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R12.3 Fluidized-Bed Reactors[1]

"When a man blames others for his failures, it's a good idea to credit others with his successes."

-- Howard W. Newton

The fluidized-bed reactor has the ability to process large volumes of fluid. For the catalytic cracking of petroleum naphthas to form gasoline blends, for example, the virtues of the fluidized-bed reactor drove its competitors from the market.

Fluidization occurs when small solid particles are suspended in an upward-flowing stream of fluid, as shown in Figure R12.3.1.

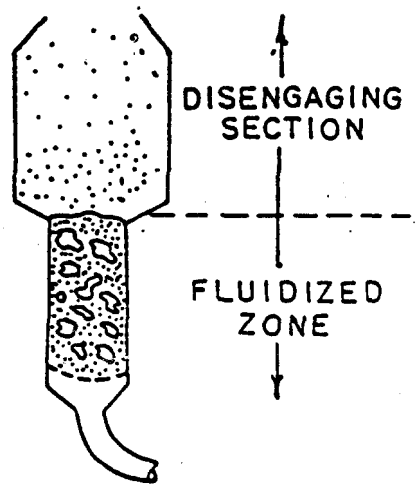

Figure R12.3-1 From Kunii and Levenspiel *Fluidization Engineering*, Melbourne, FL 32901: Robert E. Krieger Pub. Co. 1969. Reprinted with permission of the publishers

The fluid velocity is sufficient to suspend the particles, but it is not large enough to carry them out of the vessel. The solid particles swirl around the bed rapidly, creating excellent mixing among them. The material "fluidized" is almost always a solid and the "fluidizing medium" is either a liquid or gas. The characteristics and behavior of a fluidized bed are strongly dependent on both the solid and liquid or gas properties. Nearly all the significant commercial applications of fluidized-bed technology concern gas-solid systems, so these will be treated in this section. The material that follows is based upon what is seemingly the best model of the fluidized-bed reactor developed thus far–the bubbling bed model of Kunii and Levenspiel.

[1] This material is based on the article by H. S. Fogler and L. F. Brown [*Reactors*, ACS Symposium Series, vol.168, p. 31 1981, H. S. Fogler ed.], which in turn was based on a set of notes by Fogler and Brown.

R12.3.1 An Overview

We are going to use the Kunii-Levenspiel bubbling bed model to describe reactions in fluidized beds. In this model, the reactant gas enters the bottom of the bed and flows up the reactor in the form of bubbles. As the bubbles rise, mass transfer of the reactant gases takes place as they flow (diffuse) in and out of the bubble to contact the solid particles where the reaction product is formed. The product then flows back into a bubble and finally exits the bed when the bubble reaches the top of the bed. The rate at which the reactants and products transfer in and out of the bubble affects the conversion, as does the time it takes for the bubble to pass through the bed. Consequently, we need to describe the velocity at which the bubbles move through the column and the rate of transport of gases in and out of the bubbles. To calculate these parameters, we need to determine a number of fluid-mechanics parameters associated with the fluidization process. Specifically, to determine the velocity of the bubble through the bed we need to first calculate:

The Algorithm

1. Porosity at minimum fluidization, ε_{mf}
2. Minimum fluidization velocity, u_{mf}
3. Bubble size, d_b

To calculate the mass transport coefficient, we must first calculate

1. Porosity at minimum fluidization, ε_{mf}
2. Minimum fluidization velocity, u_{mf}
3. Velocity of bubble rise, u_b
4. Bubble size, d_b

To determine the reaction rate parameters in the bed, we need to first calculate

1. Fraction of the total bed occupied by bubbles, δ
2. Fraction of the bed consisting of wakes, $\alpha\delta$
3. Volume of catalyst in the bubbles, clouds, and emulsion, γ_b, γ_c, and γ_e

It is evident that before we begin to study fluidized-bed reactors, we must obtain an understanding of the fluid mechanics of fluidization. In Section R12.3B, equations are developed to calculate all the fluid mechanic parameters (e.g., d_b, u_{mf}) necessary to obtain the mass transfer and reaction parameters. In Section R12.3.3, equations for the mass transfer parameters are developed. In Section R12.3.4, the reaction rate parameters are presented, and the mole balance equations are applied to the bed to predict conversion in Section R12.3.5.

R12.3.2 The Mechanics of Fluidized Beds

In this section we shall first describe the regions of fluidization and calculate the minimum and maximum fluidization velocities. Next, the Kunii-Levenspiel

bubbling bed model is described in detail.[2] Finally, equations to calculate the fraction of the bed comprising bubbles, the bubble size, the velocity of bubble rise, and the fractional volume of bubbles, clouds, and wakes are derived.

R12.3.2A Description of the Phenomena

We consider a vertical bed of solid particles supported by a porous or perforated distributor plate, as in Figure R12.3-2(a). The direction of gas flow is upward through this bed.

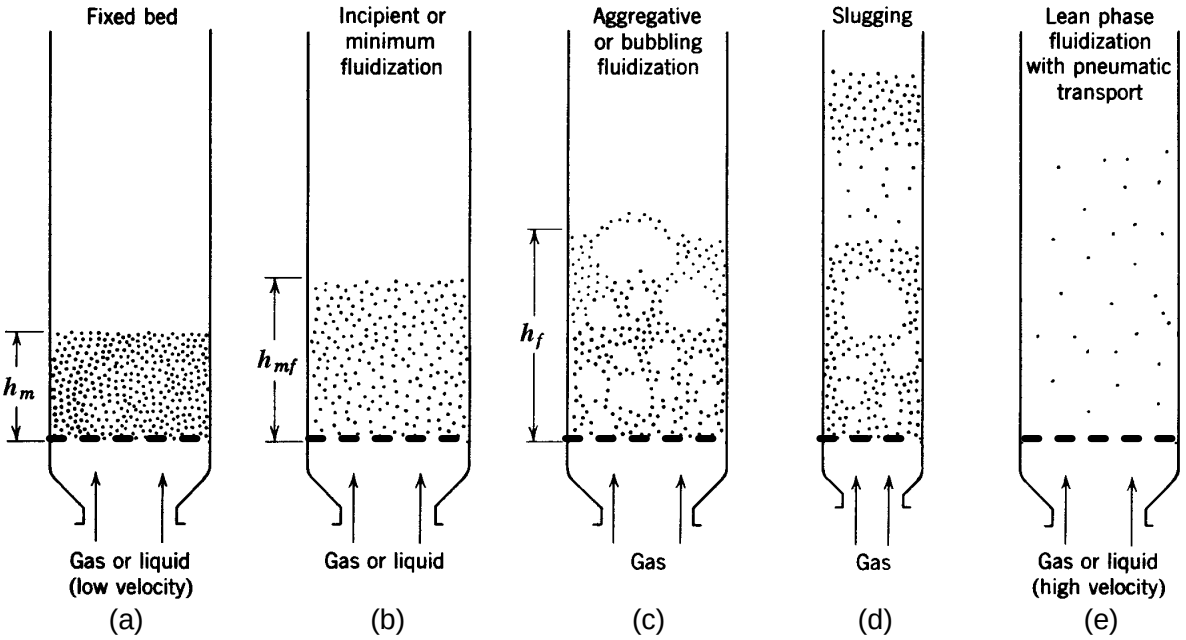

Figure R12.3-2 Various kinds of contacting of a batch of solids by fluid. Adapted from Kunii & Levenspiel, *Fluidized Engineering* (Huntington, NY: Robert E. Krieger Publishing Co., 1977).

