An analysis of the kinetics for oil agglomeration of coal

David Tyson
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An analysis of the kinetics for oil agglomeration of coal

Tyson, David, Ph.D.
Iowa State University, 1990
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by

David Tyson

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# TABLE OF CONTENTS

ACKNOWLEDGEMENTS .................................................. x

CHAPTER 1. INTRODUCTION ........................................ 1
  Background ......................................................... 1
  Oil Agglomeration Process ...................................... 3
  Research Purpose and Objectives ............................... 6

CHAPTER 2. REVIEW OF PREVIOUS WORK ....................... 8
  Coal Agglomeration .............................................. 8
  Agglomeration of Other Materials ............................ 11
  Factors Affecting General Agglomeration Processes ...... 16

CHAPTER 3. VOLUME OF PENDULAR BRIDGES ................. 20

CHAPTER 4. MATHEMATICAL MODELS ......................... 25
  Population Balance ............................................ 25
  Batch Agglomeration ........................................... 29
  Continuous Stirred Tank Agglomeration ...................... 31
    Layering/Shear breakage .................................... 31
    Layering ....................................................... 32
    Layering/Attrition .......................................... 33
# Table of Contents

Layering/Coalescence .................................................. 34
Population Balance Parameters ....................................... 34
Coal-Oil Interaction ..................................................... 34

## CHAPTER 5. EXPERIMENTAL (BATCH SYSTEM) .................... 37
Materials ................................................................. 37
Coulter Counter Measured Agglomeration ......................... 37
Oil Emulsification Tests .............................................. 40
Inversion Time Measurements ....................................... 41

## CHAPTER 6. EXPERIMENTAL (CONTINUOUS SYSTEM) ............ 42
Preliminary Tests ....................................................... 42
Materials Used .......................................................... 45
Apparatus ................................................................. 46
Size Distribution Determination ..................................... 48
Experimental Design .................................................... 52

## CHAPTER 7. DISCUSSION OF RESULTS ............................. 55
Batch Agglomeration Involving Limited Growth .................... 55
Emulsion Studies ....................................................... 65
Batch Agglomeration With Inversion Time Measurements .......... 67
Characterization of Coals Used for Continuous Agglomeration .... 70
Continuous Agglomeration Runs ....................................... 75
First Series ............................................................... 75
Second Series ............................................................ 76

## CHAPTER 8. CONCLUSIONS ........................................... 106
CHAPTER 9. RECOMMENDATIONS ................................... 109
CHAPTER 10. NOMENCLATURE .................................... 111
BIBLIOGRAPHY .................................................. 114
APPENDIX A. FORM FOR COALESCEANCE AND BREAKAGE 119
APPENDIX B. OIL DROPS ON COAL ............................... 122
APPENDIX C. DERIVATION OF PENDULAR BRIDGE VOLUME EXPRESSION ........................................ 124
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Exact vs. approximate values of bond volume.</td>
<td>24</td>
</tr>
<tr>
<td>5.1</td>
<td>Agglomerating solids for batch tests.</td>
<td>38</td>
</tr>
<tr>
<td>5.2</td>
<td>Bridging liquids for batch tests.</td>
<td>38</td>
</tr>
<tr>
<td>6.1</td>
<td>Central composite design for agglomeration with Indiana No. 6 coal</td>
<td>53</td>
</tr>
<tr>
<td>6.2</td>
<td>Central composite design for agglomeration with Upper Freeport coal</td>
<td>54</td>
</tr>
<tr>
<td>7.1</td>
<td>Results of agglomerating -200/+400 mesh Australian coal with different oils.</td>
<td>69</td>
</tr>
<tr>
<td>7.2</td>
<td>Run conditions for the continuous runs with Upper Freeport coal</td>
<td>77</td>
</tr>
<tr>
<td>7.3</td>
<td>Results of continuous agglomeration using Upper Freeport coal</td>
<td>90</td>
</tr>
<tr>
<td>7.4</td>
<td>Comparison involving agglomeration between the coarse feed and the fine feed</td>
<td>92</td>
</tr>
<tr>
<td>7.5</td>
<td>Computed t-values based on linear model</td>
<td>97</td>
</tr>
<tr>
<td>7.6</td>
<td>Values of $N_m$ for the various runs</td>
<td>99</td>
</tr>
</tbody>
</table>
Table 7.7: Layering model parameters and goodness of fit for the region of smaller agglomerates. 100

Table 7.8: Parameter values for the Gaussian distribution range of the number density curves. 101
LIST OF FIGURES

Figure 1.1: Phase diagram for agglomeration with a binder\textsuperscript{[2]}. \hspace{1cm} 5

Figure 3.1: Diagram of two particles with pendular bridge showing various angles. \hspace{1cm} 21

Figure 4.1: Various mechanisms describing particle size changes\textsuperscript{[58]}. \hspace{1cm} 27

Figure 4.2: The progress of agglomeration with respect to time, illustrating a time of wetting and a time of growth. \hspace{1cm} 36

Figure 6.1: Schematic diagram of the batch agglomeration unit employing a photometric dispersion analyzer \hspace{1cm} 44

Figure 6.2: Schematic diagram of experimental set-up for continuous runs. \hspace{1cm} 47

Figure 6.3: Agglomeration vessel for continuous agglomeration \hspace{1cm} 49

Figure 7.1: Volume percent density curves for graphite agglomeration at shorter mixing times (21,000 rpm). \hspace{1cm} 57

Figure 7.2: Volume percent density curves for graphite agglomeration at later longer mixing times (21,000 rpm). \hspace{1cm} 58

Figure 7.3: Population density curves for graphite agglomeration at 0 and 2 min (21,000 rpm). \hspace{1cm} 60
Figure 7.4: Volume percent density curves for graphite agglomeration (650 rpm). ........................................ 62
Figure 7.5: Volume percent density curves plotted against time for graphite agglomeration (650 rpm). .......................... 63
Figure 7.6: Volume percent density curves plotted against time for graphite agglomeration with emulsified oil (650 rpm). .......................... 64
Figure 7.7: Light absorbance versus time for n-heptane using various agitation modes. ........................................ 66
Figure 7.8: Turbidity analysis for Indiana No. 6 coal. ........................................ 72
Figure 7.9: Turbidity analysis for Indiana No. 6 using sodium oleate ........................................ 73
Figure 7.10: Turbidity analysis for Upper Freeport coal ........................................ 74
Figure 7.11: Histogram of number distribution for run 2 ........................................ 79
Figure 7.12: Histogram of number distribution for run 6 ........................................ 80
Figure 7.13: Histogram of number distribution for run 9 ........................................ 81
Figure 7.14: Histogram of number distribution for run 15 ........................................ 82
Figure 7.15: Histogram of number distribution for run 8 ........................................ 84
Figure 7.16: Histogram of number distribution for run 14 ........................................ 85
Figure 7.17: Histogram of number distribution for run 17 ........................................ 86
Figure 7.18: Number density data for run 2 fitted by a model assuming layering as the growth mechanism ........................................ 88
Figure 7.19: Number density data for run 9 fitted by a model assuming layering as the growth mechanism ........................................ 89
Figure 7.20: Histogram of number distribution for run 21 ........................................ 93
Figure 7.21: Histogram of number distribution for run 19 ........................................ 94
Figure 7.22: Histogram of number distribution for run 20. .......... 95
Figure 7.23: Histogram of number distribution for run 3. .......... 96
Figure 7.24: The number density curve for run 11 based on the combined layering and coalescence regimes. ............... 103
Figure 7.25: The fitting together of regime 1 (layering) and regime 2 (coalescence/breakage simulation) ............... 105
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CHAPTER 1. INTRODUCTION

Background

The difficulty of using coal as a combustible energy source is due to the presence of sulfur and ash-forming mineral constituents. The heat content of the coal is decreased due to the mineral matter, thereby reducing the quality of the coal as a fuel\[1\]. The sulfur, which is present in the form of iron pyrite (FeS$_2$), can cause equipment wear and it can oxidize to form acids which cause boiler corrosion. Excessive amounts of ash will cause slagging, fouling and erosion of various parts of a boiler, plug the air preheaters, and overload the electrostatic precipitators. Also, there is the problem of physically disposing of the ash from the boiler. The flue gas that arises from a smoke stack must be desulfurized since the combustion product of sulfur is gaseous sulfur dioxide, which is an air pollutant. Standards for acceptable sulfur emissions are set by the Environmental Protection Agency. In order to reduce the amounts of sulfur and mineral matter which are present in coal, pretreatment of the coal, i.e. coal cleaning, can be employed.

Coal cleaning methods can be broken down into three main categories: conventional physical cleaning by washing, nonconventional physical cleaning, and chemical cleaning.

Conventional physical cleaning by washing involves crushing the coal and then
separating the resulting particles. The coal is crushed in order to liberate the carbonaceous part of the coal from the mineral matter. Liberation is achieved because of the difference in grindability of the two principal constituents. Coal washers can be divided into coarse-coal washers and fine-coal washers. The most commonly used coarse-coal washers are heavy-medium vessels and Baum jigs. The most commonly used fine-coal washers are heavy-medium cyclones, hydrocyclones, Batac jigs, feldspar jigs, concentrating tables, and Humphreys spiral concentrators. The separation achieved between the carbonaceous-rich particles and the mineral-rich particles is due to their respective differences in specific gravity. The specific gravity of the mineral matter is in the range of two to five, while the specific gravity of the carbonaceous material is in the range of 1.3 to 1.7.

Nonconventional physical cleaning deals with the cleaning of very fine-size particles. The fines may be discharged to wasteponds, since conventional washing methods can not handle very small sizes. Fines may be present due to the need to pulverize coal to very fine size in order to liberate finely disseminated mineral matter. In Iowa coal, for example, electron microscope studies have shown that a large portion of the pyrite is smaller than 10 μm. Two main cleaning processes for coal fines are froth flotation and oil agglomeration. Both of these processes utilize the difference in surface properties of the mineral matter and the carbonaceous material. The surface property that is used as a basis for separation is the relative hydrophobicity of the different types of particles.

Chemical cleaning involves removing the sulfur in coal by chemical reaction. Physical cleaning methods remove only the sulfur present in the mineral matter, whereas some chemical cleaning methods remove both the organic and the inor-
ganic sulfur. Various chemical cleaning processes include: the Battelle Hydrothermal process, the Meyers process, Ames oxydesulfurization process, KVB process, chlorinolysis, and microwave desulfurization[1].

Oil Agglomeration Process

In an oil agglomeration process, an immiscible liquid (oil) is added to a well-mixed water slurry of coal fines[1]. Ideally, the oil will preferentially wet only the hydrophobic (carbonaceous) particles. The oil-wetted particles will stick together upon collision with each other to form agglomerates. Collisions are promoted by vigorous agitation. The hydrophilic (mineral matter) particles, on the other hand, are not wetted by the oil and do not agglomerate upon collision. Following agglomeration, the slurry is then screened to separate the agglomerated solids (concentrate) from the unagglomerated solids (tailings).

The type of agglomerates that are produced with a given sample of coal is dependent upon the amount of oil used and the hydrophobicity or oleophilicity of the solids[2]. At low dosages of oil, only pendular bridges can form between the particles, so that the product has an unconsolidated floe consolidate and some compact agglomerates appear until microagglomerates are formed. This is referred to as the funicular state. When more oil is added (15-20 %), the agglomerates grow in size and reach a peak of strength and sphericity in what is referred to as the capillary state. With even more oil added (greater than 20 %), the agglomerates form an amalgam, and the hydrophobic solids are essentially dispersed in the bridging liquid. Thus, the particles will be either agglomerated as loose flocs, as spherical balls, or simply transferred from the aqueous phase to the organic phase. The phase diagram for the
various product types is given in Figure 1.1.

Although most of the mineral matter (quartz, kaolin, etc.) is very hydophilic relative to the carbonaceous material, pyrite may have surface characteristics (i.e., relative hydrophobicity) similar to those of the carbonaceous material[2]. As a result of this feature, the agglomerated product may contain a substantial amount of pyrite with its accompanying sulfur. Thus, there are two main problems associated with the removal of pyritic sulfur from coal: (1) an appropriate surface conditioning agent may be needed to keep the pyrite in the aqueous phase, and (2) fine dissemination may make it difficult to liberate the pyrites from the coal. In some cases, the coal itself may be rather hydrophilic, e.g., Illinois No. 6 coal, and a surfactant such as a long-chain fatty acid may be needed to increase the hydrophobicity of the coal surface. The recovery of carbonaceous material is increased, but unfortunately the recovery of the pyrite is also increased since the fatty acid interacts with the pyrite as well. In oil agglomeration processes, it is difficult to selectively agglomerate the carbonaceous material relative to pyrite.

There are advantages of using the oil agglomeration method for the treatment of coal fines[3]. This method can treat a broad range of coal particle sizes. It can treat coal fines as small as the angstrom range or as large as 2-3 mm., which would act as nuclei for finer particles. Also, oil agglomeration can promote the dewatering of coal fines. If the cleaned coal product is left in slurry form, the resulting coal-oil-water dispersion can be used to displace oil in utility and industrial boilers and, possibly, low speed diesel engines. The major cost involved with the oil agglomeration technique is the cost of the oil itself. If a coal-oil mixture is used, then the cost of the oil is not so critical since the oil is used as fuel along with the coal. Another way in which to utilize
State of bridging liquid

Form of product

Preferred Agglomeration Equipment
Fluid mixers, high shear mills; pumps; disc and drum agglomerators; shakers; liquid-liquid contractors

Sedimentation Volume (arbitrary units)

Pendular | Funicular | Capillary | Particles dispersed in bridging liquid.

Floes | Microagglomerated | Pellets | Liquid-liquid particle transfer.

% Pore Volume Occupied by Bridging Liquid (mono-sized particles)

0 20 40 60 80 100

Figure 1.1: Phase diagram for agglomeration with a binder[2].
the agglomerated product is to prepare it in the form of microagglomerates which are mixed with coarse coal for shipment. One must consider the volatile components of the bridging oil in the agglomerates and the resulting safety aspects during shipping. Instead of mixing the microagglomerated product with coarse coal, the product can be pelletized with a suitable binder and the resulting pellets heat treated. In this manner, a hard and easy-to-ship pellet can be produced, and the heat treatment will vaporize the oil which is used for agglomeration.

In order to use oil agglomeration technology for actual application to coal fines, the National Research Council of Canada (NRCC) established a pilot plant scale study[3]. For this study, two agglomeration tanks were used in series. The first tank provided high shear mixing for the fine coal slurry/bridging liquid mixture. The residence time in the tank was on the order of 1 min. or less. The product stream of the first tank was conducted to a second tank where agglomerate growth took place under slow turbine agitation. The residence time in the second tank was on the order of 2-4 min.

**Research Purpose and Objectives**

The purposes of this investigation was to study the mechanisms governing coal particle growth phenomena in an oil agglomeration process. By monitoring the size distribution of agglomerates and phase inversion through time, it was hoped that information could be acquired to explain the growth kinetics for batch and continuous flow systems. The size distributions were analyzed either qualitatively or by using mathematical representations of specific mechanisms expressed in terms of a population balance.
The experiments performed in a batch mode were treated in a more qualitative fashion since particle size distribution analyses were found to be both costly and time consuming, particularly since so many more analyses were needed for the unsteady state batch mode. When a Coulter Counter was employed for measuring size distributions, this particular problem was greatly minimized, but agglomerate size had to be severely limited. Consequently the Coulter Counter was only used in batch tests under conditions which produced small agglomerates. A photometric dispersion analyzer was employed in batch tests which produced agglomerates of intermediate size. For conditions which produced large agglomerates, the phase inversion time was determined by monitoring stirrer torque while using a constant speed agitator.

For the continuous steady-state mode, determining the product size distribution was not as much of a problem because only the steady-state distribution was needed. The main problem was finding a way to measure the distribution over a wide range of agglomerate size. It was necessary to find a procedure which was accurate and reproducible for a given size range and strength of the agglomerates. The method chosen utilized automated image analysis of data obtained with a scanning electron microscope or SEM-AIA.

Due to the large amount of feed coal required to carry out a continuous agglomeration run, an experimental design was employed to minimize the number of runs. This required careful selection of the range of operating parameters to insure that the design could be executed and reasonable results be obtained for analysis and correlation.
CHAPTER 2. REVIEW OF PREVIOUS WORK

Coal Agglomeration

Rao et al.\[4\] worked with -200 mesh coals that were pretreated in water slurries with precalculated quantities of diesel oil and stirred at 700 rpm for 10 min. After pretreatment, furnace oil was used as a binder. The agglomeration took place with an agitator speed of 1200 rpm. In order to determine agglomerate growth rate, the materials were agglomerated for a series of predetermined times and the resulting agglomerates were wet-sieved. With a given set of dimensionless coordinates on a distribution plot, the experimental points fell on the same S-shaped curve for both the same type of coal and same feed size. This characteristic curve was found to depend only on the nature of the feed and not on other process variables. The characteristic curve was fitted by an equation similar to one developed previously for expressing the efficiency of hydrocyclones.

Vanangamudi and Rao\[5\] performed agglomeration experiments with coal and found that the growth followed second order kinetics, allowing them to determine the second order rate constant.

Hazra et al.\[6\] worked a the characteristic curve for coal and found that the feed size and oil dosage do not affect the shape of this curve, while stirring speed, temperature, and agglomeration period do affect the shape of the curve.
Drzymala et al. [7] performed agglomeration experiments with mixtures of pyrite and graphite. This mixture was supposed to represent a model version of coal. At low heptane dosages, loose agglomerates were formed which contained entrapped pyrite. At high heptane dosages, compact spherical agglomerates were formed which were relatively free of pyrite. These experiments were conducted at relatively high stirring speeds for about 5 min. with no excess air being entrapped in the slurry. The authors [8] also investigated the effects of air that was incorporated in the slurry during agglomeration. When either a large dose of oil or a long chain alkane (at any given dosage) was used, no difference in agglomerate recovery was observed due to air being present.

