S.G.; see below)

which is difficult for a jig. In addition, since the particle bed is fully fluidized, at steady-state a *number* of different density fractions, rather than just two, as in most other physical coal cleaning systems, can be removed *continuously* by hydraulic flow to simple gravity separators for recovery. Moreover, the added effect of *selective particle modification via solvent swelling* can be used to significantly improve the separation performance even beyond that in simple LFBC, and that which is currently attainable in jigs and most other commercial physical coal cleaning equipment.

1.3. The Effects of “Swelling Solvents.”

It is well known that the polymeric structure of the organic material in coal tends to swell when exposed to certain solvents. In fact, this has been widely used as a characterization technique for the macromolecular structure of coals (e.g., see Larsen *et al.*, 1985; Yun and Suuberg, 1993). Solvents have also been used to “study the behavior of coal under various conditions to determine the character of occluded material in pores to facilitate characterization of coal, and as a first step in coal liquefaction processes.” (Yürüm, 1991). Organic solvents break or relax the cross-links in the coal macromolecular network, especially the hydrogen-bonds [Yürüm, 1991; Suuberg *et al.*, 1994; Wang *et al.*, 1998]. A measure of the extent of swelling in a coal is the swelling index, which is equal to the final height of a measured, small diameter column of coal, divided by its initial height.

Both the type of solvent and the coal have a considerable effect on the degree of swelling. Many studies have shown that coal is a strong hydrogen donor. "Phenolic hydroxyl is one of the major oxygen functional groups in coals and most of the hydroxyls are hydrogen bonded. It has amply been demonstrated that hydrogen bonds are an important associative interaction holding the network together, that there are a range of hydrogen bonds structures and energies and that coal hydrogen bonds can be broken and replaced by a coal solvent hydrogen bonds to varying extent depending upon the basicity of the solvent" [1]. (9) Thus, it is expected that non-interacting solvents will diffuse slowly while interacting hydrogen-bonding solvents will diffuse more rapidly. It has been shown that for non-interacting hydrocarbons with at least six carbons, the diffusion rates are so slow that only the external surface is sampled at room temperature. Strongly interacting molecules such as pyridine, THF, and small alcohols diffuse rapidly

throughout the coal. Interactive (H-bonding) molecules can usually diffuse through coals fairly rapidly compared to non-interacting solvents (Yürüm, 1991). Another important parameter in solvent selection is the size of the molecule. In general, the larger the molecule, the more difficult it is to diffuse into the coal. In a study by Yun and Suuberg (1993) using straight chain alcohols and Utah Blind Canyon coal, the swelling index decreased from 1.2 to 1.6 as the number of carbons increased from 1 to 6.

Exposure of coal particles to a swelling solvent will cause particles to swell to different extents, depending on their organic matter content. Those with the highest organic matter content will swell considerably more than those with a high mineral matter content. For coal cleaning in a LFBC this means that solvent swelling will expand the spatial extent of the classification of the organic matter-containing particles at the expense of the mineral matter-containing particles. It is not yet known whether there is any dependence of swelling behavior specifically on organic sulfur content. If there is, a commensurately greater discrimination would occur in particle segregation according to organic sulfur content, which can be exploited to further enhance coal cleaning in LFBC.

2.0. EXPERIMENTAL

2.1. Coal Particle Sample Preparation Procedures.

Initially, four different coals were obtained from the Penn State Coal Sample Bank. Composition data are presented in Table 1.

Table 1. Summary of coals investigated and their compositions on a dry basis.

<u>Coal</u>	<u>Mineral Matter (dry) (%)</u>	<u>Sulfur (%)</u>	<u>Pyritic/Organic Sulfur</u>
Illinois #6	14.25	4.45	1.4
Kentucky #9	12.25	4.8	1.29
Ohio #4A	12.02	4.25	0.61
Pittsburgh #8	9.10	2.15	0.59

The first three coals listed have similar levels of mineral matter and sulfur, but varying pyritic/organic sulfur ratios. Ultimately, two of these coals were selected for investigation in the LFBC experiments: Illinois #6 and Kentucky #9. These latter two coals were selected based on initial favorable coal-swelling results. In addition, their favorable inorganic-to-organic sulfur ratios are positive indicators of the degree of sulfur beneficiation that may be achieved by LFBC.

The coals were received as particles approximately 1/4 inch in diameter, and were ground to obtain the desired particle sizes. Coal grinding was initially accomplished with a coffee grinder, and then sieved to two sizes: (A) 53-105 μm , and (B) 105-153 μm . This procedure was quite rapid, but was found to produce a large amount of coal fines. Therefore, subsequent ground samples were produced with a mortar and pestle.

Four different particle size ranges were obtained by grinding and sieving for the LFBC studies: (A') 56-75 μm ; (B') 106-180 μm ; (C) 355-500 μm ; and (D) 840-1000 μm . It is noted, however, that sieve fractionation is only an approximate size classification method. For example, the A', 56-75 μm fraction, for the Illinois #6 coal particles actually ranged in size from 30~141 μm when measured with image analysis. Consequently, a narrower A"-size range of 40-100 μm , as verified by image analysis, was obtained by decanting a slurry of the 56-75 μm sieve cut into a column filled with water. "Fines" from this sieve cut were removed in this manner, and the coal particles that remained in the initial container became the A" sample.

The amount of mineral matter in the coal samples was determined *via* ashing experiments. The coal was first preheated to remove moisture. The preheating process consisted of drying the coal on a hot plate at approximately 50°C for about one hour. Once dry, approximately one gram of coal was weighed and burned in a tube furnace in the presence of flowing air at approximately 750°C for about three hours. The samples were re-weighed following combustion. The weight of sample that remained was attributed to the mineral matter, or ash, present in the coal sample.

2.2. Coal Swelling and De-swelling Procedures.

Solvent swelling tests were initially performed with methanol and acetone. The final LFBC experiments were conducted with coals swollen with acetone and aqueous phenol solutions. Acetone was selected based on the initial swelling test results that showed it to be an effective swelling solvent for the coals examined. Saturated solutions of phenol in water (8g/100ml) were

investigated because, in addition to being an effective swelling solvent, phenol is produced as an objectionable byproduct in paper pulping operations (EPA, 1995), and could be available in large amounts at relatively low cost.

Swelling index measurements were performed in the same manner as described by Yun and Suuberg (1993). Small glass tubes of 3 mm inner diameter and approximately 5 cm in length were filled with roughly 1 cm of ground coal. The tubes were then centrifuged in a Savant HSC-10K high-speed centrifuge at 7500 rpm. The initial heights of the coal samples were then measured with calipers and recorded. Excess solvent was added to the tube and the samples were stirred vigorously. The samples were covered with parafilm and then allowed to sit for 2-3 hours after which the tubes were centrifuged again at 7500 rpm for 3 minutes and the coal height was measured again. The coal height was always measured after centrifugation to insure accuracy and reproducibility of results. Coal samples were allowed to swell for 3-4 days. A summary of all the swelling results is presented in Appendix A. For the LFBC experiments, larger samples of the coals were allowed to swell from seven to ten days.

De-swelling of the coal was performed in a similar manner by simply replacing the solvent with DI water and then measuring the coal column height every 20-30 minutes.

2.3. Particle Size Measurements.

Images of the coal particle samples were also taken using an optical microscope or a digital camera at three different stages: untreated, swollen, and upon de-swelling. In order to prepare the samples for this procedure, the solvent was removed, and the sample was immediately distributed on a piece of plain white paper to reduce glare, and the image was taken.

Particle size measurements were made by analysis of images taken with an optical microscope (smaller particles) or with a digital camera (larger particles). The procedures that were developed and used in the current work are presented in Appendix B. In addition, other common methods for performing particle size measurements are summarized in Appendix B.

The particle sample images were analyzed with initially analyzed with Scion Image, a particle analysis program distributed by the NIH. Scion Image was used to count the number of particles and to measure each particle's major and minor ellipse lengths and area. The data from Scion Image was converted into equivalent radii and plotted as a particle size distributions.

Microscopy with image analysis is considered to be the most direct method for particle size classification (Irani and Callis, 1963) and can yield very accurate results. There are three basic steps in the use of microscopy: slide preparation, particle observation, and the actual counting and sizing of individual particles. The standard procedure used with the light microscope is that given by the American Society for Testing Materials (ASTM) E20-51T (1951). The final procedures used in the current work were based on this approach, and are summarized in Appendix B.