There is a drag exerted on the solid particles by the flowing gas, and at low gas velocities the pressure drop resulting from this drag will follow the Ergun equation, Equation (4-22), just as for any other type of packed bed. When the gas velocity is increased to a certain value however, the total drag on the particles will equal the weight of the bed, and the particles will begin to lift and barely fluidize. If ρ_c is density of the solid catalyst particles, A_c is the cross sectional area, h_s, is the height of the bed settled before the particles start to lift, h, is the height of the bed at any time, and ε_s and ε are the corresponding porosities,[3] of the settled and expanded bed, respectively; then the mass of solids in the bed, W_s, is

$$W_s = \rho_c A_c h_s \left(1-\varepsilon_s\right) = \rho_c A_c h \left(1-\varepsilon\right) \qquad \text{(R12.3-1)}$$

[2] D. Kunii and O. Levenspiel, *Fluidization Engineering* (New York: Wiley, 1968).

[3] **Note: Nomenclature change in the text and lecture ϕ = porosity, while in this chapter ε = porosity.**

This relationship is a consequence of the fact that the mass of the bed occupied solely by the solid particles is the same no matter what the porosity of the bed. When the drag force exceeds the gravitational force, the particles begin to lift, and the bed expands (i.e., the height increases) thus increasing the bed porosity, as described by Equation (R12.3-1). This increase in bed porosity decreases the overall drag until it is again balanced by the total gravitational force exerted on the solid particles (Figure R12.3-3(b)).

If the gas velocity is increased still further, expansion of the bed will continue to occur; the solid particles will become somewhat separated from each other and begin to jostle each other and move around in a restless manner. Increasing the velocity just a slight amount further causes instabilities, and some of the gas starts bypassing the rest of the bed in the form of bubbles (Figure R12.3-3(c)). These bubbles grow in size as they rise up the column. Coincidentally with this, the solids in the bed begin moving upward, downward, and around in a highly agitated fashion appearing as a boiling frothing mixture. With part of the gas bubbling through the bed and the solids being moved around as though they were part of the fluid, the bed of particles is said to be "fluidized." It is in a state of aggregative, nonparticulate, or bubbling fluidization.

A further increase in gas velocity will result in slug flow (Figure R12.3-3(d)) and unstable chaotic operation of the bed. Finally at extremely high velocities, the particles are blown or transported out of the bed (Figure R12.3-3(e)).

The range of velocities over which the Ergun equation applies can be fairly large. On the other hand, the difference between the velocity at which the bed starts to expand and the velocity at which the bubbles start to appear can be extremely small and sometimes nonexistent. This observation means that if one steadily increases the gas flow rate, the first evidence of bed expansion may be the appearance of gas bubbles in the bed and the movement of solids. At low gas velocities in the range of fluidization, the rising bubbles contain very few solid particles. The remainder of the bed has a much higher concentration of solids in it and is known as the *emulsion phase* of the fluidized bed. The bubbles are shown as the *bubble phase*. The cloud phase is an intermediate phase between the bubble and emulsion phases.

After the drag exerted on the particles equals the net gravitational force exerted on the particles, that is,

$$\Delta P = g\left(\rho_c - \rho_g\right)(1-\varepsilon)h \qquad \text{(R12.3-2)}$$

the pressure drop will not increase with an increase in velocity beyond this point. (See Figure R12.3-2.) From the point at which the bubbles begin to appear in the bed, the gas velocity can be increased steadily over a quite appreciable range without changing the pressure drop across the bed or flowing the particles out of the bed. The bubbles become more frequent, and the bed, more highly agitated as the gas velocity is increased (Figure R12.3-2(c)); but the particles remain in the bed. This region is bubbling fluidization. Depending on the physical characteristics of the gas, the solid particles, and the distributor plate; and the internals (e.g., heat exchanger

tubes) within the bed, the region of bubbling fluidization can extend over more than an order of magnitude of gas velocities (e.g., 4 to 50 cm/s in Figure R12.3-3). In other situations, gas velocities in the region of bubbling fluidization may be limited; the point at which the solids begin to be carried out of the bed by the rising gas may be a factor of only three or four times the velocity at incipient fluidization.

Eventually, if the gas velocity is continuously increased, it will become sufficiently rapid to carry the solid particles upward, out of the bed. When this begins to happen, the bubbling and agitation of the solids are still present, and this is known as the region of fast fluidization, and the bed is know as *fast-fluidized bed*. At velocities beyond this region, the particles are well apart, and the particles are merely carried along with the gas stream. Under these conditions, the reactor is usually referred to as a *straight through transport reactor* or STTR (Figure R12.3-2(e)).

The various regions described earlier display the behavior illustrated in Figure R12.3-2. This figure presents the pressure drop across a bed of solid particles as a function of gas velocity. The region covered by the Ergun equation is the rising portion of the plot (Section I: $1 < U_0 < 4$ cm/s). The section of the figure where the pressure drop remains essentially constant over a wide range of velocities is the region of bubbling fluidization (Section II: $4 < U_0 \leq 50$ cm/s). Beyond this are the regions of fast fluidization and of purely entrained flow.

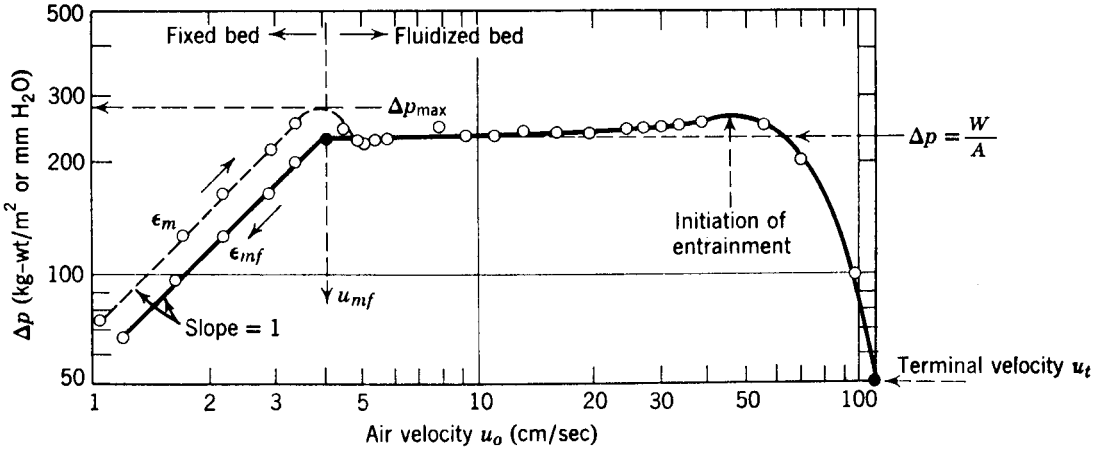

Figure R12.3-3 From Kunii and Levenspiel, Fluidization Engineering (Melbourne, FL: Robert E. Krieger, Publishing Co. 1977). Reprinted with permission of the publishers.