The floc regime for coal was studied by Darcovich et al. [9]. A laser diffraction particle sizer was employed to study the coal flocs. It was concluded that below 2 wt.% oil dosage, the bond volumes were great enough to consume available oil in forming agglomerates containing no more than two particles (doublets) or three particles (triplets).

Bensley et al. [10] experimented with Australian coal, the average size being about 250 to 350 μm. They performed agglomeration tests with 10 wt. % coal slurries and a total slurry volume of 1 liter. An agglomeration run lasted 20 min. at a stirring speed of 500 rpm with the oil added either directly to the slurry or as an oil-in-water emulsion. They also ran inversion time experiments with 35 wt. % coal slurries and again the oil was added either directly or as an oil-in-water emulsion. Depending on the method of emulsification, the oil droplets were between 3 and 15 μm. The authors used the following oils: n-heptane, kerosene, automotive diesel fuels, heavy fuel oil/automotive diesel blend, and heavy fuel oil. They concluded that
the overall results of their investigation suggested that the most striking effect of emulsification is on the kinetics of the process rather than the equilibrium properties of the system. They also believed that their data supported the view that one of the rate-controlling steps in the process involves the distribution of the oil over the surfaces of the coal particles.

Labuschagne[11] investigated several different types of oil as agglomerants, taking into account their chemical structures and physical properties. The types of oil employed were: paraffinic straight chain hydrocarbons, monocyclic saturated hydrocarbons, monocyclic aromatic hydrocarbons, and dicyclic hydrocarbons. The agglomeration runs were conducted with a slurry concentration of 20 g. of coal in 200 ml. of water. Oil dosages were varied and the agitator was operated at 1000 rpm. By using a relatively high slurry concentration, the inversion time (or time of agglomeration) could be measured. The inversion time was plotted against the volume fraction of different oil mixtures used as binders. Agglomeration experiments were also carried out with a mixture of tetralin and tetralin peroxide, with the tetralin peroxide acting to reduce the coal/oil interfacial tension and decreasing the magnitude of the contact angle[12].

Dunstan et al.[13] investigated the kinetic behavior of the oil agglomeration process. They assumed that the collisions between the coal and oil particles were the rate-limiting step for agglomeration. This assumption was based on the fact that the overall rate of agglomeration depended on both the oil concentration and the particle concentration, and also on the notion that the probability of an oil-coal interaction was much less than that of a coal-coal interaction. This was said to be especially true for oil drops which are much smaller than the coal particles. Determinations were
made to quantify the number of oil drops residing on a coal particle which enables that particle to engage in a collision that leads to coalescence. Particle coalescence was believed to be determined by the following criteria: (1) the oil must be present in sufficient quantity to form a bridge between the coal particles that is strong enough to withstand the shearing forces; and (2) the larger the amount of oil present on the coal, the greater the probability of a favorable interaction.

Klose and Lent[14] studied the agglomeration of coking coals during the softening phase. No binder was needed because of the presence of a coal-liquid phase. Wojcik and Al Taweel[15] combined the principles of agglomeration with the principles of froth flotation. They noticed that aggregates formed at low oil dosages would break and pass through the holes of a separation screen. By floating the coal aggregates with air, they could recover more material at lower oil dosages. They looked upon the process as either a flotation process in which agglomeration was used to reduce the number density of particles to be recovered, or as a selective agglomeration process in which the agglomerates were recovered by flotation rather than by screening. Takamori et al.[16] worked on the agglomeration of Japanese coals. They used kerosene, heavy oil, and crude oil as binders. They investigated the effects on the agglomeration process of the following parameters: type of binder, volume of binder added, ratio of kaolin added to coal, and impeller speed.

Agglomeration of Other Materials

Kawashima and Capes[17] conducted agglomeration experiments with silica sand, glass, and calcium carbonate powders. They performed the experiments at 30° C and suspended the powders in a carbon tetrachloride slurry. An aqueous calcium chloride
solution was used as the bridging liquid. A size distribution of the particles was obtained by using photographic analysis. All of their experimental results seemed to obey approximately first-order kinetics. They claimed that this was contrary to the idea that second-order agglomeration kinetics should prevail for dilute suspensions of very fine particles. They indicated that first-order kinetics should apply only for a system of larger particles in higher concentrations. The controlling parameters for first-order agglomeration kinetics are the shearing forces and the level of agitation. They claimed that for second-order agglomeration kinetics there exist submicron particles in low concentration, and the controlling parameters are the physico-chemical properties of the system.

A number of studies have investigated the effects of various parameters on the agglomeration process. Work was done to investigate the role of contact angle on the agglomeration process[17]. Birkner and Morgan[18] conducted studies on the number density kinetics of polymer flocculation using 1.3 μm polystyrene latex particles. Hraste and Nuber[19] worked with silica which ranged below 250 μm in size. The feed size was determined both by sieving and by using a Coulter Counter, while the agglomerates were measured optically with a OPTON TGZ-3. Grover et al.[20] performed agglomeration tests using fluidization of a dry bed. The materials used for measuring particle growth included: tryptophane, sulfamethazine, lactose, and ascorbic acid. Holm et al.[21] studied the effect of power consumption and the resulting temperature increase during agglomeration (granulation). The materials employed in this study were lactose, dicalcium phosphate, magnesium hydroxide, corn starch, and glass spheres. It was determined that with low binder dosages, the agglomerates were rigid and breakable, while at high dosages, the agglomerates were large and more
plastic. Bos and Zuiderweg[22] made agglomeration runs with an aqueous suspension of calcium carbonate. The binder used to agglomerate this solid was kerosene. Oleic acid was used to modify the surface of calcium carbonate. The agglomeration took place in a system of three vessels in series. The first vessel provided an environment for the solid fines to interact with the oil. In the other two vessels, the agglomerates grew to larger sizes through layering. The residence times in these experiments were at least three times the residence times of the longest remaining material. Samples were then removed from each of the three vessels and the size distribution was determined by photographic methods. From the ensuing data, it was concluded that the agglomeration rate was first-order with respect to both fines concentration and oil concentration. Toward the end of the wetting period, the process was considered to be zero-order for the fines due to the complete consumption of the fines.

Kawashima et al.[23] studied the spherical crystallization of salicylic acid. Without the incorporation of agglomeration, the salicylic acid would crystallize into a sharp needle-shaped product. By producing very small crystals and agglomerating the crystals, a spherical product was produced. The three growth steps were the initial crystal nucleation, simultaneous crystallization and agglomeration, and agglomeration alone. All three of these growth steps were found to be affected by temperature. It was determined that fine particles required less bridging liquid for agglomeration and produced larger agglomerates than did coarse particles. The reason for this phenomenon was the superior adhesive forces between the fine particles and the bridging liquid. Kawashima et al.[24] also performed agglomeration tests with time released drugs, using white beeswax as a binder. Since the white beeswax was a solid at room temperature, the agglomeration tests were performed either at 90° C (where
the beeswax was a liquid) or with the beeswax dissolved in benzene. A size analysis of the agglomerates was performed by sieving. Using continuous operation[25], the drug was also produced. They determined that steady state was obtained in approximately ten residence times, which was less than that for a crystallization process, because agglomeration did not require a nucleation step. For particles above a certain size, it was discovered that the growth rate was size-dependent, and for particles below that size the growth rate was size-independent.

Kent and Ralston[26] studied the separation of a chalcopyrite-quartz system. They employed the following equipment to determine the size of mineral particles and particles in stabilized emulsions: HIAC Model 320 particle size analyzer, a Coulter Nanosizer (0.04-3 μm), and a microscope with camera. Wahl and Baker[27] studied the agglomeration of titanium dioxide dispersions which did not need a binder to produce agglomerates. They determined that the kinetics of agglomeration were second-order. Their particle size measurements were performed with a Coulter Counter.

Burkhart and Voigt [28] found that two types of agglomerates were created in the precipitation of metals. The first type of agglomerate was a dense aggregate with a low porosity, and it was only a few microns in size. This type was very strong and did not break-up under liquid shearing. Agglomerates of the first type coalesced into agglomerates of the second type which the authors referred to as flocs. The flocs were found to be much more porous and were not as tightly bound together as the small aggregates. These particles experienced breakage in a shearing regime.

Glatz and coworkers[29]- [32] precipitated proteins. Particle growth and particle breakage were investigated. It was assumed that the growth of an aggregate was due only to collisions involving primary particles and smaller aggregates. Thus, growth
was viewed as the incremental additions of small units to the growing aggregates. This assumption allowed for mathematical treatment of the process as a continuous growth (length derivative) process as opposed to a discrete (incremental) growth process.

Takamori et al. [33] studied the agglomeration of barite. A suspension was made up of particles larger than 2 μm in size and was agitated at 780 rpm. The binding liquid was kerosene. Both agglomeration experiments and phase inversion experiments were conducted. Larger particle concentrations were used in the phase inversion experiments than in the agglomeration experiments. Since barite is naturally hydrophilic, sodium oleate (a fatty acid salt) was employed as a surfactant to make the barite surface more hydrophobic. After this treatment, the barite was readily wetted by the oil. The investigators were able to adjust the degree of hydrophobicity of the barite by the addition of the surfactant. They found that when the degree of particle hydrophobicity was suitably high, large agglomerates formed very quickly. When the surface of the solid was not sufficiently hydrophobic, microagglomerates formed, and after some time, the microagglomerates compacted, causing the entrapped oil to be forced out onto the surface. After this happened, large agglomerates were formed immediately without any intermediate sizes being present. With Barite particles of intermediate hydrophobicity, agglomerate growth behavior was an average of the preceding two cases. In other words, microagglomerates formed immediately, followed by growth of medium size agglomerates, and then growth of large agglomerates.

Meadus and Puddington [34] also studied the agglomeration and beneficiation of barite. The tailings consisted of copper, lead, zinc, iron, silica, and calcite minerals. The binder was vacuum still bottoms mixed with a lighter oil. Puddington [35] re-
ported agglomeration studies involving the recovery of barium sulphate from lead/zinc tailings piles, removal of phosphorous from apatite containing iron ores, and the recovery of bitumen from oil sands.

Sebba[36] employed very small air bubbles to form pseudo-agglomerates. Microbubbles of air were produced in water to form a milky emulsion. Sirianni et al.[37] studied the agglomeration and beneficiation of iron ore. Silica and phosphorus were rejected in this selective process. Fatty acids were employed to selectively treat the surface of the iron ore, rendering it more hydrophobic, so that a petroleum binder would wet the surface more effectively.

Factors Affecting General Agglomeration Processes

Warren[38] examined the issue of shear flocculation of fine particles. It was determined that the rate of shear flocculation depends on the rate at which particles collide with each other as well as on the number of those collisions which result in adhesion. Consequently the rate of shear flocculation will be controlled by the parameters which affect the collision rate and the parameters which affect the probability of adhesion. Upon examination of the turbulent collision mechanism, three main features were brought out:

1) For particles larger than about 0.1 μm, there are more collisions per unit time due to turbulent flow than due to Brownian motion.

2) The collision rate varies with the square of the number of particles per unit volume.

3) Turbulent collision rates are sensitive to particle size.

One more claim made by Warren is that particle size affects both the rate of collision
and the probability of adhesion. The reasoning is that the larger particles have a better chance of intercepting an oil drop and, because of higher momentum, find it easier to rupture the wetting film separating the drop and particle. Jacques et al.[39] made a study of the available free energy existing in the agglomeration process. They found that the stability depends on the oil droplet/particle size ratio and the three phase contact angle. Toyama et al.[40] believed that the measured capillary suction time could be utilized as an index to evaluate the relative agglomerability of materials. Smith and Van De Ven[41] concluded that the primary cause of agglomeration was due to the ability of the binder drop to deform. The two factors which allow such deformation to take place are particle collisions and the shear field. Sonntag and Russel[42] developed a model for the breakup of isolated flocs subjected to shear flow. Relationships between the floc radius and shear rate were then developed. Chandler et al.[43] claimed that the part of a particle's surface that is created through the rupture of van der Waals (residual) bonds is the hydrophobic part. Other parts of the surface formed by the rupture of ionic or covalent bonds would be highly reactive and hydrophilic since they would be capable of strongly orientating water molecules. According to Rosenbaum and Fuerstenau[44], the surface of coal is comprised of three main components: graphitic hydrophobic sites, paraffinic hydrophobic sites, and hydrophilic sites (organic functional groups and grains of mineral matter). The wetability of a particular coal can then be related theoretically to the relative amount of each component.

Mehrotra and Sastry[45] found that the force of adhesion due to the presence of a pendular bridge between two particles arose from two component forces: 1) the pressure drop over the surface produced by the curvature of the liquid meniscus, and
2) the interfacial tension exerted by the liquid along the wetted perimeter of the particles.

Rumpf[46] concluded that the main variables of importance affecting the attractive forces in an agglomerate bond were the interfacial tension, the contact angle, the distance between particles in a liquid bridge, and the volume of the liquid bridge. He stated that under normal atmospheric conditions using wetted materials, liquid bridges are formed by capillary condensation when the solid particles are in direct contact.

Mullier et al.[47] studied the role of breakage in agglomeration. They determined that breakage depends on impact velocity and agglomerate size. The strength of the agglomerate was studied in terms of the potential for break-up. The agglomerate strength was then characterized by either the critical stress intensity factor or the critical strain energy release rate. Ouchiyama and Tanaka[48] investigated the kinetics of compaction. It was believed that the coordination number increased during the compaction process. They were able to relate the coordination number and the porosity by a suitable mathematical expression.

Sunada et al.[49] developed a computer simulated agglomeration scheme. They operated with two basic considerations: 1) the model should allow for particles to encounter (collide), and 2) there should be a certain probability that particles will adhere to one another as distinct units after an encounter. The restrictions that were imposed on the simulation were: 1) agglomerates were not capable of deflocculating after formation; 2) after collision of a primary particle with an agglomerate, the direction of subsequent movement would be that of the agglomerate; 3) the movement of the agglomerate was non-rotational; and 4) the agglomerate moved a unit of grid
length per unit time, regardless of the size of the agglomerate. Upon examination of
the total number of particles as a function of time, it was shown that the simulation
produced a second-order fit.

Adorjan[50] evaluated the tensile strength of model particle assemblies due to
capillary forces. Although other forces have been shown to be significant, the capillary
component was considered to have the greatest influence on the wet strength of
agglomerates. Coca et al.[51] concluded that it was not easy to relate the contact
angle with the macroscopic properties of solid aggregates that play a significant role
in a separation process, but the interfacial properties are always an indication of
how the surface of the solid is altered in the presence of coagulating or flocculating
agents. Farnand et al.[52] believed that if enough binder liquid was available to form
multiple junctions given the fact that the mechanical action for creating spheres was
present, then indications were that the agglomeration was stepwise. Also, the larger
units eventually exuded sufficient oil to cause them to adhere strongly to a neighbor.
Further agitation converted the dumbell, triangular or pyrimidal shapes into new
larger sphere.

Good and Koo[53] investigated the relationship between contact angle and the
drop size employed for measurement of the contact angle. They reasoned that this
phenomena existed due to the tendency of the drop to spontaneously elongate. The
elongation proceeded as if a large negative line tension was present (pseudo-line ten­sion). In another work involving surface tension, van Oss et al.[54] attempted to
develop and expound a modern theory of surface tension components in agglom­er­ation. They claimed that an equation of state involving the surface tension in
agglomeration is in conflict with theories of adhesion.
CHAPTER 3. VOLUME OF PENDULAR BRIDGES

Pendular bridges can occur between solid particles when either a liquid phase in air or an immiscible second liquid phase in an already established liquid medium gets in between touching particles and serves as an adhesive for these particles. An example of a pendular bridge between two particles of equal size is given in Figure 3.1.

Oil agglomeration, as it applies to coal, is a process that deals with selective growth through the use of bridging oils. There could be some kinetic implications as to how a liquid bridge is formed combined with its resultant shape or size, and how the rate of agglomeration may be affected. Relative hydrophobicity (as represented by the contact angle) is the parameter which influences selectivity. Also, from coal to coal, the hydrophobicity of a given material is not the same. Work performed by Drzymala et al. [7] was carried out on pure materials that make up coal, with agglomeration tests performed with these pure materials either alone or in combination with each other. The contact angles for the various materials were indicative of the agglomeration response observed with these materials.

An important consideration when dealing with pendular bridges is our ability to predict the strength of such bridges. This determination will indicate whether or not a floc will stay together given the external forces placed upon the floc. In one study, the bond strength was determined only for a contact angle equal to zero. If
Figure 3.1: Diagram of two particles with pendular bridge showing various angles.
the meridian and contact angles are known, the shape and volume of the bond can be approximated, and thus, the strength of the bridge holding two particles determined.

Another important aspect of pendular bridges is the packing arrangement of solid particles in a floc. This has been treated in the literature in the same way as molecules arranged in a solid lattice. One proposed arrangement is a close packing in which the solid particles have a coordination number of twelve, i.e., each particle has twelve nearest neighbors. Another proposed arrangement is a primitive cubic arrangement which involves particles located at the corners of a cube in space and results in a coordination number of six. The particle arrangement in a floc may affect the oil dosage needed to achieve pendular bridging in an oil agglomeration process. There is believed to be a limit beyond which further oil addition would lead to a type of bridging outside of the pendular regime. Thus, bond volume information would be very useful in discerning the characteristics of these flocs.

The volume of fluid between two touching spheres, i.e., pendular bridge, has been investigated by various researchers. Fisher[55] worked with ideal soil particles that were held together by a pendular bridge of water. The bond volumes were associated with a contact angle of zero degrees. The curvature of the pendular bridge was assumed constant, such that the meniscus would form its own circle. Since the contact angle was zero, a straight line could be drawn from the center of the particle circle to the center of the meniscus circle and the resultant line intersected the contact point between the meniscus and particle, i.e., the line A-B-C. This creates a triangular situation where the trigonometric relationships are quite tractable. This situation exists only if the contact angle is zero. The equation for the bond volume
was determined as a function of particle radius $R$, and meridian angle $\theta$ such that:

$$V = 2R(\sec \theta - 1)^2[1 - (\frac{1}{2} - \theta)\tan \theta]$$  \hspace{1cm} (3.1)

It was believed that in the work with soil particles, contact angle was not a factor. Newitt and Conway-Jones [56] also used this expression to predict bond volumes in granulation.