2.4. Liquid-Fluidized Bed Apparatus.

A schematic of the liquid-fluidized apparatus is presented in Figure 1. The experimental column was constructed of a clear Lucite tube. The column is 5 cm in diameter, and 1.5 m in height. The column diameter was selected to be large enough to ensure that the relationship between the fluid-velocity and bed void-fraction was independent of the total particle loading. It has been determined that this relationship becomes independent when the column-to-particle diameter aspect ratio is 10 to 20 (Couderc, 1985). In this particular experimental setup this criteria is met for particles with an effective diameter of 2.5 mm or less. The column has a fluidizing section that is 1 m in length. This column-height to column-diameter ratio ensured minimal axial mixing while providing an adequate height for fluidization to occur. Previous experiments have demonstrated that LFBC performance is sensitive to the vertical inclination of the column (Hradil, 1991). For this reason the vertical alignment of the column was checked with a level prior to operation.

Upstream of the fluidizing section of the column is a 50 cm homogenizing section. The role of this section is to provide a uniform flow field over the entire cross section of the distributor. The homogenizing section is composed of approximately 30 cm of packed straws, topped off with approximately 20 cm of 1/8" acrylic spheres.

The fluidization and homogenizing sections are separated by the distributor. The distributor in the current work was a stainless steel wire mesh with a nominal opening of 56 μm . This mesh size was selected because it provided the lowest pressure drop while preventing the smallest particles from passing through. Particles were loaded into the bed from an opening at the top of the column. Samples were removed from the column *via* ball valves on three sampling ports

along the side of the column. The sample ports are located at distances of about 10, 30, and 40 cm above the distributor.

Liquid flow to the bed was supplied by a centrifugal pump with a maximum volumetric capacity of 10 gallons per minute (GPM). The flow into the bed was measured with a paddle wheel flow meter equipped with a digital display (calibrated for 545.142 pulses per gallon). A series of ball valves between the bypass and the column allowed for control of the flow to the column. The fluidizing liquid was water to which approximately 5 ml of surfactant (Triton X-165 and Triton N-101) was added to aid in disengaging air from the particles.

The flowrate in all the LFBC experiments for which segregated particle samples were collected was maintained at a superficial linear velocity of 1.77 cm/s, in order to maintain the bed expansion as constant as possible.

2.4-1. LFBC Sampling Procedures.

Three particle samples were taken from each LFBC run. Samples were removed from the column *via* 1/2" ball valves on three sampling ports along the side of the column. The sample ports were located at distances of about 10, 30, and 40 cm above the distributor.

The first step in the sampling procedure was to expand the bed sufficiently so that the fluidized particles were accessible from all three sampling ports. The bed was then allowed to run for approximately ten minutes to ensure steady-state classification. Samples were taken first from the upstream sampling ports so as not to disrupt the classification of the bed further down. Samples were obtained by opening the ball valve and collecting all the particles that were hydraulically transported out.

3.0. RESULTS & DISCUSSION

3.1. Initial Solvent-Swelling/De-swelling Tests.

Methanol was not found to be a very good swelling solvent for all the coal samples tested. For Pittsburgh #8 coal the swelling index never exceeded 1.2 in methanol. The effects of three other solvents on Pittsburgh #8 coal are presented in Figure 2. As shown, THF (tetrahydrofuran) was the best swelling solvent of those tested, with a maximum swelling index of 1.5, followed by acetone and octane. THF is known to be a strongly interacting solvent that diffuses rapidly and

can achieve a swelling index as high as 2.0 with Utah Blind Canyon coal (Yun and Suuberg, 1993). This is probably due to the greater electron donor strength of THF in comparison to acetone and octane. Also, THF is thought to break cross-links instead of simply relaxing cross-links, thus allowing more of the solvent to diffuse into the coal (Wang *et al.*, 1998). Octane is a nonpolar, relatively noninteracting molecule, and thus cannot effectively penetrate and relax the coal network.

Illinois #6 coal swelled more for the same solvent than Pittsburgh #8, and acetone was a more effective swelling solvent than methanol. The larger particle size sample (B: 105-153 μm) apparently swelled more than the smaller (A: 53-105 μm) particles in both solvents; e.g., 1.4 vs. 1.25, for acetone. This trend was unexpected since the smaller particles have a larger external surface area - to volume ratio. Thus the reason for this result is not known. However, it may have to do with the manner in which the inorganic and organic matter are distributed among the particles as a function of size (see below).

Kentucky #9 swelled less in both solvents than Illinois #6, and Ohio #4A swelled relatively little in acetone and did not really swell at all in methanol. The swelling indices less than unity for Ohio #4A are most probably indicative of sample loss during stirring in a series of successive handling and measurement operations. For this reason, it is felt that all the swelling results probably underestimate the swelling indices slightly.

De-swelling results for Illinois #6 in methanol are presented in Figure 3. The upper curve is the data for the B (105-153 μm) size coal, which swelled more than the A (53-105 μm) particles, as indicated above. In both cases the coal de-swelled quite slowly. Even after 200 minutes for the smaller size class, and over 400 minutes for the larger size class, the particles had still not returned to their original size. Similar results were found for the other coals and solvents as well.

These preliminary results indicated that solvent leaching from the particles in water and concomitant particle shrinkage should not be major impediments to LFBC separation.

3.1-1. Cumulative Particle Size Distributions From Initial Tests.

Particle size distribution results for Illinois #6 coal samples are presented in Figure 4a and Table 2. Comparison of the two A (53-105 μm) size curves shows that the distribution shifts to larger sizes upon swelling, as expected. For the unswollen particles, over 55% were less than 100 μm in diameter, in comparison to only 40% of the swollen particles. This 40% that remained less

than 100 μm and effectively did not swell can be attributed to particles that contain primarily mineral matter, which does not swell.

The resultant mean diameters in Table 2 support this result. That is, for the A-size (53-105 μm) sample, the unswollen coal had a mean diameter of 128 μm , in comparison to 340 μm for the coal swollen in acetone. One inconsistency in these data was that the particle diameter means for the unswollen samples determined from the particle images both fall outside the nominal particle sizes determined by the sieve analyses. It is noted, however, that the distribution for the B-size sample is shifted to the left relative to the smaller particle size sample. This shows that even if the average particle size is large, it is still possible to have many small particles and many large particles.

Table 2. Summary of Illinois #6 particle size distribution tests.

ILLINOIS #6		
Sample	# Particles	Mean Diameter (μm)
A: 53-105 μm (unswollen)	655	128
A: 53-105 μm (in acetone)	202	340
B: 105-149 μm (unswollen)		155

Similar results were found for both Kentucky #9 and Ohio #4A coal samples. The results for Kentucky #9 are presented in Figure 4b and Table 3. In Figure 4b, the B-size (105-149 μm) sample distribution is also the furthest to the left, and also has the highest percentage of particles less than 100 μm . Also, the swollen B-size sample is shifted to the right, as was observed for the Illinois #6 coal sample. However, for the smaller A-size (53-105 μm) sample the two curves are reversed. Following the same logic as above, the swollen curve is expected to be shifted to the right of the standard curve, indicating an increase in particle size; however, the opposite is evident. The results presented in Table 3 provide some insight into the probable cause of this observation.

Table 3. Summary of Kentucky #9 particle size distribution tests.

KENTUCKY #9		
Sample	# Particles	Mean Diameter (μm)
A: 53-105 μm (unswollen)	595	118
A: 53-105 μm (in acetone)	1299	122
B: 105-149 μm (unswollen)	801	100
B: 105-149 μm (in acetone)	183	243

As shown in Table 3, for the smaller A-size particles the mean diameters for the standard and swollen coal are 118 and 122 μm respectively. Although the two numbers exhibit the correct trend (i.e., the swollen diameter is greater than the standard diameter), the two numbers are still quite similar. The 3.4% difference in diameter is well within experimental error, and thus may not be significant. Also, only 595 particles were counted for the standard, in comparison to 1299 for the swollen sample for the A-size particles. As explained above, the larger the number of particles counted, the greater the accuracy of the results. Also, while the microscope data exhibited the same expected trends as predicted by the swelling experiments, the actual numbers were at times too large in comparison, and gave unreasonable swelling indices of 2.0, or over 100% swelling. In the specific case in Table 2 for Illinois #6 of over 100% swelling, the number of particles counted for the standard was 655 compared to 202 for the swollen coal. Thus the diameter of 128 μm calculated for the standard case can be considered to be more accurate than 340 μm for the swollen case. Assuming that the standard diameter of 128 μm is correct, the swelling index for this sample was 1.29. This corresponds to 29% swelling, and implies that the new swollen diameter should be approximately 165 μm instead of 340 μm . It is expected, therefore, that if the number of particles counted was increased significantly, the accuracy of the resultant distribution would also increase, and the swollen diameter would be expected to decrease to a more reasonable value.

A similar trend is evident in the data in Table 3 for Kentucky #9 coal. That is, the B-size standard sample of 801 particles exhibited a mean diameter of 100 μm . For the corresponding swollen sample, only 183 particles were counted and it exhibited a much larger and unreasonable swollen diameter of 243 μm . Consequently, it is expected that if a larger number of particles

were counted, the mean swollen diameter would decrease to more reasonable values commensurate with the measured swelling index of 1.28.