R12.3.2B The Minimum Fluidization Velocity

Fluidization will be considered to begin at the gas velocity at which the weight of the solids gravitational force exerted on the particles equals the drag on the particles from the rising gas. The gravitational force is given by Equation (R12.3-1) and the drag force by the Ergun equation. All parameters at the point where these two forces are equal will be characterized by the subscript "mf," to denote that this is the value of a particular term when the bed is just beginning to become fluidized.

The combination [$g\ (\rho_c - \rho_g)$] occurs very frequently, as in Equation (R12.3-1), and this grouping is termed [η].

$$(\Delta P/h) = g\,\eta\,(1 - \varepsilon_{mf}) \tag{R12.3-2}$$

The Ergun Equation, Equation (4-22) can be written in the form

$$\frac{\Delta P}{h} = \rho_g U^2 \left[\frac{150(1-\varepsilon)}{\mathrm{Re}_d\,\psi} + \frac{7}{4} \right] \frac{1-\varepsilon}{\psi d_p \varepsilon^3} \tag{R12.3-3}$$

where ψ = shape factor of catalyst particle, sometimes called the sphericity.

At the point of minimum fluidization, the weight of the bed just equals the pressure drop across the bed

$$W_s = \Delta P A_c$$

$$g(1-\varepsilon)(\rho_c - \rho_g)hA_c = \rho_g U^2 \left[\frac{150(1-\varepsilon)}{Re_p\,\psi} + \frac{7}{4} \right] \frac{1-\varepsilon}{\psi d_p \varepsilon^3} A_c h \tag{R12.3-4}$$

For Re_p < 10, $\left(Re_p = \dfrac{\rho_g d_p U}{\mu} \right)$, we can solve Equation (R12-5) for the minimum fluidization velocity to give

Calculate u_{mf}

$$u_{mf} = \frac{(\psi d_p)^2}{150\mu} \underbrace{\left[g(\rho_c - \rho_g) \right]}_{\eta} \frac{\varepsilon_{mf}^3}{1-\varepsilon_{mf}} \tag{R12.3-5}$$

Reynolds numbers less than 10 represents the usual situation, in which fine particles are fluidized by a gas. Sometimes, higher values of the Reynolds number do exist at the point of incipient fluidization, and then the quadratic Equation (R12.3-5) must be used.

Two dimensionless parameters in these two equations for u_{mf} deserve comment. This first is Ψ, the "sphericity," which is a measure of a particle's nonideality in both shape and roughness. It is calculated by visualizing a sphere whose volume is equal to the particle's, and dividing the surface area of this sphere by the actually measured surface area of the particle. Since the volume of a spherical particle is

$$V_p = \pi d_p^3 / 6$$

and its surface area is

$$A_s = \pi d_p^2 = \pi \left[\left(6V_p/\pi \right)^{1/3} \right]^2$$

Calculate ψ

$$\boxed{\psi = \frac{A_s}{A_p} = \frac{\left(\pi \left(6V_p/\pi \right)^{2/3} \right)}{A_p}} \tag{R12.3-6}$$

Measured values of this parameter range from 0.5 to 1, with 0.6 being a normal value for a typical granular solid.

The second parameter of special interest is the void fraction at the point of minimum fluidization, ε_{mf}. It appears in many of the equations describing fluidized-bed characteristics. There is a correlation that apparently gives quite accurate predictions of measured values of ε_{mf} (within 10%) when the particles in the fluidized bed are fairly small:[4]

Calculate ε_{mf}

$$\varepsilon_{mf} = 0.586\psi^{-0.72}\left(\frac{\mu^2}{\rho_g \eta d_p^3}\right)^{0.029}\left(\frac{\rho_g}{\rho_c}\right)^{0.021} \qquad \text{(R12.3-7)}$$

Another correlation commonly used is that of Wen and Yu

$$\varepsilon_{mf} = \left(0.071/\psi\right)^{1/3} \qquad \text{(R12.3-8)}$$

and/or

$$\varepsilon_{mf} = \frac{0.091\left(1-\varepsilon_{mf}\right)}{\psi^2} \qquad \text{(R12.3-9)}$$

When the particles are large, the predicted ε_{mf} can be much too small. If a value of ε_{mf} below 0.40 is predicted, it should be considered suspect. Kunii and Levenspiel[5] state that ε_{mf} is an easily measurable value. However, if it is not convenient to do so, Equation (R12.3-7) should suffice. Values of ε_{mf} around 0.5 are typical. If the distribution of sizes of the particles covers too large a range, the equation will not apply because smaller particles can fill the interstices between larger particles. When a distribution of particle sizes exists, an equation for calculating the mean diameter is

$$d_p = \frac{1}{\sum \frac{f_i}{d_{p_i}}} \qquad \text{(R12.3-10)}$$

where f_i is the fraction of particles with diameter d_{p_i}.

R12.3.2C Maximum Fluidization

If the gas velocity is increased to a sufficiently high value, however, the drag on an individual particle will surpass the gravitational force on the particle, and the particle will be entrained in a gas and carried out of the bed. The point at which the drag on an individual particle is about to exceed the gravitational force exerted on it is called the maximum fluidization velocity.

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[4] T.E. Broadhurst and H.A. Becker, *AIChE J.*, *21*, 238 (1975).

[5] D. Kunii and O. Levenspiel, *Fluidization Engineering* (New York: Wiley, 1968).

Maximum velocity through the bed u_t

When the upward velocity of the gas exceeds the free-fall terminal velocity of the particle, u_t, the particle will be carried upward with the gas stream. For fine particles, the Reynolds numbers will be small, and two relationships presented by Kunii and Levenspiel[6] are

$$\left.\begin{aligned} u_t &= \eta d_p^2 / 18\mu && Re < 0.4 \\ u_t &= \left(1.78\times 10^{-2}\,\eta^2/\rho_g\mu\right)^{1/3}\left(d_p\right) && (0.4 < Re < 500) \end{aligned}\right\} \qquad \text{(R12.3-11)}$$

We now have the maximum and minimum superficial velocities at which we may operate the bed. The entering superficial velocity, u_0, must be above the minimum fluidization velocity but below the slugging u_{ms} and terminal, u_t, velocities.

$$u_{mf} < u_0 < u_t$$

and

$$u_{mf} < u_0 < u_{ms}$$

Both of these conditions must be satisfied for proper bed operation.