Darcovich et al. [9] investigated the effect of varying the contact angle on the bond volume. For a contact angle greater than zero, the line passing through the center of the particle circle and the contact point of the meniscus will not pass through the center of the meniscus circle. The meniscus circle was described by a general equation in terms of the locus of the center and radius was related to the meridian angle and the contact angle, i.e., the angle formed at the contact point between the tangent lines to the particle circle and the meniscus circle. The bond volume was determined by numerical calculation using a 15-point Gaussian quadrature routine for different values of contact angle. Also, the volume was calculated at a fixed meridian angle of $45^\circ$. It was also implied that the contact angle and bond volume were directly proportional.

An objective of the present study was to obtain an analytical solution for the bridge volume expression that would relate three important variables (contact angle, meridian angle, particle radius) to the volume such that:

$$V_B = f(\Theta_c, \Theta_m, R)$$  \hspace{1cm} (3.2)

When an analytical expression exists, it can be used to predict values of $V_B$ or it can be used for other purposes such as Using mathematical techniques illustrated in Appendix C, the form of the expression for the pendular bridge between two equal
Table 3.1: Exact vs. approximate values of bond volume.

<table>
<thead>
<tr>
<th>$\Theta_C$, deg.</th>
<th>$\Theta_M$, deg.</th>
<th>Bond volume ($100V_B/R_s^2$)</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
<td>0.113</td>
<td>0.5</td>
</tr>
<tr>
<td>0</td>
<td>20</td>
<td>1.437</td>
<td>1.7</td>
</tr>
<tr>
<td>0</td>
<td>30</td>
<td>5.946</td>
<td>3.0</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>0.1234</td>
<td>0.24</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
<td>1.704</td>
<td>0.50</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>7.574</td>
<td>0.79</td>
</tr>
<tr>
<td>40</td>
<td>10</td>
<td>0.1312</td>
<td>0.08</td>
</tr>
<tr>
<td>40</td>
<td>20</td>
<td>1.916</td>
<td>0.14</td>
</tr>
<tr>
<td>40</td>
<td>30</td>
<td>8.962</td>
<td>0.18</td>
</tr>
</tbody>
</table>

sized spheres is:

$$
\frac{V_B}{V_S} = \frac{3}{2}(1 - \cos \Theta_m)^2(1 + [\sin \Theta_m + (1 - \cos \Theta_m)\tan \Theta_s] \times \\
[tan \Theta_s - (\frac{\pi}{2} - \Theta_s)(\tan^2 \Theta_s + 1)])
$$

(3.3)

where $V_S$ is the volume of the spherical particle. This approximation of the pendular bridge volume provides a good estimate as can be seen by comparison with the exact solution for constant curvature [57] (Table 3.1). The exact solution is left in the form of elliptical integrals and cannot be further manipulated with ease.
CHAPTER 4. MATHEMATICAL MODELS

Population Balance

In order to gain better insight into the agglomeration process, it is important to develop mathematical models to describe the process. A useful expression is the population balance. The main parameter in the population balance is the population density defined below.

\[ n(\ell, t) = \lim_{\Delta \ell \to 0} \frac{N(\ell, t)\Delta \ell}{\Delta \ell} \quad (4.1) \]

In this expression, \( \Delta \ell \) is a range of particle sizes and \( N(\ell, t)\Delta \ell \) is the number of particles within that size range. Another parameter which can be used to describe the size distribution is the volume percent density shown below.

\[ VPD(\ell, t) = \frac{100\ell^3 n(\ell, t)}{\int_0^\infty \ell^3 n(\ell, t) d\ell} \quad (4.2) \]

The denominator of this expression is the third moment of the size distribution. The general form of the \( i^{th} \) moment of a size distribution is:

\[ i^{th \text{ moment}} = \int_0^\infty \ell^i n(\ell, t) d\ell \quad (4.3) \]

where: \( i = 0 \) refers to the total number of particles

\( i = 1 \) refers to the total length of particles
i = 2 refers to the total area of particles
i = 3 refers to the total volume of particles.

Sastry and Fuerstenau[58] stated that the following mechanisms are involved in agglomeration processes: (1) nucleation, (2) coalescence, (3) layering, (4) shattering, (5) breakage, (6) attrition, and (7) abrasive transfer. These mechanisms are illustrated in Figure 4.1.

The authors also used the following form of the population balance:

\[
\frac{\partial n(\ell,t)}{\partial t} = \dot{n}_{in}(\ell,t) - \dot{n}_{out}(\ell,t) + \frac{\partial^2}{\partial \ell^2} [Gn(\ell,t)] - \frac{\partial}{\partial \ell} [(G_A - G_L)n(\ell,t)]
\]

\[
A \quad B \quad C \quad D \quad E
\]

\[
\quad \quad \quad + \dot{B}(\ell,t) - \dot{D}(\ell,t)
\]

\[
F \quad G
\]

The terms in equation (4.4) have the following physical meanings:

A = accumulation of particles of size \( \ell \)
B, C = input, output rates of particles of size \( \ell \)
D = abrasive transfer involving particles of size \( \ell \)
E = layering and attrition involving particles of size \( \ell \)
F, G = discrete size changes involving particles of size \( \ell \) due to nucleation, coalescence, shattering, or breakage.

The general population balance can be used to describe the specific types of processes that can be used in conjunction with oil agglomeration. The population balance approach for analyzing systems has been employed for a variety of situations.

Levine[59] used the population balance in conjunction with mass and momentum balances for analyzing agglomeration in rotating cylindrical and conical drums. For Levine's system, the geometry and velocity of mixing was represented by certain
<table>
<thead>
<tr>
<th>SIZE ENLARGEMENT</th>
<th>SIZE REDUCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation</td>
<td>Shatter</td>
</tr>
<tr>
<td>[ j_{P_i} \rightarrow P_j ]</td>
<td>[ P_j \rightarrow j_{P_i} ]</td>
</tr>
<tr>
<td>Coalescence</td>
<td>Breakage</td>
</tr>
<tr>
<td>[ P_i + P_j \rightarrow P_{i+j} ]</td>
<td>[ P_i \rightarrow P_{j} + P_{i-j} ]</td>
</tr>
<tr>
<td>Layering</td>
<td>Attrition</td>
</tr>
<tr>
<td>[ P_i + j_{P_i} \rightarrow P_{i+j} ]</td>
<td>[ P_i \rightarrow P_{i-j} + j_{P_i} ]</td>
</tr>
<tr>
<td>Abrasion Transfer</td>
<td></td>
</tr>
<tr>
<td>[ P_i + P_j \rightarrow P_{i+j} + P_{j-l} ]</td>
<td>[ \text{or} ]</td>
</tr>
<tr>
<td>Free Fines</td>
<td>Working Unit</td>
</tr>
<tr>
<td>[ j_{P_i} ]</td>
<td>[ P_i ]</td>
</tr>
</tbody>
</table>

Figure 4.1: Various mechanisms describing particle size changes[58].
terms in the population balance, which would not be the case with continuous agglomerator. The layering process was shown mathematically to be a special case of coalescence. The spherical agglomeration process was described by three sets of mass and momentum balance equations.

Jeon and Lee [60] used the population model to analyze the coalescence of liquid drops. Several additional independent variables including age and solute content were employed. Since neither an analytical nor numerical solution could be obtained, a simulation technique was needed. Also every collision between drops was considered a success with respect to coalescence, which would not be a good assumption for agglomeration.

Nuttall [61] investigated the agglomeration of radioactive wastes in groundwater. Mass transport equations were needed for the dissolved species which were present. Two population balances were needed: one for microbial colloids, and one for clay colloids. Also within the population balance, submodels were required for further explanation. Chu and Fitzpatrick [62] worked with coal in a batch agglomeration system. They solved the population balance for three different scenarios: 1) one component, one constant; 2) one component, three constants; 3) three component, six constants. In order to solve the population balance, they used a non-linear least squares estimation routine. An initial estimate of the constants was made and then the differential equations were solved by the Euler Predictor-Corrector method or the Runge-Kutta fourth order method.
Batch Agglomeration

When particle agglomeration is conducted in a batch reactor, the system operates in a transient mode. In this situation, the following terms can then be eliminated from equation (4.4):

1. Terms B and C are eliminated due to no input or output flows.
2. Terms D and E are eliminated if it is assumed that particle size changes are due only to incremental size increases and decreases caused by coalescence and breakage.

The resulting expression then becomes:

\[
\frac{\partial n(\ell, t)}{\partial t} = \dot{B}_C + \dot{B}_B - \dot{D}_C - \dot{D}_B
\] (4.5)

where \(\dot{B}_C\) and \(\dot{B}_B\) are the birth rates of particles of a certain size through coalescence and breakage, respectively, and \(\dot{D}_C\) and \(\dot{D}_B\) are the death rates of particles of a certain size through coalescence and breakage, respectively.

From Appendix A, the forms of the B and D terms are:

\[
\dot{B}_C(\ell, t) = \frac{1}{2} \int_0^\ell R(\ell^3 - \ell^3)^{1/3} n(\ell, t) d\ell
\] (4.6)

\[
\dot{B}_B(\ell, t) = \eta B(\ell^{1/3} n(\ell^{1/3}, t)
\] (4.7)

\[
\dot{D}_C(\ell, t) = n(\ell, t) \int_0^\infty R(\ell, \beta) n(\ell, t) d\beta
\] (4.8)

\[
\dot{D}_B(\ell, t) = B(\ell) n(\ell, t)
\] (4.9)

Substitution of these expressions into equation (4.5) yields:

\[
\frac{\partial n(\ell, t)}{\partial t} = -B(\ell) n(\ell, t) + \eta B(\ell^{1/3} n(\ell^{1/3}, t)
+1/2 \int_0^\ell R(\ell^3 - \ell^3)^{1/3} n(\ell^3 - \ell^3)^{1/3}, t) n(\ell, t) d\ell
-n(\ell, t) \int_0^\infty R(\ell, \beta) n(\ell, t) d\beta
\] (4.10)
The time-independent coefficients were determined by Bemer and Zuiderweg\cite{63} to be:

\begin{align*}
B(\ell) &= B_0 \ell^b \\
B(\eta^{1/3}\ell) &= B_0 \eta^{b/3} \ell^b \\
R[(\ell^3 - \bar{\ell}^3)^{1/3}, \bar{\ell}] &= \frac{R_0}{[(\ell^3 - \bar{\ell}^3)^{1/3}]^r} \\
R(\bar{\ell}, \ell) &= \frac{R_0}{[\bar{\ell}\ell]^r}
\end{align*}

The form of equation (4.10) is that of an integro-differential equation. The constants which are present in this equation as a result of the time-independent coefficients, are: \( r, b, B_0, R_0, \) and \( \eta \). The constant \( \eta \) refers to the number of pieces that result from breakage, and for simplification of the model, can be set equal to two. This would then leave four constants that need to be determined. But the constants would probably have little physical meaning. The ways in which these constants could be handled are:

1. assume conditions of agglomeration such that the breakage terms \( \dot{B}_B \) and \( \dot{D}_B \) are negligible when compared to the coalescence terms \( \dot{B}_C \) and \( \dot{D}_C \), or
2. assume reasonable values for two of the constants and then try to determine the other two constants by fitting the experimental data to the model equations.

Kawashima et al.\cite{23} assumed that in their system the coalescence of fine and coarse particles was dominant and that the breakdown of fines was negligible. By using these assumptions for the population balance, they were able to avoid the problem of an integro-differential equation. The two growth models that they wanted to
compare were growth by random coalescence versus growth by non-random coalescence. The factors which influenced non-random coalescence were particle movement, physicochemical properties, particle size, and shearing forces.

**Continuous Stirred Tank Agglomeration**

There appear to be more possible growth mechanisms for a continuous system than for a batch system. Due to this situation, there are more possible variations of equations which can be generated from the general population balance. The following subcases arising from various assumptions are: layering/shear breakage, layering, layering/attrition, and layering/coalescence.

**Layering/Shear breakage**

If the conditions are allowed to reach steady state, then the population density will be a function of particle size. The following terms can be eliminated from equation (4.4): according to Glatz and coworkers [29]-[32]

1. term A is eliminated due to steady state,
2. term D is eliminated if particle size increases are due to layering (term E), and if particle size decreases are due to incremental particle breakage (terms F and G).

The resulting expression then becomes:

\[ 0 = n_{in}(\ell) - n_{out}(\ell) + \frac{d}{d\ell} [ (G_A - G_L)n(\ell) ] + \dot{B}_B(\ell) - \dot{D}_B(\ell) \] (4.15)

or

\[ \frac{d}{d\ell} [G_Ln(\ell)] = n_{in}(\ell) - n_{out}(\ell) + \dot{B}_B(\ell) - \dot{D}_B(\ell) \] (4.16)
The expressions for $\hat{D}_B(\ell)$ and $\hat{B}_B(\ell)$ are the same as for equations (4.7) and (4.9) without the time dependence, $\hat{h}_{in}(\ell) = 0$ due to no input of agglomerates, and $\hat{h}_{out}(\ell)$ can be described as:

$$\hat{h}_{out}(\ell) = n(\ell) / \tau$$

(4.17)

where $t$ is the average residence time of the CSTA. Equation (4.16) now takes the form:

$$\frac{d}{d\ell} [G_L n(\ell)] = -n(\ell) / \tau + \eta B(\eta^{1/3} \ell) n(\eta^{1/3} \ell) - B(\ell) n(\ell)$$

(4.18)

If the growth rate, $G_L$, is expressed as a linear expression of length,

$$G_L = G_0 \ell$$

(4.19)

then equation (4.18) becomes:

$$G_0 \frac{d[ln(\ell)]}{d\ell} = -n(\ell) / \tau + \eta B(\eta^{1/3} \ell) n(\eta^{1/3} \ell) - B(\ell) n(\ell)$$

(4.20)

or

$$\frac{dn}{d\ell} = \frac{B \ell^{b-1}}{G_0} \eta^{(b+3)/3} n(\eta^{1/3} \ell) - \frac{B \ell^{b-1}}{G_0} \left( 1 + \frac{1}{G_0 \tau} \right) n(\ell)$$

(4.21)

The expression can then be solved numerically for $n(\ell)$. In this instance, the equation is an ordinary differential equation as opposed to an integro-differential expression.

Layering

If it is assumed that no breakage takes place, a more general form of the layering growth rate can be employed:

$$G_L = G_0 \ell^a$$

(4.22)
The differential equation takes the form:

$$\frac{G_0 \ell^a n(\ell)}{d\ell} + \frac{n(\ell)}{r} = 0$$  \hspace{1cm} (4.23)

and the solution becomes:

$$\ln \frac{n}{n_0} = -a \ln \frac{\ell}{\ell_0} - \frac{\ell^{1-a} - \ell_0^{1-a}}{(1-a)G_0r}$$  \hspace{1cm} (4.24)

With these particular assumptions, an analytical solution of the differential equation is obtained.

Layering/Attrition

If agglomerate size reduction is due to attrition of the surface, and if the attrition rate is independent of the size of particles:

$$G_L = G_0 \ell^a$$  \hspace{1cm} (4.25)

$$G_A = E_0$$  \hspace{1cm} (4.26)

the size distribution will take the form:

$$\ln \frac{n}{n_0} = -\ln \frac{G_0 \ell^a - E_0}{G_0 \ell_0^a - E_0} - \frac{1}{r} \sum_{i=1}^{m} \frac{E_0^{i-1}(\ell^{1-a} - \ell_0^{1-a})}{G_0^i(1-i\alpha)}$$  \hspace{1cm} (4.27)

If attrition is treated as a function of size such that:

$$G_L = G_0 \ell^b$$  \hspace{1cm} (4.28)

$$G_A = E_0 \ell^b$$  \hspace{1cm} (4.29)

the distribution will take the form:

$$\ln \frac{n}{n_0} = -\ln \frac{G_0 \ell^a - E_0 \ell^b}{G_0 \ell_0^a - E_0 \ell_0^b} - \frac{1}{r} \sum_{i=0}^{m} \frac{E_0^i(\ell^{ib+1-(i+1)a} - \ell_0^{ib+1-(i+1)a})}{(ib + 1 - (i + 1)a)G_0^{i+1}}$$  \hspace{1cm} (4.30)

The exponential term is in the form of a series.
Layering/Coalescence

If both layering and coalescence are present such that the form of the population balance looks like:

\[
\frac{d[G Ln(\ell)]}{d\ell} + \frac{n(\ell)}{\tau} = 1/2 \int_0^\ell R[(\ell^3 - \ell\tilde{\ell})^{1/3}, \ell] n[(\ell^3 - \ell\tilde{\ell})^{1/3}] n(\ell) d\tilde{\ell}
\]

\[- n(\ell) \int_0^\infty R(\ell, \tilde{\ell}) n(\tilde{\ell}) d\tilde{\ell}
\]

(4.31)

The solution of this expression will require techniques utilized for integro-differential equations.

Population Balance Parameters

The various parameters of the population balance such as the growth constants, breakage constants and exponents of particle size must themselves be modelled by theory. The growth rates have been investigated by various investigators such as Levich[64], Saffman and Turner[65], Glatz et al.[29], and Voigt[66]. Based on the assumption of the Kolmogorov scale of turbulence (2-16 mum), the following expression for collision frequency emerges:

\[
b_{ij} = 12 A_2 V_g R_{ij} N_i N_j
\]

(4.32)

Coal-Oil Interaction

If the oil agglomeration process could be broken down into two main steps, they might be:

1. particles acquire binder on their surfaces, and
2. particles collide and stick; the binder forms bridges between adhering
particles. These two steps are illustrated in Figure 4.2.