In all cases, as the number of particles counted increased, the accuracy of the mean diameter increased, and its value decreased. Thus, for an insufficient number of particles, the microscope counting method tends to overestimate the mean diameter, and only for large numbers of particles will this method yield accurate results consistent with the swelling data.

The particle size distribution results for the Ohio #4A coal samples are summarized in Figure 4c and Table 4. In this case, all the plots exhibit the expected trends, such that the distribution curves for the swollen samples are shifted to larger particle sizes. Once again, the B-size (105-149 μm) standard sample curve is the furthest to the left. However, for the B-size particles the mean diameters are reversed, such that the mean diameter of the swollen sample (213 μm) is less than that of the standard sample (235 μm). As previously, this apparent discrepancy is attributed to experimental statistical error.

Table 4. Summary of Ohio #4A particle size distribution tests.

OHIO #4A		
Sample	# Particles	Mean Diameter (μm)
53-105 μm (unswollen)	283	186
53-105 μm (in acetone)	498	293
105-149 μm (unswollen)	218	235
105-149 μm (in acetone)	464	213

3.2. Solvent-Swelling/De-swelling Results for LFBC Coal Samples.

Based upon the swelling results, for the LFBC studies it was decided to focus on two of the coals, Illinois #6 and Kentucky #9, and two solvents, acetone and an aqueous phenol solution, as discussed above (*cf.* Section 2.1). Also, four different particle size classes were investigated: (A') 56-75 μm ; (B') 106-180 μm ; (C) 355-500 μm ; and (D) 840-1000 μm . The former two are similar to the particle size classes used in the initial tests, and the latter two are larger. In addition, as described previously, a narrower size cut of the A' particles was obtained and labeled A".

Table 5. Swelling results; mean particle diameters.

Sample	Unswollen (μm)	Acetone (μm)	Phenol (μm)
Kentucky #9 (C)	349	382	397
Illinois #6 (C)	381	381	433
Kentucky #9 (D)	613	753	682
Illinois #6 (D)	644	657	670

Table 6. Percentage increases in mean diameters of coal samples upon swelling.

Sample	Acetone (%)	Phenol (%)
Kentucky #9 (C)	9.6	13.8
Illinois #6 (C)	0.1	13.7
Kentucky #9 (D)	22.8	11.1
Illinois #6 (D)	2.1	4.0

Mean diameters and corresponding percentage increases upon solvent swelling for both coals were obtained from the resultant differential particle size distributions for the C- and D-size particle samples. These are presented in Tables 5 and 6, respectively. From these data, it is apparent that both solvents swell both coals significantly. However, it was not expected that the swelling with acetone would be less than that for phenol. It was suspected, therefore, that this was an experimental artifact due to the image analysis sample preparation procedure that was used. That is, these particular samples were mounted dry because mounting them wet in water while obtaining good particle separation for image analysis proved to be difficult. In air, acetone, with the considerably higher vapor pressure, would have evaporated from the samples much more rapidly than phenol, and the particles could have de-swelled.

It was decided to examine this issue with the smaller particle size classes, A', B', and A". Consequently, a wet-mounting procedure was developed, which, although more tedious, proved to yield a more accurate assessment of the coal swelling/de-swelling behavior. The results are summarized in Figure 5(a-f). Comparisons of the particle size distributions in each case, before and after solvent-swelling, show a significant shift to larger particle sizes upon swelling for all the samples. This change seems to be the most marked for the narrower A"-size particles. The

corresponding mean diameters and ultimate swelling indices of the six samples are presented in Tables 7 and 8, respectively.

Table 7. Swelling results; mean particle diameters.

Sample	Unswollen (μm)	Acetone (μm)	Phenol (μm)
Kentucky #9 (A')	79	105	97
Illinois #6 (A')	92	128	109
Kentucky #9 (B')	169	215	198
Illinois #6 (B')	191	239	214
Kentucky #9 (A'')	70	86	79
Illinois #6 (A'')	67	88	80

Table 8. Swelling indices of coal samples.

Sample	Acetone	Phenol
Kentucky #9 (A')	1.33	1.22
Illinois #6 (A')	1.39	1.18
Kentucky #9 (B')	1.27	1.17
Illinois #6 (B')	1.25	1.12
Kentucky #9 (A'')	1.23	1.13
Illinois #6 (A'')	1.31	1.19

As previously, both acetone and phenol were shown to be effective swelling agents for both coals. That is, upon swelling, the mean diameter of all the distributions increased significantly. However, now, as expected, acetone is a better swelling solvent than phenol in all four cases. For example, the swelling index for Illinois #6 in acetone was as high as 1.39, while the corresponding value for the aqueous phenol solution was 1.18.

The smaller particles typically exhibited a greater increase in the mean diameter than the larger particles. This important result may be due to a number of factors, but from the LFBC segregation results (see below), the smaller particle sizes appear to produce a better separation between organic and inorganic matter upon grinding, such that the small particles that swell

more effectively appear to have a higher organic content. However, it may also be partially due to more rapid diffusion of solvents into the smaller particles, as well as their larger surface area-to volume ratio, although the samples were allowed to swell for seven to ten days.

The de-swelling results for the A'-size (56-75 μm) particles in water are presented in Figure 6. Being the smallest particles, these were expected to de-swell the most rapidly in water. As shown, for both coals de-swelling occurred more rapidly for the phenol-swollen particles than for the acetone-swollen particles. This was to be expected, given the relatively high solubility of phenol in water. The de-swelling times for the acetone-swollen particles were comparable to those found in the initial tests. Particles swollen with phenol de-swelled to their original size in approximately 80 min. Even though leaching of phenol from the particles was about twice as fast as for acetone, this time scale is still sufficiently long to allow LFBC separation of phenol-swollen particles.

3.3. Fluidization Behavior of Unswollen Coal.

The relationship between the superficial fluid velocity and the resultant bed expansion was investigated experimentally. This type of data has been classically using the Richardson and Zaki (1954) expression:

$$U_o = U_i \varepsilon^N \quad [1]$$

where:

ε = fluidized bed void fraction

U_o = superficial fluid velocity

U_i = terminal velocity of a “falling” particle

N = an empirical exponent

N is dependent on the Reynolds number and the ratio of diameters of the particles and the column (Hradil, 1991). Reported values of N for glass spheres range from 2.4 to 4.7, from 5 to 10 for nonspherical particles, and from 7 to 15 for porous materials (Smith *et al.*, 1978; Davies and Richardson, 1982).

The mean bed void-fraction of the bed is related to the height of the expanded column *via*:

$$\varepsilon_H = 1 - \frac{(1 - \varepsilon_s)H_s}{H} \quad [2]$$

where:

ε_H = the mean bed void fraction at height H

ε_s = the mean void fraction of the initially stationary fixed bed

H_s = the stationary bed height

H = the height of the expanded bed

The expanded bed height was measured as a function of the fluidization velocity, and Eq. [2] was then used to relate it to the mean bed void fraction. “Best-fit” values of U_i and N were determined from linear regression. The results are presented in Figure 7.

Table 9. Unswollen coal particle terminal velocity comparisons.

Sample	Richardson-Zaki Fit			Experimental Results	
	U_t (cm/s)	N	R^2	Mean U_t (cm/s)	Std. Dev. (cm/s)
Kentucky #9 (D)	3.45	7.2	1.00	2.82	0.30
Illinois #6 (D)	3.43	6.8	0.97	3.54	0.63
Kentucky #9 (D)	7.46	3.1	0.96	6.47	1.13
Illinois #6 (D)	7.47	4.0	0.93	5.60	0.60

Attempts were also made to experimentally determine particle terminal velocities. This was accomplished by measuring the time it took an individual particle to freely fall a set distance in the column filled with non-flowing water. The particles were allowed approximately 50 cm to achieve terminal velocity, and were then timed with a stopwatch as they fell an additional distance of 50 cm. Ten measurements were made for each coal sample type. It was found that the measured velocity was highly dependent on the particle shape and orientation. Comparisons of the experimentally determined values of terminal velocity and the values derived from Eq. [1] are presented in Table 9. These results indicate that the Richardson-Zaki equation describes the fluidized behavior of the coal reasonably well, even though the coal particles are porous and irregularly shaped.

3.4. LFBC Separation and Beneficiation of Coal.

3.4-1. “Larger” Coal Particle Samples (C and D).

Coal samples, both swollen and unswollen, were fluidized in the LFBC, and three fractions (bottom, middle, top) were removed from each of the corresponding sampling ports. The size classification data for the four samples investigated are presented in Figures 8-19. As shown, the mean particle diameter tended to decrease with increased height in the bed. The corresponding mean diameters of the samples are presented in Tables 10-13. Values of the mean particle diameter of the top fraction as a percent of the mean particle diameter of the bottom fraction diameter are presented in Table 14.