R12.3.2D Descriptive Behavior of a Fluidized Bed – The Model Of Kunii And Levenspiel

At gas flow rates above the point of minimum fluidization, a fluidized bed appears much like a vigorously boiling liquid; bubbles of gas rise rapidly and burst on the surface, and the emulsion phase is thoroughly agitated. The bubbles form very near the bottom of the bed, very close to the distributor plate and as a result the design of the distributor plate has a significant effect on fluidized-bed characteristics.

Literally hundreds of investigators have contributed to what is now regarded as a fairly practical description of the behavior of a fluidized bed; chief among these is the work of Davidson and Harrison.[7] Early investigators saw that the fluidized bed had to be treated as a two-phase system – an emulsion phase and a bubble phase (often called the dense and lean phases). The bubbles contain very small amounts of solids. They are not spherical; rather they have an approximately hemispherical top and a pushed-in bottom. Each bubble of gas has a wake that contains a significant amount of solids. These characteristics are illustrated in Figure R12.3-4, which were obtained from x-rays of the wake and emulsion, the darkened portion being the bubble phase.

As the bubble rises, it pulls up the wake with its solids behind it. The net flow of the solids in the emulsion phase must therefore be downward.

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[6] D. Kunii and O. Levenspiel, *Fluidization Engineering* (New York: Wiley, 1968).

[7] J. F. Davidson and D. Harrison, *Fluidized Particles* (New York: Cambridge University Press, 1963).

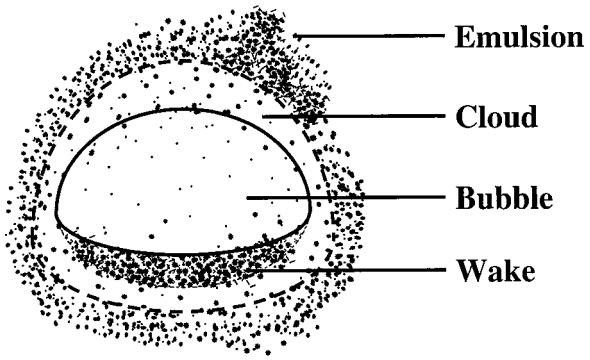

Figure R12.3-4 Schematic of bubble, cloud, and wake.

The gas within a particular bubble remains largely within that bubble, only penetrating a short distance into the surrounding emulsion phase. The region penetrated by gas from a rising bubble is called the cloud.

Davidson found that he could relate the velocity of bubble rise and the cloud thickness to the size of bubble. Kunii and Levenspiel[8] combined these observations with some simplifying assumptions to provide a practical, useable model of fluidized-bed behavior. Their assumptions are presented in Table R12.3-1.

TABLE R12.3-1. ASSUMPTIONS IN THE KUNII-LEVENSPIEL MODEL

(a) The bubbles are all of one size.

(b) The solids in the emulsion phase flow smoothly downward, essentially in plug flow.

(c) The emulsion phase exists at minimum fluidizing conditions. The gas occupies the same void fraction in this phase as it had in the entire bed at the minimum fluidization point. In addition, because the solids are flowing downward, the minimum fluidizing velocity refers to the gas velocity relative to the moving solids, that is,

$$u_e = \frac{u_{mf}}{\varepsilon_{mf}} - u_s \qquad \text{(R12.3-12)}$$

(The ε_{mf} is present in this equation because u_{mf} is the superficial velocity, i.e., based on an empty tube cross section.) The velocity of the moving solids, u_s, is positive in the downward direction here, as in most of the fluidization literature. The velocity of the gas in the emulsion, u_e, is taken as a positive in the upward direction, but note that it can be negative under some conditions.

[8] D. Kunii and O. Levenspiel, *Fluidization Engineering* (New York: Wiley, 1968).

(d) In the wakes, the concentration of solids is equal to the concentration of solids in the emulsion phase, and therefore the gaseous void fraction in the wake is also the same as in the emulsion phase. Because the emulsion phase is at the minimum fluidizing condition, the void fraction in the wake is equal to ε_{mf}. The wake, however, is quite turbulent, and the average velocities of both solid and gas in the wake are assumed to be the same and equal to the upward velocity of the bubbles

Several of these assumptions had been used by earlier investigators, particularly Davidson and Harrison.[9] With the possible exception of (c), all these assumptions are of questionable validity, and rather obvious deviations from them are observed routinely. Nevertheless, the deviations apparently do not affect the mechanical or reaction behavior of fluidized beds sufficiently to diminish their usefulness.

R12.3.2E Bubble Velocity and Cloud SSize

From experiments with single bubbles, Davidson and Harrison found that the velocity of rise of a single bubble could be related to the bubble size by

Single bubble

$$u_{br} = (0.71)(g d_b)^{1/2} \qquad \text{(R12.3-13)}$$

When many bubbles are present, this velocity would be affected by other factors. The more bubbles that are present, the less drag there would be on an individual bubble; the bubbles would carry each other up through the bed. The greater number of bubbles would result from larger amounts of gas passing through the bed (i.e., a larger value of u_0). Therefore, the larger the value of u_0, the faster should be the velocity of a gas bubble as it rises through the bed.

Other factors that should affect this term are the viscosity of the gas and the size and density of the solid particles that make up the bed. Both of these terms also affect the minimum fluidization velocity, and so this term might well appear in any relationship for the velocity of bubble rise; the higher the minimum fluidization velocity, the lower the velocity of the rising bubble.

Adopting an expression used in gas-liquid systems, Davidson and Harrison proposed that the rate of bubble rise in a fluidized bed could be represented by simply adding and subtracting these terms:

Velocity of bubble rise u_b

$$u_b = u_{br} + (u_0 - u_{mf})$$

$$\boxed{u_b = u_0 - u_{mf} + (0.71)(g d_b)^{1/2}} \qquad \text{(R12.3-14)}$$

Bubble Size. The equations for the velocity of bubble rise, Equations (R12.3-13) and (R12.3-14) are functions of the bubble diameter, an elusive value to obtain.

[9] J. F. Davidson and D. Harrison, *Fluidized Particles* (New York: Cambridge University Press, 1963).

As might be expected, it has been found to depend on such factors as bed diameter, height above the distributor plate, gas velocity, and the components that affect the fluidization characteristics of the particles. Unfortunately, for predictability, the bubble diameter also depends significantly upon the type and number of baffles, heat exchangers tubes, and so forth, within the fluidized bed (sometimes called "internals"). The design of the distributor plate, which disperses the inlet gas over the bottom of the bed, can also has a pronounced effect upon the bubble diameter.

Studies of bubble diameter carried out thus far have concentrated on fluidized beds with no internals and have involved rather small beds. Under these conditions the bubbles grow as they rise through the bed. The best relationship between bubble diameter and height in the column at this writing seems to be that of Mori and Wen,[10] who correlated the data of studies covering bed diameters of 7 to 130 cm, minimum fluidization velocities of 0.5 to 20 cm/s, and solid particle sizes of 0.006 to 0.045 cm. Their principal equation was

d_b

$$\frac{d_{bm} - d_b}{d_{bm} - d_{bo}} = e^{-0.3h/D_t} \tag{R12.3-15}$$

In this equation, d_b is the bubble diameter in a bed of diameter D_t, observed at a height h above the distributor plate; d_{bo} is the diameter of the bubble formed initially just above the distributor plate, and d_{bm} is the maximum bubble diameter attained if all the bubbles in any horizontal plane coalesce to form a single bubble (as they will do if the bed is high enough).

