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#### ABSTRACT

## DRY PARTICLE COATING AND GRANULATION IN ROTATING FLUIDIZED BEDS

## by Madhuri Kolli

The practicability of using rotating fluidized bed as dry particle coater and granulator is investigated in this study. Dry particle coating, in which fine guest particles are coated onto bigger host particles in the absence of binders or solvents, is studied for various systems of host and guest particles. Coating results are explained by considering the collisions between the host and guest particles and among themselves. Balance between collisional energy and adhesion energy is suggested to be the limiting condition for the adhesion and hence the coating of guest particles onto host particles. It is observed that the experimental and theoretical pressure drops across the fluidized bed differ about 35% on an average. This is assumed to be because of the theoretical approximations and loss of particles during fluidization. Guest particles SiC and alumina, which are fine and cohesive, are seen to agglomerate and form spherical granules during fluidization because of the collisions among the guest particles.

Dry granulation of cohesive powders in rotating fluidized bed is investigated with the aid of pressure swing. In pressure swing granulation, the powder bed is fluidized in one cycle and compacted in the other cycle. This facilitates the formation of spherical granules without any binders. It is observed that denser granules with narrow size distribution are formed as the granulation time is increased. The mechanism and forces involved in making and shaping these granules is investigated. Mathematical modeling of dry granulation in rotating fluidized beds with the aid of population balances is initiated.

## DRY PARTICLE COATING AND GRANULATION IN ROTATING FLUIDIZED BEDS

by Madhuri Kolli

## A Thesis

Submitted to the Faculty of New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering

**Department of Chemical Engineering** 

# May 2002

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## **APPROVAL PAGE**

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To my family and Jeevan: for their love, support and encouragement.

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#### **CHAPTER 1**

#### **INTRODUCTION**

#### 1.1 Overview

Particle technology deals with the production, characterization, modification, handling and utilization of organic and inorganic powders, in both dry and wet conditions. Particle products are attractive, because of the high surface to volume ratio available for reaction, solubility, coating and dispersion. In recent years, particle design, i.e., structuring and optimization of physical and chemical properties to achieve a combination of the desired effects, has grown in importance. These so-called engineered particles have become the goal in many industrial systems.

Applications of these engineered particles include paints and coatings, which achieve desirable appearance while having carefully controlled rheological and drying properties; encapsulation of pesticides, fertilizers or herbicides for controlled release of the active ingredient and coating of seeds; and pharmaceutical applications, for controlled-drug delivery within the body. Other applications include foods, which must combine a desirable appearance and aroma and enhance shelf life; ceramics, with increased strength and improved sintering properties; and biosensors, which can evaluate the risk for developing a disease by looking at specific genes.

Particle science and technology as applied in industry and taught in academia is structured on a unit operations basis. These include reaction engineering, crystallization, precipitation, coating, granulation, drying, solids transport, comminution, solid/liquid and solid/gas separation etc. Coating and granulation can be used to improve or modify

1

surface properties and/or functionality of particles like flowability, dispersibility, solubility, wettability (hydrophilic/hydrophobic properties), electrostatic, electric, magnetic, optical, color, flavor, taste, particle shape/sphericity, sinterability and solid phase reactivity.

Dry particle coating and granulation processes, as opposed to wet coating and granulation processes are relatively new. A brief description of both the wet and dry processes and the advantages of dry processes over wet processes are given below. Detailed discussion of the dry processes and the equipment used is described in detail in a subsequent chapter.

## 1.2 Coating

Particle coating or surface modification technology has been used for the synthesis of composite materials with tailored properties. It attracted special interest in many industries including pharmaceuticals, food, cosmetics, ceramics, electronics and special chemicals.

Particle coating can be accomplished using both wet and dry processes. Wet coating methods includes sol-gel processes, wet chemical deposition, spray coating, dip coating, spinning disc coaters and a variety of fluidized bed coaters such as the Wuster coater. Wet particle coating is used primarily to form a barrier or film between the host particle and its environment. The coating material in these wet methods usually consists of a solute dissolved in an organic solvent or an aqueous suspension of the solute. The organic solvent is usually highly volatile. For example, organic compounds whose vapor pressure at 20 °C exceeds 0.13 kPa are referred to as Volatile Organic Compounds

(VOCs). VOCs have been implicated as a major precursor in the production of photochemical smog, which causes atmospheric haze, eye irritation and respiratory problems. Some VOCs are even carcinogenic.

Dry coating, which attaches tiny, submicron-sized particles (guests) onto relatively larger micron-sized particles (host) without using any solvent, binders or even water, is a promising alternative approach. Here, the guest particles are brought into close contact with the host particles through the application of mechanical forces. Since the size of the guest particles is so small, van der Waals interactions are strong enough to keep them firmly attached to the host particles. Depending on a variety of operating conditions including processing time, weight fraction of the host and guest particles and particle properties, either a discrete or continuous coating of guest particles can be achieved. Thus, dry particle coating processes are environmentally benign, producing none of the organic emissions or aqueous waste streams usually present in wet coating processes. Also, dry coating is cost effective since there is no need for drying the products.

## 1.3 Granulation

Granulation is a size enlargement operation, by which fine powders are agglomerated into larger granules engineered to a specific size and shape. Granulation can result in improved flowability and appearance and improve other properties such as dissolution rate, bulk density, reduced caking formation and granule strength. It is an important technique to improve powder handling, especially for fine powders, which are difficult to handle because of their cohesiveness and low flowability. Granulation technology has a wide spectrum of applications ranging from pharmaceutical, food, fertilizer, and detergent to mineral, ceramic, waste processing, and advanced materials. Both dry and wet processes can achieve granulation. Many conventional granulators, such as pan granulators, inclined disc agglomerators, pelletizers, spray dryers, drums, extrusion processes, fluidized beds and roll compactors for compaction of dry materials are employed.

In wet granulation, usually called binder granulation, a liquid binder such as a solution or a melt is pumped, poured or atomized into an agitated bed of powders contained in a granulator whose main role is to provide shearing forces to the powder mass. Binders are used for generating cohesiveness to agglomerating powders. Consolidation by shear forces and drying result in solvent evaporation from the binder or melt thickening as a result of which, interparticle bridges strengthen, powder particles stick together, and larger granules of the original powder are formed. In many cases, binders left in the granules have some undesirable effects on the granule properties, like solubility reduction, too much strength to disintegrate etc. Fine powders are subjected to controlled agglomeration to reduce handling problems and uncontrolled agglomeration. However, it would be beneficial if these granules can be easily disintegrated again into powder form for further processing.

In such cases, dry granulation is an alternative approach where binders are not involved. Cohesive property of the powders forms the vehicle for granulation and granules are engineered specifically for a particular application. Nishii et.al., invented a novel binderless fluidized bed granulation method called pressure swing granulation (PSG). In PSG, the agglomerating nature of fine Geldart Group C powders is utilized.

#### 1.4 Objectives

The objective of this research is to investigate the practicability of using a rotating fluidized bed as a dry coater and dry granulator. Dry coating was studied using the following host-guest systems: glass beads-silicon carbide, microcrystalline fibrous cellulose-silicon carbide, glass beads-alumina, glass beads-titanium dioxide, cornstarch-silica, and microcrystalline fibrous cellulose-silica. Dry granulation was explored using zinc oxide and TiO<sub>2</sub> powders. Results of both coating and granulation are characterized using SEM-EDX. Theoretical modeling of granulation in fluidized beds with the aid of population balances is explored.

## CHAPTER 2

## **FLUIDIZATION**

Fluidization is a unit operation by which a bed of particulate solids is transformed into a fluidlike state through suspension in a gas or liquid. The particulate bed is supported over a porous plate, usually called the distributor.

When fluid is passed through a bed of particulate solids at a low flow rate, the fluid merely percolates between the particles. This is called a fixed or packed bed. When the fluid flow rate is further increased, the voidage between the particulate solids increases somewhat with the flow rate. The solids move apart, and some solids vibrate in restricted regions. This is called an expanded bed. As the fluid flow rate is further increased, a point is reached where all the particles are just suspended in the fluid. At this point, the frictional force between the fluid and solid particles (drag force) is just balanced by the weight of the particles, the vertical component of the compressive force between adjacent particles disappears, the pressure drop through any section of the bed reaches a maximum value, equal to the weight of the fluid and the particles in that section [Kunni & Levenspeil, 1993], and the distributor plate or grid which supports the bed of particulate solids does not experience any load. The bed is considered to be just fluidized and is referred to as an incipient fluidized bed or a bed at minimum fluidization velocity.

#### 2.1 Fluidlike Behavior of the Bed

At minimum fluidization, the bed just attains fluidlike properties and resembles a boiling liquid. The bed that maintains an uneven surface in static, fixed or defluidized state now has an even or horizontal surface. When the column is tipped, the upper surface of the bed is maintained at the horizontal. A heavy object that would sit on the top of a static bed would now sink to the bottom and a light object can now be easily pushed into the bed and on release would pop up and float on the top of the bed. The pressure at any point is proportional to the height of the column, as in a liquid. When two beds are connected their levels equalize. Any hole made on the vessel or column would allow the solids to flow like a liquid.

## 2.2 Regimes of Fluidization

Behavior of the bed at fluid rates greater that minimum fluidization depends on the type of system. The fluid under consideration, which flows upward, can be a gas, a liquid, or both. In liquid-solid systems, an increase in flow rate above minimum fluidization results in smooth or homogeneous (particulate) fluidization. The bed expands smoothly depending on the fluid flow rate. Gross flow instabilities are damped and large-scale voids are not observed under normal conditions.

In gas-solid systems, an increase in flow rate above minimum fluidization results in large instabilities with bubbling or channeling depending on the size and density of the particles. At even higher flow rates, the agitation becomes more violent and the movement of the solids becomes more vigorous. Such beds are termed aggregative or bubbling or heterogeneous fluidized beds. Their behavior is in contrast to that of liquidsolid systems. Under special conditions of fine light particles fluidized with dense gas at high pressures, a gas-solid system fluidizes homogeneously. Also, when low-density liquids fluidize very dense solids, a liquid-solid system behaves like a heterogeneous fluidized bed. When the solid particles are densely dispersed in the fluid stream, the fluidized bed has a clearly defined upper limit. Such a bed is considered to be a densely fluidized bed. Both gas and liquid fluidized beds can be densely fluidized. When the surface is not clearly defined at a particular velocity, the solid particles are likely to be carried away by the fluid. This situation corresponds to dilute or lean phase fluidization. The situation where the solid particles are entrained by the fluid flow corresponds to a state called pneumatic transport. Again, both gas and liquid fluidized beds can be dilute fluidized beds and pneumatically transported.

As the liquid velocity in a liquid-solid system is increased, homogeneous fluidization with smooth expansion of the bed occurs. When the liquid velocity is increased beyond the terminal velocity of the particles, hydraulic transport of the particles takes place. In gas-solid systems, bubbling is predominant. The minimum bubbling velocity is the velocity at which bubbles are just born at the distributor. As the bubbles rise, they coalesce and grow in size. When the gas velocity is increased beyond the minimum bubbling velocity, the bubbles coalesce and eventually become large enough to spread across the vessel. This phenomenon is called slugging and is more prominent in shallow beds of small diameter. In the case of fine particles, they flow smoothly down along the walls of the vessel around the raising void of gas. The slugs thus formed are called axial slugs. In the case of coarse particles, the portion of the bed above the bubble is pushed upward. Particles rain down from the slug, which finally disintegrates. These





slugs are called flat slugs. When the velocity is increased beyond the terminal velocity of the particles, the upper surface of the bed disappears and entrainment becomes appreciable. At this point instead of bubbles there is a turbulent motion of the solid clusters and voids of various sizes. This is called a turbulent fluidized bed [Kunni & Levenspeil, 1993]. At even higher gas velocities, pneumatic transport of the particles would occur. Fluidization regimes are depicted in Figure 2.1.

#### 2.3 Pressure Drop Across the Bed

The superficial velocity of the fluid is the net volume of the fluid crossing an empty horizontal plane per unit area per unit time. This superficial velocity is many times smaller than the interstitial fluid velocity inside the bed [Gupta & Sathiyamoorthy, 1999]. The variation of the pressure across the bed and thus the fluidization quality, with superficial fluid velocity depends mainly on the size distribution of the particulate solids along with many other factors like fluid-solid density ratio, vessel geometry, gas inlet arrangement, type of solids used etc.

The pressure drop across the bed,  $\Delta P$  behaves differently with increasing superficial gas velocity and decreasing superficial gas velocity because of the variation in the bed voidage. When the bed is initially a well-settled bed, the bed voidage is relatively low. Thus, the pressure drop obtained across the fixed bed is of a relatively high magnitude as predicted by the Ergun equation:

$$\frac{\Delta P}{L_f}g_c = 150 \frac{\left(1 - \varepsilon_f\right)^2}{\varepsilon_f^3} \frac{\mu u_0}{\left(\Phi_s d_P\right)^2} + 1.75 \frac{1 - \varepsilon_f}{\varepsilon_f^3} \frac{\rho_g u_0^2}{\Phi_s d_P}$$
(2.1)

In the Ergun equation for pressure drop,  $\varepsilon_f$  corresponds to the fixed bed voidage,  $\mu$  is the viscosity of the fluidizing air,  $u_0$  is the superficial gas velocity and  $L_f$  is the length of the

bed,  $\Phi_S$  the sphericity and  $d_P$  the particle size for isotropic solids. For beds with particle size distribution,  $d_P$  is replaced by  $\overline{d}_P$  given by

$$\overline{d}_{P} = \frac{1}{\frac{alli}{\sum} \left( x/d_{P} \right)_{i}}$$
(2.2)

With further increase in the gas velocity, the fixed bed slowly transforms to a bed at minimum fluidization. The voidage increases from  $\varepsilon_{\rm f}$  to  $\varepsilon_{\rm mf}$ , resulting in a decrease in pressure drop to the static pressure of the bed [Kunni & Levenspeil, 1993]. At the transition from fixed bed to fluidized bed, a bed with isotropic particles and a bed with particles having wide size distribution behave differently. In the case of a bed with isotropic particles, all the particles start to fluidize at almost the same superficial velocity. Thus, the pressure drop decreases during the transition as illustrated in the Figure 2.2 [Kunni & Levenspeil, 1993].



Figure 2.2 Pressure drop versus superficial velocity for uniformly sized sharp sand.

However, in the case of a bed having particles of wide size distribution, as the gas velocity is increased, the smaller particles are apt to slip into the void spaces between the

larger particles and fluidize while the larger particles remain stationary. Then partial fluidization occurs. With increasing gas velocity, the pressure drop equals the weight of the particles and fluid in the bed, showing that all the solids eventually fluidize. This phenomenon is depicted in the Figure 2.3 [Kunni & Levenspeil, 1993].



Figure 2.3 Pressure drop versus superficial velocity for a wide distribution of solids.

In either case, once the entire bed is completely fluidized, the pressure drop across the bed,  $\Delta P_b$  remains constant even though the superficial gas velocity is increased. At this point, the drag force between the particles and the gas moving upward balances the weight of the particles.