Table 10. Mean particle diameters of LFBC fractions for Kentucky #9, 355-500 μm (C) and 840-1000 μm (D) samples.

Solvent	Bottom (μm)	Middle (μm)	Top (μm)
Unswollen (C)	419	358	339
Acetone	415	376	294
Phenol	409	361	335
Unswollen (D)	711	697	628
Acetone	816	714	711
Phenol	785	740	680

Table 11. Mean particle diameters of LFBC fractions for Illinois #6, 355-500 μm (C) and 840-1000 μm (D) samples.

Solvent	Bottom (μm)	Middle (μm)	Top (μm)
Unswollen (C)	368	364	320
Acetone	398	448	333
Phenol	418	378	328
Unswollen (D)	693	693	666
Acetone	712	723	650
Phenol	838	724	737

Table 12. Mean particle diameters of LFBC fractions for Kentucky #9, 840-1000 μm (D).

Solvent	Bottom (μm)	Middle (μm)	Top (μm)
Unswollen	711	697	628
Acetone	816	714	711
Phenol	785	740	680

Table 13. Mean particle diameters of LFBC fractions for Illinois #6, 840-1000 μm (D).

Solvent	Bottom (μm)	Middle (μm)	Top (μm)
Unswollen	693	693	666
Acetone	712	723	650
Phenol	838	724	737

Table 14. Mean particle diameters of the top LFBC fraction as a percent of the bottom LFBC fraction.

Sample	Unswollen (%)	Acetone (%)	Phenol (%)
Kentucky #9, C (355-500 μm)	80.9	70.8	82.1
Illinois #6, C (355-500 μm)	86.9	83.7	78.3
Kentucky #9, D (840-1000 μm)	88.3	87.2	86.6
Illinois #6, D (840-1000 μm)	96.1	91.3	88.0

From these data, it appears that the LFBC did indeed separate particles according to size, with the largest particles consistently appearing in the bottom fraction. However, there is relatively little evidence of solvent-dependent effects in these data. That is, all the fractions exhibited an almost uniform increase in size with solvent-swelling. Also, the data in Table 14 show that neither acetone nor phenol demonstrated a consistent trend in changing the *distribution* of particle sizes within the column.

The ashing data for the LFBC fractions for the unswollen coal samples are presented below in Table 15.

Table 15. Ashing results for the unswollen LFBC fractions.

Sample	Bottom (wt % ash)	Middle (wt % ash)	Top (wt % ash)	Unclassified (wt % ash)
Kentucky #9, C (355-500 μm)	5.7	3.1	3.6	-
Illinois #6, C (355-500 μm)	6.1	4.3	3.4	9.4
Kentucky #9, D (840-1000 μm)	6.0	5.3	3.8	7.3
Illinois #6, D (840-1000 μm)	7.5	4.6	5.1	7.9

One apparent discrepancy in these data is that the measured ash content of the unclassified coal samples was consistently greater than in the bottom sample. It was expected that the ash content of the unclassified sample would be an average of that in the entire expanded, segregated bed. Consequently, it should have an ash content somewhere in between that of the top and bottom fractions. These results can only be explained by a systematic error in the sample preparation method; e.g., loss of a fraction of the heaviest, presumably highest mineral-matter containing particles during the multiple transfer and handling operations. In any case, the trends observed in the classified fractions appear to be consistent.

In addition to the preceding problem, the measured ash contents of the unclassified samples were consistently less than the averages reported in the data for the two coals. It is possible that the particular sample fractions investigated had less total ash than the reported averages. In addition, however, it is possible that the preheating procedure was not sufficient to remove all the moisture from the coal samples. Moisture effectively increases the percentage of non-ash matter in the coal, and results in underestimation of the true ash content of the dry sample. However, since all the samples were exposed to the same conditions and handling procedures, this should not affect the measured relative ash percentages. Therefore, the conclusions remain valid.

The data indicate that the LFBC separated the C- and D-size particles based primarily on ash content. The top fraction consistently had less ash than the bottom fraction for all the samples investigated. However, the ash content of some of the middle fractions did not lie between those of the top and bottom fractions, as would be expected. The three samples for each run were ashed in the furnace at the same time to minimize variations in ashing conditions.

However, due to the limited size of the furnace tube, one of the samples had to be about half the size of the other two. For consistency, this was always taken to be the middle fraction. Consequently, there could have been a systematic experimental error that resulted in the observed discrepancies for the middle fractions.

A summary of the ashing data for all the LFBC fractions, both swollen and unswollen, for the Illinois #6, C-size (355-500 μm) sample is presented in Table 16. It is noted that the fractions were all fairly consistent, irregardless of the swelling treatment. Consequently, for the larger particles there was no evidence of improved beneficiation due to solvent-swelling beyond that expected for separation based on natural density in the LFBC.

Table 16. Ash content summary of LFBC fractions for standard and solvent-swollen samples of Illinois #6, C-size (355-500 μm) particles.

Fraction	Bottom (%)	Middle (%)	Top (%)
Standard	6.1	4.3	3.4
Acetone	7.9	5.1	3.8
Phenol	7.6	4.9	3.3

3.4-2. “Smaller” Coal Particle Samples (A' and A").

It was hypothesized that the larger particles did not exhibit improved beneficiation due to solvent-swelling primarily because the mean organic/inorganic composition did not vary significantly enough. Thus, it was decided to focus on the smaller particles. As previously, the coal samples, both swollen and unswollen, were fluidized in the liquid fluidized bed, and the same three fractions (bottom, middle, top, middle and bottom) were removed from each of the sampling ports. Particle size distributions were determined by image analysis.

Experimental results for the A' and A" samples, for both coals, both unswollen and solvent-swollen, are presented in Tables 16-19. From these data, it is apparent that the mean particle size decreased with increasing bed height for all the unswollen coal particle samples. This trend was the same as found for the “larger” (C- and D-size) particles.

Table 17. Mean particle diameters of LFBC fractions for Kentucky #9, A'-size.

Fractions	Bottom (μm)	Middle (μm)	Top (μm)
No Solvent	115	119	67
Phenol	128	123	87
Acetone	151	145	96

Table 18. Mean particle diameters of LFBC fractions for Illinois #6, A'-size.

Fractions	Bottom (μm)	Middle (μm)	Top (μm)
No Solvent	123	78	82
Phenol	129	111	77
Acetone	149	126	109

Table 19. Mean particle diameters of LFBC fractions for Kentucky #9, A"-size.

Fractions	Bottom (μm)	Middle (μm)	Top (μm)
No Solvent	79	75	64
Phenol	94	89	76
Acetone	81	93	109

Table 20. Mean particle diameters of LFBC fractions for Illinois #6, A"-size.

Fractions	Bottom (μm)	Middle (μm)	Top (μm)
No Solvent	72	68	67
Phenol	69	75	91
Acetone	74	83	101

The data for the solvent-swollen particles were even more interesting. First of all, it was noted that the expansion observed for the liquid-fluidized beds of these solvent-swollen coal samples was considerably greater than that for the corresponding unswollen particle samples at the constant liquid velocity of 10.6 cm/min that was used in these studies. At this fluidization velocity, the unswollen particle samples expanded to about two-thirds of the column height, or approximately 1 m. For the same initial sample size for the solvent-swollen particles, the bed

expanded essentially to the full column height of about 1.5 m. This behavior is consistent with a significantly decreased mean particle density. The latter decreases the particle terminal settling, which, according to the Richard-Zaki equation would increase the mean bed void fraction. Consequently, particle swelling had a considerable effect of the bed behavior.

For the A"-size particles, for three of the four solvent-swollen samples, it was observed that the top LFBC fraction exhibited the *largest* particle size. This could only occur if the density of these particles was considerably less than the smaller particles at the bottom of the bed. This means that these particles were predominantly organic in nature and were sufficiently swollen to overcome the natural propensity of the larger particles (when of similar densities) to accumulate at the bottom of the bed. This effect was observable only for the A"-size particles because of their narrower size distribution. The bulk of these particles had a mean diameter lying between about 60 μ m and 80 μ m. Consequently, upon swelling the original smaller (primarily organic) particles could easily exceed in size the original larger (primarily inorganic) particles. This behavior is a good indicator of the degree of added beneficiation effect of solvent-swelling over that obtained with just segregation of unswollen particles.

For distributions of ground coal particles, it has been reported that the organic matter is concentrated in the *smaller* particles (Kaufmann *et al.*, 1994, 1995, and Senior *et al.*, 2000). This same effect was demonstrated in the current work. The A"-size particles were further separated into three size fractions using the water-filled column approach that was used to eliminate a significant fraction of the “fines” from the original A'-size particles. These three samples were then ashed. The results are presented in Table 21. As shown, the smaller particles do indeed exhibit a larger fraction of organic matter than the larger particles.