For the batch and CSTA agglomeration models to be accurate representations of the real systems, it would seem as though step (2) should be rate limiting \( t_2 >> t_1 \). If step (1) is rate limiting \( t_1 >> t_2 \), the significance of the oil phase has to be considered. From Appendix B (based on the work of Dunstan et al.[13]):

\[
\frac{dC_i}{dt} = KO(t)[C_{i-1}(t) - C_i(t)]
\]  

(4.33)

where \( O(t) \) is the oil drop concentration at any time \( t \), \( C_i(t) \) is the concentration of particles with \( i \) oil drops attached to the particle surface, and \( K \) is the rate constant for successful collisions of oil drops and particles. This model can be tested experimentally by monitoring the power supplied to a stirrer motor in a system undergoing agglomeration. The assumption was made that a rise in stirring motor power is an indirect result of the enlargement of particles. Experimentally, it is usual for the current input to stay constant for a relatively long time and then rise quickly to a new input level. The time when the change takes place (short time interval of change) is referred to as the inversion time. When equation (4.33) was solved and graphed, the curves contained inflection points for all values of \( i \). The time at which the inflection points are found can be compared with the experimental inversion times.
Figure 4.2: Agglomeration progress with respect to time displaying times of wetting and times of growth.
CHAPTER 5. EXPERIMENTAL (BATCH SYSTEM)

Materials

The solids agglomerated in the batch experiments were Upper Freeport coal from the Lucerne No. 6 mine in Indiana County, Pennsylvania; Australian A coal from the Ulan coal mine in New South Wales, Australia; and pure graphite from Sri Lanka. The oils employed as binders for these solids were n-heptane, 1-heptanol, hexadecane, 1-hexanol, paraffin oil, and tetralin. Sodium chloride was used as an electrolyte in the slurry during agglomeration. Sodium oleate was used as an ionic surfactant which would adsorb on to the solid surface, whereas the alcohols would act as a nonionic surfactants. The list of materials, as well as their properties, is given in Table 5.1 and Table 5.2.

Coulter Counter Measured Agglomeration

Slurries of graphite particles were agglomerated with various oils. The graphite was -400 mesh (i.e., particles smaller than 37 μm). In all of these runs, a 2 wt.% slurry was used (15 g. of graphite in 750 ml. of deionized water). The slurry was agitated at moderate speeds for at least 10 min. prior to the addition of a binder. The oil (heptane, hexadecane, or paraffin oil) was introduced into the slurry with the use of a syringe. In all of the runs, a 10 v/w % oil dosage (1.5 ml. of oil for 15 g. of
<table>
<thead>
<tr>
<th>Solid Type</th>
<th>Ash, %</th>
<th>Sulfur, %</th>
<th>Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Freeport Coal</td>
<td>11-12</td>
<td>0.5</td>
<td>-200 &lt;74</td>
</tr>
<tr>
<td>Lucerne No. 6 Mine</td>
<td></td>
<td></td>
<td>-200/+400 37-74</td>
</tr>
<tr>
<td>Indiana County, Penn.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Australian A Coal</td>
<td>17.73</td>
<td>—</td>
<td>-200/+400 37-74</td>
</tr>
<tr>
<td>Ulan Coal Mine LTD, Ulan - New South Wales</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure Graphite, Sri Lanka</td>
<td>—</td>
<td>—</td>
<td>-400 &lt;37</td>
</tr>
</tbody>
</table>

Table 5.2: Bridging liquids for batch tests

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Density, $g/cm^3$</th>
<th>Viscosity, centipoise</th>
<th>Dipole moment, D</th>
<th>Surface tension, dyne/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-heptane</td>
<td>0.6838</td>
<td>0.418</td>
<td>0</td>
<td>20.140</td>
</tr>
<tr>
<td>1-heptanol</td>
<td>0.8219</td>
<td>8.53</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>0.7733</td>
<td>3.34</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1-hexanol</td>
<td>0.8136</td>
<td>4.592</td>
<td>1.55</td>
<td>26.208</td>
</tr>
<tr>
<td>paraffin oil</td>
<td>0.865</td>
<td>23.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>tetralin</td>
<td>0.9632</td>
<td>2.202</td>
<td>0.60</td>
<td>33.642</td>
</tr>
</tbody>
</table>
coal) was used, except in those cases where additional oil was introduced at 60 min.
In some of the runs, the oil was added in the form of an emulsion. In such cases, the
graphite (15 g.) was mixed initially with 500 ml. of water while 1.5 ml. of oil was
emulsified in another 250 ml. of water using an agitator speed of 21,000 rpm for 2
min. The agglomeration took place in a variable speed kitchen blender (operated at
21,000 rpm) or a Plexiglas cylindrical vessel containing four baffles. The agitation
for this second container was supplied by a variable speed stirring motor with a three
blade stirrer, operated at 100 or 600 rpm. After the slurry was conditioned, the
oil was introduced and the clock started. As the agglomeration proceeded, 0.3 ml.
samples were removed with a Pipetman at 1, 2, 4, 15, 30, and 60 min. and analyzed
with a Coulter Counter, model TAI. Each sample was diluted with 200 ml. of a
microfiltered 3 wt. % sodium chloride solution. The highly diluted agglomerates-
in-electrolyte slurry was then stirred at moderate speeds for about 1 min. It was
assumed that no further agglomeration would take place due to the diluteness of
the slurry. After stirring, approximately 2 ml. of the suspension was drawn into
the Coulter Counter and analyzed using a 240 μm aperture. The agglomerates were
counted using 16 different channels. The channels were calibrated to upper and
lower size limits based on the size of aperture used. The information provided by the
Coulter Counter was then analyzed in terms of population density or volume percent
density. The population density for the \( i^{th} \) channel was given by:

\[
n_i = \frac{N_i}{\Delta \ell_i}
\]  

(5.1)

while the volume percent density for the \( i^{th} \) channel was given by:

\[
VPD_i = \frac{\pi \ell_i^3 N_i}{6 \Delta \ell_i}
\]  

(5.2)
where: \( N_i \) is the number of particles in channel \( i \)
\( \ell_i \) is the average size of a particle in channel \( i \)
\( \Delta \ell_i \) is the size width of a channel.

**Oil Emulsification Tests**

Different oils (heptane, hexanol, and tetralin) were emulsified in water. Three methods were used for producing the emulsions: mixing in a kitchen blender at 18,000 rpm, mixing in a baffled, cylindrical vessel at 1000 rpm, and treating in an ultrasonic bath. The emulsions were made by mixing 20 ml. of oil with 200 ml. of water, and then agitating this mixture for 2 min. The ultrasonic bath emulsification utilized a 20 ml. test tube, which contained 15 ml. of liquid with 1 part oil to 10 parts water immersed in the bath. After the emulsions were prepared, they were transferred to sampling tubes for analysis with either a spectrophotometer or turbidimeter to monitor both the extent of emulsification and the decay with time by measuring the light absorbance and turbidity. To measure the extent of emulsification and the stability of the emulsions, the following equipment was used: a Coleman spectrophotometer, a Hach model 2100A Turbidimeter, and a Coulter Counter. The spectrophotometer indicated the relative absorbance and/or transmittance of the emulsion. The turbidimeter was used to measure the turbidity of an emulsion. The Coulter Counter gave an indication of the oil droplet size distribution of an emulsion. The readings of all three instruments were monitored over time in order to observe the stability of the emulsions.
Inversion Time Measurements

Concentrated slurries of Australian coal (-200/+400 mesh) were used in several agglomeration runs. The slurries contained 10 wt. % solids. The oil dosages ranged from 40 v/w % to 80 v/w %. The agglomeration tests were performed with an agitator speed of 1000 rpm using a Morat R20 digitronic stirrer. A digital voltmeter was connected between the current source and the stirrer motor to detect an increase in power consumption by the motor resulting from a phase inversion of the slurry. At phase inversion, the viscosity of the slurry changed rapidly as the system achieved a state of maximum flocculation. During the agglomeration process, the time when there was a sharp rise in voltage was noted with the voltmeter and recorded as the inversion time. For this set of experiments, a small container (500 ml. canning jar) was employed for the agglomeration process. A four blade impellor was employed together with an adjustable metal baffle placed near the impellor. When this baffle was placed in the proper location, the effect of the increasing slurry viscosity was magnified slightly which improved the signal to noise ratio. The time when visible particle enlargement was seen initially was also recorded and referred to as the striation time. When the agglomeration was completed following phase inversion, the agglomerates were recovered on a 100 mesh sieve. If the resulting agglomerates were spherical, their size was measured with an optical microscope. The agglomerates and refuse were analyzed for ash by placing approximately one gram samples in crucibles and then heating the samples to 750°C.
CHAPTER 6. EXPERIMENTAL (CONTINUOUS SYSTEM)

Preliminary Tests

In order to launch a successful series of continuous runs, it was necessary to choose the proper parameters and conditions that would adequately reflect the model system that was to be used. Only certain conditions produced the type of product that could be used for population counting. If too little oil was used, the coal particles formed loose flocs that could not be counted accurately. If too much oil was used, the coal particles formed an amalgam which again could not be counted due to the fact that there was no definite boundary between particles. If the coal was too hydrophilic, adequate spherical agglomerates could not be produced. The agglomerates (small flocs) tended to form a tight structure (secondary agglomeration) which again became hard to size. The use of surfactants or alcohols did not prevent this from occurring. With a hydrophilic coal, the choice of oil was important as well as the range of dosage. If the oil was too volatile, the risk of evaporation became a problem in an open system. If longer chain hydrocarbons (e.g., 16 carbons) were employed, the coal became spherically agglomerated, but the individual agglomerates tended to stick together.

A way to characterize the agglomeration of a particular coal was described by Drzymala and Wheelock[67]. The schematic representation of both a batch unit
along with a turbidity measuring device is given in Figure 6.1. A 500 ml. canning jar was used in a kitchen blender set-up, which was operated as a closed system with no air present. The system was fitted with an external loop of tubing which conveyed some of the material being agglomerated to a photometric dispersion analyzer and back to the agglomerator. The dispersion analyzer (PDA 2000), was manufactured by Rank Brothers Ltd. of Cambridge, England, and it measured the turbidity of the suspension. For the runs utilizing this apparatus, 8 g. of coal was suspended in 500 ml. of deionized water. An effort was made to exclude air bubbles from the vessel prior to the start of a run. The coal slurry was stirred for 5 min. at 5000 rpm. Oil was introduced through the top of the closed jar with a hypodermic syringe inserted through a rubber septum. The oil was added in the following increments: 0.1, 0.1, 0.2, 0.4, 0.8, and 1.6 ml.. These additions yielded the following net oil dosages: 1.25, 2.5, 5, 10, 20, and 40 v/w %. The output signal from the dispersion analyzer was converted to turbidity values by using the Lambert-Beer law. The turbidity values were then plotted against oil dosage on a semi-log graph. Extrapolation of the data to zero turbidity provided an indication of the theoretical dosage required for complete agglomeration of the coal. This dosage referred to as the critical dosage was indicative of the relative agglomeribility of the coal. Of the coals that were readily available for continuous runs (Illinois No.5, Pittsburgh No.8, and two kinds of Upper Freeport Coal), only the Upper Freeport coal from the Helvetia mine proved hydrophobic enough to produce good results in the continuous runs.
Figure 6.1: Schematic diagram of the batch agglomeration unit employing a photometric dispersion analyzer
Materials Used

The coals used for the continuous runs were from the Indiana No.6 seam (same as the Illinois No.5 seam) and from the Upper Freeport seam in the Helvetia mine. The coals were received in barrels that were purged with an inert gas. Each barrel was riffled into two portions and then each of those two portions was riffled into two more portions. The four riffled portions were then stored under nitrogen. The coal was then passed through a high-speed impact mill and sieved with a Rototap shaker. The coal fines that were employed in the study of Indiana No.6 coal was between 200 and 325 mesh, while the study of Upper Freeport coal was either less than 200 mesh or greater than 200 mesh. This fraction was not so small as to require large oil additions due to a high specific surface area and not so large as to interfere with spherical agglomeration. The heat of wetting as well as induction time measurements were made with this coal size.

The oils employed in the continuous runs were: tetralin for Indiana No.6 coal and hexadecane for the Upper Freeport coal (Helvetia mine). From batch tests, it was apparent that the Indiana No.6 coal was fairly hydrophilic and that straight chain hydrocarbons would not produce spherical agglomerates. Spherical agglomerates were produced with tetralin (an aromatic compound), and with a mixture of heptane and heptanol (a straight chain hydrocarbon and a straight chain alcohol). This mixture was not employed because a single component binder was desired for purposes of simplification. For the Upper Freeport coal, hexadecane did a good job in producing spherical agglomerates. The Upper Freeport coal seemed to be much more hydrophobic than the Indiana No.6 coal. The shorter chain hydrocarbons did not perform as well because they seemed to produce weaker agglomerates. Although tetralin pro-
duced fairly strong, compact agglomerates when applied to Upper Freeport coal, the agglomerates lacked sphericity.

**Apparatus**

The experimental set-up shown in Figure 6.2 was used to carry out the series of continuous runs. The various components of this set-up included a feed tank, plastic tubing, pumps, and agglomeration cell. The coal/water slurry was pumped into the agglomeration cell through the plastic tubing and was mixed with oil which was also pumped to the cell. The flow of both the slurry as well as the oil could be controlled. Agglomerates were then formed and exited the cell at a mass flow rate equal to the combined flow rates of the slurry and oil. Agitation in the cell provided the environment for the coal to grow into agglomerates.

The agitator employed for the feed tank was a Denver flotation cell with no air flow. The Denver cell was used because the agitation was very vigorous near the bottom of the cell and lifted the fines into suspension, thus preventing settling. The bottom outlet of the feed tank enabled the slurry to be pumped out of the bottom. The Tygon tubing connecting the feed tank and the agglomeration cell was as vertical as possible to minimize particle settling. Thus, loops in the tubing were avoided. Based upon the volumetric flow rates, the diameter of the tubing was chosen so that a velocity could be maintained that would prevent particle settling or classification. Spells\[68\] developed a relationship between pipe or tube diameter and flow velocity of slurries which would prevent particle settling or classification. The feed tank was placed above the agglomeration unit. Prior to a run, the feed pump was calibrated at different volumetric flow rates, using only deionized water. The slurry
Figure 6.2: Schematic diagram of experimental set-up for continuous runs
flow rate was then determined by collecting 2 to 3 samples over a timed interval and weighing them. The solids content of the samples was also determined to give an indication of the solids feed rate. The oil pump was then calibrated to deliver the oil dosage required for the solids flow rate. For a given stirring speed, it was hoped that settling of particles would not be a problem, based on the work by Aeschbach and Bourne[69] who investigated different CSTR arrangements for particles-in-liquid. With ineffective stirring, large particles would remain in the tank while small particles would leave in the output stream. Although larger and more uniform particles would be formed, steady-state would not be attained. The agglomeration tank consisted of a 2 liter stainless steel beaker with a baffled-draft tube insert (Figure 6.3). The draft tube had both internal and external baffles. Also, the stirring blade had a reversed 45° pitch, i.e., the fluid was forced upward as opposed to downward. The upward motion of the slurry allowed for a flow of agglomerates up and around the draft tube. The outlet tube from the tank was placed so that it would intercept the flow streamlines, and thus provide an output which was representative of the tank's content. A representative output was crucial for achieving steady-state. The outlet tube was 2.0 cm in diameter at an angle of 30° with the side of the vessel. The feed slurry inlet and oil inlet to the agglomerator were placed outside of the draft tube to reduce the possibility of short circuiting.

Size Distribution Determination

The size distribution of agglomerates was measured by automatic image analysis. Other methods of particle size analysis which were considered included using a Coulter Counter, sieving (wet or dry), in situ light scattering, or simple photog-
Figure 6.3: Agglomeration vessel for continuous agglomeration
raphy. The problem with the Coulter Counter is that it does not work well with larger sizes of particles. When measuring particles above 300 \( \mu m \), too much material is drawn through the aperture and the sample container may be sucked dry. The Coulter Counter is ideally suited for particles much smaller than 300 \( \mu m \). Also, when a particle approaches the aperture, it is subjected to shearing forces. The instrument is designed so that only one particle will pass through the aperture at a time. Smaller agglomerates, or loose flocs, may be too weak to withstand the shear and consequently break into several pieces. Thus, in order to use results from a Coulter Counter, an assumption has to be made that the fragments resulting from the breakage of a single agglomerate can be counted as one particle. The Coulter Counter is better suited for agglomerates composed of particles about 1 \( \mu m \) in size so that the adhesion forces are greater.

Sieving did not seem to work well because there was too much opportunity for breakage when the agglomerates were screened causing an artificially high number of small particles to be counted. The breakage was caused by the large amounts of vibration, suction, and washing required. Wet sieving was better suited for analyzing the feed material, where breakage was not a problem.

The insitu light scattering method required a properly set-up agglomeration vessel and probably would be more applicable to a batch system which then could be monitored with respect to time. The photography method would require taking a series of photomicrographs of collected samples. Each photomicrograph would then be analyzed individually to determine a size distribution.

The automatic image analysis method is closely related to the photographic method, except that the images are recorded by a computer. At steady-state a
sample of the output stream from the agglomerator was collected in a 50 ml. beaker and was then diluted quickly with water. The dilute sample was spread onto sheets of filter paper placed in Pyrex dishes which had been lined with absorbent tissues (Kimwipes). The liquid drained through the filter paper, leaving the agglomerates sitting on top of the paper. The Pyrex dishes were then covered with cellophane to retain moisture. By retaining sufficient moisture, the agglomerates were able to retain their integrity. When a sample was ready for analysis, the filter paper was removed from the dish and the sample was dried in an oven for a few minutes. A blank sheet of white paper was sprayed with an adhesive, after which the dried agglomerates were carefully sprinkled onto the sheet. The sheet was then placed under a microscope where the particles were illuminated by a ring of light. On top of the microscope was a television camera which recorded the image and also displayed the image on a television monitor. The camera interfaced with a computer, using a Lemont program (OASYS). The program took advantage of the fact that the coal particles were very black while the background was white. There was a grey bar color chart which allowed for the coloring of particles which ranged in various shades of grey with one shade of a primary color, i.e., yellow. The program then counted everything that appeared yellow. If two or more particles touched, there was an automatic function which allowed for a white line to be drawn to separate the particles. An individual sample from a single run could produce a number of images which were stored on floppy disks as frames. Particle size distributions based on projected areas were then determined. These distributions were then converted to number density curves where the length parameter was actually a particle diameter based on the projected area of a circle. For the larger particles which undergo spherical agglomeration, this assumption was
acceptable.