(Drag force between particles and gas moving upward) = (Weight of particles)

or

(Pressure drop across bed)(Cross-sectional area) = (Volume of bed) (Fraction of -solids)

(Specific weight of solids)

12

or

$$\frac{\Delta P_b}{L_{mf}} = (1 - \varepsilon_{mf})(\rho_s - \rho_g)\frac{g}{g_c}$$
(2.3)

where  $\varepsilon_{mf}$  and  $L_{mf}$  are the voidage and length of the fluidized bed at minimum fluidization,  $\rho_s$  and  $\rho_g$  are the densities of solids and fluidizing gas. The superficial velocity at minimum fluidizing conditions,  $U_{mf}$  can be obtained by combining Equations 2.1 and 2.3 as:

$$\frac{1.75}{\varepsilon_{mf}^3 \Phi_s} \left(\frac{d_P U_{mf} \rho_g}{\mu}\right)^2 + \frac{150(1 - \varepsilon_{mf})}{\varepsilon_{mf}^3 \Phi_s^2} \left(\frac{d_P U_{mf} \rho_g}{\mu}\right) = \frac{d_P^3 \rho_g (\rho_s - \rho_g)g}{\mu^2}$$
(2.4)

For a bed of isotropic solids,  $d_P$  corresponds to the particle size and for a bed of nonisotropic solids; d<sub>P</sub> corresponds to  $\overline{d}_{P}$  defined in Equation 2.2. The velocity at which bubble are first observed is called the minimum bubbling velocity. At velocities higher than minimum fluidization velocity, the excess gas goes through the bed as bubbles, which rise through the bed. In gas-solid systems, depending on the size of the particles being fluidized, bubbles may appear as soon as the velocity exceeds the minimum fluidizing velocity or may appear at even higher flow rates. In liquid-solid systems, bubbles have no meaning as smooth fluidization usually takes place. As the superficial velocity reaches the terminal velocity of the particles, the bed pressure drop no longer remains constant and increases in a manner similar to an empty bed because of particle elutriation. When the superficial velocity is gradually decreased, the bed defluidizes and the pressure drop assumes its original path as long as the bed continues to be in a state of fluidization. But the path followed for a fixed bed is lower than that obtainable for increasing superficial gas velocity as shown in Figure 2.4 [Gupta et al, 1999]. This is because the bed voidage is greater.



Figure 2.4 Variation in pressure drop with superficial velocity.

## 2.4 Classification of Particles

Numerous attempts have been made to devise a criterion to predict the mode of fluidization. Among them, Geldart empirically developed a classification to predict the fluidization behavior in gas based on the size and density of the particles. Other criteria proposed by Molerus (1982) based on interparticle forces, by Clark et al., based on certain dimensionless numbers have also been widely accepted.

## **Geldart Classification of Particles:**

Geldart classified uniformly sized powders into four groups and designated them by the letters A, B, C and D. Starting from the smallest to the largest particles, all the particles are grouped into any of these four groups based on the density difference between the fluidizing gas and particles and the mean size of the particles.

 $Group \ C \ (Cohesive)$ : Very fine or cohesive powders. They are extremely difficult to fluidize because the interparticle forces dominate the drag forces between the fluidizing

air and the particles. The density of these powders is typically less than  $1400 \text{ kg/m}^3$ . The bed lifts as a plug in small diameter columns. In larger beds, the particles channel or rathole badly. Hence, bubbling is usually absent. They can be fluidized as agglomerates or by using agitators or vibration to break the channels.

*Group A (Aerated):* Materials having small mean particle size and/or low particle density  $(\rho_S < 1.4 \text{ g/cc})$  are classified into this group. They are usually aeratable and fluidize easily with smooth fluidization at low fluid velocities. The bed expands rapidly before bubbles appear. Small bubbles appear at higher gas velocities,  $U_{mf}/U_{mb} < 1$ . These gas bubbles appear to split and coalesce as they rise through the bed. The bed expands very rapidly and collapses very slowly. Mixing is very rapid even with a few bubbles. Examples of materials included in this group are cracking catalysts.

Group B (Bubbling): Sandlike materials whose size lies typically in the range of  $40\mu m < \overline{d}_p < 500 \ \mu m$  and density in the range of  $1.4 < \rho_S < 4$  g/cc. Bed expansion is very small and the bed collapses very fast. Solids fluidize well with vigorous bubbling action and mixing is insignificant in the absence of bubbles. Bubbles appear after minimum fluidization velocity  $U_{mf}/U_{mb} \sim 1$ . At higher gas velocities, bubble size is found to be almost independent of the particle size.

*Group D (Spoutable):* Coarse particles with particle size  $d_P > 500 \mu m$  and very dense particles are classified into this group. The bed collapses very fast compared with beds of powders of other groups. Particle mixing is relatively poor because of severe channeling and large exploding bubbles. Deep beds of these particles are difficult to fluidize and hence shallow beds are usually used. Bubbles coalesce rapidly and grow to a large size. Bubbles rise slowly compared to the rest of the gas percolating through the emulsion.

#### 2.5 Rotating Fluidized Beds

In rotating fluidized beds, fluidization is achieved by passing the gas radially through the distributor that is rotated at a desired speed. The particulate solids are thrown to the walls of the distributor due to the centrifugal force. The fluidizing air that enters the distributor radially fluidizes the bed layer by layer starting from the innermost free surface and finally fluidizing the particulate solid layer just beside the distributor. Since the bed can be rotated at different speeds, the centrifugal force and hence the gravitational force acting on the bed can be varied. Thus, the minimum fluidization velocity required to fluidize particulate solids can be increased by several orders of magnitude and therefore minimum fluidization can be achieved virtually at any flow rate by varying the rotating speed of the bed. A schematic diagram of the rotating fluidized bed is shown in Figure 2.5. Rotating fluidized beds are described in more detail in later chapters of this thesis.



Figure 2.5 Rotating Fluidized Bed.

#### **CHAPTER 3**

#### FLUIDIZATION OF FINE PARTICLES IN ROTATING FLUIDIZED BEDS

A rotating fluidized bed is cylindrical in shape and rotates about its axis of symmetry. As a consequence of this circular motion, the bed material is forced to the annular region at the circumference of the cylinder. Fluid is introduced through the porous surface of the cylindrical distributor in the radial direction to fluidize the particles. The gravitational field is an adjustable parameter in rotating fluidized beds determined by the rotational speed and radius of the cylindrical distributor, unlike conventional fluidized beds where the gravitational field is fixed at 1g. There are many advantages of rotating fluidized beds over conventional fluidized beds that make them suitable for a variety of applications. Because of the advantage of varying the rotating speed and hence the gravitational force, much higher gas flow rates per unit area of the distributor can be achieved. In principle minimum fluidization can be achieved at any gas flow rate by changing the rotating speed of the bed.

#### 3.1 Minimum Fluidization

In rotating fluidized beds, the granules or powders are fluidized layer by layer from the inner free surface outward at increasing radius as the gas velocity is increased. Chen (1987) proposed a theory for calculating the minimum fluidization velocity in a rotating fluidized bed. The system configuration used by Chen (1987) is shown in Figure 3.1 where  $r_0$  is the radius of the distributor and  $r_i$  is the radius of the inner surface of the particle bed. Gas is introduced from the distributor to the inner surface of the particle bed.

Chen assumed that the centrifugal force is dominant and the gravitational force is relatively small. Under this assumption, the free surface of a horizontal rotating bed is symmetrical around its axis of rotation. Furthermore, he assumed that the pressure drop through the particle bed is not large and hence the gas phase can be taken to be incompressible. The interstitial gas velocity,  $u_r$  is assumed to be uniformly distributed over the distributor. At steady state the equation of continuity for the gas phase is:

$$\frac{d}{dr}(\varepsilon r u_r) = 0 \tag{3.1}$$

The above equation can be integrated to:

$$r\overline{u}_r = r_o\overline{u}_o = \text{Constant}$$
 (3.2)

where  $\overline{u}_r = u_r \varepsilon$  is the local superficial gas velocity.



Figure 3.1 System configuration of a centrifugal particle bed.

Unlike the model proposed by Fan et al. (1985), where the voidage  $\varepsilon$  was assumed constant, Chen (1987) considered variable voidage in his model. If the drag force exerted on the particles by the gas is given by the Ergun equation, the local momentum balance of the gas phase becomes (Jackson, 1971):

$$\frac{dP}{dr} = -\Phi_1 \overline{u}_r + \Phi_2 \overline{u}_r^2 + \rho_g r \omega^2 - \rho_g u_r \frac{du_r}{dr}$$
(3.3)

where  $\omega$  is the angular velocity. Combining Equations 3.2 and 3.3,

$$\frac{dP}{dr} = -\Phi_1 \overline{u}_r + \Phi_2 \overline{u}_r^2 + \rho_g r \omega^2 + \frac{\rho_g \overline{u}_r^2}{\varepsilon^2 r} + \rho_g \frac{\overline{u}_r^2}{\varepsilon^3} \frac{d\varepsilon}{dr}$$
(3.4)

$$\Phi_1 = \frac{150(1-\varepsilon)^2 \mu}{\varepsilon^3 (\phi_s d_p)^2} \text{ and } \Phi_2 = \frac{1.75(1-\varepsilon)\rho_g}{\varepsilon^3 \phi_s d_p}$$
(3.5)

Since  $\Phi_1$  and  $\Phi_2$  are both sensitive functions of voidage and a slight change in voidage will result in considerable change in pressure drop, Chen's model is more accurate compared to the model proposed by Fan et al. (1985), where voidage is assumed to be constant. Jackson (1971) proposed the following equation for the local momentum balance of the solid phase, taking the superficial solid velocity to be zero.

$$\frac{1}{r}\frac{d}{dr}(r\sigma_r) = -\frac{dP}{dr} + (1-\varepsilon)\rho_s r\omega^2 + \varepsilon\rho_g r\omega^2 + \rho_g \frac{\overline{u}_r^2}{\varepsilon} (\frac{1}{r} + \frac{1}{\varepsilon}\frac{d\varepsilon}{dr})$$
(3.6)

Combining Equations 3.4 and 3.6,

$$\frac{1}{r}\frac{d}{dr}(r\sigma_r) = \Phi_1 \overline{u}_r - \Phi_2 \overline{u}_r^2 + (1-\varepsilon)(\rho_s - \rho_g)r\omega^2 - (1-\varepsilon)\rho_g \frac{\overline{u}_r^2}{\varepsilon^2}(\frac{1}{r} + \frac{1}{\varepsilon}\frac{d\varepsilon}{dr})$$
(3.7)

where  $\sigma_r$  is the normal stress in the radial direction and is taken to be positive. Chen (1987) defined the criterion of fluidization in a more fundamental sense so that when the fluid drag of the interstitial gas is large enough to balance the centrifugal and

gravitational forces, the normal stress will vanish. When the fluid drag exceeds these other forces, a tensile stress will act on the solid phase. If the particles are cohesionless, the solid phase cannot withstand any tensile stress and will be fluidized. In rotating fluidized beds, superficial gas velocity is a function of position r. Hence, the centrifugal force, fluid drag, and gas inertia are all functions of the position r. When all the three forces balance one another, the bed is fluidized.

The superficial gas velocity and fluid drag both decrease with increasing r, and the centrifugal force increases with increasing r. Thus, when the air rate increases from zero, the stress gradient becomes zero first at the inner surface of the particle bed. The superficial velocity at which this phenomenon occurs is called the surface fluidization velocity,  $U_{mfs}$ . For air rates smaller than this velocity the stress gradient in the fluid bed is positive at all levels and the bed remains packed.

As the air velocity increases beyond the surface fluidization velocity, the point of zero normal stress in the particle bed moves outward. Thus, the particle bed is fluidized layer by layer, from the inner surface outward, as the superficial gas velocity increases. For a given air rate, the position at which the bed is fluidized can be determined by setting Equation 3.7 to zero.

As the point of zero stress moves towards the distributor, the whole particle bed fluidizes completely. The superficial gas velocity at which the entire particle bed fluidizes is called the critical fluidization velocity  $U_{mfc}$ . Thus, a centrifugal fluidized bed is fluidized layer by layer in a range of superficial velocities and the span of this range depends on the thickness of the particle bed. The system configurations at different stages of fluidization are shown in Figure 3.2 (Chen, 1987).


Figure 3.2 System configurations at different stages of air flow rate.

Kao et al. (1987) simplified the equations proposed by Chen (1987) for the pressure drop and minimum fluidizing velocities based on the theory that the drag force is the major contributor for the pressure drop in a fixed bed and the total mass of the particles is the major contributor to the pressure drop in the fluidized bed region. They proposed that the effect of inertia and variable porosity contribute less than one percent of the total pressure drop and therefore can be neglected. Hence, the equations for pressure drops in fixed and fluidized bed regions reduce to:

$$\frac{dP}{dr} = \Phi_1 (\frac{U_o r_o}{r}) + \Phi_2 (\frac{U_o r_o}{r})^2$$
(3.8)

$$\frac{dP}{dr} = (\rho_g - \rho_f)(1 - \varepsilon)r\omega^2$$
(3.9)

where  $\Phi_1$  and  $\Phi_2$  are defined in Equation 3.5. If the sphericity,  $\phi_s$ , is not known the correlations suggested by Wen and Yu (1966) can be used:

$$\frac{1}{\phi_s \varepsilon^3} \approx 14 \text{ and } \frac{(1-\varepsilon)}{\phi_s^2 \varepsilon^3} \approx 11$$
 (3.10)

Thus  $\Phi_1$  and  $\Phi_2$  become:

$$\Phi_1 = \frac{1650(1-\varepsilon)\mu}{d_p^2}, \ \Phi_2 = \frac{24.5(1-\varepsilon)\rho_g}{d_p}$$
(3.11)

Integrating the pressure drop equations for the fixed and fluidized beds, an equation for the average minimum fluidization velocity  $U_{mf}$  can be obtained as:

$$\frac{U_{mf}\rho_f d_g}{\mu} = \left[ (33.7\frac{C_2}{C_1})^2 + 0.0408\frac{\rho_f(\rho_g - \rho_f)d_g^3\omega^2}{\mu^2}\frac{C_3}{C_1} \right]^{1/2} - 33.7\frac{C_2}{C_1}$$
(3.12)

where

$$C_{1} = r_{o}^{2} \left(\frac{1}{r_{i}} - \frac{1}{r_{o}}\right)$$

$$C_{2} = r_{o} \ln\left(\frac{r_{o}}{r_{i}}\right)$$

$$C_{3} = \frac{\left(r_{o}^{2} - r_{i}^{2}\right)}{2}$$
(3.13)

The equation for the surface fluidizing velocity  $U_{mfs}$ , reduces to:

$$\frac{U_{mfs}\rho_f d_g}{\mu} \frac{r_0}{r_i} = \left[ (33.7)^2 + 0.0408 \frac{\rho_f (\rho_g - \rho_f) d_g^3 \omega^2 r_i}{\mu^2} \right]^{1/2} - 33.7$$
(3.14)

Similarly, the equation for the critical fluidizing velocity  $U_{mfc}$  reduces to:

$$\frac{U_{mfc}\rho_f d_g}{\mu} = \left[ (33.7)^2 + 0.0408 \frac{\rho_f (\rho_g - \rho_f) d_g^3 \omega^2 r_o}{\mu^2} \right]^{1/2} - 33.7$$
(3.15)

From these equations, the pressure drop across the bed is determined depending on the superficial velocity  $U_0$ . When the superficial velocity  $U_o$  is less than the surface minimum fluidizing velocity  $U_{mfs}$ , the entire bed is in a packed condition. In this case, the pressure drop across the packed bed is given by:

$$\Delta P_{P} = \Phi_{1} U_{o} r_{o} \ln(\frac{r_{o}}{r_{i}}) + \Phi_{2} U_{o}^{2} r_{o}^{2} \left(\frac{1}{r_{i}} - \frac{1}{r_{o}}\right)$$
(3.16)

When the superficial gas velocity lies between the surface minimum fluidizing velocity and critical minimum fluidizing velocity, the bed is in a condition of partial fluidization and the pressure drop across the fluidized bed and the packed bed:  $\Delta P = \Delta P_f + \Delta P_P$ :

$$\Delta P = (1 - \varepsilon) (\rho_g - \rho_f) \omega^2 (r_{pf}^2 - r_i^2) + \Phi_1 U_o r_o \ln(\frac{r_o}{r_{pf}}) + \Phi_2 U_o^2 r_o^2 \left(\frac{1}{r_{pf}} - \frac{1}{r_o}\right)$$
(3.17)

where  $r_{pf}$  is the interface between the fluidized and packed beds. When the air velocity exceeds the critical minimum fluidization velocity  $U_{mfc}$ , the bed is completely fluidized and the pressure drop is given by:

$$\Delta P_f = \frac{(1-\varepsilon)(\rho_g - \rho_f)\omega^2(r_o^2 - r_i^2)}{2}$$
(3.18)

### **3.2** Factors Affecting the Pressure Drop

The pressure drop and hence, the fluidization in a rotating fluidized bed are affected by many factors including the type of distributor, fluidizing gas, particle density and size distribution and rotation speed. Qian et al, (1998) have studied the pressure drop in a horizontal rotating fluidized bed using slotted and sintered metal cylindrical gas distributors. They reported that the pressure drop response obtained at the transition from the packed bed to the fluidized bed regime is quite different for the two types of distributors.