Table. 21. Relationship between unswollen particle size and ash content.

Sample	Fraction 1		Fraction 2		Fraction 3	
	Mean diameter (μ m)	Ash content (%)	Mean diameter (μ m)	Ash content (%)	Mean diameter (μ m)	Ash content (%)
Kentucky #9	70	8.2	88	9.9	114	11.8
Illinois #6	67	11.3	73	12.1	104	12.8

3.5. Ashing Results.

As noted above, significant bed expansion was observed for the solvent-swollen particle samples. For this reason, a direct comparison of the particle samples obtained from the same three fixed sampling ports cannot be expected to provide an accurate measure of the improvement in the degree of beneficiation associated with solvent-swelling. For this reason, only two fractions were analyzed for ash content: a sample from the bottom sampling port, and a sample of the particles overflowing the fluidized bed. The latter was collected by removing the retaining screen in the overflow tank at the top of the column, and intercepting the flow of fluidized particles that were carried out of the bed.

Table 22. Weight percent ash in LFBC bottom sample.

Samples	KY #9 (A') (%)	IL #6 (A') (%)	KY #9 (A'') (%)	IL #6 (A'') (%)
Standard	10.4	12.3	8.2	11.3
Unswollen	12.7	15.5	8.8	11.8
Acetone	14.2	15.8	9.6	13.2
Phenol	13.1	15.9	9.4	12.5

Table 23. Weight percent ash in LFBC overflow sample.

Samples	KY #9 (A') (%)	IL #6 (A') (%)	KY #9 (A'') (%)	IL #6 (A'') (%)
Standard	10.4	12.3	8.2	11.3
Acetone	3.9	5.2	3.2	4.7
Phenol	3.8	4.3	4.9	6.4

The ash contents of these samples are summarized in Tables 22 and 23, respectively. As shown, in all four cases, comparisons of the ash content of the top and bottom fractions clearly show a significant beneficiation effect of segregation in the liquid-fluidized bed for the solvent-swollen samples, ranging from ratios of 2-4 in bottom/top ash content.

The significant effect of solvent-swelling was also observed in another telling manner. After fluidization of the A'-size particle sample of Kentucky #9 swollen with phenol, the sample was allowed to remain immersed in water for five days, over which time most of the phenol was

leached out of the particles. The sample was then re-fluidized under the same conditions, and samples were collected from the three sampling locations as usual. The ash content of the resultant samples was determined to be 15.1, 13.9, and 12.1% for the bottom, middle, and top samples, respectively. It is noted that these values were almost the same as determined for the unswollen particles: 15.5, 14.4, and 11.9%, for the bottom, middle, and top samples, respectively. These results underscore the significant effect of solvent-swelling on improving coal beneficiation in liquid-fluidized beds.

It is also noted that the size range where solvent-swelling appears to be the most effective with respect to improving beneficiation is quite similar to the size of particles commonly used in pulverized coal combustion; that is, a mass mean diameter of $50\text{ }\mu\text{m}$ with 70-80 wt % less than $75\text{ }\mu\text{m}$, and 0.2-0.5 wt % larger than $300\text{ }\mu\text{m}$. This is potentially quite convenient since the LFBC beneficiation with solvent-swelling could be performed on the power plant PC grind just before it is used, without incurring any additional grinding costs.

4.0. SUMMARY & CONCLUSIONS

The concept of coal beneficiation due to particle segregation in water-fluidized beds, and its improvement *via* selective solvent-swelling of organic material-rich coal particles, was investigated in this study. Particle size distributions and their behavior were determined using image analysis techniques, and beneficiation effects were explored *via* measurements of the ash content of segregated particle samples collected from different height locations in a 5 cm diameter water-fluidized bed apparatus.

Both acetone and phenol were found to be effective swelling agents for both Kentucky #9 and Illinois #6 coals, considerably increasing mean particle diameters, and shifting particle size distributions to larger sizes. Illinois #6 was swollen somewhat more by these solvents than Kentucky #9. Acetone was a somewhat more effective swelling solvent than phenol. Leaching of solvent out of the coal particles into water was observed to occur. This was found to be more rapid for phenol than for acetone. Phenol-swollen particles were observed to return to their original size in about an hour. However, this process is still slow enough to allow sufficient time for segregation and separation of solvent-swollen coal particles in a water-fluidized bed.

For unswollen coal particles, the trend of increasing particle size from top to bottom in the LFBC was observed in all cases. Since the organic matter in the coal tends to concentrate in the smaller particles, the larger particles are typically denser. Consequently, the LFBC naturally tends to separate coal particles according to mineral matter content, both due to density and size.

For the larger coal particle sizes investigated in the current study (355-500 μm (C) and 840-1000 μm (D) samples), it was found that solvent-swelling did not have a significant effect on improving beneficiation over that obtained for the unswollen coal particles. This was attributed to the larger particles being relatively homogeneous with respect to their organic/inorganic composition.

For the smaller coal particle samples however, a significant improvement in beneficiation due to solvent-swelling was observed. In fact, in the case of A" (40-100 μm) particles swollen with acetone, the *larger* particles appeared in the *top* fraction of the bed and the *smaller* particles in the *bottom* fraction after swelling. This, of course, is the opposite of what was always observed for the unswollen samples. This is because the original smaller and lighter particles, containing a higher proportion of organic matter than the larger particles, swelled more than larger particles, thereby reducing their density and causing them to accumulate preferentially at the top of the water-fluidized bed. The data for the small, solvent-swollen particles clearly showed improved beneficiation with respect to segregation in the water-fluidized bed than was achieved with the corresponding unswollen particles.

The size range of the smaller particles investigated here is quite similar to that used in pulverized coal combustion. Therefore, additional grinding is unnecessary in order to implement improved beneficiation *via* selective solvent-swelling in LFBC. Moreover, as demonstrated, the process can utilize waste solvents, such as phenol, in order to swell the particles, while minimizing costs.

In summary, the original hypothesized concept was amply demonstrated in this project. Additional work remains to be done, however, in order to develop this concept into a full-scale process.

LITERATURE REFERENCES

- Al-Dibouni, M.R., and Garside, J. *Trans. Instn. Chem. Eng.* **57**, 94 (1979).
- Cadle, R.D., *Particle Size Determination*, Interscience Publishers, NY, 1955.
- Calo, J.M., Lilly, W.D., Hradil, G., and Mohsen, P., *Adv. Filtration Separation Tech.* **10**, 399 (1996).
- Couderc, J.P. in *Fluidization*, 2nd ed., J.F. Davidson, R. Cliff, and D. Harrison, eds., Academic Press, London, 1985.
- Davidson, R.M. *Fuel* **73**, 988 (1994).
- Davies, L., and Richardson, J.F., *Chem Eng. Sci* **37**, 1079 (1982).
- EPA/310-R-95-015, EPA Office of Compliance Sector Notebook Project, Profile of Pulp and Paper Industry, 1995.
- Gibbs and Hill, Inc., *Coal Preparation for Combustion and Conversion*, EPRI AF-791, 1978.
- Hradil, G., A Study of Liquid-Fluidized Reactors for the Enzymatic Hydrolysis of Biomass, Ph.D. Dissertation, Division of Engineering, Brown University, May, 1991.
- Irani, R., and C.F. Callis. Particle Size: Measurement, Interpretation, and Application, John Wiley and Sons, New York, 1963.
- Kaufman, E.N., Scott, T.C., *Powder Technology*, **78**, 239(1994).
- Kaufman, E.N., Petersen, J.N., Wang, Y., Little, M.H., *Chem Eng. Sci.* **50**, 3703 (1995).
- Larsen, J.W., Green, T.K., and Kovac, J., *J. Org. Chem.* **50**, 4729 (1985).
- Lawlor, D.L., Fester, J.I., and Robinson, F.E., *Fuel* **42**, 2 (1963).
- Richardson, J.F., and Zaki, W.N. *Trans. Instn. Chem. Eng.* **32**, 35 (1954).
- Senior, C.L., Zeng, T., Che, J., Ames, M.R., Sarofim, A.F., Olmez, I., Huggins, F.E., Shah, N., Huffman, G.P., Kolker, A., Mroczkowski, S., Palmer, C., Finkelman, R., *Fuel Processing Technology*, **63**, 215 (2000).
- Smith, E.L., James, A., and Fidgett, M. (1978) in *Fluidization*, Cambridge University Press, Cambridge, England, p. 196.
- Tsai, S.C., *Fundamentals of Coal Beneficiation and Utilization*, Elsevier, 1982.
- Vorres, K.S., *Users Handbook for the Argonne Premium Coal Sample Program*, October, 1993.
- Yun, Y. and E. M. Suuberg, *Fuel* **72**, 1245, (1993).