The data received as an output of the OASYS program were presented as the number of particles within a given interval of projected particle areas on a logarithmic scale. The size limit intervals were then recalculated as equivalent diameters, and the geometric mean was determined. The number of particles in a particular size interval were then divided by the length of the interval to determine the number density. The number density was then adjusted to number density per liter of solution by using the following relation:

\[ n_{\text{per liter}} = n_{\text{sample}} \times f. \]  \hfill (6.1)

where:

\[ f = \frac{10^{12} SC}{\rho \frac{\pi}{6} \sum_{i=1}^{m} N_i (\ell_i)^3} \]  \hfill (6.2)

\[ SC = \text{slurry concentration (g}_\text{coal}/g_{\text{slurry}}) \]

**Experimental Design**

In the continuous runs, the main operating parameters examined included: slurry concentration, oil dosage, stirring speed, and residence time. An experimental design was used to determine response curves for these runs. The design was called the half fraction central composite method. This method takes determined responses, such as model parameters, R-squared values from model fits, range of particle diameters, median size of agglomerates, average size of agglomerates, standard deviation of size distribution, and range of middle 50% of particles and analyzes them for the different run conditions. The purpose was to determine if any coupling/interaction
existed between the different run conditions with regard to particular responses. The experimental design utilized five levels of each of the four run parameters. There are two types of designs that can be used: full or half fraction. For a full fraction, the number of runs to be performed equals $2^P + 2P + R_P$, and for a half fraction, the number of runs equals $\frac{1}{2}(2^P) + 2P + R_P$. In these expressions, $P$ is the number of operating parameters and $R_P$ is the number of replications of the center point. For the Indiana No. 6 coal, a half fraction was performed and the center point was replicated 5 times which required 21 total runs. For Upper Freeport coal, a full fraction was performed and the center point was duplicated 2 times which required 16 runs. Also, 3 additional runs were performed with the Upper Freeport coal at a different particle size, and these experiments were external to the main experimental design. The design matrix is shown in Table 6.1 and Table 6.2. The runs were randomized and then performed in the resultant order to eliminate any systematic bias.
Table 6.2: Central composite design for agglomeration with Upper Freeport coal.

<table>
<thead>
<tr>
<th>Operating Parameter Levels</th>
<th>-2</th>
<th>-1</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil Dosage, v/w%</td>
<td>20</td>
<td>25</td>
<td>30</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>Stirring Speed, rpm</td>
<td>500</td>
<td>750</td>
<td>1000</td>
<td>1250</td>
<td>1500</td>
</tr>
<tr>
<td>Residence Time, min.</td>
<td>2</td>
<td>3.5</td>
<td>5</td>
<td>6.5</td>
<td>8</td>
</tr>
</tbody>
</table>
CHAPTER 7. DISCUSSION OF RESULTS

Batch Agglomeration Involving Limited Growth

Initially, agglomerates of graphite particles were created using operating conditions that promoted very small growth. During a single agglomeration run a series of samples were collected and the particle size distribution of each sample was determined in terms of the volume percent density. By observing the shift in particle size distribution with agglomeration time it was possible to learn something about the kinetics of agglomeration. The graphite was crushed so as to pass a 400 mesh (37 μm) screen. In all cases, the concentration of the slurry was about 2 wt.% (15 g. of slurry in 750 g. of slurry). After 10 min. of agitation of the slurry, oil was introduced either as an emulsion or as a pure liquid. The amount of oil added was about 10 v/w%. In employing a Coulter Counter to measure particle size distributions, a 240 μm aperture was utilized. Larger apertures did not seem to work well with the Coulter Counter model available because the amount of material drawn into the apparatus would have exceeded the amount in the sample glass. With the 240 μm aperture, the largest particle that could be measured was 100 μm in size. Thus, experimental conditions were limited by the Coulter Counter such that the agglomerates could not exceed 100 μm. In order to maintain limited growth, low slurry concentrations, low oil dosages, and small particle sizes were used. Graphite was used as a feed
material because its surface is fairly hydrophobic, it is available as a relatively pure material, and it is a good model for coal in an agglomeration process. It was also advantageous to use a single component material because a Coulter Counter can’t distinguish between carbonaceous particles and mineral particles, which was important when dealing with agglomerates that did not exceed the feed size by very much. The feed particles were smaller than 37 μm and the agglomerates were found to be smaller than 100 μm. Due to the low growth conditions in the batch mode, the competing mechanisms involved in the agglomeration were coalescence and breakage. In these runs, growth appeared to be due to particle coalescence and their mechanism seemed to be dominant in the early stages of agglomeration. After the maximum amount of growth took place, breakage seemed to dominate.

To obtain the results presented in both Figure 7.1 and Figure 7.2, a single run was made and the following experimental conditions were employed in an open kitchen blender: a slurry concentration of 2 wt.% graphite in deionized water, an oil dosage of 10 v/w % heptane, and a stirring speed of 21,000 rpm. Samples of the slurry were removed with a pipet at various times during agglomeration and analyzed with a Coulter Counter.

Figure 7.1 shows that for short mixing times the particle size distribution curves shifted to the right due to particle growth. However, after a certain mixing time, breakage seemed to dominate over growth and the distribution curves shifted back toward the left and approached the feed distribution curve. Breakage may have been the result of not using enough oil to create strong agglomerates and a strong shear field. As can be seen in Figure 7.1, the maximum shift in the volume distribution towards the larger sizes occurred at about 2 min. In other words, if agglomeration had
Exp. Conditions: 2% Slurry (15 g. in 750 ml water)
Graphite, 10% v/w Heptane [1.5 ml]
Stirring Speed = Highest mode on kitchen blender
21,000 rpm
- 0 min, $L_{max} = 24.4 \mu m$
- 1 min, $L_{max} = 40.4 \mu m$
- 2 min, $L_{max} = 45.0 \mu m$
- 4 min, $L_{max} = 38.8 \mu m$
- 15 min, $L_{max} = 35.7 \mu m$

Figure 7.1: Volume percent density curves for graphite agglomeration at early time readings (21,000 rpm).
Exp. Conditions: 2% Slurry (15 g. in 750 ml water)
Graphite, 10% v/w Heptane [1.5 ml]
Stirring Speed = Highest mode on kitchen blender
21,000 rpm

- 0 min, $L_{\text{max}} = 24.4 \, \mu m$
- 15 min, $L_{\text{max}} = 35.7 \, \mu m$
- 30 min, $L_{\text{max}} = 33.8 \, \mu m$
- 60 min, $L_{\text{max}} = 26.4 \, \mu m$

Figure 7.2: Volume percent density curves for graphite agglomeration at later time readings (21,000).
been halted after 2 min., the largest agglomerate size distribution would have been obtained. Up until 2 min., the mechanism of growth dominated over the mechanism of breakage. After 2 min., the mechanism of breakage dominated over the mechanism of growth. It is evident from Figure 7.2 that the agglomerate volume distribution for a mixing time of 60 min. resembled the initial size distribution.

Some of the results of the first run are also reproduced in Figure 7.3 which shows the logarithm of the population density plotted against particle size. In this graph, only the initial size distribution and the size distribution corresponding to 2 min. of mixing are shown.

To obtain the results presented in Figure 7.4, a cylindrical Plexiglas vessel was used and the following experimental conditions were employed: a slurry concentration of 2 wt.% of graphite in water, an oil dosage of 10 v/w% heptane, and a stirring speed of 650 rpm. As can be seen in Figure 7.4, the maximum shift in particle size distribution occurred at about 4 min. Another interesting feature was the size distribution at 60 min. and the way in which it very nearly matched the initial feed distribution. In the case of the previous run made at 21,000 rpm, the 60 min. size distribution did not reflect the extent of breakage necessary to match the initial feed distribution. In comparison with the first run, one possible reason for the slower shift to the maximum size distribution at 650 rpm could have been the reduced interaction between the oil phase and the graphite fines due to the slower agitation. The oil droplet size may not have been small enough in comparison with the size of the graphite particles for optimum interaction, and thus it may have taken longer for sizable agglomerates to appear. Also, due to this phenomenon, the agglomerates may not have been as strong. Thus, even though the shearing force acting upon the
Exp. Conditions: 2% Slurry (15 g. in 750 ml water)
Graphite, 10% v/w Heptane [1.5 ml]
Stirring Speed = Highest mode on kitchen blender
21,000 rpm

Figure 7.3: Population density curves for graphite agglomeration at 0 and 2 minutes (21,000).
agglomerates were reduced, the agglomerate strength may also have been reduced.

In order to further investigate this idea, a third run was executed with the Plexiglas vessel using the following conditions: slurry concentration of 2 wt.%, oil dosage of 10 v/w% of heptane, and a stirring speed of 650 rpm. In this case, the oil was added as an emulsion. The emulsion was prepared by adding 1.5 ml. of oil to 250 ml. of water and 21,000 for 2 min. in a kitchen blender. Thus, the oil was exposed to a shearing environment which was similar to that encountered in the first run. The maximum shift in the particle size distribution occurred after about 1 min. of mixing at 650 rpm. For easier comparison, the results of the preceding run were replotted in Figure 7.5 showing the volume density as a function of mixing time for a series of particle sizes. The results of the third run are presented in a similar way in Figure 7.6.

For the case involving an emulsified oil, the oil was in a condition where it was immediately ready to interact with the coal fines, thus greatly shortening the time required for the maximum size of agglomerates to be created. Also, the breakage of agglomerates was not so complete with prolonged mixing. The reason appears to be a combination of increased particle strength coupled with reduced shearing force.

The oil agglomeration is looked upon as a two step process, i.e., interaction of oil droplets with particles, and interaction of various oil-coated particles with each other. It then seems logical that if the oil is introduced to the agitated slurry in an emulsified form at time equal to zero, the interaction of coal and oil for purposes of agglomeration with the given agitation would result in more rapid overall agglomeration.
Exp. Conditions: 2% Slurry (15 g. in 750 ml water)
Graphite, 10% v/w Heptane [1.5 ml]
Stirring Speed=650 rpm

- 0 min, $L_{\text{max}} = 22.5 \, \mu\text{m}$
- 1 min, $L_{\text{max}} = 22.5 \, \mu\text{m}$
- 2 min, $L_{\text{max}} = 22.5 \, \mu\text{m}$
- 4 min, $L_{\text{max}} = 35.7 \, \mu\text{m}$
- 15 min, $L_{\text{max}} = 22.5 \, \mu\text{m}$
- 30 min, $L_{\text{max}} = 22.5 \, \mu\text{m}$
- 60 min, $L_{\text{max}} = 22.5 \, \mu\text{m}$

Figure 7.4: Volume percent density curves for graphite agglomeration (650 rpm).
Conditions: 2% Slurry (1-5 g in 7-50 ml water)
Graphite. 10% v/w Heptane ml
Stirring Speed=650 rpm

Experiment Conditions: 2% Slurry (15 g in 750 ml water)
Time (min)

Volume Percent Density (μm⁻¹)

Figure 7.5: Volume percent density curves plotted against time for graphite agglomeration (650 rpm).

[Graph showing volume percent density curves plotted against time for graphite agglomeration (650 rpm).]

63
Exp. Conditions:

2% Slurry (15 g. in 750 ml water)
Graphite, 10% v/w Heptane (1.5 ml pre-emulsified in 250 ml)

Stirring Speed=650 rpm

\[22.3 \mu m\]
\[35.7 \mu m\]
\[56.7 \mu m\]
\[71.4 \mu m\]
\[89.9 \mu m\]

Figure 7.6: Volume percent density curves plotted against time for graphite agglomeration with emulsified oil additions (650 rpm).
Emulsion Studies

The preparation of oil-in-water emulsions for use in particle agglomeration was investigated. The purpose of this investigation was to characterize the emulsions produced with various oils to see how the kinetics of coal agglomeration would be affected by emulsification. The three methods used to create emulsions were high speed mixing in a kitchen blender (21,000 rpm), low speed mixing (1000 rpm) in a glass jar vessel equipped with a four-blade propeller, and ultrasonic mixing in a test-tube placed in an ultrasonic bath. In the case of the high and low speed mixing, 20 ml. of oil was mixed with 200 ml. of water for 2 min., and then the mixture was transferred to a 20 ml. test-tube. In the case of ultrasonic mixing a 10:1 mixture of water to oil was placed in a test tube and treated for 2 min. in an ultrasonic bath. Different emulsions were made with various oils and the various mixing techniques to examine oil drop formations. When n-heptane was used as the oil, the ultrasonic bath treatment yielded the most stable emulsions. Both high speed mixing (21,000 rpm) and low speed mixing (1000 rpm) produced relatively unstable emulsions. This is illustrated in Figure 7.7 which shows the change in light absorbance with time of different emulsions.

When 1-hexanol was used, both the high speed mixing and the lower speed mixing produced stable emulsions. The stability was probably due to the interaction (hydrogen bonding) between the alcohol and the water. When tetralin was used as the oil, the high speed mixing produced stable emulsions while the low speed mixing produced unstable emulsions. A Coulter Counter was used to measure the droplet size distribution of an emulsion after 2 min. of high speed mixing. A tetralin-in-water (21,000 rpm) emulsion was used since it was fairly stable. The oil droplet size
Figure 7.7: Light absorbance versus time for n-heptane using various agitation modes.
distribution when plotted on a log n versus size coordinate system yielded a straight line. The average drop size for this emulsion was 5 to 6 μm. This would represent the drop size distribution of a tetralin-in-water emulsion used for agglomeration provided it was prepared by the same technique.

**Batch Agglomeration With Inversion Time Measurements**

Inversion time measurements were used to obtain kinetic information in batch agglomeration experiments without resorting to detailed particle size analyses. Instead of working with pure graphite particles, a real coal was used (Australian A coal from the Ulan coal mine). Emulsificated oils were used in some experiments to determine the effect of emulsification on the size of agglomerates, recovery of the carbonaceous material, and the rate of agglomeration (inversion time). A detailed size distribution analysis would have been difficult to obtain since larger agglomerates were required to achieve a high recovery. Therefore, a Coulter Counter could not be employed for these experiments. Other particle sizing techniques would have been costly and time consuming. Since a relatively large amount of material would have had to be removed from the agglomeration vessel for each size distribution analysis during a given run, many agglomeration experiments would have had to be conducted. In performing such experiments, achieving consistent results can be very difficult. In order to obtain kinetic information without a detailed particle size analysis, the inversion time measurement method was employed. This method is based on the existence of a definite time of wetting by oil before coal particles form larger aggregates. The concept suggests that the oil phase interaction with coal particles is very important. The measurement of inversion time leads to consideration of the effect of emulsification
as well as the choice of oil. A series of runs was carried out using a glass jar mixing vessel equipped with four baffles and a four blade agitator driven by a constant stirring speed at 1000 rpm. The solids concentration was 10 wt.%. The oils that were used included tetralin, n-heptane, and a n-heptane/1-heptanol mixture. The oils were added directly or as an emulsion prepared in a kitchen blender operating at 21,000 rpm. The dosage varied from 40 v/w% to 80 v/w%. The inversion time was recorded as the time when a sudden increase in slurry viscosity occurred as indicated by a sudden power surge to the stirrer motor. The recovery of material on a 100 mesh screen (total and organic) as well as the average particle diameter (average for about 10 particles) were also recorded. The results of these runs are listed in Table 7.1.

The inversion time (or agglomeration time) was shortest when the n-heptane/1-heptanol mixture was employed at any given dosage. The inversion time observed with tetralin was between that observed with heptane or the heptane/heptanol mixture. This result suggests that the rate of agglomeration is a function of the product of collision frequency and collision efficiency of the coal particles. Since both the solids concentration and the stirring speed were constant for all the runs, the collision frequency should have been constant. The change of oils should only have affected the collision efficiency, which is related to the wetting period of the coal by the oil. Since the coal was not perfectly hydrophobic, the alcohol acted both to enhance the coal hydrophobicity and to reduce the interfacial tension. Consequently, the oil/alcohol combination produced the fastest agglomeration. Heptane, alone should have produced the slowest agglomeration unless the surface of the coal had been strongly hydrophobic. The oil dosages did not seem to have a great effect (or definitive trend) upon the agglomeration time or recovery on a 100 mesh screen,
Table 7.1: Results of agglomerating -200/+400 mesh Australian coal with different oils.