In a slotted distributor for alumina and glass beads with size distribution, the pressure drop increases steadily until minimum fluidization is achieved and then suddenly decreases by approximately 60% of its peak value. Further increase in the flow rate maintains the pressure nearly constant with a slight upward trend. If the flow rate is then decreased from its maximum value, a different curve is followed which is nearly linear without any discontinuities. Furthermore, the sudden decrease in pressure drop is insignificant at low rotational speeds for a narrow size distribution of the particles. For the sintered metal distributor, the pressure drop increases until the bed fluidizes and then

becomes constant. However, they reported that when the gas flow rate is decreased from its maximum value, the pressure drop versus velocity follows a slightly different path from the fluidization curve.

Kroger et al. (1980) investigated the effects of particle density and size distribution on centrifugal fluidization. They reported that the pressure drop in the bed increases with the bed mass at the same airflow rate. Also, particle size does have an influence on the pressure drop in the packed state, but in fully fluidized region, the pressure drop is independent of the particle size. When there is a size distribution of the particles in the bed, smaller particles are fluidized first while the larger particles are fluidized at a higher radial flow rate and at the outer radius of the bed. The width of the size distribution has negligible influence in the fully packed and fluidized states. However, the transition region from packed to fluidized state is strongly influenced by the width of the size distribution.

The fluidizing fluid also influences the pressure drop. When a denser fluid is used, the pressure drop decreases in both the packed and fluidized states and when a less dense fluid is used, the pressure drop increases. When the bed is packed and partially fluidized, the pressure drop is directly proportional to the viscosity of the fluidizing air. Thus, more viscous fluidizing air would give greater pressure drops. However, viscosity of the fluidizing air has no effect on the pressure drop across the bed once the bed is completely fluidized.

#### **3.3** Inter-Particle Forces between Fine Particles

Geldart Group C powders are very fine and cohesive. They exhibit adhesion between particles and any surface in contact with them, and have the tendency to form channels and rise like a plug when fluidized. A bed of cohesive powders tends to channel at low superficial velocity, but can be disrupted to form agglomerates at a higher superficial gas velocity. Sugihara (1966) found that fine particles can be fluidized as agglomerates, and this is termed agglomerating fluidization. The forces acting between these fine particles are primarily van der Waals forces, intermolecular and surface forces. Group C powders are apt to agglomerate because of these very strong inter-particle forces.

The properties of bulk powders, e.g., during mixing, powder flow, drug delivery, compaction, granulation, etc. are governed by the nature and the degree of interaction between particles and between particles and surfaces. The major mechanisms of these interactions are adhesion and friction. Adhesion between particles and between particles and surfaces is due to the forces that exist between them. Depending on the conditions that exist between two surfaces in contact, adhesion can be classified into dry, boundary, static and dynamic adhesion. Dry adhesion exists between surfaces that completely exclude adsorption and capillary condensation in the contact zone. If the contact zone is so narrow that the properties of the contact surface differ from the properties of the entire surface, then the adhesion that occurs in that narrow contact zone is termed as boundary adhesion. Static adhesion is measured by applying the minimum force required for detachment at an infinitely slow rate, while dynamic adhesion is determined by applying a detachment force at a finite rate [Fridrun, 1998]. Adhesion occurring between particles and surfaces of the same nature is termed as cohesion. With respect to single particle

interactions, the term cohesion is applicable only when the particles are as close as an atomic distance between each other. Friction is the force preventing the tangential displacement of two solid or particle surfaces in contact.

### 3.3.1 Forces Causing Adhesion of Particles to Particles or Surfaces

Adhesion between particles and between particles and surfaces are primarily due to van der Waals Forces, capillary forces, electrical forces and electrostatic coulomb forces. They usually arise because of the interactions between dipole-dipole, charge-dipole, charge-charge, covalent, charge-non-polar, dipolar-non-polar, non-polar-non-polar and also hydrogen bonding [Seville et al. 1997].

# van der Waals Forces:

The long-range interaction between molecules, collectively know as van der Waals forces consists of three types of forces, Debye-induction force, Keesom-orientation force and dispersion force. Debye-induction forces usually exist between dipole and non-polar molecules, Keesom-orientation forces between dipole-dipole, and dispersion forces between two non-polar molecules. A dipolar molecule can induce an electric dipole in apolar but polarizable molecules resulting in a Debye-induction force. When two polar molecules are in contact, they orient themselves so that negative pole of one faces the positive pole of the other, resulting in a Keesom-orientation force. Dispersion forces arise from the local polarizations produced in molecules by random fluctuations of electrons. When these dipoles interact, finite attractive forces are generated between the atoms called dispersion forces.

Van der Waals was the first to point out that the deviations from the ideal-gas law at high pressures could be explained by assuming that the molecules in the gas attract each other (Visser, 1989). London (1930, 1937) proposed that the force acting between two molecules varies inversely with the sixth power of distance d, between the centers of the molecules:

$$F_w = -\frac{3}{4}h\gamma_0 \frac{\alpha^2}{d^6}$$
(3.19)

where h is Plank's constant,  $\alpha$  is the polarizability and  $\gamma_0$  the characteristic frequency. However, his theory is not valid if the distance between the molecules is very close or if the distance is very large or more than 1nm.

Hamaker (1937) assumed that molecular interactions are additive and calculated the interaction energy between two semi-infinite solid bodies at a separation distance H by summarizing all the possible individual molecular interactions. He obtained an expression for the force per unit of surface area, P, given by (Visser, 1989):

$$P = \frac{A}{6\pi H^3} \tag{3.20}$$

where A is the Hamaker coefficient, a material property, that can be directly related to the molecular properties.

Lifshitz (1955, 1956) developed a macroscopic theory to circumvent Hamaker's assumption of the additivity of molecular interactions that explains the attractive forces in the range between 1 and 100nm, the range not covered by London's theory. The Lifshitz theory calculates the magnitude of forces from the bulk properties such as dielectric constants or refractive indices and surface properties like surface roughness, surface free energy, hardness, elasticity and also particle size and true area of contact. The Lifshitz

theory takes into account the natural fluctuations in the density electron cloud surrounding the nucleus of an atom, which leads to consistent fluctuation of the appearance of dipole moments and hence fluctuations of an electromagnetic field surrounding the atom. This electromagnetic field acts over a wide distance, and interacts with other electromagnetic fields and hence attractive forces between solid bodies beyond the London distance. For spherical particles, Lifshitz-van der Waals forces can be calculated for three cases of contact,

Two spheres:

$$F_{VdW} = \frac{\hbar \varpi}{16\pi z_0^2} R \tag{3.21}$$

Sphere and plane surface:

$$F_{VdW} = \frac{\hbar \sigma}{8\pi z_0^2} R \tag{3.22}$$

Two plane surfaces:

$$F_{\nu dW} = \frac{\hbar \varpi}{8\pi^2 z_0^3} \tag{3.23}$$

Here  $F_{vdW}$  is the Lifshitz-van der Waals force,  $\hbar \varpi$  is the Lifshitz-van der Waals constant, R is the particle radius, and  $z_0$  is the distance of separation between contiguous bodies. The Lifshitz-van der Waals constant is independent of the medium of separation of the two bodies and is related to the Hamaker coefficient by:

$$A = \frac{3}{4\pi}\hbar\varpi \tag{3.24}$$

According to Israelachvili (1992), the van der Waals force between two spherical particles of diameter  $d_1$  and  $d_2$  is given by:

$$F_{V} = \frac{A_{12}}{12\delta^{2}} \frac{d_{1}d_{2}}{d_{1} + d_{2}}$$
(3.25)

where  $\delta$  is the distance of separation between the centers of the two particles and A<sub>12</sub> is Hamaker constant or Lifshitz-van der Waals interaction coefficient obtained to a good approximation by taking the geometric mean of the individual coefficients A<sub>11</sub> and A<sub>22</sub>.

Kendall (1994a) proposed that van der Waals forces could be much greater than the gravitational force, depending on the particle size and roughness of the surfaces in contact. Under normal conditions, i.e., in the absence of a high-voltage field and at close distances between the contiguous bodies, van der Waals forces are about 10 times larger than electrical forces and at least 10 times larger than electrostatic image forces (Rumpf, 1977).

# Capillary Forces:

Capillary forces arise from the moisture in the gap between contiguous bodies that form liquid bridges to adhered surfaces. They are very important for powder flow. Moist powders usually exhibit poor flow properties, sticking to the walls of hoppers or other surfaces during powder handling. In the case of hydrophilic porous materials, moisture is trapped in the pores that build up liquid bridges to adhered surfaces. In some cases, moisture in the gap between contiguous bodies condenses, giving rise to capillary forces. Capillary forces due to moisture condensation depend on the geometry of the gap, properties of the materials in contact, surface free energy, wettability and surface roughness. Moisture starts condensing in the gap in air at a relative humidity of about 50% [Zimon 1982]. Also, above a relative humidity of 65% to 75%, capillary forces dominate the adhesion force.

According to Colbeck (1996), during contact, the liquid pressure is less than the air pressure, which results in a concave meniscus and a state of tension. Many theories are being developed to calculate the capillary forces acting between a spherical particle and a surface. When the liquid condenses between a sphere and a surface, the Laplace pressure developed due to the curved liquid surface pulls the sphere and the plane together. Fisher and Israelachvili (1981) proposed an equation to calculate the capillary force:

$$F_C = 4\pi\gamma_L(\cos\theta) + 4\pi R\gamma_{sl} \tag{3.26}$$

where  $\gamma_L$  is the surface tension of the condensed liquid [mNm<sup>-1</sup>], and  $\gamma_{sl}$  is the solidliquid interfacial free energy [mJm<sup>-2</sup>], R is the radius of the adhered sphere;  $\theta$  is the contact angle between the adhered particle and the liquid. Colbeck (1997) proved that capillary forces are proportional to the product of the wetted area of surfaces and the tension arising from the liquid pressure. Consequently, there will be a maximum capillary force at an intermediate value of the liquid tension, which is the quotient between surface tension and the radius of curvature of the liquid meniscus.

## Electrostatic Image Forces (Coulomb forces):

Rumpf (1977) found that when non-conductors come into adhesion contact, the excess charges give rise to electrostatic image forces. The interaction force between a spherical particle of radius R, having a particle charge Q, interacting with an adjacent uncharged particle at a separation distance H due to its own image charge, is given by the Coulomb equation (Bailey, 1984)

$$F_{EI} = \frac{Q^2 \left[ 1 - \frac{H}{\left(R^2 + H^2\right)^{1/2}} \right]}{16\pi\varepsilon_0 H^2}$$
(3.27)

where  $\varepsilon$  is the permittivity of vacuum.

# Electrical Forces:

When two particles or a particle and surface are in contact, the difference in contact potential results in electrical forces. When the two surfaces are in air or vacuum, and if moisture is present in the gap between them, then electrical forces do not arise. However, when the particles come into contact in the presence of a liquid medium like suspensions or emulsions, electrical forces are very important for the stability of such systems [Fridrun, 1998]. The charge density of the electrical double layer and the true area of contact are used to calculate the electrical forces:

$$F_e = 2\pi \sigma_A^2 A \tag{3.28}$$

where  $\sigma_{A}$  [c] is charge density and A [m<sup>2</sup>] is the true area of contact.

# **3.3.2 Factors Influencing Adhesion of Particles to Particles or Surfaces**

There are four main factors influencing adhesion namely: surface roughness, particle size and shape, material hardness and elasticity and the work of adhesion and surface free energy. Surface roughness is one of the most important mechanisms influencing adhesion because it is strongly related to the geometry of contact. Johnson (1976) proposed that when two particles or a particle and surface contact, real contact occurs only at the crests of the surface asperities where the contact pressure is very high.

Along with surface roughness, other factors like particle shape and particle size also influence adhesion. If the particle size is much larger than the distance between the asperities, then only few contacts will occur between the particle and the asperities. Thus, the contact area is proportional to the number of asperities, and increasing the particle size will increase the contact area. If the particle size is smaller than the distance between the asperities, the particles will be placed in the valley between asperities. This is called nesting and is depicted in the Figure 3.3 [Fridrun, 1998].



**Figure 3.3** Relationship between particle size and asperity size and spacing with respect to increase or decrease of the adhesion force.

Thus, surface roughness increases the adhesion because of the greater number of contacts and hence larger true area of contact. This effect is further promoted if the particles are needle shaped. The adhesion force is smallest for ideal spherical particles and largest for cubical shaped particles [Fidrun, 1998]. However, spheres will exhibit the strongest adhesion when protuberances are present on the surface such as adhered fine particles.

Since these strong inter-particle adhesion forces are greater than the drag force that the fluid exerts on the particle, Geldart Group C particles are very difficult to fluidize; the powder lifts as a plug in small diameter tubes, or channels with gas bypassing the bed, through large voids from the distributor to the bed surface.

#### 3.4 Fluidization of Group C Particles

Fluidization of fine particles is becoming an emerging field because of the rapidly growing applications of ultra fine particles in the industry. Qian et al., (2000) proposed a theoretical model for the transition between Group C and Group A particles in a centrifugal field. Group A particles can be fluidized individually, while Group C particles will tend to agglomerate due to the large inter-particle forces and can be fluidized only as agglomerates.

According to Horio (2001), in a conventional fluidized bed, when the bed is completely uniform without any voidage distribution, the maximum tensile strength in the bed appears at the bed bottom where the pressure due to the gas flow is a maximum. A slow increase in the air velocity produces a rupture at the bed bottom forming the whole bed into a plug. Thus, there is no possibility of fluidization. However, when the bed is broken into agglomerates, fluidization can take place. Qian's model predicts that certain Group C particles that cannot be fluidized individually in a conventional fluidized bed will behave as Group A particles under different gravitational forces and hence can be fluidized individually. In a rotating fluidized bed, every single particle in the bed is acted upon by the drag force, centrifugal and buoyancy force, and cohesive force.