- Yürüm, Y., in *Clean Utilization of Coal*, NATO ASI Series, Series C, Vol. 370, Y. Yürüm, ed., Kluwer Academic Publishers, The Netherlands, 1992, p. 153.
- Washington, C., *Particle Size Analysis in Pharmaceuticals and Other Industries*, Ellis Horwood Ltd., UK, 1992.
- Wang, N., M. Sasaki, T. Yoshida, and T. Kotanigawa, *Energy & Fuels*, **12**, 531-535 (1998).

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Figure 1. Schematic of LFBC apparatus.

Figure 2. Pittsburgh #8 swelling results in three solvents.

Figure 3. De-swelling results in water for Illinois #6 coal samples (B: 105-149 μm), originally swollen in methanol and acetone.

Figure 4(a,b). Cumulative particle size distributions for: (a) Illinois #6; and (b) Kentucky #9 coal samples.

Figure 4(c). Cumulative particle size distributions for (c) Ohio #4A coal samples.

Figure 5(a,b). Differential particle size distributions for unswollen and solvent-swollen A'-size (56-75 μm) particles for: (a) Kentucky #9; (b) Illinois #6.

Figure 5(c,d). Differential particle size distributions for unswollen and solvent-swollen B'-size (106-180 μm) particles for: (c) Kentucky #9; (d) Illinois #6.

Figure 5(e,f). Differential particle size distributions for unswollen and solvent-swollen A"-size (40-100 μm) particles for: (e) Kentucky #9; (f) Illinois #6.

Figure 6. De-swelling results in water for Illinois #6 and Kentucky #9 coal samples, A'-size (56-75μm), originally swollen in methanol and acetone.

Figure 7. Mean bed void fraction as a function of superficial liquid velocity; Richardson-Zaki correlation.

Figure 8. Size comparisons of LFBC fractions for Kentucky #9, C-size (355-500 μm) particles.

Figure 9. Size comparisons of LFBC fractions for Kentucky #9, C-size (355-500 μm) particles swollen with acetone.

Figure 10. Size comparisons of LFBC fractions for Kentucky #9, C-size (355-500 μm) particles swollen with phenol.

Figure 11. Size comparisons of LFBC fractions for Illinois #6, C-size (355-500 μm) particles.

Figure 12. Size comparisons of LFBC fractions for Illinois #6, C-size (355-500 μm) particles swollen with acetone.

Figure 13. Size comparisons of LFBC fractions for Illinois #6, C-size (355-500 μm) particles swollen with phenol.

Figure 14. Size comparisons of LFBC fractions for Kentucky #9, D-size (840-1000 μm) particles.

Figure 15. Size comparisons of LFBC fractions for Kentucky #9, D-size (840-1000 μm) swollen with acetone.

Figure 16. Size comparisons of LFBC fractions for Kentucky #9, D-size (840-1000 μm) particles swollen with phenol.

Figure 17. Size comparisons of LFBC fractions for Illinois #6, D-size (840-1000 μm) particles.

Figure 18. Size comparisons of LFBC fractions for Illinois #6, D-size (840-1000 μm) particles swollen with acetone.

Figure 19. Size comparisons of LFBC fractions for Illinois #6, D-size (840-1000 μm) particles swollen with phenol.

Appendix A. Summary of Coal Swelling and De-swelling Data.

(1) All coal swelling time series begin at a swelling index of unity at time zero.

(2) Coal Samples: Pitt = Pittsburgh #8; Illinois = Illinois #6; Kent = Kentucky #9; Ohio = Ohio #4A.

Particle Sizes: A - 53-105 μm ; B - 105 - 149 μm]

Sample# (Size)	Sample/ Solvent														
Time(h)		2	4	5	22	26.33	28.33	46	48	50.5	52.5	68.5	70	72	74
11 (A)	Pitt/ MeOH	1.1	1.1	1.12	1.1										
12 (A)	Pitt/ MeOH	1.137	1.137	1.176	1.12	1.127	1.039	1.137	1.12						
13 (A)	Pitt/ MeOH	1	1	0.96	0.98	0.955	0.95	0.98	0.96						
14 (A)	Pitt/ MeOH	1.16	1.16	1.2	1.18	1.12	1.12	1.16	1.17						
Time(h)		2.75	4.75	20.8	22.3	24.3	27.25	51.3							
15 (B)	Pitt/ MeOH	1.153	1.07	1.1	1.1	1.1	1.08	1.05							
16 (B)	Pitt/ MeOH	1.119	1.04	1.06	1.06	1.04	1.07	1.04							
17 (B)	Pitt/ MeOH	1.068	1.04	1.03	1.03	0.99	1.01	0.96							
18 (B)	Pitt/ MeOH	1.049	1.03	1.02	1.01	1.02	1.02	1.01							
Time(h)		1	3	4	24	25	27	29	30.5	47	50	51.5	54	72	98.75
25 (A)	Illinois/ MeOH	1.084	1.15	1.131	1.15	1.14	1.12	1.121							
26 (A)	Illinois/ MeOH	1.14	1.15	1.15	1.12	1.16	1.15	1.15	1.15	1.13	1.1				
27 (A)	Illinois/ MeOH	1.14	1.095	1.095	1.162	1.16	1.105	1.104	1.114	1.123	1.090	1.07	1.076	1.11	
28 (A)	Illinois/ MeOH	1.143													
Time(h)		1.5	3.5	5	21.33	25.33	26.75	29	46.3	49.15	69.3	71.5	73	75	76.8
29 (B)	Pitt/ Acetone	1.1	1.09	1.12	1.1	1.08	1.09	1.09	1.16	1.14	1.2				
Time(h)		2.33	3.75	6	23.33	26.2	46.25	48.5	50	52	53.75	118.3			
30 (B)	Pitt/ THF	1.125	1.192	1.23	1.365	1.38	1.471	1.49							
31 (B)	Pitt/ Octane	1.010	1.083	1.09	1.01	1.04	1								
32 (B)	Illinois/ MeOH	1.333	1.276	1.31	1.343	1.3	1.238	1.257	1.224	1.19	1.2				

33 (B)	Illinois/ MeOH	1.316	1.242	1.26	1.389	1.23	1.305	1.253							
34 (B)	Illinois/ MeOH	1.32	1.23	1.24	1.22	1.26	1.265	1.28	1.23	1.21	1.21				
35 (B)	Illinois/ MeOH	1.318										1.255			
Time(h)	Pitt/ Acetone	1	2.15	4.15	6.15	24	26.25	27.5	28.7	30.5	47.5	49.67	51.85	54.15	71.67
36 (A)	Pitt/ Acetone	1.16	1.179	1.253	1.211	1.216	1.2	1.179	1.16	1.137					
37 (A)	Pitt/ Acetone	1.14	1.145	1.19	1.19	1.16	1.16	1.18	1.17	1.19	1.2	1.2	1.18	1.175	
38 (A)	Pitt/ Acetone	1.14	1.14	1.2	1.19	1.16	1.16	1.18	1.2	1.2	1.2	1.2	1.18	1.16	1.13
39 (A)	Pitt/ Acetone	1.143	1.143												
Time(h)		2.667	4.67	6.667	23.5	25.75	27	28.15	31	47	49.15	51.33	53.67	71	73.15
40 (B)	Pitt/ Acetone	1.16	1.111	1.1	1.13	1.093	1.093	1.065	1.09	1.074	1.111	1.074	1.1		
41 (B)	Pitt/ Acetone	1.184	1.117	1.117											
42 (B)	Pitt/ Acetone	1.13	1.04	1.047	1.03	1.02	1.03	1.02	1.04	1	1.04	1.03	1	1	1
43 (B)	Pitt/ Acetone	1.2													
Time(h)		2	4.5	7.5	24.5	27.75	30	71.5	74	76	78	79.7	96	98	101.7
44 (A)	Illinois/ Acetone	1.297	1.26	1.261	1.25	1.189									
45 (A)	Illinois/ Acetone	1.31	1.284	1.29	1.305	1.25	1.211	1.242	1.23	1.26					
46 (A)	Illinois/ Acetone	1.21	1.233	1.23	1.243	1.21	1.194	1.184	1.18	1.25	1.18	1.18	1.18	1.19	
47 (A)	Illinois/ Acetone	1.28	1.229	1.23	1.211	1.19									
Time(h)		3.25	5.5	23	25.5	27.5	29.5	31	47.5	49.5	53	55	71.3	74	76
48 (B)	Illinois/ Acetone	1.318	1.26	1.27	1.29	1.28	1.25								
49 (B)	Illinois/ Acetone	1.38	1.39	1.31	1.34	1.29	1.33	1.32	1.36	1.34					
50 (B)	Illinois/ Acetone	1.35	1.34	1.3	1.34	1.33	1.32	1.34	1.34	1.34	1.27	1.3	1.26	1.34	1.33
51 (B)	Illinois/ Acetone	1.305													1.35

