Particle Size Analysis in the SRC Process by Coulter Counter

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Introduction

This work was undertaken to develop an effective rapid technique for determining particle size of undissolved solids in the Solvent Refined Coal (SRC) Process. Particle size distributions for SRC filter feed from the Wilsonville SRC Pilot Plant and autoclave reaction mixtures from the Auburn Coal Conversion Laboratory were measured using a Coulter Counter Model TA.

The Coulter principle was originally applied to blood cell counting[1] and is now widely used in the biomedical area for cell counting and size distribution.[2] Industrial use of the Coulter technique is now widespread.[3] The Coulter technique has been applied in coal research in the size analysis of pulverized coal, coal dust, and fly-ash.[4] Presently, the Coulter technique is being applied to the study of particle size distributions in the SRC process. Interest in the effect of the mean particle size in the effluent from the SRC dissolver on filtration along with the problem of dissolver solids accumulation[5] has shown the need for a reproducible method of determining particle size in SRC process streams.

Experimental

Equipment

Particle size determinations were performed on a Coulter Counter Model TA (Coulter Electronics, Hialeah, Florida) equipped with a Model TA External Size Calibrator II and an adjacent sample stand. The orifices normally used for the analyses were 100, 140, 200 and 280 μm.

Electron microscopy was performed using an AMR Model 1000 scanning Electron Microscope operating at 20KV with a tungsten source and an aluminum coated detector. The samples were coated with 60:40 gold-palladium using a Denton DV 502 vacuum evaporator. Optical microscopy was performed using a Wild Model M21 microscope equipped with a Polaroid MP-3 Land Camera.

Chemicals

Reagent grade ammonium thiocyanate (NH_4SCN) and dimethylformamide (DMF) obtained from Mallinckrodt prepared in a 5% solution was the electrolyte used for Coulter analysis. Metricel alpha -8 filters with 0.20μm pore size were used for filtering the electrolyte solution. Carbowax 400 obtained from Union Carbide was the dispersant used for optical microscopy.

Procedure

Calibration of each orifice was performed using polystyrene calibration standards of known diameter (supplied by Coulter Electronics) dispersed in isoton.

Autoclave reaction samples and Wilsonville filter feed were sonicated using a low energy ultrasonic bath, dispersed in the 5% NH_4SCN - DMF electrolyte and again sonicated. The samples were diluted with electrolyte and immediately analyzed. For each sample 100,000 particles were counted and the particle size distribution was obtained. Extensive filtering with 0.2μm filters was necessary to maintain the necessary background of the electrolyte.

For scanning electron microscopy samples were prepared by sonicating and further diluting the Coulter samples. The particles were filtered on a 0.2μm filter and air dried. For optical microscopy, autoclave reaction mixtures were first sonicated and then dispersed in Carbowax 400. Hanging drop as well as slide preparations were used.

Verification

Verification of the Coulter technique by optical microscopy can be seen in Figure 1. Rigid polystyrene calibration spheres (9.99μm in diameter supplied by Coulter Electronics) were measured by optical microscopy under 500x magnification to have a diameter of 10.0μm. Subsequent analysis of the polystyrene's particle size by Coulter Counter agreed fully with the microscopy.

Results and Discussion

The Coulter technique measures the particle volume size distribution. The smallest particles measured had a diameter of 1.59μm with an overall diameter range of 1.59 to 128μm. All measurements were taken within the optimum range of the orifice. Particle size distributions were obtained for autoclave reaction mixtures and Wilsonville filter feed of Amax, Western Kentucky, Pittsburgh Seam, and Monterey coals. The particle size distribution measurements for each coal sample can be accurately reproduced within ± 10%. A mean particle size is obtained graphically by plotting the normalized cumulative particle volume percent versus particle diameter and then obtaining the mean particle size at the 50% volume level.