<table>
<thead>
<tr>
<th>Oil Type</th>
<th>Oil dosage, ml.</th>
<th>Recovery, %</th>
<th>Ash redn., %</th>
<th>Time, sec.</th>
<th>Diam., mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Runs w/o pre-emulsification</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>tetralin</td>
<td>8</td>
<td>93.5</td>
<td>32.6</td>
<td>240</td>
<td>0.6</td>
</tr>
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<td>33.0</td>
<td>190</td>
<td>3.1</td>
</tr>
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<td>12</td>
<td>93.7</td>
<td>34.1</td>
<td>185</td>
<td>amalgam</td>
</tr>
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<td>heptane</td>
<td>8</td>
<td>88.1</td>
<td>55.5</td>
<td>1300</td>
<td>0.5</td>
</tr>
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<td>heptane</td>
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<td>88.7</td>
<td>51.8</td>
<td>1500</td>
<td>2.1-2.6</td>
</tr>
<tr>
<td>heptane</td>
<td>12</td>
<td>89.4</td>
<td>49.7</td>
<td>1785</td>
<td>amalgam</td>
</tr>
<tr>
<td>heptane/heptanol</td>
<td>8</td>
<td>93.0</td>
<td>31.3</td>
<td>70</td>
<td>0.3</td>
</tr>
<tr>
<td>heptane/heptanol</td>
<td>10</td>
<td>93.0</td>
<td>29.7</td>
<td>60</td>
<td>2.0</td>
</tr>
<tr>
<td>heptane/heptanol</td>
<td>12</td>
<td>95.0</td>
<td>20.7</td>
<td>30</td>
<td>amalgam</td>
</tr>
<tr>
<td>Runs with pre-emulsification</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tetralin</td>
<td>8</td>
<td>95.2</td>
<td>25.9</td>
<td>145</td>
<td>0.4</td>
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<td>tetralin</td>
<td>10</td>
<td>93.3</td>
<td>32.0</td>
<td>147</td>
<td>2.1</td>
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<tr>
<td>tetralin</td>
<td>12</td>
<td>93.4</td>
<td>33.2</td>
<td>126</td>
<td>amalgam</td>
</tr>
<tr>
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<td>89.3</td>
<td>50.5</td>
<td>300</td>
<td>0.3</td>
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<td>heptane</td>
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<td>90.2</td>
<td>45.2</td>
<td>400</td>
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<td>heptane</td>
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<td>89.7</td>
<td>47.8</td>
<td>600</td>
<td>3.0</td>
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<td>heptane/heptanol</td>
<td>8</td>
<td>92.1</td>
<td>28.1</td>
<td>30</td>
<td>0.2</td>
</tr>
<tr>
<td>heptane/heptanol</td>
<td>10</td>
<td>92.1</td>
<td>34.9</td>
<td>15</td>
<td>1.3</td>
</tr>
<tr>
<td>heptane/heptanol</td>
<td>12</td>
<td>92.6</td>
<td>32.4</td>
<td>20</td>
<td>amalgam</td>
</tr>
</tbody>
</table>
although this parameter did seem to affect the agglomerate form and size. Emulsification of the oil prior to addition to the coal slurry seemed to reduce the time of agglomeration, although the organic recovery and the de-ashing of the coal product seemed unaffected. The shortening of the inversion time seemed to be due to the fact that pre-emulsification helps reduce the time needed for the coal to interact with the oil, or in other words, for enough water to be displaced from the coal surface by oil so that effective collisions can take place. Of the three oils used, tetralin produced the largest agglomerates, while n-heptane/1-heptanol mixture produced the smallest agglomerates. Finally, although the organic recovery was nearly the same for all three oils, the use of n-heptane seemed to give better ash rejection.

Characterization of Coals Used for Continuous Agglomeration

In order to characterize the coals used for a series of continuous agglomeration runs, the apparatus and technique employed by Drzymala and Wheelock [67] were utilized. As a coal slurry is agglomerated, the turbidity of the suspension is monitored with a photometric dispersion analyzer. As agglomeration proceeds, fewer particles are present and the turbidity drops. The oil is added in a series of small increments and after each addition the system is allowed to stabilize and the turbidity is measured. A plot of the turbidity versus oil dosage provides a useful characterization of the coal/oil agglomeration system. The data points tend to fall on a straight-line when the turbidity is plotted against the logarithm of the oil dosage with the x-intercept being termed the critical oil dosage.

The following coals were tested on the photometric dispersion analyzer: Upper Freeport coal, Upper Freeport coal (Helvetia), and Indiana No.6. Figure 7.8 and
Figure 7.9 indicate that that Indiana No.6 coal had the following critical oil dosages: 74 v/w% for tetralin, 1.26x10^4 v/w% for heptane, 80 v/w% for the tetralin/sodium oleate (pH=7) combination, and 80 v/w% for the heptane/sodium oleate (pH=7) combination. There are two indications from these results that Indiana No.6 coal is fairly hydrophilic. One indication is that the heptane did a very poor job of agglomerating the coal while the tetralin did a fair job. The second indication is that sodium oleate did not help the agglomeration with tetralin, while it improved the agglomeration with heptane significantly. Of the coals examined, the choices for coals which were hydrophobic enough to be used in the continuous system came down to the two Upper Freeport coals (Figure 7.10).

Both coals gave low values for the critical dosage. Another method was desired to differentiate between the two coals. The continuous agglomeration vessel was employed for batch tests with these two coals to examine the agglomerated products appearance for various levels of oil dosage. For the different conditions employed, the Upper Freeport coal from Helvetia had good agglomerating qualities for the continuous runs. At low oil dosages, the agglomerates were small distinct spheres. At high oil dosages, the spheres were larger and distinct. The agglomerates for the other Upper Freeport coal were small and in clusters for the range of oil dosages. Another indication that the coal from Helevetia was better for producing spherical agglomerates involved the respective pH of the coals. The pH for the Helvetia coal was 5.7, while the pH of the other Upper Freeport coal was 3.4. The Upper Freeport that was used had pH similar to the Helvetia Upper Freeport coal, while the pH of the oxidized Upper Freeport coal that they had is similar to the other Upper Freeport coal. In their paper, oxidation of coal was shown to have significant effect
1.6% Slurry (8 g. in 500 ml water)
Indiana No.6 coal, Stirring Speed=21,000 rpm
-200 mesh coal

- [Heptane]
- [Tetralin]

Figure 7.8: Turbidity analysis for Indiana No.6 coal.
Exp. Conditions:
1.6% Slurry (8 g. in 500 ml water)
Indiana No. 6 coal, Stirring Speed = 21,000 rpm
- 200 mesh coal

- Tetralin/Sodium oleate
- Heptane/sodium oleate

Figure 7.9: Turbidity analysis for Indiana No. 6 coal using sodium oleate.
Exp. Conditions:
1.6% Slurry (8 g. in 500 ml water)
Stirring Speed = 21,000 rpm
200 mesh coal

- Heptane/Upper Freeport
- Tetralin/Upper Freeport
- Heptane/Upper Freeport (EPRI)

Figure 7.10: Turbidity analysis for Upper Freeport coal.
upon spherical agglomeration. Thus, it seems that by observing only the pH in this instance, the potential for agglomeration can be determined.

Continuous Agglomeration Runs

First Series

Initially, a series of runs was performed using the Indiana No.6/Illinois No.5 coal according to the experimental design specifications listed in Table 6.1. The runs were randomized, so as not to incorporate bias into the results. At steady-state (greater than approximately 8 residence times), a sample of the output stream was collected, and the particle size distribution was determined using the automatic image analyzer. For analyzing the size distribution, the layering expression (equation (4.24)) was fitted to the data, thus determining constants $a$ and $G_0$. The fitting procedure involved using a non-linear Gaussian iteration routine. The mean particle size was also determined for each of the runs. Two major problems arose during the runs.

1. The agglomerates were not as robust as they appeared in preliminary tests.

2. A statistical analysis of the results indicated that the properties of the coal changed as the series of runs progressed through time.

This series of runs showed the importance of the coal preparation step for a series of runs relying on surface properties. In the coal preparation step, fresh new surfaces were created without adequate control of the surrounding gaseous and thermal environment. Each run required about 1 kg of feed. For every 1 kg of material in the required size range, 3-5 kg of material had to be crushed and sieved. For 20 runs made with certain size fraction, 100 kg of coal had to be sieved which required a
sieving time of 800-1200 hr. This value does not include the time spent in material handling and pulverizing the coal. Thus, the coal spent a considerable amount of time in an oxidizing atmosphere which very likely affected the surface properties of the coal.

Second Series

The second series of continuous runs was made using Upper Freeport coal and hexadecane as the binder. To alleviate the problem of coal preparation, this series of experiments utilized a much wider size fraction of coal than was used in the previous series. By utilizing a wider size range, the feed preparation time was greatly reduced. Also, all the coal that would be used for this series was sized and stored before the first run. The coal was homogenized and riffled to obtain 22 equal portions needed for the individual runs. These portions were stored in sealed paint cans which were placed in barrels purged continuously with nitrogen. This procedure prevented the properties of the coal from changing during the course of the experiments. The size fraction of coal used for most of the runs was -200 mesh (< 74 μm). However, three of the runs used +200 mesh material. The slurry concentration used in all of these runs was 6 wt.%. The runs could be easily classified into one of two categories: experimental runs in which agglomerates were all smaller than approximately 1000 microns (1 mm.) or experimental runs in which the top size of agglomerates were much larger than 1000 microns. Other experimental conditions are given in Table 7.2.

Each run was continued until the operating conditions approached steady-state. This involved maintaining a constant feed rate until the contents of the mixing tank had been displaced eight times or more. At this point several samples of the product
Table 7.2: Run conditions for the continuous runs with Upper Freeport coal.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Feed Size, mesh</th>
<th>Slurry Conc., wt. %</th>
<th>Oil Dosage, v/w %</th>
<th>Agitator Speed, rpm</th>
<th>Residence Time, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-1</td>
<td>-200</td>
<td>6</td>
<td>10</td>
<td>1000</td>
<td>5</td>
</tr>
<tr>
<td>U-2</td>
<td>-200</td>
<td>6</td>
<td>20</td>
<td>1000</td>
<td>5</td>
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<tr>
<td>U-3</td>
<td>-200</td>
<td>6</td>
<td>40</td>
<td>1000</td>
<td>5</td>
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<td>1250</td>
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stream were collected for sizing by automatic image analysis. The resulting particle size distributions were examined and analyzed by various methods. The first method involved studying and comparing the number frequency histograms which represented the size distributions of the agglomerates produced by the different runs.

In some runs where the largest agglomerates were not much greater than 1000 μm, the number frequency histograms were like a normal distribution. Examples of such histograms are presented in Figure 7.11 (for run 2) and Figure 7.12 (for run 6). In run 2, the oil dosage was 20 v/w%, the stirring speed was 1000 rpm, and the residence time was 5 min. In run 6, the oil dosage was 25 v/w%, the stirring speed was 1250 rpm, and the residence time was 3.5 min. In other runs where the maximum agglomerate size was limited to about 1000 μm, the histograms displayed a steady downward trend from left to right. Examples are shown in Figure 7.13 (run 9) and Figure 7.14 (run 15).

In run 9, the oil dosage was 25 v/w%, the stirring speed was 750 rpm, and the residence time was 6.5 min. In run 15, the oil dosage was 25 v/w%, the stirring speed was 750 rpm, and the residence time was 3.5 min.

The size distributions seemed to be influenced by the operating parameters as follows:

1. High stirring speed seemed to promote a normal distribution.
2. Low stirring speed seemed to a descending distribution.
3. High residence time seemed to promote a perfectly descending distribution.
4. The oil dosage in this size regime seemed to have no obvious influence on the distribution.

For runs which produced agglomerates that grew well beyond 1000 μm the his-
Figure 7.11: Histogram of number distribution for run 2.
Figure 7.12: Histogram of number distribution for run 6.
Figure 7.13: Histogram of number distribution for run 9.
Figure 7.14: Histogram of number distribution for run 15.
ograms displayed two main trends: a descending distribution in the lower size range and a normal distribution in the upper size range. For run 8 (Figure 7.15), the descending distribution in the lower size range seemed to be much more predominant than the normal distribution in the larger size range. In run 8, the oil dosage was 30 v/w%, the stirring speed was 1000 rpm, and the residence time was 8 min. In run 14 (Figure 7.16), the descending distribution in the lower particle size range and the normal distribution in the larger particle size were of comparable magnitude. In run 14, the oil dosage was 30 v/w%, the stirring speed was 1000 rpm, and the residence time was 5 min. In run 17 (Figure 7.17), the normal distribution in the larger size range was much more pronounced than the descending distribution in the smaller size range. In run 17, the oil dosage was 30 v/w%, the stirring speed was 1500 rpm, and the residence time was 5 min.

An examination of the effects of the operating parameters on the size distributions led to the following conclusions:

1. Both high stirring speeds and low oil dosages caused the normal distribution in the larger particle size region to be more predominant.

2. Both low stirring speeds and high oil dosages caused the descending distribution in the lower particle size region to be more predominant.

3. High residence times made the descending distribution in the lower particle size region to drop steadily and smoothly.

4. Low residence times made the descending distribution in the lower particle size region to be less smooth.

The second method used for analyzing the particle size distributions produced by continuous agglomeration involved mathematical modelling of the agglomeration
Figure 7.15: Histogram of number distribution for run 8.
Figure 7.16: Histogram of number distribution for run 14.
Particle Size (μm)

Figure 7.17: Histogram of number distribution for run 17.

O=30 v/w%
S=1500 rpm
τ=5 min
process by application of a population balance. For the runs which produced smaller particles (below 1000 μm), one mechanism seemed to prevail so that modelling was straight-forward. In this case it was assumed that growth of agglomerates was due to layering. Equation (4.24) was used to fit the data. The analytical expression was fitted to the data by using a non-linear Gaussian technique, employing least-squares regression for many iterations. For run 2 (Figure 7.18) and run 9 (Figure 7.19), the distribution curve based on layering seemed to fit the data points reasonably well.

Results of fitting the layering model to the experimental data are presented in Table 7.3. The goodness of fit is indicated by $R^2$ where $R$ is the multiple correlation coefficient. In runs where only one growth regime appeared to be involved, the $R^2$ values were close to 1.00 indicating a good fit. In some of the runs where two growth regimes seemed to be involved, the $R^2$ values were very low. The number of regimes is based on a visual inspection of the histograms.

Where only one mechanism was involved, layering seemed to provide explanation for the growth of agglomerates. In the runs where more than one mechanism was suspected, the $R^2$ values suggested that layering was the mechanism governing the small agglomerate region of the histograms. Where there was a poor fit throughout the whole range of sizes, as indicated by the $R^2$ values, two mechanisms appeared needed to explain the growth. When a breakage term was added to the model, i.e., shear breakage down to feed size (shatter), the quality of fit was not improved. The significance of the breakage constants was negligible. Also present in Table 7.3 are the arithmetic mean particle size $\bar{\ell}$, the volume weighted mean particle size $\ell_w$, and
Figure 7.18: Number density data for run 2 fitted by a model assuming layering as the growth mechanism.
Figure 7.19: Number density data for run 9 fitted by a model assuming layering as the growth mechanism.
Table 7.3: Results of continuous agglomeration using Upper Freeport coal.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>No. Regimes</th>
<th>a</th>
<th>$G_o$</th>
<th>$R^2$</th>
<th>$\bar{\ell}$</th>
<th>$\bar{\ell}_w$</th>
<th>$\ell_{50}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
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<td>-0.694</td>
<td>1345.0</td>
<td>0.968</td>
<td>260</td>
<td>302</td>
<td>241</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>0.89</td>
<td>0.49</td>
<td>0.984</td>
<td>647</td>
<td>1436</td>
<td>323</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>0.37</td>
<td>18.69</td>
<td>0.976</td>
<td>403</td>
<td>688</td>
<td>272</td>
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<tr>
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<tr>
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<td>0.14</td>
<td>13.35</td>
<td>0.960</td>
<td>232</td>
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<tr>
<td>8</td>
<td>2</td>
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<td>0.05</td>
<td>0.960</td>
<td>645</td>
<td>1817</td>
<td>223</td>
</tr>
<tr>
<td>9</td>
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<td>5.10</td>
<td>0.965</td>
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<td>0.963</td>
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<td>1.53</td>
<td>0.03</td>
<td>0.099</td>
<td>1935</td>
<td>2737</td>
<td>2103</td>
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<tr>
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<td>1.19</td>
<td>0.43</td>
<td>0.967</td>
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<td>313</td>
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<tr>
<td>13</td>
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<td>1.25</td>
<td>0.12</td>
<td>0.192</td>
<td>1796</td>
<td>2288</td>
<td>2037</td>
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<tr>
<td>14</td>
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<td>0.03</td>
<td>0.971</td>
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<td>344</td>
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<tr>
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<td>0.986</td>
<td>245</td>
<td>371</td>
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<tr>
<td>16</td>
<td>1</td>
<td>1.04</td>
<td>0.08</td>
<td>0.982</td>
<td>210</td>
<td>287</td>
<td>163</td>
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<tr>
<td>17</td>
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<td>0.10</td>
<td>0.152</td>
<td>1500</td>
<td>2100</td>
<td>2406</td>
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</tbody>
</table>

The equations for calculating $\bar{\ell}$ and $\bar{\ell}_w$ are:

$$\bar{\ell} = \frac{\sum N_i \ell_i}{\sum N_i} \quad (7.1)$$

$$\bar{\ell}_w = \left( \frac{\sum N_i \ell_i^2}{\sum N_i} \right)^{1/3} \quad (7.2)$$

Several runs were also performed with larger particle sizes (+200 mesh). Instead of employing an elaborate experimental design, only the oil dosage was varied among runs. Only three experiments were performed with the larger size fraction due to a shortage of feed material. The operating conditions for these three runs included
oil dosages of 20, 30, and 40 %v/w, a stirring speed of 1000 rpm and residence time of 5 min. These runs represented conditions used in the experimental design for the extreme values and mid-value of oil dosage and mid-values of the other operating parameters. With an oil dosage of 20 %v/w, a relatively flat histogram of the number distribution was created, (Figure 7.20). With an oil dosage of 30 % (Figure 7.21), a normal distribution was formed which covered the same range of particle size as the previous one. With an oil dosage of 40 %v/w (Figure 7.22), the number distribution exhibited two regimes, and the particles grew to a much greater size than for the other two oil dosages. In Table 7.4 the results are compared of runs made with two different feed particle sizes but otherwise similar conditions. For the two lower oil dosages and the coarse feed material The resulting particle size distributions exhibited only one growth regime and fitting the layering model to the data produced negative values of a. For the high oil dosage the size distribution exhibited two regimes, and fitting the data produced a large value of a (1.40). Oil dosages of 20 or 30 %v/w produced results with the coarse material which were similar to those produced by an oil dosage of 20 %v/w with the fine material (Figure 7.11). An oil dosage of 40 %v/w caused the coarse material to behave like an oil dosage of 30 %v/w caused the fine material to behave (Figure 7.16). An oil dosage of 40 %v/w applied to the fine material (Figure 7.23 may have been so high that the resulting agglomeration pattern began to change, and above this dosage, the agglomerates would probably be classified as amalgams. Patterns of growth at this oil dosage seemed to deviate from existing trends, based on the fact that the two regime distribution was not as predominate as would have been expected. Upon comparing the results obtained with the two feed size fractions, it appeared as though the same growth characteristics were evident
Table 7.4: Comparison involving agglomeration between the coarse feed and the fine feed

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Feed Size, mesh</th>
<th>Dosage, v/w%</th>
<th>a</th>
<th>Go</th>
<th>l</th>
<th>lw</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-200</td>
<td>20</td>
<td>-0.694</td>
<td>1345</td>
<td>260</td>
<td>302</td>
</tr>
<tr>
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<td>-0.96</td>
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<td>697</td>
</tr>
<tr>
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<td>30</td>
<td>1.44</td>
<td>949</td>
<td>1653</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>+200</td>
<td>30</td>
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<td>823</td>
<td>1007</td>
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</tr>
<tr>
<td>3</td>
<td>-200</td>
<td>40</td>
<td>0.89</td>
<td>647</td>
<td>1436</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>+200</td>
<td>40</td>
<td>1.40</td>
<td>1478</td>
<td>2685</td>
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</tbody>
</table>

with both fine and coarse feed, although it appeared that more oil was required for the coarse particles to achieve the same effect as the fine particles.