# 3.4.1 Forces Acting in Rotating Fluidized Bed

# Drag Force:

Khan and Richardson (1990) have shown that if a particle is in a suspension of like particles supported by a fluid having a superficial flow velocity  $u_r$ , the drag force on a single particle in the suspension of voidage,  $\varepsilon$ , is  $\varepsilon^{-4.8}$  times that on a single isolated

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particle. This applies to both the Stoke's and Newton's law regions. If the particle is in the Newton's law region (Reynold's number, Re>500), the drag force is given by [Zhou et al., 1999] as:

$$F_{y} = 0.055\pi\rho_{f}d^{2}u_{r}^{2}\varepsilon^{-4.8}$$
(3.29)

where  $\rho_f$  is the fluid density. For the Stoke's law region (Re<0.2), the drag force is given as:

$$F_{v} = 3\pi\mu du_{r}\varepsilon^{-4.8} \tag{3.30}$$

For particles with Reynold's number in the range 0.2<Re<500, a complicated equation was proposed by Khan and Richardson (1990).

Centrifugal and Buoyancy Forces:

The centrifugal force  $W_g$  for a particle with diameter  $d_p$  and density  $\rho_p$  is:

$$W_g = \frac{\pi d_p^3}{6} \rho_p g \tag{3.31}$$

When the bed is in fluidized state, it has fluid-like behavior and the density of the bed is:

$$\rho_a = \varepsilon \rho_f + (1 - \varepsilon) \rho_p \tag{3.32}$$

The buoyancy force W<sub>b</sub> on a spherical particle is given by:

$$W_{b} = \frac{\pi d_{p}^{3}}{6} (\varepsilon \rho_{f} + (1 - \varepsilon) \rho_{p})g \qquad (3.33)$$

Thus, the effective weight of the particle or centrifugal-buoyant force is:

$$W_e(F_g) = W_g - W_b = \frac{\pi d_p^3}{6} (\rho_p - \rho_f) g\varepsilon$$
(3.34)

### Cohesive Force:

The van der Waals forces are the dominant inter-particle forces in the absence of capillary forces. They are described in detail in Section 3.3.1. The van der Waals force between two perfectly spherical and rigid particles of diameter  $d_1$  and  $d_2$  is expressed as

$$F_{V} = \frac{A_{12}}{12\delta^{2}} \frac{d_{1}d_{2}}{d_{1} + d_{2}}$$
(3.35)

Where  $A_{12}$  is Hamaker Constant and  $\delta$  is the distance of separation between the centers of the two particles.

## 3.4.2 Transition Equation Between Group A and Group C

For Group A particles at flow velocity  $u_m$  greater than minimum fluidization velocity,  $F_{d\epsilon} > W_e + F_c$ , and for Group C particles because of the high cohesive forces,  $F_{d\epsilon} < W_e + F_c$ .

The transition equation can be expressed as

$$F_{d\varepsilon} = W_e | u_{=} u_m + F_c | u_{=} u_m$$
(3.36)

Substituting equations for  $F_d$ ,  $W_e$  and  $F_c$ , and flow velocity  $u_m$  by the terminal velocity  $u_t$ , into Equation 3.36, the transition equation for Group A/C particles was obtained by Qian et al., (2000) as:

$$\frac{\pi d_p^3}{6} (\rho_p - \rho_f) g(\varepsilon^{-4.8} - \varepsilon) = \frac{Al}{24\delta^2}$$
(3.37)

The transition equation is sensitive to voidage. In rotating fluidized beds the voidage is smaller when compared to the voidage in conventional bed because of the centrifugal force, which tends to pack the particles closer (Mutsers et al., 1977). The g in Equation 3.37 refers to centrifugal acceleration. As the centrifugal acceleration is increased, the

boundary curve between Group C and Group A shifts to the left as shown in Figure 3.4. However, at very high centrifugal acceleration, the particles can behave as Group D making them very difficult to fluidize again. Thus, Qian et al., (2000) showed that it should be possible to fluidize certain Group C particles without agglomeration in a centrifugal field depending on the value of the centrifugal acceleration.



Figure 3.4 Group A/C transition for fluidization by air at different centrifugal accelerations.

#### CHAPTER 4

### EXPERIMENTAL SETUP AND PROCEDURE

The objective of this study is to investigate the practicability of using a rotating fluidized bed for dry coating and binderless granulation. The experimental setup and procedure followed for coating and granulation is described in detail in the following sections.

## 4.1 Rotating Fluidized Bed Coater

# 4.1.1 Setup

The rotating fluidized bed coater (RFBC) consists of an outer chamber that acts as plenum, a fluid inlet into the plenum, a shaft that supports the distributor and rotates the distributor at the desired speed, a motor that rotates the shaft and hence the distributor, a manometer that measure the pressure drop between plenum chamber and the freeboard, a cylindrical distributor, flowmeters that measure the air flow rate into the plenum and an exhaust connected to a hood. A schema of the RFBC is shown in Figure 4.1.

The plenum chamber of the RFBC is 15 cm in length and 11 cm in diameter. The distributor back plate, front plate and exhaust is made of acrylic, while the plenum is made of PVC. A sintered metal distributor with average pore size of 55  $\mu$ m is used in this research, and has the dimensions of 8.7 cm in length and 5.72 cm in diameter. It is mounted on the shaft inside the plenum chamber and rotated along the horizontal axis. A DC motor, whose speed varies from 0 to 2000 RPM, controls the speed of the distributor. Equation 4.1 gives the force experienced by powder particles inside the distributor due to the rotation.

$$F = ma = mr\omega^2 \tag{4.1}$$

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where a is the centrifugal acceleration,  $\omega$  is the angular velocity, m is the mass, r the radius of the distributor and g is the acceleration due to gravity.



Figure 4.1 Schema of the Rotating Fluidized Bed Coater (RFBC).

## 4.1.2 Procedure

For all the coating experiments, 30 g of the host sample are used and where the density of the host sample is relatively low, 20 g are used. Before any coating experiments are conducted, the minimum fluidization velocity  $U_{mf}$  of the host particles needs to be measured experimentally. The empty distributor is first mounted on the shaft and the motor is run at the desired speed. Allowing 2-3 minutes for the motor to attain the desired speed, the airflow is then slowly increased and the pressure drop across the distributor for various airflow rates is noted. The desired amount of host particles are then put into the distributor and the distributor is mounted on the shaft. The motor is adjusted to the

desired speed and run for about 2-3mins without any airflow. The centrifugal force throws the particles to the walls of the distributor, and forms a layer of almost constant thickness.

The airflow rate is then slowly increased and the air enters the distributor radially fluidizing the particles layer by layer as described in Chapter 3. The pressure drop across the bed for various flow rates is noted. Subtracting the pressure drop across the distributor without any powder present from the pressure drop across the distributor with the powder gives the pressure drop due to the powder layer. When this becomes constant, the minimum fluidization velocity at the desired RPM and for a given weight of the host particles is measured. The guest particles are then added to the host particles and fluidized at air velocities about 1.5  $U_{mf}$  to 2  $U_{mf}$ . The weight percent of guest particles to be used in the experiment is usually calculated based on the assumption of 100 % surface coverage of the host particles with a monolayer of the guest particles. The host and the guest particles are assumed to be spherical and all of the guest particles are of the same size. It is also assumed that the host particles do not deform during coating.

The number of guest particles N, required to coat one host particle with a continuous monolayer is given by the following expression [Ramlakhan, 2001]:

$$N = \frac{S_{d+D}}{S_d} = \frac{\pi (D+d)^2}{\frac{\pi d^2}{4}} = \frac{4(D+d)^2}{d^2}$$
(4.2)

where  $S_{D+d}$  is the surface area of the sphere with diameter D+d and  $S_d$  is the cross sectional area of the guest particle of diameter d. Using the value of the number ratio N, the mass ratio of the guest particles can be calculated as:

$$W(wt\%) = \frac{\left(N \times d^3 \times \rho_d\right)}{\left(\left(D^3 \times \rho_D\right) + \left(N \times d^3 \times \rho_d\right)\right)} \times 100$$
(4.3)

where  $\rho_d$  is the density of the host material and  $\rho_D$  is the density of the guest material. Thus, W (wt%) of the guest particles are added to the host particles and fluidized at a velocity up to 2 U<sub>mf</sub>.

When the air velocity is increased from  $U_{mf}$ , within the range of 1.5  $U_{mf}$  to 2  $U_{mf}$ , some of the powder may elutriate from the bed. The air velocity is set at the desired rate and the bed is allowed to fluidize at this velocity for about one hour. Then motor is then stopped and the powder particles are taken out and weighed to calculate the amount of the powder lost due to elutriation. The samples are then analyzed using FESEM and EDX to observe the change in the surface morphology and the extent of coating.

## 4.2 Rotating Fluidized Bed Granulator

## 4.2.1 Setup

The setup of rotating fluidized bed granulator (RFBG) is more complex because of the incorporation of the pressure swing mechanism into the fluidized bed. For granulation by pressure swing, the bed is fluidized in a forward air cycle and then compacted in a reverse air cycle [Nishii et al., 1993]. These cycles of short duration (1 – 15 seconds) are repeated again and again. PSG is discussed in more detail in Chapter 5. The RFBG consists of a plenum chamber, hollow shaft, motor, exhaust or freeboard connected to hood, manometer for pressure measurement, bank of rotameters and a venturi to measure the air flow rate, cylindrical distributor and a cylindrical metal filter. A microprocessor is used for adjusting the cycle time for the forward and reverse air cycles. There is an air inlet that allows the air to flow into the plenum chamber radially during the forward air

cycle and acts as an exhaust during the reverse air cycle. Solenoid valves control the direction of the airflow rate in the RFBG and a stroboscope measures the rotating speed. Rotary union is used to connect the air inlet for reverse air cycle and the rotating shaft. A schema of the RFBG is shown in Figure 4.2.

The plenum chamber of the RFBG is 25 cm in length and 15 cm in diameter. The distributor back plate, front plate and the plenum are made of acrylic. A sintered metal distributor with average pore size of 55  $\mu$ m and a woven metal distributor with average pore size of 20  $\mu$ m were used. These distributors are 15 cm in length and 10 cm in inner diameter. The distributor is mounted onto the hollow shaft inside the plenum chamber. The shaft is hollow and has 32 holes of 2 mm diameter drilled into it to facilitate the reverse airflow that compacts the bed. The motor has an AC Inverter manufactured by Motortronics, which has a numerical display that allows us to see the speed in RPM or hertz (frequency) and also to vary the rotating speed.

The speed of the motor can vary from 0 to 2000 RPM, generating a centrifugal acceleration many times larger than the gravitational acceleration. Equation 4.1 gives the force experienced by the particles due to rotation. The microprocessor consists of 3 time delays from Dayton, Inc. that can be used to set the time for the forward, reverse and delay cycles. Once these time delays are set, the microprocessor needs to be set for the total cycle time that includes the forward cycle, reverse cycle and the delay. Depending on the individual cycle time and the total cycle time, the solenoid valves that control the airflow direction are opened and shut accordingly.



Figure 4.2 Schema of the Rotating Fluidized Bed Granulator (RFBG).

Compressed air is used for fluidization and hence granulation. A bank of flowmeters and venturi from Dwyer Instruments and Tri-Flow Tech, Inc. controls the airflow rate. During the forward air cycle dry compressed air at 120 psi is used and for reverse air cycle dry compressed air at about 60 psi is used. The cylindrical metal filter and the inner side of the distributor are covered with Goretex<sup>TM</sup> cloth donated by T.L.Gore and Associates, with pore size of about 1-2  $\mu$ m to prevent the powder particles from elutriating and/or clogging the distributor. The cylindrical metal filter prevents elutriation of fines during fluidization and returns them to the bed during the reverse air pulse. Goretex<sup>TM</sup> cloth is glued at the edges onto the distributor and the metal filter. A metal mesh (No. 8 sieve) is then placed inside the distributor on the top of Goretex<sup>TM</sup> cloth. This is done to ensure that the filter cloth stays in place during fluidization.

### 4.2.2 Procedure

For granulation to take place, the bed must be fluidized. The procedure described in Section 4.1.2 for calculating the minimum fluidization velocity for a given powder and at a given RPM is used for RFBG as well. However the much more complicated RFBG needs some extra steps to be followed for measuring the minimum fluidization velocity  $U_{mf}$ . Before measuring the pressure drop across the empty distributor and the distributor with powder, the cylindrical metal filter needs to be mounted into the grove on the back plate of the distributor. Powder should be put into the gap between the metal mesh and the distributor. After the powder is loaded into the distributor, the distributor is carefully mounted onto the hollow shaft. Granulation experiments are conducted at velocities greater than the minimum fluidization velocity. The time delays for forward air, reverse air and delay cycle are usually set to 15 s, 1 s and 1 s. The microprocessor is then set for a total cycle time of 18 s (17 s + 1 s). During the forward air cycle, air flows through the inlet into the plenum, fluidizes the powder in the bed radially and goes out through the exhaust. After 15 s, the solenoid valves at the air inlet and exhaust that are open during the air flow close and the solenoid valves for the reverse air inlet and exit open. After 1 s of reverse air cycle the solenoid valves for the reverse air inlet and exit close and the solenoid valves at the air inlet and exit close and the solenoid valves at the air inlet and exit close and the solenoid valves at the air inlet and exit close and the solenoid valves at the air inlet and exit close and the solenoid valves at the air inlet and exit close and the solenoid valves at the air inlet and exit close and the solenoid valves at the air inlet and exit close and the solenoid valves at the air inlet and exit close and the solenoid valves at the air inlet and exit close and the solenoid valves at the air inlet and exhaust open. The delay time is set to 1 s to depressurize the RFBG. The cycles are allowed to continue till the desired number of cycles is completed. To bring the experiment to stop, the airflow needs to be closed first and then the motor is brought to a stop in order to avoid the particles from being blown away from the distributor.