The maximum bubble diameter, d_{bm} has been observed to follow the relationship

d_{maximum}

$$d_{bm} = 0.652\left[A_c\left(u_0 - u_{mf}\right)\right]^{0.4} \tag{R12.3-16}$$

cm $\quad$ cm^2 $\quad$ cm/s

for all beds, while the initial bubble diameter depends upon the type of distributor plate. For porous plates, the relationship

$$d_{b0} = 0.00376\left(u_0 - u_{mf}\right)^2, \text{ cm} \tag{R12.3-17}$$

d_{minimum} is observed, and for perforated plates, the relationship

$$d_{b0} = 0.347\left[A_c\left(u_0 - u_{mf}\right)/n_d\right]^{0.4} \tag{R12.3-18}$$

appears to be valid, in which n_d is the number of perforations. For beds with diameters between 30 and 130 cm, these relations appear to predict bubble diameters with an accuracy of about ± 50%; for beds with diameters between 7 and 30 cm, the accuracy of prediction appears to be approximately + 100%, – 60% of the observed values.

[10] S. Mori and C. Y. Wen, *AIChE J.*, *21*, 109 (1975).

Werther developed the following correlation based on a statistical coalescence model:[11]

$$\frac{d_b}{\text{cm}} = 0.853\sqrt[3]{1+0.272\frac{u_0-u_{ms}}{\text{cm/s}}}\left[1-0.0684\ \frac{\text{h}}{\text{cm}}\right]^{1.21} \qquad \text{(R12.3-19)}$$

The bubble size predicted by this model is close to that predicted by Mori and Wen[12] for large diameter beds (2 m) and smaller than that suggested by Mori and Wen for small diameter beds (0.1 m).

R12.3.2F Fraction of Bed in the Bubble Phase

Using the Kunii-Levenspiel model, the fraction of the bed occupied by the bubbles and wakes can be estimated by material balances on the solid particles and the gas flows. The parameter δ is the fraction of the total bed occupied by the part of the bubbles that does not include the wake, and α is the volume of wake per volume of bubble. The bed fraction in the wakes is therefore ($\alpha\delta$). (c.f. Figure R12.13-5)

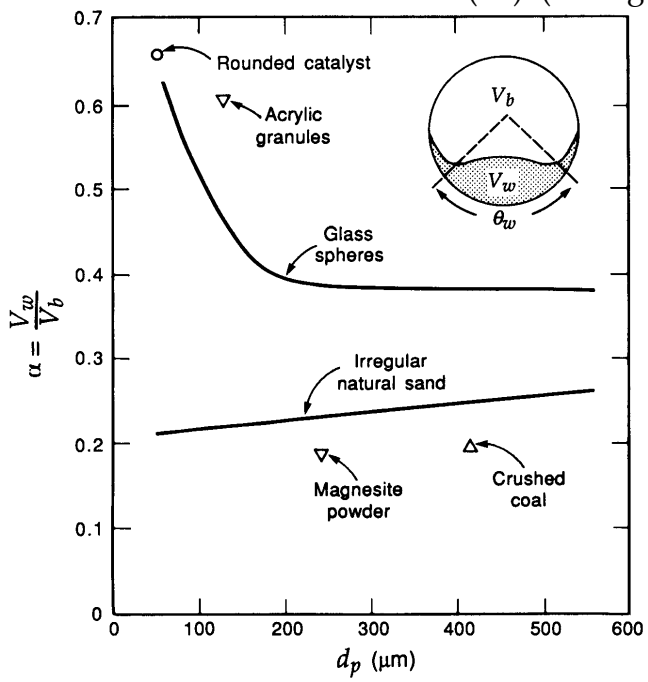

Figure R12.3-5 Wake angle θw and wake fraction of three-dimensional bubbles at ambient conditions; evaluated from x-ray photographs by Rowe and Partridge. Adapted from Kunii & Levenspiel, *Fluidized Engineering*, 2nd ed. (Stoneham, MA: Butterworth-Heinemann, 1991).

The bed fraction in the emulsion phase (which includes the clouds) is ($1 - \delta - \alpha\delta$). Letting A_c and ρ_c represent the cross-sectional area of the bed and the density of the solid particles, respectively, a material balance on the solids (Figure R12.3-4) gives

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[11] J. Werther, *ACS Symposium Series.*, *72*, D. Luss & V. W. Weekman, eds. (1978).
[12] S. Mori and C. Y. Wen, *AIChE J.*, *21*, 109 (1975).

$$\begin{matrix}\text{Solids flowing} \\ \text{downward in emulsion}\end{matrix} = \begin{matrix}\text{Solids flowing} \\ \text{upward in wakes}\end{matrix}$$

$$A_c\rho_c(1-\delta-\alpha\delta)u_s \quad = \quad \alpha\delta u_b\rho_c A_c$$

or

Velocity of solids u_s

$$u_s = \frac{\alpha\delta u_b}{1-\delta-\alpha\delta} \tag{R12.3-20}$$

A material balance on the gas flows gives

$$A_c u_0 \quad = \quad A_c\delta u_b \quad + A_c\varepsilon_{mf}\alpha\delta u_b \; + A_c\varepsilon_{mf}(1-\delta-\alpha\delta)u_e$$

$$\begin{pmatrix}\text{Total gast} \\ \text{flow rate}\end{pmatrix} = \begin{pmatrix}\text{Gas flow} \\ \text{in bubbles}\end{pmatrix} + \begin{pmatrix}\text{Gas flow} \\ \text{in wakes}\end{pmatrix} + \begin{pmatrix}\text{Gas flow in} \\ \text{emulsion}\end{pmatrix} \tag{R12.3-21}$$

The velocity of rise of gas in the emulsion phase is

Velocity of gas in emulsion u_e

$$\boxed{u_e = \frac{u_{mf}}{\varepsilon_{mf}} - u_s} \tag{R12.3-22}$$

(In the fluidization literature, u_s is almost always taken as positive in the downward direction.) Factoring the cross-sectional area from Equation (R12.3-21) and then combining Equations (R12.3-21) and (R12.3-22), we obtain an expression for the fraction δ of the bed occupied by bubbles

Volume fraction bubbles δ

$$\boxed{\delta = \frac{u_0 - u_{mf}}{u_b - u_{mf}(1+\alpha)}} \tag{R12.3-23}$$

The wake parameter, α, is a function of the particle size in Figure R12.3-5. The value of α has been observed experimentally to vary between 0.25 and 1.0, with typical values close to 0.4. Kunii and Levenspiel assume that the last equation can be simplified to

$$\delta = \frac{u_0 - u_{mf}}{u_b} \tag{R12.3-24}$$

which is valid for $u_b >> u_{mf}$, (e.g. $u_b \approx \frac{5\ u_{mf}}{\varepsilon_{mf}}$)

Example R12-1 Maximum Solids Hold-Up

A pilot fluidized bed is to be used to test a chemical reaction. The bed diameter is 91.4 cm. You wish to process 28.3×10^3 cm^3 of gaseous material. The average particle diameter is 100 μ. The reactor height is 10 feet. Allowing for a disengaging height of 7 feet, this means we have a maximum bed height of 91.4 cm. The distributor plate is a porous disc.