The initial mean particle size for unreacted coal was between 28.8 - 40.0μm. Table I shows the mean particle size in terms of particle diameter for four autoclaved coals reacted at 410°C for three different time intervals. Under autoclave conditions, the mean particle size varies significantly among the different coals. Within the time range studied the mean particle size for Monterey and Pittsburgh Seam coals remained essentially constant; however, the mean particle size of Western Kentucky coal increased with time while that of Amax coal decreased. The mean of Amax coal leveled off at 9.6μm after 4 hours. The temporal behavior of the particle size of each coal can be directly correlated to its dissolution rate and behavior. Both Monterey and Pittsburgh Seam coals dissolve very rapidly, leaving essentially only mineral matter after 15 minutes of reaction. Amax coal, however, is a slow dissolver which accounts for the decrease in particle size over the time period studied. Western Kentucky coal dissolves very rapidly but is sticky and adhesive; increasing reaction time allows the particles time to adhere to one another forming larger particles.[6]

The Wilsonville filter feed particle size distributions for each coal closely resembled the autoclave reaction distribution (an example is shown in Table II) except for Western Kentucky coal which showed a significant shift to smaller particles. Generally, the Wilsonville filter feed distributions showed greater variation within each sample than did the autoclave reactions resulting in a larger standard deviation for each volume range. A comparison of the mean particle size of Wilsonville filter feed to Auburn autoclave reaction mixtures is shown in Figure III. For each coal the mean particle sizes compare very closely with the exception of Western Kentucky coal. This difference can again be attributed to the adhesive nature of the Western Kentucky particles. In the filter feed the particles will tend to adhere to one another forming larger particles which stay in the dissolver while the smaller particles are elutriated out of the dissolver.

Optical and electron microscopy verified the presence, size, and character of the particles being counted by the Coulter Counter. Optical microscopy allowed observation of the particles in a solution matrix. Scanning electron microscopy permitted isolation of the particles from the oil matrix and allowed the particles to be individually observed. The unregular nature and individual character of the particles are shown in the micrographs in Figure 2-7.

Process Applications

Filterability of a solid/liquid slurry depends on the size distribution of the particulates entrained in the slurry as well as other factors such as viscosity, adhesive forces among the particles (i.e., whether the particles are sticky or discrete and unattractive) etc. A major objective of this work is to determine whether mean particle size determined by Coulter Counter analysis can be correlated to filterability or, more specifically, cake resistivity. To this end: the mean particle size of particulates in the SRC dissolver effluent for the coals studied are compared with their associated cake resistivities.

Filtration rates for Amax, Western Kentucky and Monterey coal/oil slurries have been extensively studied under test conditions and without the incorporation of bodyfeed at the Wilsonville SRC Pilot Plant. Pittsburgh Seam coal/oil slurries have only been tested with bodyfeed. Table IV shows the cake resistivities calculated for the slurries run without bodyfeed. Indeed, correlations are evident between the ease of filtration (i.e., cake resistivity) and mean particle size. Amax coal/oil slurries which have the lowest cake resistivity and are, therefore, the most easily filtered of the three types of slurries considered have the largest mean particle size. Monterey coal/oil slurries have the highest cake resistivity, are the most difficult to filter, and have the smallest mean particle size. When screen blinding is taken into account, Western Kentucky ranks second in filterability as well as mean particle size. Cake resistivity is a function of the porosity of the cake which is directly related to particle volume. Particle volume is measured directly by the Coulter technique. In conclusion, the Coulter Counter can give a good indication of the filterability of a particular SRC process stream and, thus, should prove to be a useful tool in optimizing operational conditions for solids separation.

The present Coulter technique has two main limitations. First, since particles less than 1.6μm are difficult to detect, the total particle size range of the SRC effluents cannot be studied. The effect of the very small particles on filterability is not precisely known; however, it is very likely that particles below 2μm play a significant role in screen blinding. The second limitation is that carbonaceous agglomeration of SRC itself is difficult to detect because approximately 96% of SRC dissolves in the electrolyte. Detection of the formation of solid agglomerates would be highly desirable; for the accumulation of solids in the SRC dissolver has presented significant problems in processing certain types of coals, particularly those containing high concentrations of calcium. One reason for this accumulation, however, is commonly thought to be the formation and growth of calcium carbonate ($CaCO_3$) crystals. Inorganic agglomeration due to $CaCO_3$ crystal formation should be easily detectable by the Coulter technique presented herein since $CaCO_3$ is essentially insoluble in DMF.