Time(h)		3	6	23.3	28.3	30.7	47	50	71	75					
52 (A)	Kent/ MeOH	1.01	0.98	0.97	1.01										
53 (A)	Kent/ MeOH	0.98	0.98	0.98	1.01	0.99	1.04	1.01							
54 (A)	Kent/ MeOH	0.94	0.94	0.94	0.99	0.95	0.96	0.972	0.99	0.945					
55 (A)	Kent/ MeOH	0.96	0.96	0.96	0.96	0.96	0.96	0.962							
56 (A)	Kent/ Acetone	1.17	1.19	1.19	1.22										
57 (A)	Kent/ Acetone	1.2	1.22	1.25	1.23	1.19	1.2	1.221							
58 (A)	Kent/ Acetone	1.14	1.15	1.15	1.19	1.17	1.18	1.144	1.16	1.153					
59 (A)	Kent/ Acetone	1.18	1.19	1.22	1.2	1.2	1.19	1.2	1.19	1.18					
60 (B)	Kent/ MeOH	1	0.98	0.95	0.99										
61 (B)	Kent/ MeOH	0.91	0.94	0.92	0.96	0.94	0.93	0.938							
62 (B)	Kent/ MeOH	0.95	0.94	0.89	0.94	0.94	0.94	0.925	0.9	0.943					
63 (B)	Kent/ MeOH	0.97	0.96		0.99	0.96	0.96	0.959							
Time(h)		3.33	6.25	23.5	28.5	30.75	47	50.5	71.5	75.33					
64 (B)	Kent/ Acetone	1.19	1.2	1.2	1.167										
65 (B)	Kent/ Acetone	1.23	1.2	1.24	1.272	1.196	1.217	1.217							
66 (B)	Kent/ Acetone	1.2	1.22	1.26	1.217	1.217	1.217	1.217	1.207	1.196					
67 (B)	Kent/ Acetone	1.14	1.19	1.2	1.212	1.15	1.168	1.204	1.199	1.221					
Time(h)		2.75	5.667	23	28	30.5	46.5	50	71	75					
68 (A)	Ohio/ MeOH	0.98	0.935	0.923	0.94										
69 (A)	Ohio/ MeOH	0.97	0.953	0.968	0.94	0.945	0.945	0.93							
70 (A)	Ohio/ MeOH	0.91	0.896	0.922	0.92	0.87	0.879	0.84	0.852	0.86					
Time(h)		2.75	5.667	23	28	30.5	46.5	50	71	75					
71 (A)	Ohio/ Acetone	1.09	1.103	1.121											

72 (A)	Ohio/ Acetone	1.1	1.1	1.1	1.12	1.062	1.077	1.06							
73 (A)	Ohio/ Acetone	1.14	1.123	1.131	1.13	1.098	1.107	1.1	1.098	1.07					
Time(h)		3	5.75	23	28	30	47	50	71	74.5					
74 (B)	Ohio/ MeOH	0.992	0.98	1	0.992										
75 (B)	Ohio/ MeOH	0.945	0.94	0.961	0.953	0.93	0.913	0.91							
76 (B)	Ohio/ MeOH	0.955	0.95	0.954	0.970	0.96	0.97	0.94							
77 (B)	Ohio/ Acetone	1.19	1.16	1.152	1.171										
78 (B)	Ohio/ Acetone	1.077	1.08	1.084	1.098	1.08	1.07	1.07							
79 (B)	Ohio/ Acetone	1.22	1.2	1.22	1.22	1.2	1.211	1.21	1.211	1.22					
Time (min)		0	10	15	20	25	30	40	50	55	65	70	85	90	195
25 (A)	Illinois/ MeOH	1.12	1.12		1.12		1.12	1.12		1.10		1.10		1.08	
26 (A)	Illinois/ MeOH	1.14				1.1		1.1							1.09
27 (A)	Illinois/ MeOH	1.2		1.1			1.1		1.1		1.1			1.1	
28 (A)	Illinois/ MeOH	1.13	1.13			1.15		1.16		1.14			1.11		
32 (B)	Illinois/ MeOH	1.3		1.3			1.3		1.2		1.2			1.2	
33 (B)	Illinois/ MeOH	1.24	1.24			1.21		1.18	1.16				1.16		
34 (B)	Illinois/ MeOH	1.24	1.24			1.24		1.2				1.2		1.2	1.18

Appendix B. Image Analysis - Background and Procedures.

B.1. Introduction.

Particle size distribution analysis is an important step in assessing the performance of the liquid fluidized bed for its coal separation and beneficiation capabilities. For the purpose of this project, a method of analyzing coal particle samples extracted from different heights in a liquid fluidized bed column for size distributions was developed. There are a number of different techniques utilized for particle analysis, among the most accurate and readily available being microscopy and image analysis. An optical microscope with frame grabber or a digital camera can be used to capture an image to be read by a computer analysis program, such as IPLab Spectrum™ or Scion Image™. This image can then be analyzed for particle size distribution.

B.2. Background.

B.2-1. Methods of Particle Size Analysis.

Particle size analysis is important in many different fields and for a multitude of purposes. There are several major methods for particle size analysis, depending on the size of the particles, their shape, and the desired results; and each has their limitations.

Sieving. Dry granulated samples can be sized using standard sieves. This method divides large portions of coal into size ranges according to the sieve sizes used, and is generally applicable to particle sizes of greater than about 40 μm . Sieves can be operated manually or automatically using a standard mechanical sieve shaker. Each sieve is numbered with a certain ‘mesh’ size that corresponds to the size of the openings in the sieve screen. Any particle smaller than the sieve size will pass through that sieve. When beginning any new sample, it is important to use the smallest size sieve (largest mesh size) first in order to eliminate as much of the ‘fines’ as possible from the sample. Once this is accomplished, samples can then be sieved through a series of sieves of decreasing size. Particles collected in a sieve that will no longer pass through are assigned to the corresponding size range between sieves.

The accuracy of this procedure depends on a number of highly variable factors. For example, the size of the sample being sieved at any time cannot be too large because the likelihood of particles not passing through the openings will increase due to decreased chance of having sufficient contact time with the mesh screen. This factor will cause particles to remain in

a size range that is larger than their actual size. The variability of manual shaking is also a factor. It requires judgement concerning the point at which no additional particles are passing through the sieve before they are assigned to a particular size range.

Sedimentation. Sedimentation methods are also widely used to analyze particle size distributions ranging from about 0.5 to 300 μm .⁶ The advantage of sedimentation techniques lies in the fact that the equipment is simple, and a wide range of sizes can be readily measured with considerable accuracy. Liquid sedimentation is often used, and in the case of very small particles, centrifugation can also be used to help separate the particles. Sedimentation techniques are based on gravity and Stokes' law, such that a sphere falling through a liquid will be acted on by two forces: the accelerating force due to gravity and the viscous drag from the fluid.⁶ Gravitational sedimentation methods for particle size analysis are divided into two categories—incremental and cumulative methods. Actual procedures include the pipette method, the fixed-time method, the density method, and the cumulative weight method.⁵

Electrical Zone Sensing. Electrical zone sensing is another method used to measure particle sizes, and is best suited for particles in suspension. The principle of the instrument is fairly simple and can yield very accurate results. A pinhole set into a glass tube is immersed in a suspension of particles. A negative pressure is applied to the interior of the tube causing the particles to be sucked through the pinhole. When a particle passes through, it partly blocks the orifice and the resistance of the electrical orifice therefore rises. The smaller the particle that passes through the hole, the smaller the resistance, consequently the size of the particle can be found due to the resistance.⁶ This method produces good results because it reports a size for each individual particle. It is important to already have the size range of particles classified so that a proper sized pinhole can be selected for analysis. The equipment is expensive, however, and can be difficult to operate. It is also very sensitive to vibrations, such that the electrodes could respond to movements other than particles passing through the pinhole.

Laser and Light Scattering. Light scattering has been used for many years to measure the size of small particles, as well as molecular weights and diffusion coefficients (Washington, 1992). The technique has become more commonly used today due to the use of lasers as light sources. There are three properties that can be used for the measurement of particle size from light scattering data: diffraction, single particle scattering, and photon correlation spectroscopy. Scattered light intensity is measured as a function of the angle through which it was scattered,

and the resulting “scattering pattern” contains information regarding the particle size. The sizes are found by appropriate calculations, utilizing the Mie and Rayleigh theories of light scattering. Photon correlation measures the statistical intensity fluctuations (due to the random Brownian motion of the particles) in light scattered from the particles measured (Washington, 1992).

Microscopy. Microscopy is a very common and reliable method for determining particle size distributions. The typical size range of particles that can be analyzed optically is about 0.1 to 500 μm . A significant problem for microscopic analysis, however, is that only a small number of particles can be examined at a time. In order to get the most accurate results, a large number of particles in the sample must be measured; ideally at least 400. The statistical error in counting a certain number of particles, N , is the square root of N using Poisson statistics. Therefore, the largest number of particles possible must be counted in order to ensure good precision.