#### **CHAPTER 5**

# **MECHANISM OF COATING AND GRANULATION**

The driving force behind both coating and granulation is the particle-particle interactions because of the collisions between particles inside the rotating fluidized bed. Timoshenko and Goodier (1970) elucidated the collision force experienced by two colliding spheres. They considered the central impact of two spheres with an approach velocity V. The relative displacement  $\alpha$  of the centers of two spheres at the instant of maximum compression is given by:

$$\alpha = \left[\frac{5V^2}{4nn_1}\right]^{2/5} \tag{5.1}$$

where n and  $n_1$  are :

$$n = \sqrt{\frac{8}{9\pi^2 (k_1 + k_2)^2} \frac{d_1 d_2}{d_1 + d_2}}$$
(5.2)

$$n_1 = \frac{m_1 + m_2}{m_1 m_2} \tag{5.3}$$

In the above equation  $m_1$  and  $m_2$  are the masses of the two colliding spheres.  $k_1$  and  $k_2$  are the k factor for spheres 1 and 2 given by:

$$k = \frac{1 - \upsilon^2}{\pi E} \tag{5.4}$$

where E is Young's Modulus and v is Poisson's ratio. The approach velocity V is given by:

$$V = \left(1.5P_s D_b r \omega^2 \varepsilon\right)^{1/2} \tag{5.5}$$

where  $D_b$  is the bubble diameter,  $\omega$  the angular velocity,  $\varepsilon$  the bed voidage and  $P_S$  is the average dimensionless particle pressure of a non-sticky system. Research on bubble diameters in rotating fluidized beds is not yet available, but since these beds are very shallow the value of the bubble diameter is assumed to be equal to the initial bubble diameter in conventional bubbling fluidized beds. The collision force is given by the following expression:

$$F_c = n\alpha^{3/2} \tag{5.6}$$

Once two particles have collided, whether adhesion will take place or not is determined by considering the model presented by Rogers and Reed (1984). Their model is based on an energy balance during the interaction between two spherical bodies or a sphere and plane surface. It is assumed that the impact is elastic-plastic, and the elastic yield limit is constant throughout the impact. If  $Q_I$  is the initial kinetic energy and  $Q_A$  is the adhesive energy due to attractive forces, the total energy involved in the impact is  $(Q_I + Q_A)$ . It is assumed that energy loss occurs only because of plastic deformation and that  $Q_A \ll Q_I$ . The energy criterion for a rebound of the sphere is then,

$$(Q_I - Q_P) > Q_A^1 \tag{5.7}$$

where  $Q_A^1$  is the adhesive energy after impaction. The initial kinetic energy  $Q_I$  is given by:

$$Q_I = \frac{1}{2}m_1 v^2$$
 (5.8)

where  $m_1$  is the mass of sphere and v is the impact velocity :

$$v = \sqrt{\frac{2*F_1*d}{m_2} + V^2}$$
(5.9)

Here  $F_I$  is the force of impact, V is the approach velocity and d is the annular distance of the other particle (around  $4A^0$ ). The van der Waals force of attraction acts in the direction in which the particle is moving and gives it an acceleration. Since the collision force is usually many times greater than the drag force, centrifugal force and van der Waals force, the velocity in the annulus region d is taken to be approach velocity of the particle. The force of impact  $F_I$  is the resultant force acting on the particle at the time of impact.

$$F_{I} = F_{y} + F_{v} - F_{g} \tag{5.10}$$

The energy loss due to plastic deformation is given by the following expression:

$$Q_{P} = \left(\frac{\left(2mv^{2} - \frac{1}{8}m\varphi^{2}\right)^{1/2} - \left(\frac{15}{8}m\varphi^{2}\right)^{1/2}}{2}\right)^{2}$$
(5.11)

where  $\varphi$  is the limiting elastic velocity given by:

$$\varphi = \left(\frac{2\pi}{3K}\right)^2 \left(\frac{2}{5\rho}\right)^{1/2} y^{5/2}$$
(5.12)

and  $\rho$  is the density of the impacting particle and K is:

$$K = \frac{4}{\left[3\pi(k_1 + k_2)\right]}$$
(5.13)

Here  $k_i = \frac{(1 - \gamma_i^2)}{\pi E_i}$ . v<sub>I</sub> is Poisson's ratio and E<sub>i</sub> is Young's modulus of the colliding sphere

i. Johnson et al., (1971) presented a theoretical description of the adhesive forces acting between elastically deformable bodies. They proposed that the total adhesive energy  $Q_A^1$   $(U_T)$  is composed of mechanical energy  $U_M$  and surface energy  $U_S$ . The two energy components are given by the following expressions:

$$U_{M} = P_{0} \frac{\left(P_{1}^{2/3} + 2P_{0}P_{1}^{-1/3}\right)}{3K^{2/3}R_{C}^{1/3}}$$
(5.14)

$$U_{s} = \Delta \gamma \pi \left(\frac{R_{c} P_{1}}{K}\right)^{2/3}$$
(5.15)

where  $P_0$  is the external force applied to the contacting bodies and  $P_1$  is defined as:

$$P_{1} = P_{0} + 3\Delta\gamma\pi R_{C} + \left[ \left( P_{0} + 3\Delta\gamma\pi R_{C} \right)^{2} - P_{0}^{2} \right]^{1/2}$$
(5.16)

 $\Delta \gamma$  is the surface energy per unit area of contact and R<sub>C</sub> is the contact geometry parameter defined as  $\frac{1}{R_C} = \frac{1}{R_1} + \frac{1}{R_2}$ .

#### 5.1 Coating

It is shown that particle-particle collisions are the driving force behind dry particle coating, which involves adhesion of sub micron sized particles onto the surface of larger micron sized host particles. Guest particles, which are usually sub-micron are Group C particles and exist as agglomerates. These agglomerates collide with the bigger host particles, adhere, and distribute themselves on the surface of the host particles. When two host particles collide, the guest particles on their surfaces may redistribute. Two guest agglomerates may also collide and form larger agglomerate. If the forces in the bed are strong enough, these agglomerates will be broken and subsequently distributed on the host particles. However, if the forces in the bed are not strong enough, then some agglomerates of guest particles might exist in the bed even after coating. These various

interactions governed by the equations described previously are depicted in the Figure 5.1.



**Figure 5.1** Particle-Particle Collisions in RFBC (A) Collisions between host and guest (B) collisions between two host particles (C) Collisions between two guest particles.

### 5.2 Granulation

Unlike coating experiments where host and guest particles of different particle size and properties are present, in granulation experiments all the particles have the same properties although a particle size distribution is present. In this work, powders are granulated using the pressure swing technology invented by Nishii et al., (1993). In pressure swing granulation (PSG) particles are granulated by cyclic fluidization and downward gas flow compaction as shown in Figure 5.2.









The powder is densified during the compaction cycle and agglomerated into spherical granules in the fluidization cycle. Weak agglomerates are attrited during the fluidization and compaction cycle. Alternate fluidization and compaction cycles convert the powder into granules of relatively spherical shape and uniform size. During the compaction period entrained fines are returned to the bed and the metal filter is cleaned (Nishii et al., 1993). Granule formation is more intensive during the initial phases of the process. There are various mechanisms by which the granules are formed. Rumpf (1958) proposed that there are two major mechanisms for particle buildup. They are particle agglomeration and particle layering and are shown schematically in Figure 5.3 (Kiran, L. Kadam, 1991).





In the pressure swing granulation (PSG) technique, both particle agglomeration and particle layering are major mechanisms driving granulation. Granules are assumed to be shaped into spheres during fluidization because of bubble motion. Particle interaction either by agglomeration or layering is due to collisions and whether they adhere, or not, is governed by the Equation 4.10.

#### CHAPTER 6

# MATHEMATICAL MODELING OF DRY PARTICLE GRANULATION USING POPULATION BALANCES

Dry particle granulation in rotating fluidized beds is a technique for producing engineered particulates. Granulation results are discussed in Chapter 7. In this chapter, theoretical concepts to model granulation in rotating fluidized beds with population balances is presented. Section 6.1 talks about the mechanism by which granules are formed by pressure swing granulation in fluidized beds. In Section 6.2, population balance equations are discussed.

# 6.1 Granulation Mechanism

The mechanism by which granules are formed due to pressure swing in fluidized beds is a very interesting topic. Horio et al., (1999), have discussed granulation mechanism and quantified their results with I-H model (Iwadate et al., 1999). They have observed the internal structure of the granules formed by pressure swing granulation (PSG) by breaking the agglomerates into two hemispherical parts by needle insertion. The I-H model predicts the equilibrium granule size by equating the hydrodynamic expansion force to the cohesive rupture force between the two agglomerates. The various models developed till now to predict the equilibrium agglomerate size in fluidized beds is shown in the Figure 6.1 (Iwadate et al., 1999).

In I-H model, they have assumed that the bed consists of spherical agglomerates of uniform size and voidage. This assumption is not accurate because of the presence of size distribution of the granules throughout the granulation process as illustrated in

Model External force/energy Cohesion force/energy Comments FGa Fep FGa = Fpp 1 No bubble T da hydrodynamic Aeffects included Force balance van der Waals force gravity force#drag force between primary particles No bubble Etatal=(Ekin+Etam) Esolit V TEL hydrodynamic Etotai=(Ekin+Elam) Eluminar =37010-00 effects included. hwi1-Ea)da2 =Espiri Escala 2 carl. If 3µumt < hw(1-Ea)  $E_{\text{termin}} = m U_{\text{curr}}^2/2$ Etotal /132x6doca). Energy balance energy required to laminar shear + kinetic force negative dals break an aggiomerate obtained. O'expansion Feature Jeip = - Ps Feep = Foot,rup Bed expansion force caused by tada(1-Ea) 3 bubbles is 245 equated with Force balance cohesive rupture force. bed expansion force cohesive rupture force

Chapter 7. The particle size distribution of the initial powder indicates the presence of lot of fines. Iwadate et al., (1998) have reported that during the initial phases of granulation.

**Figure 6.1** Models for Agglomerate Size Prediction (Iwadate et al., 1999) (1) Chaouki et al (1985) (2) Morooka et al., (1988) (3) Iwadate (1999)

these fines and the natural agglomerates present in the powder coalesce to form granules. These granules formed during the initial phases of granulation act as core and become denser by the accumulation of fines on their surface. While some granules are formed by this mechanism, remaining granules are formed by coalescence of smaller granules. In either case, granules are shaped into spheres by attrition during tumbling. Thus, nucleation, coalescence, growth and breakage can be viewed as the various granulation regimes in rotating fluidized bed granulator. Nucleation regime is assumed to take place during the very initial phases of granulation followed by coalescence regime. As time proceeds, coalescence is accompanied by growth. Once the granules are big enough, breakage takes place simultaneously to maintain an equilibrium size of the granules.

Experimental evidence of these mechanisms is discussed in Chapter 7. It will be shown that there is a granule size distribution present in the granulator at all times. Hence, a model that takes into consideration these particle size distributions (PSD) is developed with the aid of population balance equations.

### **6.2 Population Balance Equations**

Population balance equations (PBE) take as known the dependence of particle coalescence, nucleation and growth on the particle environment, and incorporate this dependence into differential equations, showing how such quantities as average particle size vary with position in the processing unit being analyzed. PBE is a statement of continuity relating particle size distributions (PSD) to underlying rate processes such as the rates of growth and aggregation. These differential equations can then be placed along side corresponding differential equations in bulk velocity, composition etc and the overall set of equations viewed as a mathematical characterization of the processing system (Hulburt and Katz, 1964). In words PBE can be written as:

Accumulation = Nucleation + Growth + Aggregation + Breakage

For each particle, a phase space is defined whose coordinates specify the location of the particle as well as its quality. Equations of motion, in the form of ordinary differential equations are then developed showing how these phase coordinates change with time. From these ordinary differential equations, partial differential equations for the number density in the phase space are developed. The phase coordinates can be separated into a set of external coordinates which specify the location of the particle in the processing unit and a set of internal coordinates which specify the particle size and other aspects of particle quality. Number density of particles in the phase space as a whole defines the particle distribution over the internal coordinates with external coordinates appearing as parameters (Hulburt and Katz, 1964).

The population balance equation for a well mixed batch system of constant volume is given by Randolph and Larson (1971) as:

$$\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial v} = B - D \tag{6.1}$$

This is the particle-number continuity equation over a fixed sub region of particle phase space. Here, n is the number-density function defined by Equation 6.2 and G is the growth rate defined by Equation 6.3. B is the birth rate and D is the death rate described by the various granulation regimes.

$$n = \frac{dN}{dv} \tag{6.2}$$

$$G = \frac{dv}{dt} \tag{6.3}$$

where N is number of particles per unit volume and v is particle volume.

# Assumptions:

The following assumptions are made for the development of PBE for rotating fluidized bed granulator.

- 1. Only binary collisions occur
- 2. Particles are spherical
- 3. Collisions are both elastic and plastic
- 4. Total volume of two agglomerating particles is conserved
- 5. Growth, coalescence and breakage take place by successful collisions of particles.
- 6. Growth rate is independent of particle size

Each collision is binary in nature. Collisions, which involve three or more particles, can be reduced as set of binary collisions. Observation of granules at various stages of granulation indicates that granules are more or less spherical. Hence the assumption that particles are spherical is valid. When two particles collide, they form new particle(s). Dissolution of particles does not take place. To reduce the complexity of the problem, one or more of these granulation regimes can be assumed to be negligible. The rate processes of nucleation, growth, coalescence and breakage processes are described in detail in the following subsection.

## Rate Processes

*Nucleation:* Nucleation is the process by which new particles are formed from matter that is considered to be non-particulate. In fields such as granulation, it is allowed that the very fine primary powder is not, in fact particulate, and grains of this powder must clump together, i.e. nucleate, before they can be reckoned particulate (Hounslow, 1998). It is assumed that new granule formation is because of the nucleation of non-particulate matter during the initial phases of granulation. This is also proved by the rapid reduction of the bed height during the initial phases of granulation. The rate of nucleation  $B^0$  is the rate of appearance of new particles per unit volume. Nucleation term can be simplified by splitting into two factors, one depending on the particle environment and the other depending on the size distribution as shown in Equation 6.4 (Hounslow, 1998).

$$-r_{N} = B^{0} f_{N}(v,t)$$
(6.4)

 $f_N(v,t)$  is the probability density in the sizes of the newly nucleated particles. If we assume that all non-particulates will nucleate at the same size  $v_0$ , then  $f_N(v,t) = \delta(v-v_0)$
where  $\delta$  is the Dirac delta function. Thus, the appropriate term for inclusion in the PBE is:

$$-r_N = B^0 \delta(v - v_0) \tag{6.5}$$

*Growth:* Growth is the process by which non-particulate matter become incorporated within a particle. Since particulate matter is available in small amounts when compared to the non-particulate matter, growth is necessarily a differential process (Hounslow, 1998). Thus, growth rate is the rate of change of size of a particle as described in Equation 6.6.

$$G(v,t) = \frac{dv}{dt} \tag{6.6}$$

Since growth is assumed to take place due to collisions between particles, when a non-particulate matter collides with a particle of considerable size collision is seen as between the non-particulate matter and the individual non-particulate matter comprising the particle instead of a particle of size v. hence, the linear growth rate is independent of particle size.

*Coalescence / Aggregation:* Coalescence is the process in which new large particles are formed by combination of smaller particles. Random coalescence is considered when successful collisions are independent of the size of particles that collide. Nonrandom coalescence is considered when successful collisions are dependent of particle sizes. Since binary collisions are only considered, aggregation involves only two particles. The rate of aggregation per unit volume, for particles of type 1 and 2 is given by Hounslow (1998) as:

$$r_{1,2} = \beta(v_1, v_2, t) N_1 N_2 \tag{6.7}$$

Hulbert and Katz (1964), Hounslow et al., (1988) and Litster et al., (1995) have developed equations for birth and death rates for aggregation alone in a batch vessel. While Hulbert and Katz (1964) assumed only one interaction for birth and death rates, Hounslow et al., (1988) assumed two interactions each for birth and death rates and Litster et al., (1995) assumed q interactions each for birth and death rates where value of  $q \ge 1$ . These interactions will be discussed in detail in Section 6.3.