What is the maximum weight of solids (i.e., holdup) in the bed? Other data:

Color of Pellet: Brown

ψ:	0.7	ρ_g:	1.07×10^{-3} g/cm^3
ρ_c:	1.3 g/cc	μ:	1.5×10^{-4} poise

Solution

The amount of solids in the reactor is given by Equation (R12.3-1)

$$W_s = \rho_c A_c h_s \left(1-\varepsilon_s\right) = \rho_c A_c h \left(1-\varepsilon\right) \qquad \text{(R12.3-1)}$$

The two parameters which need to be found are ε_{mf} and δ.

A. Calculation of ε_{mf}

$$\varepsilon_{mf} = 0.586\psi^{-0.72}\left(\frac{\mu^2}{\rho_g \eta d_p^3}\right)^{0.029}\left(\frac{\rho_g}{\rho_c}\right)^{0.021} \qquad \text{(R12.3-7)}$$

1. Calculate gravity term

$$\eta = g\left(\rho_c - \rho_g\right) = \left(980\ cm^2/s\right)\left(1.3 - 0.00107\right) g/cm^3$$

$$= 1270\ \ g/(cm)^2\left(s^2\right)$$

2. Cross-sectional area

$$A_c = \frac{\pi D^2}{4} = (\pi)\left(91.4\ cm\right)^2/4 = 6.56\times10^3\ \ cm^2$$

Superficial velocity

$$u_0 = \left(v_0/A_c\right) = 2.83\times10^4/6.56\times10^3 = 4.32\ \ cm/s$$

Porosity at minimum fluidization (Equation (R12.3-4))

$$\varepsilon_{mf} = (0.586)(0.7)^{-0.72}\left[\frac{\left(1.5\times10^{-4}\ \text{g/cm}\bullet\text{s}\right)^2}{\left(0.00107\ \ \text{g/cm}^3\right)\left(1270\ \ \text{g/cm}^2\bullet\text{s}^2\right)\left(10^{-2}\text{cm}\right)^3}\right]^{0.029}$$

$$\times\left(0.00107\ \ \text{g/cm}^3/1.3\ \ \text{g/cm}^3\right)^{0.021}$$

$$\varepsilon_{mf} = 0.58$$

B. Calculation of Volume Fraction of Bubbles

$$\delta = \frac{u_0 - u_{mf}}{u_b - u_{mf}\left(1+\alpha\right)} \qquad \text{(R12.3-23)}$$

Here we see we must calculate u_{mf} and u_b.

Step 1. First the minimum fluidization velocity is obtained from Equation (R12.3-3)

$$u_{mf} = \frac{\left[(0.7)(10^{-2}\ \text{cm})\right]^2}{150}\left(\frac{1270\ \text{g/cm}^2\bullet\text{s}^2}{1.5\times10^{-4}\ \text{g/cm}\bullet\text{s}}\right)\left(\frac{0.58^3}{1-0.58}\right)$$

$$u_{mf} = 1.28\ \text{cm/s}$$

Step 2. To calculate u_b we must know the size of the bubble d_b., that is,

$$u_b = u_0 - u_{mf} + (0.71)(gd_b)^{1/2} \qquad \text{(R12.3-14)}$$

Step 3. The average size of the bubble, d_b, is determined by evaluating Equation (R12.3-15) at (h/2).

$$\frac{d_{bm} - d_b}{d_{bm} - d_{b0}} = e^{-0.3h/D_t} \qquad \text{(R12.3-15)}$$

Where d_{bm} and d_{bo} are given in Equations (R12.3-16) and (R12.3-17) respectively.

Maximum bubble diameter

$$d_{bm} = 0.652\left[A_c(u_0 - u_{mf})\right]^{0.4},\ \text{cm} \qquad \text{(R12.3-16)}$$

$$d_{bm} = (0.652)\left[\left(6.56\times10^3\text{cm}^2\right)(4.32 - 1.28)\ \text{cm/s}\right]^{0.4}$$

$$d_{bm} = 34.2\ \text{cm}$$

Minimum bubble diameter

$$d_{b0} = 0.00376(u_0 - u_{mf})^2,\ \text{cm} \qquad \text{(R12.3-14)}$$

$$d_{b0} = (0.00376)(4.32\ \text{cm/s} - 1.28\ \text{cm/s})^2$$

$$d_{b0} = 0.0347\ \text{cm}$$

Solving for d_b

$$\frac{34.2 - d_b}{34.2 - 0.0347} = e^{-0.3h/91.4}$$

$$d_b = 34.2\left(1 - e^{-0.3h/91.4}\right)$$

At h = 45.7 cm $(h/2)$	d_b = 4.76 cm

At the top of the bed (h = 91.4 cm), d_b = 8.86 cm

For purposes of the Kunii-Levenspiel model, we shall take the bubble diameter to be 5 cm.

Step 4. We now can return to calculate the velocity of bubble rise and the fraction of bed occupied by bubbles from Equation (R12.3-14) we have

$$u_b = 4.32 \text{ cm/s} - 1.28 \text{ cm/s} + (0.71)\left[(980 \text{ cm/s}^2)(5 \text{ cm})\right]^{0.5}$$

$$u_b = 52.8 \text{ cm/s}$$

From Figure (R12.3-5) we see that a 100 μ size particle corresponds to a value of α of 0.5. Substituting this value into Equation (R12.3-23), the fraction of the bed occupied by the bubble is

$$\delta = \frac{4.32 - 1.28}{52.8 - (1.28)(1.5)}$$

$$\delta = 0.060$$

Thus 94% of the bed is in the emulsion phase plus the wakes.

C. The Amount of Solids Hold-Up, W_s

$$W_s = A_c h(1-\delta)(1-\varepsilon_{mf})\rho_s = (6.56 \times 10^3)(91.4)(0.94)(0.42)\rho_s$$

$$= (2.37 \times 10^5 \text{ cc of solid})\rho_s$$

$$= (2.37 \times 10^5)(1.3) = 3.08 \times 10^5 \text{ g of solid}$$

or

$$W_s = 678 \text{ lb of solid particles}$$

R12.3.3 Mass Transfer In Fluidized Beds

There are two types of mass transport important in fluidized-bed operations. The first is the transport between gas and solid. In some situations this can affect the analysis of fluidized-bed behavior significantly, and in others it might not enter the calculations at all. In the treatment of this type of transfer, it will be seen that this type of transport is quite similar to gas-solid mass transfer in other types of operations.