The following parameters were analyzed using a statistical approach: the layering parameters $G_o$ and $a$, the weighted averages $l$ and $\bar{l}$, and the median size $\ell_{50}$. The statistical approach was based on a central composite design to determine which operating parameters were significant when employing linear combinations of the operating parameters. The following expression was then deduced:

$$P = C_1 + C_2\gamma_o + C_3\gamma_s + C_4\gamma_r + C_5\gamma_o^2 + C_6\gamma_s^2 + C_7\gamma_r^2 + C_8\gamma_o\gamma_s + C_9\gamma_o\gamma_r + C_10\gamma_s\gamma_r$$  \hspace{1cm} (7.3)

where

$$P = a, G_o, l, \bar{l}, \ell_{50}$$ \hspace{1cm} (7.4)

$$\gamma_o = \frac{O - 30}{5}$$ \hspace{1cm} (7.5)

$$\gamma_s = \frac{S - 1000}{250}$$ \hspace{1cm} (7.6)

$$\gamma_r = \frac{\tau - 5}{1.5}$$ \hspace{1cm} (7.7)

The results of the significance test are presented in Table 7.5, in terms of the statistical parameter $t$. Equation (7.3) is an expression containing 10 constants that can be
Figure 7.20: Histogram of number distribution for run 21.

$O = 20 \text{ v/w}\%$

$S = 1000 \text{ rpm}$

$\tau = 5 \text{ min}$
Figure 7.21: Histogram of number distribution for run 19.
Figure 7.22: Histogram of number distribution for run 20.

O=40 v/w%
S=1000 rpm
τ=5 min
Figure 7.23: Histogram of number distribution for run 3.

Figure 7.23: Histogram of number distribution for run 3.
Table 7.5: Computed t-values based on linear model

<table>
<thead>
<tr>
<th></th>
<th>$\gamma_0$</th>
<th>$\gamma_1$</th>
<th>$\gamma_2$</th>
<th>$\gamma_0^2$</th>
<th>$\gamma_1^2$</th>
<th>$\gamma_0\gamma_1$</th>
<th>$\gamma_0\gamma_2$</th>
<th>$\gamma_1\gamma_2$</th>
<th>$\gamma_0\gamma_1\gamma_2$</th>
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<tr>
<td>$a$</td>
<td>2.26</td>
<td>0.82</td>
<td>1.31</td>
<td>-2.38</td>
<td>-1.28</td>
<td>-1.09</td>
<td>1.10</td>
<td>-0.28</td>
<td>1.75</td>
</tr>
<tr>
<td>$G_O$</td>
<td>-2.81</td>
<td>1.17</td>
<td>-1.21</td>
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<td>0.02</td>
<td>-1.68</td>
<td>1.68</td>
<td>-1.69</td>
</tr>
<tr>
<td>$\bar{\ell}$</td>
<td>1.43</td>
<td>6.35</td>
<td>2.89</td>
<td>-1.94</td>
<td>-0.33</td>
<td>-1.67</td>
<td>0.99</td>
<td>-0.72</td>
<td>3.57</td>
</tr>
<tr>
<td>$\bar{\ell}_w$</td>
<td>3.39</td>
<td>7.42</td>
<td>3.53</td>
<td>-2.39</td>
<td>-1.38</td>
<td>-1.22</td>
<td>2.46</td>
<td>-1.36</td>
<td>2.81</td>
</tr>
<tr>
<td>$t_{50}$</td>
<td>0.15</td>
<td>5.44</td>
<td>2.18</td>
<td>-0.16</td>
<td>2.44</td>
<td>-0.25</td>
<td>0.07</td>
<td>-0.01</td>
<td>3.21</td>
</tr>
</tbody>
</table>

determined by the creation of 15 equations based upon 17 executed runs. This leaves a total of 5 degrees of freedom. The t-values were used to test the hypothesis that any given $C_i$ was equal to zero. A relatively high degree of certainty was required to refute the hypothesis, in order to retain any given term in the equation. By employing the t-test, it could be determined which operating parameter or group of operating parameter affected the variables of interest. The level of significance for the t-test was 92%, and this corresponded to absolute t-values of 2.0 or greater.

The t-test showed that the order of layering, $a$, is a function of oil dosage and oil dosage squared. The parameter is a reflection of the particle size's contribution to the rate of growth.

$$a = f(\gamma_0, \gamma_1^2) \quad (7.8)$$

The growth constant, $G_O$, is a function of oil dosage alone:

$$G_O = f(\gamma_0) \quad (7.9)$$

The average agglomerate length, $\bar{\ell}$, is affected by the stirring speed, the residence time, and the interaction of these two parameters. The greater the stirring speed and the longer the residence time, the larger the agglomerate becomes:

$$\bar{\ell} = f(\gamma_1, \gamma_2, \gamma_1\gamma_2) \quad (7.10)$$
The weighted average of agglomerate length, $\bar{\ell}_W$, is affected by the oil dosage, the stirring speed, the residence time, the oil dosage squared, and two interaction terms:

$$\bar{\ell}_W = f(\gamma_0, \gamma_s, \gamma_T, \gamma_0 \gamma_s, \gamma_s \gamma_T, \gamma_T^2)$$  \hspace{1cm} (7.11)

The median agglomerate length, $\ell_{50}$, is affected by stirring speed, residence time, the square of oil dosage, and the interaction of stirring speed and residence time:

$$\ell_{50} = f(\gamma_s, \gamma_T, \gamma_0 \gamma_T, \gamma_T^2)$$  \hspace{1cm} (7.12)

Since the different regimes exhibited by a number density distribution curve seemed to reflect the different growth mechanisms, it was apparent that a correlation between the number of different regimes and the various operating parameters could be useful for predicting conditions which would lead to one growth mechanism or more than one mechanism. For the runs conducted there seemed to be either one regime or two regimes. The number of regimes ($N_m$) was correlated with the values of oil dosage ($\gamma_0$), stirring speed ($\gamma_s$), and residence time ($\gamma_T$) shown in Table 7.6 using the empirical equation (7.3). After eliminating terms which were not statistically significant, the following equation was obtained:

$$N_m = 1.50 + 0.3137 \gamma_s + 0.188(\gamma_0 + \gamma_T)$$  \hspace{1cm} (7.13)

The $R^2$ value for this expression was 0.672, which was considered acceptable for an expression which would be used as a rough indicator. Values of $N_m$ calculated or predicted by equation (7.13) are also shown in Table 7.6. When these values are rounded to one significant figure, the agreement between the observed and predicted numbers is good in most cases. For runs 14 and 16, the predicted values of $N_m$
Table 7.6: Values of $N_m$ for the various runs

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$\gamma_0$</th>
<th>$\gamma_s$</th>
<th>$\gamma_r$</th>
<th>Number of Regimes</th>
<th>$N_m$</th>
</tr>
</thead>
<tbody>
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<td>2</td>
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</tr>
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<tr>
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<td>2</td>
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<td>0</td>
<td>0</td>
<td>2</td>
<td>1.500</td>
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</table>

were 1.50 and 1.56, respectively. In these two runs, the predicted values of $N_m$ were midway between 1 and 2 where the predictability was most difficult. It must be noted that equation (7.13) would only apply for the range of conditions used in the runs on which it is based.

The third method used for analyzing the particle size distributions involved fitting a more complicated mechanistic model to some size distributions where the agglomeration size exceeded 1000 $\mu$m. As was mentioned previously, some of the size distributions exhibited two distinct regions. In most cases the layering mechanism fitted the data points representing the region of smaller particle sizes. This was verified by fitting the model based on the layering mechanism to the data representing agglomerates smaller than 1000 $\mu$m. The results of this fitting are presented in
Table 7.7: Layering model parameters and goodness of fit for the region of smaller agglomerates.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>a</th>
<th>Go</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
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<td>0.968</td>
</tr>
<tr>
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</tr>
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</tr>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
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<td>0.971</td>
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<td>0.08</td>
<td>0.982</td>
</tr>
<tr>
<td>17</td>
<td>1.30</td>
<td>0.10</td>
<td>0.969</td>
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</table>

Table 7.7. For every run the resulting $R^2$ is quite high indicating a good fit.

For larger particle sizes, the number density curve took on the appearance of a normal distribution. It was suspected that this region of the curve was the result of agglomerate coalescence. In previous papers [45] and [52], integral terms representing coalescence were used either directly or indirectly to model particle growth systems. A parabolic form of the size distribution was usually present. Thus, it was reasoned that the parabolic region of the data obtained by the present author could be modelled using coalescence. In solving the integral equation, representing coalescence. Bemer and Zuiderweg[63] used a spline fit with parabolic runout. An explicit mathematical form representing the region needed to be used. In a log n versus $\ell$ plot, a parabolic
Table 7.8: Parameter values for the Gaussian distribution range of the number density curves

<table>
<thead>
<tr>
<th>Run No.</th>
<th>O, v/w%</th>
<th>S, rpm</th>
<th>$\tau$, min.</th>
<th>$A_1$, $\mu m^{-1}$</th>
<th>$10^4 A_2$, $\mu m^{-2}$</th>
<th>$\ell_M$, $\mu m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>35</td>
<td>1250</td>
<td>6.5</td>
<td>0.078</td>
<td>4.45</td>
<td>3135</td>
</tr>
<tr>
<td>12</td>
<td>35</td>
<td>1250</td>
<td>3.5</td>
<td>0.040</td>
<td>2.66</td>
<td>3252</td>
</tr>
<tr>
<td>13</td>
<td>25</td>
<td>1250</td>
<td>6.5</td>
<td>0.171</td>
<td>3.32</td>
<td>1898</td>
</tr>
<tr>
<td>14</td>
<td>30</td>
<td>1000</td>
<td>5.0</td>
<td>0.332</td>
<td>5.57</td>
<td>1713</td>
</tr>
<tr>
<td>17</td>
<td>30</td>
<td>1500</td>
<td>5.0</td>
<td>0.113</td>
<td>5.47</td>
<td>2578</td>
</tr>
</tbody>
</table>

The values for these parameters are given in Table 7.8.

The second analysis attempted with the large growth sizes was to directly compare the coefficients of fit to the Gaussian distribution for the various runs to one another. The result of comparing the results produces the following expressions:

\[ A_1 = C_1 \left( \frac{\tau^3}{\Omega^{1/2} S^2} \right)^{1/3} \]

\[ A_2 = C_2 \Omega \tau \]

\[ \ell_M = C_3 (\Omega^3 S^2)^{1/2} \]
When the two agglomerate growth regimes were combined, the curves representing these regimes fit the data points for run 11 rather well as can be seen in Figure 7.24. Since two curves were used to represent the data, there is a differential discontinuity where the two curves meet. In other words, at the intersection of the two curves, the derivative is undefined.

It was hoped that the expression for \( n(\ell) \) would satisfy the following integral equation which represents both the birth and death of particles of size \( \ell \) by coalescence:

\[
\frac{n(\ell)}{\tau} = \frac{1}{2} \int_0^\ell \frac{C}{[\ell^3 - \ell^3]^{1/3} \ell^2} n(\ell) d\ell - \frac{C n(\ell)}{\ell^3} \int_0^\infty \frac{n(\tilde{\ell})}{\tilde{\ell}^3} d\tilde{\ell} \quad (7.22)
\]

Values of \( R \) and \( r \) were estimated to obtain values of \( n(\ell) \), and quadrature routines were used for the integrals assuming that the form for \( n(\ell) \) was explicitly given by equation (7.14). Initially, plots of \( n \) versus \( \ell \) were made to see what general shape of the distribution curve was found based on the estimates of \( R \) and \( r \). The shape of the curve produced by equation (7.18) was not very close to the parabolic shape of the particle size distribution data. Also the shape was not affected greatly by the choice of \( R \) and \( r \). The same basic shape always resulted. One problem seemed to be that the rate of birth of agglomerates of size \( \ell \) due to coalescence was smaller numerically than the rate of death of agglomerates of size \( \ell \). Only for larger values of \( \ell \) did the relative magnitude of these rates reverse. Thus, for most values of \( \ell \), \( n(\ell) \) from equation (7.11) was negative. It was then deduced that the reason for the lack of fit was due to neglecting the breakage terms:

\[
\text{Breakage} = B \eta^{1+b/3} \ell^b n(\eta^{1/3} \ell) - B \ell^b n(\ell)
\]

It was anticipated that when the breakage terms were combined with the coalescence
Figure 7.24: The number density curve for run 11 based on the combined layering and coalescence regimes.
terms, positive values would resurface.

For one set of R and \( r \) values, an attempt was made to fit a curve through the resulting \( n_B \) versus \( \ell \) curve, where:

\[
\begin{align*}
n_B &= n(\ell)_{\text{data}} - n(\ell)_{\text{eqn 7.11}} \\
\end{align*}
\]  

(7.24)

When the expression for breakage (equation (7.19)) was plotted on the same graph as the expression \( n_B \), there seemed to be some correlation between the two curves, indicating that the breakage terms were a necessary feature. The values of \( b \) and \( B \) were obtained through non-linear least square fitting of equation (7.19) to equation (7.20). The value of \( \eta \) was the parameter which was iterated until the regression was minimized (around 1.1). Physically, the parameter \( \eta \) refers to the average number of pieces an agglomerate breaks into upon rupture due to the shearing field. Simulations based on equation (7.22) and (7.23) were conducted. In order to simplify the analysis, an assumption was made that the growth of particles was a result of random coalescence (\( r=0 \)). This assumption removed one adjustable constant from consideration. A plot for run 11 is given in Figure 7.25. In this figure the value of the constants are: \( R_0=0.011 \), \( b=0.977 \), and \( B_0=0.0027 \). From this figure, the coalescence/breakage model fitted the distribution points in the lower size range of the normal regime (1500-3000 \( \mu \)m), but the model did not predict growth to exceed 4000 \( \mu \)m, even though the actual growth of particles was up to 5000 \( \mu \)m. This trend was evident for all of the runs exhibiting two regime growth.
Figure 7.25: The fitting together of regime 1 (layering) and regime 2 (coalescence/breakage simulation)
CHAPTER 8. CONCLUSIONS

The following conclusions were drawn from the work with batch agglomeration systems:

1. When operating conditions did not favor extensive growth, a maximum change in the particle size distribution of the product was achieved rather quickly. This change was followed by a period of particle size reduction toward the feed size distribution.

2. Emulsification of the oil phase used for agglomeration greatly reduced the time needed to achieve the maximum growth size. Apparently the time of coal wetting by oil was greatly reduced because the oil phase was dispersed as very small droplets (approximately 5-6 µm) which interacted with the coal in a form that encouraged immediate particle growth.

3. For a given solid and binder system, the speed of agglomeration seemed to be affected predominantly by the agitation environment for the binder, whereas the extent of agglomeration was affected predominantly by the agitation environment of the solid. These two agitation environments are usually the same except for cases of pre-emulsification.

4. From the standpoint of staying power, the least selective oils formed the most stable emulsions. From the standpoint of turbidity, the ultrasonic treatment formed the emulsions with the greatest turbidity.
5. For a given agitation system and choice of coal, nonpolar oils were more selective, but these oils were much slower to achieve agglomeration.

The following conclusions were drawn from the work with a continuous agglomeration system:
1. The layering mechanism seemed to adequately describe the growth of agglomerates in a continuous system when that growth was limited so that the maximum agglomerate size was less than about 1000 µm. Least squares analysis was used to verify this observation.
2. When the growth of agglomerates in a continuous system exceeded about 1000 µm, layering seemed to describe the growth up to this size, but for the production of larger agglomerates a combination of coalescence and breakage was needed to explain the resulting size distribution.
3. A statistical analysis of the effects of heptane dosage, stirring speed, and particle residence time on various system parameters showed the following:
   a. The order of layering, a, is a function of oil dosage, oil dosage squared, and the interaction of stirring speed and residence time.
   b. The growth constant, $G_0$, is a function of oil dosage alone.
   c. The average agglomerate length, $\bar{\ell}$, is affected by the stirring speed, the residence time, and the interaction of these two parameters.
   d. The weighted average of agglomerate length, $\bar{\ell}_w$, is affected by the oil dosage, the stirring speed, the residence time, the oil dosage squared, and two interaction terms.
   e. The median agglomerate length, $\ell_{50}$, is affected by stirring speed,
residence time, the square of oil dosage, and the interaction of stirring speed and residence time.
CHAPTER 9. RECOMMENDATIONS

When performing the set of experimental runs involving continuous agglomeration, particle growth exceeding 1000 \( \mu \text{m} \) was exhibited in some of the runs. This growth to larger sized particles was related to the operating parameters, based on the assumption that the mechanism of particle size changes was influenced by the operating parameters. One potential complication in analyzing the data involves the fact that there may exist agglomerates which are too large to be discharged from the agglomeration cell at some stirring speeds. As a result, these larger sized particles may reside too long in the agglomeration cell and thus, grow to unrealistic sizes. A series of runs should be carried out operating the agglomeration cell at various stirring speeds in order to determine the maximum particle size which can be discharged readily from the cell to ensure that the stream leaving the cell is representative. Artificial mixtures of different size particles could be used as long as the specific gravity of the particles is fairly close to that of coal (1.5).