*Breakage*: Breakage is the mechanism that reduces size of a particle producing smaller particles. Description of rate of breakage requires the definition of two functions: the selection rate constant S(v,t) with units s<sup>-1</sup> and a breakage function,  $b(v_1,v_2,t)$  (Hounslow, 1998). S is termed specific rate of breakage and is the rate constant for the selection of particles. The breakage function b, gives the distribution of the smaller particles formed when the bigger particle is broken. Thus, the rate of breakage may be written as:

$$-r(v,t) = \int_{0}^{\infty} S(\varepsilon,t)b(v,\varepsilon,t)n(\varepsilon,t)d\varepsilon - S(v,t)n(v,t)$$
(6.8)

Since in the present study particle volume is the internal coordinate, it is necessary that volume be conserved as shown in expression 6.9.

$$\int \varepsilon b(\varepsilon, v, t) d\varepsilon = v \tag{6.9}$$

Breakage function b can have different forms corresponding to certain kinds of limiting behavior. For attrition, in which a single small particle of volume  $v_0$  is broken off a bigger particle has:

$$b(v_0,\varepsilon,t) = \delta(v-v_0) + \delta(v-\varepsilon+v_0)$$
(6.10)

For uniform fragmentation where the bigger particle is broken entirely into small particles of size  $v_0$  had:

$$b(v_0,\varepsilon,t) = \frac{\varepsilon}{v} \delta(v - v_0)$$
(6.11)

## **6.3 Discretized Population Balance Equations**

Substituting the rate of aggregation, rate of breakage, growth rate and nucleation rate for birth and death rates in the PBE yields integro partial differential equations. The direct solution of these equations by use of conventional finite differential techniques is complicated by the presence of the integral terms and results in a computational load far greater than desirable. Application of initial conditions and auxiliary equations to the population balance results in a set of integro-partial-differential equations of mixed dimensions. The PBE can be transformed that will average the distribution with regard to the internal coordinate properties and reduce the dimensionality to that of the transport equations. This closed set, with appropriate side conditions can be thought of as a complete mathematical representation of particulate systems. The jth moment of the distribution is defined as:

$$m_j = \int_0^\infty n(v) v^j dv \tag{6.12}$$

The first four moments are related to total number, length, area and volume of particles per unit volume by:

$$N_T = m_0$$
 (6.13a)

$$L_{\rm T} = k_{\rm L} m_1 \tag{6.13b}$$

$$A_{\rm T} = k_{\rm A} m_2 \tag{6.13c}$$

$$V_{\rm T} = k_{\rm v} m_3 \tag{6.13d}$$

The values of the shape factors  $k_I$ ,  $k_A$ ,  $k_v$  depend on the shape of the particles and the type of the particle analyzer being used. Discretizing the internal coordinates and assuming that the particle-size distribution (PSD) function is constant within each of these intervals yields a system of ordinary differential equations called discretized population balance (DPB) that can be solved easily. In discrete form, Equation 6.12 can be rewritten in a discrete form:

$$m_j = \sum_i \overline{v}_i^j N_i \tag{6.14}$$

The DPB vary in the choice of discretization (linear, geometric, arbitrary). Batterham et al., (1981) have assumed linear discretization of the particle size domain as  $v_{i+1}-v_i = \text{constant}$ . Hounslow et al., (1988) considered a fixed geometric discretization as  $v_{i+1}-v_i = 2$ . Litster et al., (1995) considered an adjustable geometric discretization of form  $v_{i+1}/v_i = 2^{1/q}$ , where q is an integer greater than or equal to one. DPB are developed for aggregation, growth and nucleation, breakage separately and then combined to solve to obtain the PSD.

## **Case I: Aggregation**

For aggregation only in a batch vessel, the population balance is of the form:

$$\frac{dn(v)}{dt} = B(v) - D(v) \tag{6.15}$$

Litster et al., (1995) proposed five types of interactions that change the number of particles to the  $i^{th}$  interval. The three that as particles to the  $i^{th}$  interval are:

Type 1: Some of the interactions give particles in the i<sup>th</sup> interval and some give particles smaller that the i<sup>th</sup> interval.

Type 2: All interactions give particles in the i<sup>th</sup> interval.

Type 3: Some interactions give particles in the i<sup>th</sup> interval and some give particles larger than the i<sup>th</sup> interval.

The two interactions that remove particles from the i<sup>th</sup> interval are:

Type 4: Some interactions remove particles from the i<sup>th</sup> interval

Type 5: All interactions remove particles from the i<sup>th</sup> interval

Figure 6.2 shows the discretization of the size domain schematically. Litster et al., (1995) elucidated in detail the interactions that change the number of particles in the i<sup>th</sup> interval for values of q from 1 to 4.



Figure 6.2 Discretization of Size Domain.

The DPB for aggregation alone derived by Litster et al., (1995) is shown in Equation 6.16 as:

$$\left(\frac{dN_{i}}{dt}\right)_{agg} = \sum_{j=1}^{i-S(q)-1} \beta_{i-1,j} N_{i-1} N_{j} \frac{2^{(j-i+1)/q}}{2^{1/q} - 1} + \sum_{k=2}^{q} \sum_{j=i-S(q-k+2)-k+1}^{i-S(q-k+1)-k} \beta_{i-k,j} N_{i-k} N_{j} \frac{2^{(j-i+1)/q} - 1 + 2^{-(k-1)/q}}{2^{1/q} - 1} + \frac{1}{2} \beta_{i-q,i-q} N_{i-q}^{2} + \sum_{k=2}^{q} \sum_{j=i-S(q-k+2)-k+2}^{i-S(q-k+1)-k+1} \beta_{i-k+1,j} N_{i-k+1} N_{j} \frac{-2^{(j-i)/q} - 2^{1/q} + 2^{-(k-1)/q}}{2^{1/q} - 1} - \sum_{j=i-S(q)+1}^{\infty} \beta_{i,j} N_{i} N_{j} \frac{2^{(j-i)/q}}{2^{1/q} - 1} - \sum_{j=i-S(q)+1}^{\infty} \beta_{i,j} N_{i} N_{j}$$
(6.16)

Equation 6.16 is tested for both size independent aggregation kernel  $\beta_0$  and size dependent aggregation kernel  $\beta_0(U+V)$  where U and V are the velocities of the colliding particles. This equation is now verified for constant aggregation kernel with change of zero moment and third moment as:

$$\frac{dm_0}{dt} = -\frac{1}{2}\beta_0 m_0^2$$

$$\frac{dm_3}{dt} = 0$$
(6.17)

## Case II: Growth and Nucleation

For size-independent growth and nucleation only in a batch vessel, the population balance is:

$$\frac{dn(v)}{dt} + G\frac{d(n(v))}{dt} = B_0\delta(L)$$
(6.18)

The DPB for size-independent growth and nucleation is given by Hounslow et al., (1988) and Litster et al., (1995) as:

$$\left(\frac{dN_i}{dt}\right)_{growth} = \frac{2G}{\left(2^{1/q} + 1\right)v_i} \left(\frac{2^{1/q}}{2^{2/q} - 1}N_{i-1} + N_i - \frac{2^{1/q}}{2^{2/q} - 1}N_{i+1}\right)$$
(6.19)

## Case III: Breakage

It is assumed that single breakage takes place at a time. Breakage function was developed by Gaudin-Meloy (1962) as:

$$B_{i,j} = 1 - \left(1 - \frac{d_i}{\bar{d}_j}\right)^{N_b}$$
(6.20)

The selection function is depicted in the Figure 6.3 and consists of three parts. The first part consists of a region where it is assumed that particles below a certain size,  $d_{low}^{s}$ , are not selected for breakage. The second part consists of a region where it is assumed that particles above a certain size d<sup>S</sup><sub>upp</sub> are all selected for breakage. For the intermediate part a smooth power type curve is used to represent the selection function. For the total range of particle sizes the selection function is given by:

$$S_{i} = \begin{cases} 1 & \overline{d}_{i} \geq d_{uyy}^{s} \\ 1 - \left[ \frac{d_{uyy}^{s} - \overline{d}_{i}}{d_{uyy}^{s} - d_{low}^{s}} \right]^{N_{i}} \\ 0 & \overline{d}_{i} \leq d_{low}^{s} \end{cases}$$

$$(6.21)$$

Substituting these selection and breakage functions, the DPB for breakage alone is:

$$\frac{dN_i}{dt} = \sum_{j=i+1}^{\infty} B_{i,j} 2^{1/q} S_j N_j - N_i S_i$$
(6.22)



Figure 6.3 Selection Function.

In order to solve these DPB for aggregation, growth and nucleation, breakage either individually or together, knowledge of kernels or rate constants is essential as they relate the particle environment such as process and material variables to the DPB. Taking into consideration coalescence alone, one of the most difficult tasks in the development of a population balance model for a coalescence model is the determination if the form and nature of the coalescence kernel. Due to the limited knowledge of the forces involved in the granulation process, the kernels available in the literature are only empirical and semi-empirical (Adetayo and Ennis, 2000). The granulation kernel can be divided into two parts (Adetayo et al., 1995):

$$\beta_{i,j} = \beta_0 \beta(v_i, v_j) \tag{6.23}$$

The coalescence rate constant  $\beta_0$  determines the rate of granulation and is a function of the granulator operating conditions such as rotating speed, cycle time etc. It controls the rate of change of mean of the granule size distribution and is usually determined from experimental data. The dependence of the granulation process on the particle size is described by  $\beta(v_i, v_j)$  which determines the shape of the granule size distribution. Ennis et al., (1991) investigated the forces involved in the collision of two spherical particles covered with layer of binder in order to understand the fundamental mechanism of granule formation. The viscous stokes number, St<sub>v</sub>, was defined as the ratio of the relative kinetic energy between the colliding particles to the viscous dissipation brought about by the pendular bond, and is given by:

$$St_{\nu} = \frac{8\rho_g \bar{r}V}{9\mu} \tag{6.24}$$

where V is the velocity of granule collision,  $\rho_g$  is the granule density,  $\bar{r}$  is the effective granule size and  $\mu$  is the viscosity of the binding fluid. The critical viscous Stokes number St<sup>\*</sup><sub>v</sub> for rebound of colliding particles to occur is:

$$St_{v}^{*} = \left(1 + \frac{1}{e}\right) \ln\left(\frac{h}{h_{a}}\right)$$
(6.25)

where e is the particle coefficient of restitution, h is thickness of the binder layer and  $h_a$  a measure of the granule's surface asperities. The three granulation regimes defined in terms of the magnitude of  $St_v$  in comparison to  $St_v^*$  are:

St<sub>v</sub> << St<sup>\*</sup><sub>v</sub> non-inertial regime (all collisions successful)

 $St_v \cong St_v^*$  inertial regime (some collisions successful)

 $St_v >> St_v^*$  coating regime (no collisions successful)

Cryer (1999) proposed a new empirical coalescence kernel for fluid-bed granulation with binder as:

$$\beta = \beta_0 \int_{-\infty}^{St} f(\phi, t) d\phi$$
(6.26)

where  $f(\phi,t)$  is the discrete probability density function for the Stokes number, and  $\beta_0$  is the constant determined from the experimental data. The critical Stokes number St<sup>\*</sup> is not a constant but varies within the experimental time frame as:

$$St^* = \alpha_1 \left( 1 + e^{t - \alpha^2} \right) \tag{6.27}$$

The coefficients  $\alpha_1$ ,  $\alpha_2$  and  $\beta_0$  are determined through comparison between model predictions and experimental observations.

The present model for dry granulation is proposed on similar lines. Rogers and Reed theory of particle adhesion undergoing an elastic-plastic impact with a surface described in greater detail in Chapter 5 will be considered to model the coalescence rate constant  $\beta(v_i, v_j)$ . According to their theory, particle adhesion would occur when  $(Q_I - Q_P) < Q_A$  and particle rebounds when  $(Q_I - Q_P) < Q_A$ , where  $Q_I$  is the impact energy,  $Q_P$ is the energy dissipated in plastic deformation and  $Q_A$  is the adhesive energy. Thus, if

$$Q = \left(\frac{Q_I - Q_P}{Q_A}\right)$$
, then the three granulation regimes could be defined as:

Q << Q<sup>\*</sup> (All collisions are successful)

 $Q \cong Q^*$  (some collisions are successful)

 $Q >> Q^*$  (No collisions are successful)

Where  $Q^*$  is the critical energy value. An empirical correlation for the coalescence rate constant  $\beta(v_i, v_j)$  as a function of  $Q^*$  and other factors that take into consideration the fluidized bed dynamics should be derived.

## **CHAPTER 7**

## **RESULTS AND DISCUSSION**

The practicability of using rotating fluidized bed as dry particle coater and dry granulator is tested using various host and guest systems. Coating results are presented in Section 7.1 of this chapter and granulation results are presented in Section 7.2. Efforts made to model the dynamics of rotating fluidized bed theoretically using population balances are presented in Section 7.3.

## 7.1 Coating Results

Coating experiments are conducted with various powder particles as hosts and guest particles and are summarized in Table 7.1.

Host Particles	Guest Particles
Glass Beads (~150µm)	Alumina (~1-2µm)
Glass Beads (~150µm)	Titania (0.25µm)
Glass Beads (~150µm)	SiC (0.5µm)
Microcrystalline Fibrous Cellulose (180µm)	Hydrophobic Fumed Silica (0.3µm)
Microcrystalline Fibrous Cellulose (180µm)	SiC (0.5µm)
Cornstarch (~14µm)	Hydrophobic Fumed Silica (0.3µm)

**Table 7.1**Host and Guest Particles

The physical properties of these host and guest particles are summarized in Table 7.2. For each system of host and guest particles the operating conditions and results are discussed

in this section. The experimental results are validated using the model proposed by Rogers and Reed (1984).

Properties	Glass Beads	Cellulose	Corn- starch	Alumina	Silica	Titania	SiC
Size (µm)	150	180	14	1-2	0.03	0.021	0.5
Density (Kg/m <sup>3</sup> )	1500	350	2500	3965	2200	3700	3200
Young's Modulus (GPa)	60/62	1.5		345	300		400
Poisson's Ratio	0.24	0.35		0.26	0.4		0.19
Dispersive Surface Energy (mJ/m <sup>2</sup> )	75	24		68	31		214
Yield Strength (MPa)	55	40		70			

**Table 7.2** Physical Properties of Host and Guest Particles

# 7.1.1 Microcrystalline Fibrous Cellulose

Avicel microcrystalline fibrous cellulose (grade PH-200) from FMC Corporation is used for coating experiments. The experimental operating conditions for this system of host and guest particles are specified in Tables 7.3 and 7.4. The minimum fluidization velocity of cellulose is found initially for the same weight of the host particles and at the same rotating speed at which the coating experiments is conducted. The pressure drop for the empty distributor and distributor with cellulose is noted with increasing air velocity and the difference in the pressure drops is plotted against the air velocity as shown in the Figure 7.1.



**Figure 7.1** Minimum Fluidization Velocity of Cellulose at 800RPM: Theoretical and Experimental Values.

The difference in theoretical and experimental pressure drop is about 33.67%. This could be due to many reasons. In theoretical calculations, particles are assumed to be spherical, voidage is calculated from bulk density as 0.47 at minimum fluidization, all the particles are taken to be of the same size, presence of fines is neglected, and that there is no loss of particles from the bed. Once the minimum fluidization velocity  $U_{mf}$  of cellulose is found, silica and silicon carbide guest particles whose weight% is

predetermined from Equation 4.3 are added to 15g of cellulose particles and coated at the operating conditions specified in Tables 7.3 and 7.4.

Operating Parameters	
Weight of Cellulose	15 g
Weight % of Hydrophobic Fumed Silica	1.33%
RPM	800
Air Velocity	1.8U <sub>mf</sub>
Coating Time	1hr
Weight % of Cellulose + Silica lost during fluidization	13%

 Table 7.3 Operating Conditions for Cellulose-Silica System

The SEM of uncoated fibrous cellulose and fibrous cellulose coated with hydrophobic fumed silica are shown in Figure 7.2. It can be observed from these pictures that very discrete coating has taken place.



Figure 7.2 Scanning Electron Micrographs of (A) Uncoated Cellulose (B) Cellulose coated with silica.

Operating Parameters	Value
Weight of Cellulose	15 g
Weight % of SiC	10%
RPM	800
Air Velocity	1.9U <sub>mf</sub>
Coating Time	1hr
Weight % of Cellulose + SiC lost during fluidization	13%

 Table 7.4
 Operating Conditions for Cellulose-Silicon Carbide (SiC) System



**Figure 7.3** Scanning Electron Micrographs of (A) Uncoated Cellulose (B) Cellulose coated with SiC.

The weight percent of SiC to be used is calculated from Equation 4.3. Thus, 10 wt% of SiC particles are mixed with 15g of cellulose and the mixture is then fluidized at 800RPM and 1.9U<sub>mf</sub> for one hour. After one hour, the powder is taken out and analyzed using SEM. It can be seen from the SEM pictures that good coating has taken place with SiC.