The second type of mass transfer is unique to fluidized-bed operations. It concerns the transfer of material between the bubbles and the clouds, and between the clouds and the emulsion (Figures R12.3-3, R12.3-5, and R12.3-6). In almost every type of fluidized-bed operation, there are significant gas-phase concentration differences between the various elements of the fluidized bed. Consequently, calculations involving this type of mass transfer occur in almost every fluidized-bed analysis.

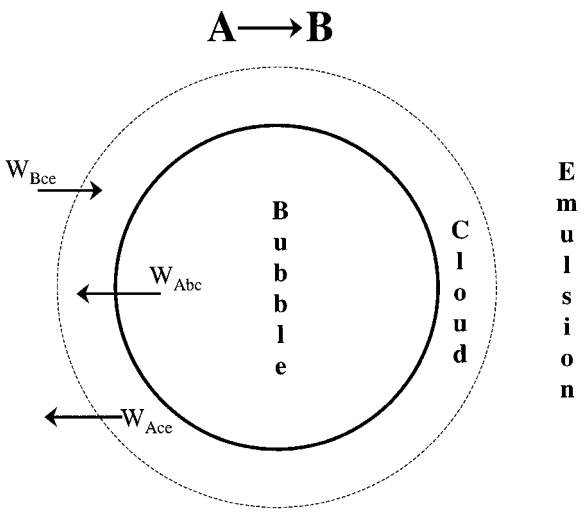

Figure R12.3-6 Transfer between bubble, cloud, and emulsion.

R12.3.3A Gas-Solid Mass Transfer

In the bubble phase of a fluidized bed, the solid particles are sufficiently separated so that in effect there is mass transfer between a gas and single particles. The most widely used correlation for this purpose is the 1938 equation of Fröessling (1938) for mass transfer to single spheres given in Chapter 11.

$$\mathrm{Sh} = 2.0 + (0.6)(\mathrm{Re})^{1/2}(\mathrm{Sc})^{1/3} \qquad \text{(R12.3-25)}$$

The relative velocity between the solid particle and the gas used in calculating the Reynolds number will be taken as u_0.

In the emulsion phase, the equation would be one that applied to fixed-bed operation with a porosity in the bed equal to ε_{mf} and a velocity of u_{mf}. The equation recommended by Kunii and Levenspiel:[13]

Transport from gas to single

$$\mathrm{Sh} = 2.0 + (1.5)(\mathrm{Sc})^{1/3}\left[(1-\varepsilon)(\mathrm{Re})^{1/2}\right] \qquad \text{(R12.3-26)}$$

for $5 < \mathrm{Re} < 120$, and $\varepsilon < 0.84$

Mass transfer coefficients obtained from these relationships may then be combined with mass transfer among the various phases in the fluidized bed to yield the overall behavior with regard to the transport of mass. Owing to the small particle sizes and high surface area per volume of solids used in fluidized beds, the mass transfer from the gas to the solid surface is usually quite rapid and consequently it seldom limits the reaction.

[13] D. Kunii and O. Levenspiel, *Fluidization Engineering* (New York: Wiley, 1968).

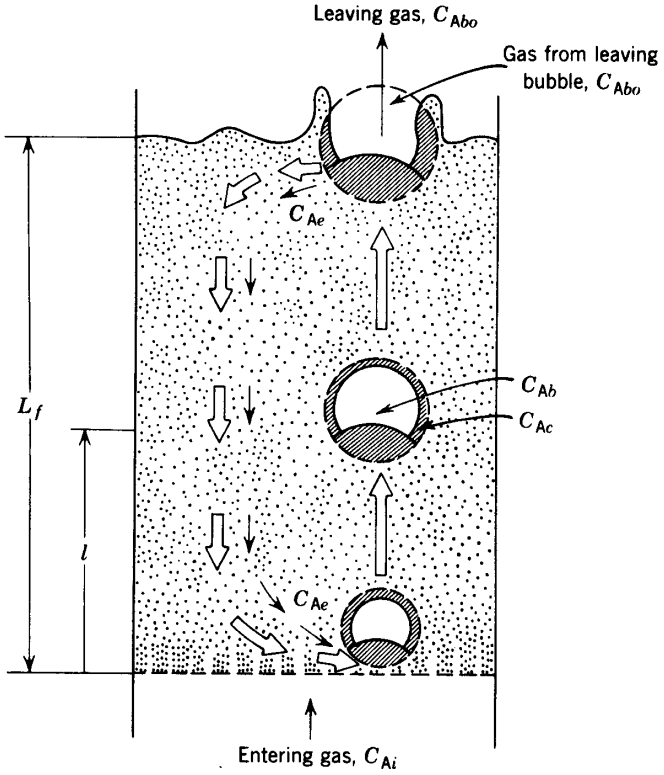

Figure R12.3-7 Sketch of flow pattern in a fluidized bed for downflow of emulsion gas, $u_e/u_0 < 0$ or $u_0/u_{mf} > 6$ to 11. Adapted from Kunii & Levenspiel, *Fluidized Engineering*, Robert E. Krieger Publishing Co., Huntington, New York, 1977.

R12.3.3B Mass Transfer Between The Fluidized-Bed Phases

For the gas interchange between the bubble and the cloud, Kunii and Levenspiel[14] defined the mass transfer coefficient K_{bc} (s^{-1}) in the following manner:

$$W_{Abc} = K_{bc}(C_{Ab} - C_{Ac}) \qquad \text{(R12.3-27)}$$

Where C_{Ab} and C_{Ac} are the concentration of A in the bubble and cloud respectively, (mole/dm^3) and W_{Abc} represents the number of moles of A transferred from the bubble to the cloud per unit time per unit volume of bubble (mole/dm^3/s). The concept of basing all mass transfer (and later, all reaction) on the bubble volume proves to simplify the calculations markedly. For the products, (e.g., B in A $\rightarrow$ B) the rate of transfer into the bubble from the cloud is given by a similar equation

$$W_{Bcb} = K_{cb}(C_{Bc} - C_{Bb}) \qquad \text{(R12.3-28)}$$

The mass transfer coefficient K_{bc} can also be thought of as an exchange volume q between the bubble and the cloud.

$$W_{Bcb} = q_b C_{Ab} - q_c C_{Ac} = q_o(C_{Ab} - C_{Ac}) \qquad \text{(R12.3-29)}$$

where q_b = Volume of gas flowing from the bubble to the cloud per unit time per unit volume of bubble

q_c = Volume of gas flowing from the cloud to the bubble per unit time per unit volume of bubble

q_o = Exchange volume between the bubble and cloud per unit time per unit volume of bubble (i.e., K_{bc})

$$(q_o = q_c = q_b)$$

Using Davidson's expression for gas transfer between the bubble and the cloud, and then basing it on the volume of the bubble, Kunii and Levenspiel[15] obtained this equation for evaluating K_{bc}:

Mass transfer between bubble and cloud

$$K_{bc} = 4.5\left(\frac{u_{mf}}{d_b}\right) + 5.85\left(\frac{D_{AB}^{1/2}\, g^{1/4}}{d_b^{5/4}}\right), \qquad \text{(R12.3-30)}$$

where u_{mf} is in cm/s, d_b is in cm, D_{AB} is the diffusivity (cm^2/s) and g is the gravitational constant (980 cm/s^2).