On-line Coulter analysis of the SRC process stream would allow immediate detection of changes in the size distribution of the solvent stream particles. Through on-line analysis more precise correlations between mean particle size and filterability would be possible. Also, by monitoring the size distribution of particulates in the upstream and downstream to the filter, a direct reading on filtering efficiency could be obtained. Coulter analysis is also an effective method for determining the efficiency of other solid-liquid separation techniques, such as centrifuging and hydrocloning, currently being tested in the SRC process.

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TABLE I

Mean Particle Size of Autoclave Reacted Coals
at 15, 30 and 60 Minutes

Autoclave Conditions
Temperature: 410°C
Pressure: Hydrogen 2000 psi
Solvent/Coal: 3/1
Stirrer: 1000 rpm

Time (min)	Mean Particle Size (µm)*			
	Amax	Western Kentucky	Monterey	Pittsburgh Seam
15	14.0	7.0	5.2	6.0
30	9.1	8.2	5.5	5.5
60	8.0	10.6*	4.8	6.0

*Through subsequent calculations, the population mean can be calculated. For example, Western Kentucky coal, reacted for 60 minutes, has a population of 2.0µm.

TABLE II

Particle Size Distributions of Amax Coal Autoclave Reaction Mixture and Wilsonville Filter Feed

Particle Diameter (μm)	% Volume Distributions Amax Autoclave 60 minute	Amax Wilsonville filter feed
1.59	10.9 ± 0.6	10.4 ± 1.8
2.00	8.7 ± 1.2	6.3 ± 1.4
2.52	6.6 ± 0.64	5.7 ± 0.6
3.17	5.5 ± 0.35	6.7 ± 0.7
4.00	5.6 ± 0.36	7.6 ± 0.8
5.04	6.4 ± 0.42	9.3 ± 0.7
6.35	6.9 ± 0.49	8.6 ± 1.0
8.00	8.2 ± 0.57	8.8 ± 1.1
10.08	9.0 ± 0.68	9.2 ± 1.3
12.7	9.7 ± 1.6	9.2 ± 1.7
16.0	9.2 ± 1.5	5.7 ± 0.8
20.2	7.0 ± 1.8	4.6 ± 2.0
25.4	4.6 ± 2.6	4.6 ± 2.8
32.0	1.3 ± 1.0	2.3 ± 2.7
40.3	0.6 ± 0.05	0.6 ± 0.1

TABLE III

Comparison of the Mean Particle Size of Wilsonville Filter Feed and Auburn Autoclave Reaction Mixtures

Coal Type	Date	Wilsonville Filter Feed Mean Particle Size μm	Auburn Autoclave Mean Particle Size μm
Monterey	10-20-76	4.5	
Monterey	11-15-76	3.7	
Monterey	11-10-76	3.8	
Monterey	Average	4.0	4.8
Amax	- - - -	7.2	
Amax	12-19-76	6.4	
Amax	1-28-77	7.5	
Amax	Average	7.0	8.0
Western Kentucky	4-17-76	6.8	
Western Kentucky	5-29-76	4.6	
Western Kentucky	Average	5.7	10.6
Pittsburgh Seam	7-22-75	6.2	6.0

TABLE IV

Correlation between Cake Resistivity and Mean Particle Size of Wilsonville Filter Feed

Coal	Cake Resistivity ft/lbm	ΔP (psi)	Mean Particle Size (μm)	
Amax	0.8×10^{12}	45	7.0	(Ref 7)
Western Kentucky	1.13×10^{12}	60	5.7	(Ref 8)
Monterey	1.22×10^{12}	60	4.0	(Ref 8)