### 7.1.2 Glass Beads

Glass beads of about 150µm are used for the coating experiments. The minimum fluidization velocity of 30g glass beads at 600RPM and 800RPM calculated theoretically and experimental values are shown in the Figures 7.4 and 7.5.



**Figure 7.4** Minimum Fluidization Velocity of Glass Beads at 800RPM: Theoretical and Experimental Values.



**Figure 7.5** Minimum Fluidization Velocity for Glass Beads at 600RPM: Theoretical and Experimental Values.

The difference in theoretical and experimental pressure drop at 600RPM is about 27.51% and at 800RPM is about 43%. This could be due to the various reasons mentioned previously for the case of cellulose. Once the  $U_{mf}$  is found, Alumina, Titania and silicon carbide guest particles whose weight% is predetermined from Equation 4.3 are added to 30 g of glass beads and coated at the operating conditions specified in Tables 7.5-7.7. Titania guest particles obtained from Degussa Corporation (Grade P25) are of size 21 nm. Though the equation indicates that 0.2 wt% of titania is sufficient for 100% surface coverage, 1% titania is used because it was observed that during fluidization titania is elutriated from the bed at air velocities just above  $U_{mf}$ .

<b>Operating Parameters</b>	Value
Weight of Glass Beads	30 g
Weight % of Titania	1%
RPM	800
Air Velocity	1.5U <sub>mf</sub>
Coating Time	1hr
Weight % of Glass Beads + Titania lost during fluidization	2.6%

 Table 7.5
 Operating Parameters for Glass Beads – Titania system

Host and guest particles are then fluidized and coated at  $1.5U_{mf}$  for about an hour. After fluidization the particles are taken out and analyzed using SEM. Visual observation of the SEM indicate that good coating has taken place for glass beads with titania.



(A)



**Figure 7.6** Scanning Electron Micrographs of (A) Coated Glass Bead with Titania (B) Uncoated Glass Bead.

Fused aluminum oxide powder obtained from AEE, is used for coating glass beads. The operating conditions for glass beads and alumina system are shown in Table 7.6.

<b>Operating Parameters</b>	Value
Weight of Glass Beads	30 g
Weight % of Alumina	10%
RPM	600
Air Velocity	1.8U <sub>mf</sub>
Coating Time	1hr
Weight % of Glass Beads + Alumina lost during fluidization	5.6%

 Table 7.6 Operating Parameters for Glass beads–Alumina system

Coating of glass beads with alumina is conducted at superficial gas velocity of  $1.8U_{mf}$  for one hour. It is observed that after fluidization, alumina forms some

agglomerates apart from discrete coatings. The coating of glass beads is then analyzed using SEM-EDX. These pictures indicate that discrete coating has taken place. SiC used for coating glass beads is the same that was used to coat cellulose. The operating conditions used for this system is shown in the Table 7.7.



**Figure 7.7** Scanning Electron Micrographs of (A) Uncoated Glass bead (B) Coated glass bead with Alumina (C) Alumina EDX mapping.

Table 7.7	Operating	Parameters	for Glass	beads-SiC	system
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<b>Operating Parameters</b>	
Weight of Glass Beads	30 g
Weight % of SiC	5%
RPM	600
Air Velocity	2U <sub>mf</sub>
Coating Time	1 hr
Weight % of Glass Beads + SiC lost during fluidiza	tion 3.6%



**Figure 7.8** Scanning Electron Micrographs of (A) Uncoated glass bead (B) Glass bead coated with SiC.

After fluidization, it was observed that some SiC forms agglomerates, though there number of agglomerates is less when compared with the number of agglomerates formed while coating glass beads with alumina.

## 7.1.3 Analysis and Discussion

Coating results are analyzed using Rogers and Reed (1984) theory for elastic-plastic collisions described in Chapter 5. All the graphs illustrated in this section are generated from the program in Appendix. The limiting elastic velocity  $\varphi$  for plastic deformations to occur for various systems of host and guest particles is shown in Table 7.8. This velocity must be less than the impaction velocity V, which us assumed to be 1m/s.

Host-Guest System	φ (m/s)
Cellulose – Silica	0.116206
Cellulose-SiC	0.0962247
Glass Beads – SiC	0.0001768
Glass Beads – Alumina	0.0001643

**Table 7.8** Limiting Elastic Velocity φ for Various Host-Guest Systems

The limiting elastic velocity is function of the density of the guest particles and elastic yield limit(y) and Young's Modulus(E) of the host particles.  $\varphi$  is proportional to  $\frac{y^{2.5}}{E^2}$  of the host particles. Properties of cellulose and glass beads indicate that this value is smaller for glass beads making them more susceptible for deformation when compared to cellulose. Hence, limiting elastic velocity  $\varphi$  for glass beads is less than that of cellulose. Again,  $\varphi$  is inversely proportional to the density of the guest particles. Hence, denser guest particles require less limiting velocity to deform the host particles.

The initial kinetic energy  $Q_1$  of the guest particles is directly dependent on their mass, which is again dependent on the density and size of the particle. The  $Q_1$  for various guest particles of various sizes at an impaction velocity of 1m/s is depicted in the Figure 7.9. The energy expended in producing plastic deformation in the host particle at impaction velocity of 1m/s, as function of guest particle size is shown in Figures 7.10 and 7.11.



Figure 7.9 Initial kinetic energy Q<sub>1</sub> of guest particles as function of their size.





Figure 7.10 Energy expended to deform cellulose for various guest particles of different sizes. Guest Size (µm)



Figure 7.11 Energy expended to deform glass beads for various guest particles of different sizes.

The energy expended to deform host particles is mainly dependent on the size of the guest particles and hence on their kinetic energy Q<sub>1</sub>, and the deformability of the host

particles. From the Figures 7.10 and 7.11, we see that  $Q_P$  for alumina is greater than SiC, which is greater than silica. Also, for the same guest particle of SiC,  $Q_P$  for glass beads is less than that of cellulose because of the easy deformability of glass beads.

The total adhesion force is directly dependent on the dispersive surface energy,  $\Delta\gamma$ . Hence,  $Q_A$  for cellulose-SiC system is greater than that of cellulose-silica and is illustrated in the Figure 7.12.



Guest Size (µm)

Figure 7.12 Adhesion Energy for cellulose host particle and various guest particles.

For glass beads as host particles, the adhesion energy,  $Q_A$  with alumina and SiC as guest particles is shown in Figure 7.13. From this figure it is evident that SiC with higher dispersive surface energy than alumina has greater adhesion energy. Comparing the adhesion energies of cellulose and glass beads with the same guest particle of SiC from Figure 7.14, we can conclude that cellulose has greater adhesion energy. This is also confirmed from the experimental results. Figure 7.15 shows the SEM pictures of

cellulose and glass beads coated with SiC for one hour. 10 wt% SiC is used for cellulose and 5 wt% is used for glass beads, which are calculated from the Equation 4.3. It can be seen that cellulose has good coating compared with glass beads.







**Figure 7.14** Adhesion Energy for different host particles as function of particle size of guest particle SiC.



Figure 7.15 Surface coverage of (A) Cellulose with SiC and (B) Glass bead with SiC.

Figure 7.16 shows the rebound energy plotted against adhesion energy for glass beads and SiC. It can be seen from this figure that when SiC agglomerates are less than 70  $\mu$ m, adhesion energy is greater than rebound energy. However, when the SiC agglomerate size is greater than 70  $\mu$ m, adhesion energy is less than rebound energy. Hence, collisions of guest particles or agglomerates less than 70  $\mu$ m with the host particles lead to coating.

#### Guest Agglomerate Size (µm)



**Figure 7.16** Adhesion Energy Vs Rebound Energy for Glass beads-SiC for different sizes of guest particle agglomerates.



**Figure 7.17** Adhesion Energy Vs Rebound Energy for Cellulose-SiC system for different sizes of guest particle agglomerates.

Similar analysis with cellulose and SiC shows that for guest agglomerate size greater than 4.5  $\mu$ m, coating does not take place. For the system of glass beads and alumina, adhesion energy, Q<sub>A</sub> plotted against rebound energy Q<sub>I</sub> – Q<sub>P</sub> is illustrated in the Figure 7.18.



Figure 7.18 Adhesion Energy Vs Rebound Energy for glass beads-alumina system for different sizes of guest particle agglomerates.

It can be seen that when the guest agglomerate size is greater than 38  $\mu$ m, coating does not take place. Experimental observation shows that when alumina and SiC are used as guest particles, some of them form agglomerates. For alumina collisions between agglomerates of different sizes, the adhesion and rebound energies for various sizes of the agglomerates is plotted in the Figure 7.19.



**Figure 7.19**  $Q_A$  Vs  $Q_I$ - $Q_P$  between 5µm alumina agglomerate and alumina agglomerates of other sizes.

Thus, coating results are analyzed using Rogers and Reed (1984) theory for elasticplastic collisions.

#### 7.1.4 Cornstarch

Cornstarch is very commonly used in the food industry as a food-thickening agent and in pharmaceutical industry as an inactive compound (Watano et al., 1996). However, cornstarch is very cohesive and hydrophilic creating problems during handling, premature biodegradation, increased stickiness under humid conditions. Modifying the surface of silica by coating can reduce this. Cornstarch is coated with hydrophobic fumed silica. The minimum fluidization velocity,  $U_{mf}$  of cornstarch is found experimentally and is shown in the Figure 7.20. The operating conditions are listed in the Table 7.9.



**Figure 7.20** Experimental value of minimum fluidization velocity, U<sub>mf</sub> of cornstarch at 800RPM.

 Table 7.9
 Operating Parameters for Cornstarch-Fumed Silica system

<b>Operating Parameters</b>	Value
Weight of Cornstarch	20 g
Weight % of Fumed Silica	1-2%
RPM	800
Air Velocity	1.6U <sub>mf</sub>
Coating Time	1 hr
Weight % of Cornstarch + Fumed Silica lost during fluidization	20%

Coating experiment is conducted in the same procedure described for glass beads and cellulose. Results are then analyzed using SEM. The SEM pictures in Figure 7.21 show that very discrete coating of cornstarch with silica has taken place.



(A)

(B)

**Figure 7.21** (A) and (B) Scanning Electron Micrographs of cornstarch coated with silica.

Discrete coatings of cornstarch might be due to the very less percentage of silica used for coating and because of the high elutriation rate from the fluidized bed during coating. However, the flowability of cornstarch increased drastically even with such discrete coatings. Zinc oxide and titanium dioxide powders are used to study the practicability of using a rotating fluidized bed with pressure swing for granulation. The properties of the powders used for granulation are shown in the Table 7.10.

Property	ZnO	TiO <sub>2</sub>
Diameter (µm)	0.6	0.23
Density (Kg/m <sup>3</sup> )	5606	4100
Voidage	0.789	0.75

<b>Table 7.10</b>	Properties	of powders
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## 7.2.1 ZnO Granulation

Zinc oxide from Aldrich with a primary particle size of  $0.6\mu m$  is used for granulation purposes. Various experiments are conducted by varying the operating parameters. Though the primary particle size is  $0.6 \mu m$ , because of the cohesiveness of the powder, it exists as agglomerates. Hence the particle size distribution (PSD) of the initial powder should be measured using a dry method. A Beckman Coulter counter tornado LS13-320 is used to obtain the initial particle size distribution, which is shown in Figure 7.22. The median diameter of initially ZnO powder with some natural agglomerates is 18.8  $\mu m$ . Granulation of these powders is then performed in the RFBG at the operating conditions specified in Table 7.11



**Figure 7.22** Frequency size distribution of initial ZnO powder.

<b>Operating</b> Parameter	Value
Forward air cycle time	17s
Reverse air cycle time	1s
Delay between the two cycles	2s
Rotating Speed	500 RPM, 700RPM
Superficial airflow rate	1050 SCFH, 800SCFH
Weight of the sample	75g, 130g
Initial powder sieved through mesh No.	12, 140

**Table 7.11Operating conditions for ZnO granulation** 

Granulation experiments are conducted for 1-3hrs. After granulation, the powder is taken out and the size distribution of the granules greater than 106µm is analyzed. Two sets of experiments are conducted. In one set, initial ZnO powder is sieved through No. 12 mesh that allows the presence of some natural agglomerates prior to granulation. In the other set, initial ZnO powder is sieved through No. 140 mesh, which prevents the presence of any natural agglomerates greater than 106µm. Granulation results for these two sets of experiments are tabulated in the Table 7.12.

ZnO Granulation	Weight of the sample	Wt% of sample granulated
1hr – No.12 mesh	75g	78.56%
1hr – No. 140 mesh	130g	4.92%
2hr – No. 140 mesh	130g	7.92%
3hr – No. 140 mesh	130g	16.25%

**Table 7.12Results of ZnO granulation experiments** 

From these results it is evident that the presence of some initial granules enhances granulation. Also, as the granulation time is increased, wt% of ZnO granulated is almost doubled.

## 7.2.2 TiO<sub>2</sub> Granulation

Titania powders of primary particle size 0.23  $\mu$ m from DuPont, Ti-Pure R-104 is used for granulation. Since the particles are very cohesive, they exist as agglomerates. The size distribution of the initial powder, measured using the dry technique along with wet technique results from DuPont is shown in Figure 7.23. The Beckman Coulter counter with a dry powder module is used for the dry analysis of the particle size. This instrument can measure particles within a size range 0.375  $\mu$ m and 2000  $\mu$ m. The X-Ray centrifuge used for the wet technique can measure particles in the size range 10nm to 100 $\mu$ m. The median diameter for initial TiO<sub>2</sub> powder measured by the dry technique is 130.1  $\mu$ m. The large difference in the size distribution is because in X-Ray Centrifuge technique, the particles are suspended in a liquid medium, which causes the agglomerates to break and size of individual primary particles is measured. In Coulter Counter dry technique, the particles are suspended in the air, which allows agglomerates to be intact and measures

the size of agglomerates as well. The operating conditions for  $TiO_2$  granulation experiments are shown in the Table 7.13. The experiment time is varied and the size distribution of the granules is analyzed using standard sieves.



**Figure 7.23** Cumulative and frequency size distribution of initial TiO<sub>2</sub> measured from X-Ray Centrifuge (wet technique) and Coulter Counter (dry technique).

**Table 7.13**Operating conditions for TiO2 granulation

Operating Parameter	Value
Forward air cycle time	17s
Reverse air cycle time	1s
Delay between the two cycles	2s
Rotating Speed	700 RPM

Operating Parameter	Value
Superficial airflow rate	800 SCFH
Weight of the sample	150g, 130g
Initial powder sieved through mesh No.	12, 140

Granulation experiments are conducted for 1-3hrs. After granulation, the powder is taken out and the size distribution of the granules greater than  $106\mu$ m is analyzed. Two sets of experiments are conducted. In one set, initial TiO<sub>2</sub> powder is sieved through No. 12 mesh and in the other, initial TiO<sub>2</sub> powder is sieved through No. 140 mesh. Granulation results for these two sets of experiments are tabulated in the Table 7.14.

<b>TiO<sub>2</sub> Granulation</b>	Weight of the sample	Wt% of sample granulated
1hr – No.12 mesh	150g	89.65%
2hr – No.12 mesh	150g	96.07%
1hr – No. 140 mesh	130g	24.82%
2hr – No. 140 mesh	130g	33.55%
3hr – No. 140 mesh	130g	44.52%

**Table 7.14Results of TiO2 granulation experiments** 

From these results it is evident that the presence of some initial granules enhances granulation. Also, as the granulation time is increased, wt% of  $TiO_2$  granulated increases drastically.