In addition to not having a sufficient number of particles in the sample window, there is also a problem of particle overlap. This often makes sample preparation the most difficult task in analyzing particle samples with an optical microscope. Considerable care must be taken in preparing the slide so that particles do not touch and can be measured separately. When analyzing dry samples, it is often easy to prepare the slide. The dry particles can be ‘puffed’ onto the slide using a pipette. One could also dip a small brush into the sample and then touch it to the slide surface. Both of these techniques can result in a great number of sufficiently separated particles on the slide.

The principal advantage of image analysis techniques is that the particle profile itself is measured. Since particles are visible, the reliability of a properly dispersed sample can be assessed immediately. Image analysis involves a few separate stages. A good representative picture with sharp contrast between the particles and background must first be captured with an optical microscope or camera. This can be accomplished with a vidicon tube camera or CCD (charge—coupled device) camera and frame grabber so that the image can be digitally displayed on a screen, or with a digital hand-held camera. The frame grabber operates by dividing the continuous analog video signal into an array of points known as pixels, each corresponding to a point in the picture. Each pixel is assigned a number based on its intensity, typically from 0 (black) to 255 (white). This is known as a 256 grayscale. These images can then be saved in a suitable format, and then operated upon with image analysis software for particle size distribution analysis.

B.2-2. Data Presentation.

The size of a particle is the representative dimension that best describes that particle (Irani and Callis, 1963). For a spherically symmetric particle the characteristic dimension is the particle diameter. The coal particles of interest here are irregular in shape, but are assumed to be spherical for simplification. The “diameter” of the particle can be determined from the projected area as measured using the formula for the area of a circle. Although this is an estimated size, it is reliable because of the large number of particles in the representative sample, and because a size distribution is the only data desired.

The particle size distribution of a sample is not the only data one can present for particle analysis. Average particle sizes, maximum and minimum particles sizes, and nonuniformity (the measure of the spread in particle sizes around the average size) can also be measured. Distribution data can be plotted in the form of a histogram, which shows the frequency of occurrence of particles as a function of size range, and this can be “smoothed—out” to produce a size frequency curve. Another convenient presentation of data is with cumulative plots. These involve plotting the percent of particles greater than a given particle size against the particle size, which results in limiting values of the ordinate from 0 to 100%. Any of these methods, along with applicable distribution functions, are adequate for reporting the size distribution of a sample (Irani and Callis, 1963).

B.3. Optical Image Analysis Procedure.

B.3-1. Sample Preparation.

The preparation of slides for use in optical microscopy is very important for particle size distribution analysis. In order to obtain the most accurate results, it is desirable to have at least 400 particles in the field of view, all separate from each other and not touching (Washington, 1992). This is done by comparison of the particles with a graticule or a calibration. The most common graticule is the ‘comparison circle’ type, where a range of circles of appropriate diameters is provided for sizing by comparison. Graticules with directly calibrated linear scales are not often used and usually lead to systematic overestimation on particle size

Many methods have been explored for mounting slides. For dry particles, it is possible to ‘puff’ the sample onto a slide, or to touch the slide with a brush that has been previously dipped into the sample. This method is generally accurate and can result in a sufficient number of

particles on the slide. This is the method that was used for the dry, unswollen, sieved coal particles.

Wet particles are somewhat more difficult and tedious to mount. Several liquids were explored as solvents; for example rubber in xylol and polystyrene in xylene (Irani and Callis, 1963). In the current project, however, the swollen and unswollen coal particles should be mounted in water because that is the liquid used in the liquid fluidized bed (from which samples are extracted). For this reason, it was not attempted to mount the particles using another solvent. The swollen particles had already been swollen in a solvent, and further modification of particle size due to the introduction of other liquids could result in alteration of the swelling index and could skew the distribution results.

Samples of particles in a liquid should be taken with an excess of water and stirred vigorously. Two tools could be used to mount the sample onto the slide. A stirring rod can be dipped into the stirred sample and then touched to the slide. A pipet could also be used to transfer particles to the slide. In both cases, after the sample has been mounted, the slide should be covered with a glass cover slip to prevent evaporation. The cover slip may also be used to separate particles by moving it around gently on top of the slide to disperse particles. Care must be taken not to scratch the glass or fracture the particles. The larger the particles, the easier it is to separate them on the slide. However, then fewer particles will fit into the field of view under the microscope, and the results become less accurate. For particle sizes approaching 1 mm, it is not necessary to capture the image through a microscope. Useable sample pictures could be taken using a digital camera.

B.3-2. IPLab Spectrum™ Analysis Procedure.

Particle images can be analyzed using various software packages, such as IPLab Spectrum™ or Scion Image™. Both were used in the current project, but IPLab Spectrum™ was judged to be more flexible.

Prior to image analysis, the program must be calibrated for different magnifications. This is accomplished by taking a picture of a calibration tool, in this case a 1 mm standard, at all available magnifications; i.e., 5x, 10x, 20x, and 50x. These images can then be opened by the program and their pixel counts calibrated. Images of the samples can be captured in a similar manner and analyzed.

A detailed explanation of the procedure developed and followed using IPLab Spectrum™ follows. The italicized words represent commands as they appear in the program toolbar.

Calibrating the Program:

- *Analyze— Define XY Units*— allows new calibration according to the magnification of the open image.
- *Interactive* — the mouse can be used to measure a known length on the image (for instance, 0.1 mm), and this value can be recorded. Each pixel will then be assigned a certain length according to the calibration.

Preparation for Analysis of Images:

- *Analyze- Set XY Units* — used to set the units to whatever magnification at which the image was taken.
- *Analyze— Set Measurements* - allows selection of the factors the program will measure when analysis commences. It is important to measure *Area*, *Perimeter*, *Mean*, and perhaps *Major* and *Minor Axis*.
- *Analyze— Measurement Options*- a segment color should be chosen other than black or white so that particles can stand out against the background; segments touching the ROI (Region of Interest) should be ignored so that they are not included in measurements; it should be indicated that segments are to be outlined and numbered.

Segmentation of Particles:

- *Analyze— Segmentation*— the most crucial and difficult step in particle analysis.
- *Show ROI Histogram*- allows the user to adjust the minimum and maximum segment numbers while viewing the image. It is suggested that the minimum segmentation number be adjusted so that anything not to be measured as a particle is the segment color chosen previously. It is important to adjust segmentation number so that all background noise (i.e., particle dust, scratches on slide, etc.) is eliminated.

Modifying the Segments:

- *Analyze— Modify Segments- Complement*- inverts the particle color (black) and the segment color so that the background becomes white and the particles become the segment color.
- *Analyze— Modify Segments— Erode* and *Analyze— Modify Segments— Dilate*— these features attempt to separate any overlapping particles by removing pixels at the particle

edges (*Erode*) and then inserting some to compensate for previous removal (*Dilate*).

- *Zoom Icon*— can be used to examine particles more closely.
- *Paint Icon*- can be used to manually separate any obviously overlapping particles by painting over the ‘overlapped’ segment color with the background color.

Measuring the Segments:

- *Analyze— Measure Segments*- the program analyzes the segments, and the measurements selected previously will be displayed in a new window entitled *Measurement Results*.

The preceding procedure was used to analyze most of the particle images in the current work. The procedure is significantly easier for larger particles and clear images, and becomes more laborious when the background noise is difficult to separate from the selected particles. Although IPLab Spectrum™ does have statistical analysis options, it was found that manipulation of the data was more facile using other plotting programs, such as Kaleidagraph™ or Microsoft Excel™.

Results from IPLab Spectrum™ can be copied to Kaleidagraph™ for statistical analysis. If *Area* is chosen to represent particle size, then this column can be highlighted and *Functions— Bin Data* selected. The desired number of bins must also be selected. The left column will show how the bins were separated (its units will be in whatever the measurements were taken in) and the right column can show either the number of particles in each bin or the percentage of particles in each bin. This option reports useful information, but the values must be copied and pasted to a spreadsheet for further manipulation and analysis. The results can then be as particle size distributions. Other relevant statistical information can be found under *Functions— Statistics*. In this window the minimum and maximum particle value is presented, as well as the mean and median particle size, the total number of particles, the standard deviation, and the skewness factor.

IPLab Spectrum™ results can also be copied to an Excel spreadsheet for analysis. From the area, the ‘rough’ diameter can be calculated by assuming the particles are spherical. Bins can then be created manually according to the maximum and minimum diameter values, and the number of particles that fall into each bin range can be counted and entered into a cell. When all bins have been filled the resulting numbers can be used as the particle size distribution. The number of particles can also be converted to a percentage of the total number of particles or to the percentage of the particles less than a given size.