Some conditions should be changed in future continuous runs to determine how these changes affect particle size distribution as well as layering growth parameters. These changes should include:

(1). employment of emulsions as the input flow of the oil phase,

(2). employment of coals having varying hydrophobicities,
(3). employment of surfactants of differing chemical properties.

(4). employment of multiple reactor schemes.
CHAPTER 10. NOMENCLATURE

a \quad \text{Empirical constant which describes the length dependence on growth by layering.}

A \quad \text{Constant.}

A_1, A_2 \quad \text{Constants.}

b \quad \text{Exponential term in shear breakage.}

b_{ij} \quad \text{Collision frequency between particle i and particle j.}

B \quad \text{Breakage function. min}^{-1}.

B_0 \quad \text{Breakage constant. min}^{-1} \mu m^{-b}.

\dot{B} \quad \text{Birth rate of particles, } \mu m^{-1} \ell^{-1} \text{min}^{-1}.

\dot{B}_B, \dot{B}_C \quad \text{Birth rates of particles through breakage and coalescence, respectively, } \mu m^{-1} \ell^{-1} \text{min}^{-1}.

C \quad \text{Coalescence Constant.}

C_i \quad \text{Concentration of particles with i oil drops contained at particle surface, } (cm^3)^{-1}.

\dot{D} \quad \text{Death rate of particle, } \mu m^{-1} \ell^{-1} \text{min}^{-1}.

\dot{D}_B, \dot{D}_C \quad \text{Death rates of particles through breakage and coalescence, } \mu m^{-1} \ell^{-1} \text{min}^{-1}.

e \quad \text{Exponential term in attrition.}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_o$</td>
<td>Attrition rate constant, $\mu m^{1-b}min^{-1}$.</td>
</tr>
<tr>
<td>$f$</td>
<td>Factor relating the number density of the sample to a per liter bases.</td>
</tr>
<tr>
<td>$G$</td>
<td>Rate expression for abrasive transfer, $\mu m^2min^{-1}$.</td>
</tr>
<tr>
<td>$G_o$</td>
<td>Layering rate constant, $\mu m^{1-a}min^{-1}$.</td>
</tr>
<tr>
<td>$G_A, G_L$</td>
<td>Rate expressions for attrition and layering, respectively, $\mu m min^{-1}$.</td>
</tr>
<tr>
<td>$K$</td>
<td>Rate constant for successful collisions of oil drops and particles, $cm^3 min^{-1}$.</td>
</tr>
<tr>
<td>$\ell$</td>
<td>Agglomerate diameter, $\mu m$.</td>
</tr>
<tr>
<td>$\ell$</td>
<td>Agglomerate diameter, integration dummy variable, $\mu m$.</td>
</tr>
<tr>
<td>$\ell_o$</td>
<td>Smallest considered agglomerate diameter, $\mu m$.</td>
</tr>
<tr>
<td>$\ell_M$</td>
<td>Median diameter in a Gaussian distribution, $\mu m$.</td>
</tr>
<tr>
<td>$n$</td>
<td>Number density of agglomerates, $\mu m^{-1} \ell^{-1}$.</td>
</tr>
<tr>
<td>$n_o$</td>
<td>Number density of agglomerates of diameter $\ell_o$, $\mu m^{-1} \ell^{-1}$.</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of agglomerates.</td>
</tr>
<tr>
<td>$N_m$</td>
<td>Number of growth regimes.</td>
</tr>
<tr>
<td>$O(t)$</td>
<td>Oil drop concentration at time $t$, $\ell^{-1}$.</td>
</tr>
<tr>
<td>$O$</td>
<td>Oil Dosage, v/w%.</td>
</tr>
<tr>
<td>$r$</td>
<td>Exponent describing the length dependence of coalescence growth from binary collisions.</td>
</tr>
<tr>
<td>$R$</td>
<td>Empirical expression which numerically describes effects of collision frequency and efficiency upon coalescence, $\mu m \ell min^{-1}$.</td>
</tr>
<tr>
<td>$R_{ij}$</td>
<td>Collision radius of particles $i$ and $j$, $\mu m$.</td>
</tr>
<tr>
<td>$S$</td>
<td>Stirring Speed, rpm.</td>
</tr>
<tr>
<td>$SC$</td>
<td>Slurry concentration of the feed, weight %.</td>
</tr>
<tr>
<td>Symbol</td>
<td>Expression</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$t$</td>
<td>time, min.</td>
</tr>
<tr>
<td>$V_B$</td>
<td>Volume of pendular bridge between two particles, $\mu m^3$.</td>
</tr>
<tr>
<td>$V_S$</td>
<td>Volume of a spherical particle, $\mu m^3$.</td>
</tr>
<tr>
<td>VPD</td>
<td>Volume percent density of the agglomerate, $\mu m$.</td>
</tr>
<tr>
<td>$V_g$</td>
<td>Velocity gradient relating to the turbulent mixing, $min^{-1}$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Parabolic constants of a Gaussian distribution curve fit.</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Adjusted operating parameters levels.</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Number of breakage fragments.</td>
</tr>
<tr>
<td>$\Theta_C$</td>
<td>Contact angle.</td>
</tr>
<tr>
<td>$\Theta_M$</td>
<td>Meridian angle.</td>
</tr>
<tr>
<td>$\Theta_S$</td>
<td>Sum of contact and meridian angles.</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density of agglomerate, $g/cm^3$.</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Residence time, min.</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY


APPENDIX A. FORM FOR COALESCENCE AND BREAKAGE

The form of the population balance for this system is very analogous to a simplified binary gas phase reaction. If the effects of the suspending media upon the particles is ignored in this analysis, it can be assumed that each particle can be viewed like an individual gas atom or molecule. The two different types of species in the gas phase reaction are distinguished from one another by their atomic numbers; whereas in the slurry, the particles are distinguished by their sizes. Thus, where a gas phase reaction may have only two species interacting (e.g., chlorine reacting with hydrogen), there is virtually an infinite number of sizes of particles, and thus, a series of binary interactions are involved. A further analogy to gas phase reactions would be that the agitation which causes collisions between coal particles would be analogous to the temperature effect (kinetic energy) which causes gas particles to interact. Chemical type reactions could then be written for these particle interactions. In order to write out these expressions, allow [ℓ] to represent a particle of size ℓ, and \( N(\ell) \) to represent the number concentration of particles of size \( \ell \). For all interactions involving the creation of particles of size ℓ due to combinations of particles of size \( \ell' \), where \( \ell' < \ell \), with other sized particles:

\[
[\ell] + \left[ (\ell^3 - \ell'^3)^{1/3} \right] \xrightarrow{K_1} [\ell]
\]
for one such particle of size $\tilde{\ell}$:

$$r_1 = K_1 N(\tilde{\ell}, t) N[(\tilde{\ell}^3 - \tilde{\ell}^3)^{1/3}, t] \tag{A.1}$$

for all such particles of size $\tilde{\ell}$ such that $\tilde{\ell} < 1/2$:

$$r_1 = \sum_{\tilde{\ell}=0}^{\tilde{\ell}=1/2} K_1 N(\tilde{\ell}, t) N[(\tilde{\ell}^3 - \tilde{\ell}^3)^{1/3}, t] \tag{A.2}$$

For all interactions such that particles of size $\ell$ are lost due to combinations with all possible size $\tilde{\ell}$s:

$$[\ell] \overset{K_2}{\longrightarrow} [((\tilde{\ell}^3 + \tilde{\ell}^3)^{1/3}]

for one such particle of size $\tilde{\ell}$:

$$r_2 = K_2 N(\ell, t) N(\tilde{\ell}, t) \tag{A.3}$$

for all such particles of size $\tilde{\ell}$ that exist:

$$r_2 = \sum_{\tilde{\ell}=0}^{\tilde{\ell} = \infty} K_2 N(\ell, t) N(\tilde{\ell}, t) \tag{A.4}$$

For particles of size $\ell$ which are lost by breaking into $\eta$ number of particles of size $\ell / \eta^{1/3}$:

$$[\ell] \overset{K_3}{\longrightarrow} \eta[\ell / \eta^{1/3}]

r_3 = K_3 N(\ell, t) \tag{A.5}$$

For $\eta$ number of particles of size $\ell$ created by the breakage of particles of size $\eta^{1/3}\ell$:

$$[\eta^{1/3}\ell] \overset{K_4}{\longrightarrow} \eta[\ell]

r_4 = K_4 N(\eta^{1/3}\ell, t) \tag{A.6}$$
A population balance can now be performed on particles of size $\ell$:

$$\frac{\partial N(\ell,t)}{\partial t} = r_1 - r_2 - r_3 + \eta r_4 = \sum_{\ell=0}^{\ell=1/2} K_1 N(\ell,t) N[(\ell^3 - \ell^3)1/3,t]$$

$$- \sum_{\ell=0}^{\ell=\infty} K_2 N(\ell,t) N(\ell,t) - K_3 N(\ell,t) + \eta K_4 N(\eta^{1/3}\ell,t) \quad (A.7)$$

$$\frac{\partial [N(\ell,t)\Delta \ell]}{\partial t} = \sum_{\ell=0}^{\ell=1/2} K_1 \frac{N(\ell,t) N[(\ell^3 - \ell^3)1/3,t]}{\Delta \ell} \Delta \ell \Delta \ell$$

$$- \sum_{\ell=0}^{\ell=\infty} K_2 \frac{N(\ell,t) N(\ell,t)}{\Delta \ell} \Delta \ell \Delta \ell - K_3 \frac{N(\ell,t)}{\Delta \ell} \Delta \ell + \eta K_4 \frac{N(\eta^{1/3}\ell,t)}{\Delta \ell} \Delta \ell \quad (A.8)$$

The limit of $\Delta \ell$ approaching zero can be incorporated into equation (A.8) to yield:

$$\frac{\partial n(\ell,t)}{\partial t} = \int_0^{\ell/2} K_1 n(\ell,t) n[(\ell^3 - \ell^3)1/3,t] d\ell - \int_0^\infty K_2 n(\ell,t) n(\ell,t) d\ell - K_3 n(\ell,t)$$

$$+ \eta K_4 n(\eta^{1/3}\ell,t) \quad (A.9)$$

For the kinetic constants $K_1, K_2, K_3,$ and $K_4$, it can be assumed that they are functions of the sizes of the particles involves (using Bemer's nomenclature):

$$K_1 = R[\ell,(\ell^3 - \ell^3)1/3] \quad (A.10)$$

$$K_2 = R(\ell,\ell) \quad (A.11)$$

$$K_3 = B(\ell) \quad (A.12)$$

$$K_4 = B(\eta^{1/3}\ell) \quad (A.13)$$

Substitution of equations (A.10)-(A.13) into equation (A.9), noting that the 1$st$ integral term is that of an even function, yields:

$$\frac{\partial n(\ell,t)}{\partial t} = 1/2 \int_0^\ell R[\ell,(\ell^3 - \ell^3)1/3] n(\ell,t) n[(\ell^3 - \ell^3)1/3,t] d\ell$$

$$- n(\ell,t) \int_0^\infty R(\ell,\ell) n(\ell,t) d\ell - B(\ell) n(\ell) + \eta B(\eta^{1/3}\ell) n(\eta^{1/3}\ell) \quad (A.14)$$
APPENDIX B. OIL DROPS ON COAL

It must be assumed that an oil drop is much smaller than a coal particle during the time that the oil is interacting (colliding) with the coal particle. The assumption is also made that the rate constant, $K$, is the same for all successful particle-oil drop interactions. The concentration of coal particles which has $i$ oil drops attached to them is represented by $C_i(t)$. The sequence of particle-oil drop interactions can be represented by (assuming irreversibility):

\begin{align*}
    r_1 &= KO(t)C_0(t) \\
    r_2 &= KO(t)C_1(t) \\
    r_3 &= KO(t)C_2(t) \\
\vdots \\
    r_i &= KO(t)C_{i-1}(t) \\
    r_{i+1} &= KO(t)C_i(t) \\
\end{align*}
The rate of change in the concentration of particles with one oil drop on them is:

\[ \frac{dC(t)}{dt} = r_1 - r_2 = KO(t)C_0(t) - KO(t)C_1(t) \]  \hspace{1cm} (B.6)

In the general case, the rate of change in the concentration of particles with \( i \) oil drops on them is:

\[ \frac{dC_i(t)}{dt} = r_i - r_{i+1} = KO(t)C_{i-1}(t) - KO(t)C_i(t) \]

\[ = KO(t)[C_{i-1}(t) - C_i(t)] \]  \hspace{1cm} (B.7)

Dunstan et al. [13] solved this equation analytically and obtained the following expression:

\[ C_i(t) = C \frac{[K \int_0^t O(t) \, dt]^i}{i!} \exp[-K \int_0^t O(t) \, dt] \]  \hspace{1cm} (B.8)
APPENDIX C. DERIVATION OF PENDULAR BRIDGE VOLUME EXPRESSION

In order to determine the volume of a liquid bridge between two particles, two-dimensional analysis will be employed. There are two main circles: the particle circle consisting of a center at \((0,R)\) and radius \(R\), and a meniscus circle consisting of a center at \((a,0)\) and radius \(b\). The equations of the particle and meniscus circles are:

\[ \begin{align*}
    x^2 - (y - R)^2 &= R^2 \\
    (x - a)^2 + y^2 &= b^2
\end{align*} \]  

Equations (C.1) and (C.2) can be rewritten in terms of heights above the x-axis:

\[ \begin{align*}
    y &= h_1(x) = R - (R^2 - x^2)^{1/2} \\
    y &= h_2(x) = (b^2 - (x - a)^2)^{1/2}
\end{align*} \]

In order to obtain a volume for the liquid bridge, the area below the heights and above the x-axis are rotated around the y-axis, such that:

\[ V_B = \text{volume of bridge between particles} \]

\[ = 2 \sum_{i=1}^{n} \left( \text{Perimeter about y-axis}_i \cdot \text{Differential Area}_i \right) \]

\[ = 2 \sum_{i=1}^{n} \left( 2\pi x_i \cdot (h_i(x) \Delta x) \right) \]  

(C.5)
The limit as $\Delta x$ approaches zero yields:

$$V_B = 2 \int_0^x 2\pi x h_1(x) \, dx + 2 \int_x^{a+b} 2\pi x h_2(x) \, dx$$

$$= 4\pi \int_0^x (xR - x(R^2 - x^2)^{1/2}) \, dx + \int_x^{a+b} x(b^2 - (x-a)^2)^{1/2} \, dx \quad (C.6)$$

Integration of this expression yields:

$$V_B = \frac{2}{9} \pi \left[ 3Rx_c^2 - 2R^3 + 2(R^2 - x_c^2)^{3/2} \right] + \frac{4}{3} \pi [b^2 - (x_c - a)^2]^{3/2}$$

$$- 2\pi a[(x_c - a)\sqrt{b^2 - (x_c - a)^2} + b^2(\arcsin \frac{x_c - a}{b} - \frac{\pi}{2})] \quad (C.7)$$

where: $+\frac{\pi}{2}$ for $(\Theta_c - \Theta_m) > 90^\circ$  
$-\frac{\pi}{2}$ for $(\Theta_c - \Theta_m) < 90^\circ$

These equations represent the volume of a pendular bond in terms of the geometrical variables of the bond boundaries. The next step that needs to be executed is to get the bond volume in terms of the particle variables, such that the pendular bond volume can be expressed as a function of particle radius, meridian angle, and contact angle. The parameters $x_c, y_c, a,$ and $b$ can be expressed in terms of $\Theta_c, \Theta_m,$ and $R$ by:

$$a = x_c + y_c \tan \Theta_s \quad (C.8)$$

$$b = y_c \sqrt{\tan^2 \Theta_s + 1} \quad (C.9)$$

$$x_c = R \sin \Theta_m \quad (C.10)$$

$$y_c = R(1 - \cos \Theta_m) \quad (C.11)$$

$$\Theta_s = \Theta_c + \Theta_m \quad (C.12)$$

Upon substitution of these expressions into equation (C.6) produced:

$$V_B = V_1 + V_2 + V_3 \quad (C.13)$$
\[ V_1 = V_s (1 - \cos \Theta_m)^2 \left( \frac{2 \cos \Theta_m - 1}{2} \right) \]  
\[ V_2 = V_s (1 - \cos \Theta_m)^3 \]  
\[ V_3 = \frac{3}{2} V_s (1 - \cos \Theta_m)^2 \left[ \sin \Theta_m + (1 - \cos \Theta_m) \tan \Theta_s \right] \left[ \tan \Theta_s - \left( \frac{\pi}{2} - \Theta_s \right) (\tan^2 \Theta_s + 1) \right] \]
\[ V_s = \frac{4}{3} \pi R^3 \]

Combination of these equations yields:
\[ \frac{V_B}{V_S} = \frac{3}{2} (1 - \cos \Theta_m)^2 \left( 1 + \sin \Theta_m + (1 - \cos \Theta_m) \tan \Theta_s \right) \left[ \tan \Theta_s - \left( \frac{\pi}{2} - \Theta_s \right) (\tan^2 \Theta_s + 1) \right] \]
\[ \frac{V_B}{V_S} = (1 - \cos \Theta_m)^2 \left( \frac{2 \cos \Theta_m + 1}{2} \right) \]

In the case of \( \Theta_s = \frac{\pi}{2} \):
\[ \frac{V_B}{V_S} = (1 - \cos \Theta_m)^2 \left( \frac{2 \cos \Theta_m + 1}{2} \right) \]

This expression reduces down to the expression derived by Fisher in the instance of the contact angle being equal to zero:
\[ \frac{V_B}{V_S} = 2 \pi R^3 (\sec \Theta - 1)^2 (1 - \left( \frac{\pi}{2} - \Theta \right) \tan \Theta) \]