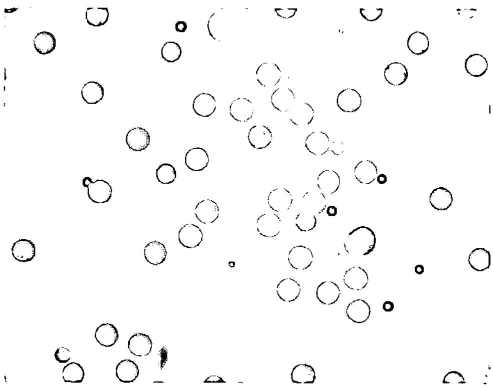


Figure 1

Verification of polystyrene particle size

1 cm = 20μm

Figure 2

Photomicrograph of Amax coal particles (suspended in Carbowax) after 60 minute autoclave reaction (500x)

1 cm = 20μm

Figure 3

Photomicrograph of
Pittsburgh Seam coal particles
(suspended in carbowax) after
60 minute autoclave reaction
(500x)

1 cm = 20μm

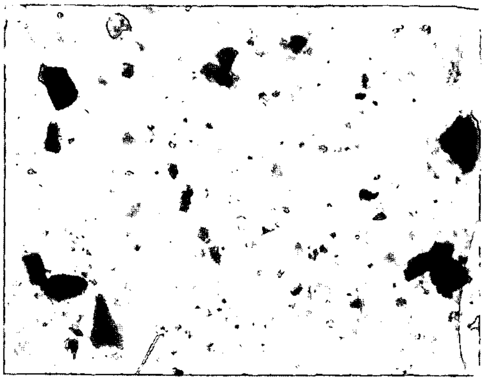


Figure 4

Photomicrograph of
Western Kentucky coal particles
(suspended in carbowax)
after 60 minute autoclave
reaction (500x)

1 cm = 20μm

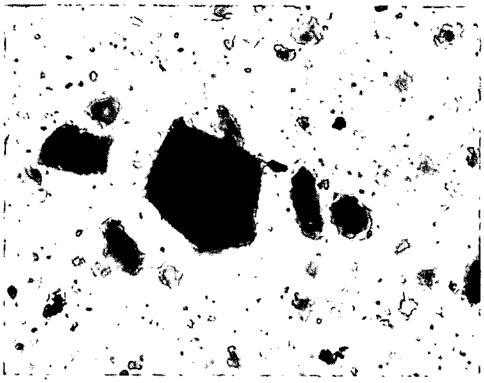


Figure 5

Electronicrograph of
Western Kentucky coal particles
(on a Metricel filter)
after 60 minute autoclave
reaction (2000x)

1 cm = 5μm

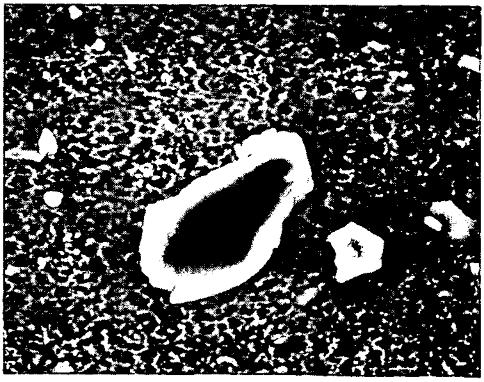
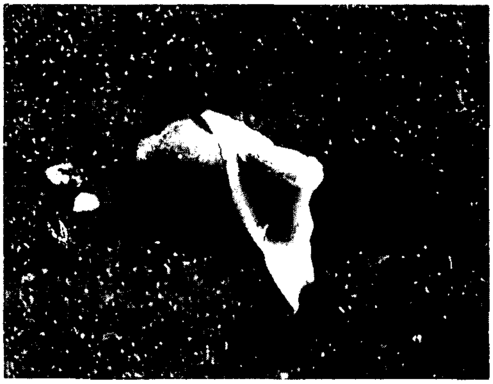


Figure 6

Electronmicrograph of Monterey coal particles (on a Metricel filter) after 60 minute autoclave reaction (2000x)



1 cm = 5μm

Figure 7

Electromicrograph of Monterey coal particle (on a Metricel filter) after 60 minute autoclave reaction (10,000x)

1 cm = 1μm