### 7.2.3 Analysis and Discussion

Quantifying the granulation results by some theoretical model is yet another topic of this research. In this section a mechanism by which granules grow in the RFB is investigated using experimental results. A theoretical investigation of the growth mechanism using population balances is presented in Chapter 7. Figure 7.24 shows the SEM picture of the ZnO primary particles.



Figure 7.24 Scanning Electron Micrograph of ZnO primary particles.

The frequency size distribution of the initial ZnO powder shown in Figure 7.22 reveals the presence of lots of fines and weak natural agglomerates. As discussed in Chapter 6, it is proposed that there are four granulation regimes. During the initial phases of granulation, nucleation of the fines and coalescence of the weak natural agglomerates take place simultaneously to form initial granules. Coalescence and growth then take place, and are the major mechanisms by which these granules densify. Once the granules are big enough, forces in the fluidized bed break the bigger granules to maintain an equilibrium size of the granules. Thus, the size of the granules is a strong function of the bed operating conditions, which control the forces in the RFBG. Figure 7.25 shows the plot of weight of ZnO granules formed Vs oversize granule diameter for different granulation times. Figure 7.26 shows the plot of weight of TiO<sub>2</sub> granules formed Vs

oversize granule diameter for different granulation times. Granules greater than 106µm are considered for analysis.



**Figure 7.25** Weight of ZnO granules formed for different granulation times Vs oversize granule diameter with initial powder sieved through No. 140 mesh.



**Figure 7.26** Weight of  $TiO_2$  granules formed for different granulation times Vs oversize granule diameter with initial powder sieved through No. 140 mesh.
Under the same operating conditions of 700 RPM, 750SCFH and 130g sample, it is observed from Tables 7.12 and 7.14 that TiO<sub>2</sub> granulates well compared to ZnO. This could be because the particle size of TiO<sub>2</sub> is less than ZnO, more surface area is available for contact and hence more van der Waals forces are acting between the particles. It can be observed from Table 7.15, that for both ZnO and TiO<sub>2</sub> with initial powder sieved through No. 140 mesh, large number of granules exists in the size range 106µm-500µm and 710µm-1400µm. This could be due to the formation of many smaller granules from fines due to growth and nucleation, and coalescence of small granules, and formation of many compacts during compaction cycle, which are further shaped during fluidization.

Figure 7.27 shows the frequency size distribution of  $TiO_2$  after one to three hours of granulation and the frequency size distribution of ZnO after one to three hours of granulation. These distributions are prepared using Fritsch Particle Sizer Analysette 22, by extrapolating the granule size distribution data obtained from standard sieves.

	TiO <sub>2</sub>		ZnO	
	106µm- 500µm	710μm- 1400μm	106µm- 500µm	710μm- 1400μm
0hr Granulation- No. 140 Mesh	0%	0%	0%	0%
1hr Granulation- No. 140 Mesh	67.65%	22.86%	100%	0%
2hr Granulation- No. 140 Mesh	59.83%	30.93%	68.25%	20.73%
3hr Granulation- No. 140 Mesh	62.89%	30.17%	54.45%	37.13%

**Table 7.15** Weight percent of  $TiO_2$  and ZnO granules that lie in the size range 106 $\mu$ m-500 $\mu$ m and 710 $\mu$ m-1400 $\mu$ m



Figure 7.27 Frequency size distribution of TiO<sub>2</sub> and ZnO for 1-3 hours granulation.

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Figure 7.28 Scanning Electron Micrographs of ZnO granules.

Formation of many small granules due to nucleation and compaction is confirmed from the SEM of granules shown in Figure 7.27. Observation of the size distributions of TiO<sub>2</sub> from Figure 7.27 shows that as the granulation time increases, more and more fine particles nucleate and small granules coalesce to form bigger granules. With increasing granulation time, the frequency of fine particles decreases, and the frequency of bigger particles increases. Hence, growth and nucleation is one of the major mechanism by which granules are formed. SEM picture of TiO<sub>2</sub> granule in Figure 7.29 shows the growth of granules by layering of fines. Equation 6.19 as gives the discretized population balances (DPB) of particles due to growth and nucleation:

$$\left(\frac{dN_i}{dt}\right)_{growth} = \frac{2G}{\left(2^{1/q}+1\right)v_i} \left(\frac{2^{1/q}}{2^{2/q}-1}N_{i-1} + N_i - \frac{2^{1/q}}{2^{2/q}-1}N_{i+1}\right)$$
(6.19)

where G is the growth rate, and the term in the brackets gives the nucleation rate. Figure 7.28 shows the SEM of ZnO granules. Observation of these pictures confirms that some of the granules are formed by coalescence of very small granules. Equation 6.16 gives the discretized population balance (DPB) for aggregation alone. Thus, coalescence/ aggregation is the second major mechanism by which granules are formed. Formation of large particles in the size range 710 $\mu$ m-1400 $\mu$ m is assumed to be due to the formation of many compacts during the compaction cycle of pressure swing granulation. These compacts are assumed to be broken and shaped during fluidization cycle. Equation 6.22 gives the discretized population balance for breakage:

$$\frac{dN_i}{dt} = \sum_{j=i+1}^{\infty} B_{i,j} 2^{1/q} S_j N_j - N_i S_i$$
(6.22)

SEM of  $TiO_2$  and ZnO granules in Figure 7.30 confirm that the forces in the RFBG break the big granules and/or compacts to maintain an equilibrium size of the granules.





(b)

**Figure 7.29** Scanning Electron Micrographs of (a) ZnO granule (b) TiO<sub>2</sub> granule.







(b)



Also, it is observed that within the size range  $500\mu$ m- $710\mu$ m, there exists minimum number of granules. It is assumed that this behavior is due to the insufficient forces in the fluidized bed to allow the coalescence/ agglomeration of smaller granules to form bigger granules and also to break big granules/ compacts to form smaller granules. Putting together all the granulation regimes, the size distributions in Figure 7.27 can be described by the following DPB for i<sup>th</sup> size interval:

$$\begin{aligned} \frac{dN_{i}}{dt} &= \left\{ \frac{2G}{(2^{1/q}+1)v_{i}} \left( \frac{2^{1/q}}{2^{2/q}-1} N_{i-1} + N_{i} - \frac{2^{1/q}}{2^{2/q}-1} N_{i+1} \right) \right\} + \\ \left\{ \sum_{j=i+1}^{\infty} B_{i,j} 2^{1/q} S_{j} N_{j} - N_{i} S_{i} \right\} + \\ \begin{cases} \sum_{j=i+1}^{i-S(q)-1} \beta_{i-1,j} N_{i-1} N_{j} \frac{2^{(j-i+1)/q}}{2^{1/q}-1} \\ + \sum_{k=2}^{q} \sum_{j=i-S(q-k+1)-k}^{i-S(q-k+1)-k} \beta_{i-k,j} N_{i-k} N_{j} \frac{2^{(j-i+1)/q}-1+2^{-(k-1)/q}}{2^{1/q}-1} \\ + \frac{1}{2} \beta_{i-q,i-q} N_{i-q}^{2} + \sum_{k=2}^{q} \sum_{j=i-S(q-k+2)-k+2}^{i-S(q-k+1)-k+1} \beta_{i-k+1,j} N_{i-k+1} N_{j} \frac{-2^{(j-i)/q}-2^{1/q}+2^{-(k-1)/q}}{2^{1/q}-1} \\ - \sum_{j=1}^{i-S(q)} \beta_{i,j} N_{i} N_{j} \frac{2^{(j-i)/q}}{2^{1/q}-1} - \sum_{j=i-S(q)+1}^{\infty} \beta_{i,j} N_{i} N_{j} \end{cases} \end{aligned}$$

$$(7.1)$$

Further research needs to be done to relate the rate constants or kernels in the above equation to the fluidized bed dynamics, and solve the above equation to predict the granule size distribution.

#### CHAPTER 8

### **CONCLUSIONS AND RECOMMENDATIONS**

### 8.1 Conclusions

Dry particle coating for the synthesis of engineered particulates in rotating fluidized beds is demonstrated successfully. Rotating fluidized bed is a good coater for some host and guest systems while, for some systems of host and guest particles good coating could not be achieved. It is observed that for all the coating experiments, the experimental pressure drop is less than the theoretical pressure drops by 35% on an average. This could be due to many approximations made in the theoretical calculations like constant voidage, monodisperse particles, absence of elutriation etc. For some systems of host and guest particles, particle elutriation rate was very high which prevented from running the experiment at higher gas flow rates. Rogers and Reed (1984) theory for adhesion of particles undergoing elastic-plastic collisions is used to quantify the coating results. It is found that this theory predicts the coating results well. Since the guest particles used for coating are very fine and cohesive (Group C particles), some of these guest particles like SiC and alumina are observed to agglomerate and form small spherical granules during the coating process. RFBC may be a good device to coat cornstarch with silica. The flowability of cornstarch improved after the experiment, even though only 1 wt% of silica is used for coating.

Dry granulation of cohesive powders in rotating fluidized beds with the aid of pressure swing is tested successfully in the case of ZnO and Titania powders. It has been observed than with the increase of granulation time, denser granules with a more narrow

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size distribution are obtained. The forces in the RFBG involved in shaping the granules are complex and tough to understand. However, observation of the product granules confirms the existence of various granulation regimes like nucleation, coalescence, growth and breakage. Theoretical modeling of granulation is attempted using population balance equations. More experimental results are required to propose and test a new coalescence kernel for dry granulation in rotating fluidized beds. On account of the poor design and complexity of the RFBG, an extensive study of dry coating could not be achieved.

#### 8.2 **Recommendations**

The operating parameters like rotating speed, superficial air velocity, weight% of the guest particles, processing time can be varied for each of the host and guest system discussed in this thesis and results need to be analyzed for optimal operating conditions. Rogers and Reed theory for adhesion of particles undergoing elastic-plastic collisions should be extended to include the fluidized bed dynamics.

More studies on PSG with a variety of powders need to be done. Also, the operating parameters like the reverse air pressure, cycle times, rotating speed etc should be varied and results be compared for optimal conditions. The RFBG design needs to be improved for many reasons. The outer chamber of the RFBG is opaque and it prevents us from observing the fluidization phenomena, taking place in the bed. The distributor is mounted on one end of the shaft, which makes the shaft to wobble due to the load imbalance. The distributor was designed with its length greater than the diameter. Due to the small diameter and large length of the distributor, the rotating speed needs to be

increased many times in order to achieve greater centrifugal forces. Also, the surface area of the distributor is very large because of its large length, which requires very high airflow rates to attain reasonable superficial gas velocity in the fluidized bed.

All these problems can be overcome by having a distributor with large diameter and shorter length. This will also allow for a greater bed thickness with the same amount of powder used for the present experiments. While conducting the experiments it is observed that the microprocessor skips the forward air or reverse air cycles sometimes. To prevent this, the microprocessor that controls these cycles needs to be further improved to obtain accurate time cycles. Presently, the air inlet to the outer chamber is concentrated to the center of the chamber. This leads to non-uniform distribution of the fluidizing air into the distributor. To prevent this, the air inlet should be spread across the entire chamber. Modeling dry granulation in rotating fluidized beds using population balances is a very interesting topic. Empirical correlations for the kernels in population balance equation need to derived and validated, using experimental results.

## APPENDIX

# PROGRAM FOR THE CALCULATION OF ADHESION ENERGY

This program calculates the adhesion energy between two particles using the theory proposed by Rogers and Reed (1984). It takes the properties of the two particles as input and outputs the initial kinetic energy,  $Q_I$ , energy dissipated in plastic deformation,  $Q_p$ , and the adhesion energy  $Q_A$  into an excel file and the screen.

# include<iostream.h>

# include <math.h>

# include<fstream.h>

# include<iomanip.h>

# include<stdlib.h>

main()

# {

ofstream ostream;

ostream.open("values1.xls");

double y1,den1,den2,pr1,pr2,ym1,ym2,dse1,dse2;

double phi,K,k1,k2,m1,m2,impactv=1,r1,r2;

double p1,p0,rc,rp,d1,d2;

double Qa,Um,Us,Qi,Qp,Qr;

double eyl1,eyl2,deltadse;

double temp1,temp2,temp3;

int i;

cout<<"Enter the diameter, density, Poisson's Ratio, Young's Modules of host"; cin>>d1;

cin>>den1;

cin>>pr1;

cin>>ym1;

r1=d1/2;

cout << "Enter the Elastic Yield Limit and Dispersive Surface Energy of host";

cin>>eyl1;

cin>>dse1;

cout << "Enter the density Poisson's Ratio , Young's Modules of guest";

cin>>den2;

cin>>pr2;

cin>>ym2;

cout<<"Enter the Dispersive Surface Energy of guest";</pre>

cin>>dse2;

for(i=0;i<8;i++) // Loop to calculate the output for different guest particle size

# {

cout<<"Enter the diameter of guest"<<"\t";

cin>>d2;

r2=d2/2;

k1=(1-pow(pr1,2))/(3.14\*ym1); // Equation 5.4

```
k2=(1-pow(pr2,2))/(3.14*ym2); // Equation 5.4
```

```
K=4/(3*3.14*(k1+k2)); // Equation 5.13
```

```
phi=pow(((2*3.14)/(3*K)),2)*pow(2/(5*den2),0.5)*pow(eyl1,2.5); // Equation 5.12
cout<<"The limiting elastic velocity is \t"<<phi<<"\n";
ostream<<setw(10)<<setprecision(6)<<d2<<setw(10)<<setprecision(6)<<phi;
```

```
if(phi>=1)
{
cout<<"error";
exit(1);
}</pre>
```

```
m1=den1*4.1888*pow(r1,3); // Mass of host particles
m2=den2*4.1888*pow(r2,3); // Mass of guest particles
cout<<"mass of guest is\t"<<m2<<"\n";
Qi=pow(impactv,2)*0.5*m2; // Equation 5.8
ostream<<"\t"<<setw(10)<<setprecision(6)<<Qi;
cout<<"The initial kinetic energy, Q<sub>I</sub> is\t";
cout<<Qi<<"\n";
temp1=(2*m2*impactv*impactv)-(0.125*m2*phi*phi);
temp2=1.875*m2*phi*phi;
Qp=pow((0.5*(pow(temp1,0.5)-pow(temp2,0.5))),2); // Equation 5.11
```

```
ostream<<"\t"<<setw(10)<<setprecision(6)<<Qp;
```

```
cout << "The plastic deformation energy Q_P is \t";
```

```
cout<<Qp<<"\n";
```

```
Qr=Qi-Qp; // Rebound Energy
```

```
ostream<<"\t"<<setw(10)<<setprecision(6)<<Qr;
```

```
cout<<"The energy needed for rebound is\t";</pre>
```

```
cout<<Qr<<"\n";</pre>
```

```
rc=r1*r2/(r1+r2);
```

```
deltadse=2*pow((dse1*dse2),0.5);
```

```
p0=m2*9.81;
```

```
temp3=pow((p0+(3*deltadse*3.14*rc)),2)-pow(p0,2);
```

```
p1=p0+(3*deltadse*3.14*rc)+pow(temp3,0.5); // Equation 5.16
```

```
Us=deltadse*3.14*pow((rc*p1/K),0.667); // Equation 5.15
```

```
Um=p0*((pow(p1,0.667)+(2*p0*pow(p1,-0.333)))/(3*pow(K,0.667)*pow(rc,0.333))); //
```

Equation 5.14

```
Qa=Us+Um;
```

```
ostream<<"\t"<<setw(10)<<setprecision(6)<<Qa<<"\n";
```

```
cout<<"The adhesive energy is\t";</pre>
```

```
cout<<Qa<<"\n";
```

```
}
```

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