We note

$$K_{bc} = K_{cb}$$

$K_{bc} \cong 2\ s^{-1}$

and a typical value of K_{bc} is 2 s^{-1}.

Similarly, these authors defined a mass transfer coefficient for gas interchange between the cloud and the emulsion:

$$W_{Ace} = K_{ce}(C_{Ac} - C_{Ae})$$
$$W_{Bce} = K_{ce}(C_{Be} - C_{Bc}) \qquad \text{(R12.3-31)}$$

where W_{Ace} is the moles of A transferred from the cloud to the emulsion per unit time per unit volume of bubble. Note that even though this mass transfer does not involve the bubble directly, it is still based on the bubble volume.

Using Higbie's penetration theory and his analogy for mass transfer from a bubble to a liquid, Kunii and Levenspiel[16] developed an equation for evaluating K_{ce}:

Mass transfer between cloud and emulsion

$$K_{ce} = 6.77\left(\frac{\varepsilon_{mf} D_{AB} u_b}{d_b^3}\right)^{1/2} \qquad \text{(R12.3-32)}$$

where u_b is velocity of bubble rise in cm/s and the other symbols are as defined at Equation (R12.3-30). A typical value of K_{ce} is 1 s^{-1}. K_{ce} can also be thought of as the exchange volume between the cloud and the emulsion.

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[14] D. Kunii and O. Levenspiel, *Fluidization Engineering* (New York: Wiley, 1968).
[15] D. Kunii and O. Levenspiel, *Fluidization Engineering* (New York: Wiley, 1968).
[16] D. Kunii and O. Levenspiel, *Fluidization Engineering* (New York: Wiley, 1968).

With knowledge of the mass transfer coefficients, the amount of gas interchange between the phases of a fluidized bed can be calculated and combined to predict the overall mass transfer behavior or reaction behavior of a fluidized-bed process.

R12.3.4 Reaction Behavior in a Fluidized Bed

To use the Kunii-Levenspiel model to predict reaction rates in a fluidized-bed reactor, the reaction rate law for the heterogeneous reaction per gram (or other fixed unit) of solid must be known. Then the reaction rate in the bubble phase, the cloud, and the emulsion phase, all per unit of bubble volume, can be calculated. Assuming that these reaction rates are known, the overall reaction rate can be evaluated using the mass transfer relationships presented in the preceding section. All this is accomplished in the following fashion.

We consider an *n*th order, constant-volume catalytic reaction. In the bubble phase

$$r_{Ab} = -k_b C_{Ab}^n$$

in which the reaction rate is defined per unit volume of bubble. In the cloud,

RATE LAWS

$$r_{Ac} = -k_c C_{Ac}^n$$

and similarly in the emulsion,

$$r_{Ae} = -k_e C_{Ae}^n$$

where k_e, k_c and k_b are the specific reaction rates in the emulsion cloud, and bubble respectively. In the latter two equations, the reaction rate is also defined per unit volume of bubble.

R12.3.5 Mole Balance on the Bubble, the Cloud, and the Emulsion

Material balances will be written over an incremental height Δz for substance A in each of the three phases (bubble, cloud, and emulsion) (Figure R12.3-7).

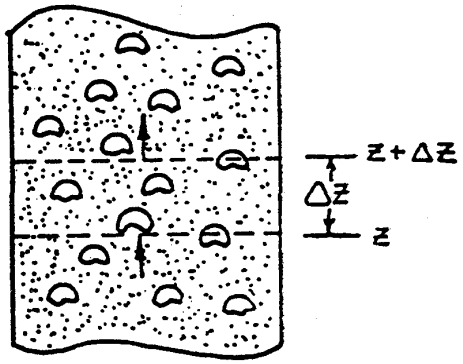

Figure R12.3-8 Section of a bubbling fluidized bed

R12.3.5A Balance on Bubble Phase

The amount of A entering at z is the bubble phase by flow,

$$(u_b A_c C_{Ab})(\delta) = \begin{pmatrix}\text{Molar flow rate}\\ \text{of A assuming the}\\ \text{entire bed is filled}\\ \text{with bubbles}\end{pmatrix}\begin{pmatrix}\text{Fraction of the}\\ \text{bed occupied}\\ \text{by bubbles}\end{pmatrix}$$

A similar expression can be written for the amount of A leaving in the bubble phase in flow at z + Δz.

In by flow	Out by flow	+	Out by mass Transport	+	Generation

$$(u_b A_c C_{Ab})(\delta)\big|_x - (u_b A_c C_{Ab}\delta)_{z+\Delta x} - K_{bc}(C_{Ab} - C_{Ac})A_c \Delta z\delta - k_b C_{Ab}^n A_c \Delta z\delta = 0$$

Dividing by $A_c \Delta z\delta$ and taking the limit as $\Delta z \to 0$

A balance on A in the bubble phase for steady state operation in section Δz.

Balance on the bubble

$$\boxed{u_b \frac{dC_{Ab}}{dz} = -k_b C_{Ab}^n - K_{bc}(C_{Ab} - C_{Ac})} \qquad \text{(R12.3-33)}$$

R12.3.5B Balance on Cloud Phase

In the material balance on the clouds and wakes in the section Δz, it is easiest to base all terms on the volume of bubble. The material balance for the clouds and wakes is

Balance on the clouds

$$\boxed{u_b \delta\left[\frac{3(u_{mf}/\varepsilon_{mf})}{u_{br} - (u_{mf}/\varepsilon_{mf})} + \alpha\right]\frac{dC_{Ac}}{dz} = K_{bc}(C_{Ab} - C_{Ac}) - K_{ce}(C_{Ac} - C_{Ae}) - k_c C_A^n} \qquad \text{(R12.3-34)}$$

R12.3.5C Balance on the Emulsion

The fraction of the bed in the emulsion phase is (1 – δ – αδ). The material balance for A in the emulsion the following expression for the emulsion-phase material balance on A results in

Balance on the emulsion

$$\boxed{u_e\left(\frac{1-\delta-\alpha\delta}{\delta}\right)\frac{dC_{Ae}}{dz} = K_{ce}(C_{Ac} - C_{Ae}) - k_e C_{Ae}^n} \qquad \text{(R12.3-35)}$$

The three material balances thus result in three coupled ordinary differential equations, with one independent variable (z) and three dependent variables (C_{Ab}, C_{Ac}, C_{Ae}). These equations can be solved numerically. The Kunii-Levenspiel model simplifies these still further, by assuming that the derivative terms on the left-hand side of the material balances on the cloud and emulsion are negligible in comparison

with the terms on the right-hand side. Using this assumption, and letting $t = z/u_b$ (i.e., the time the bubble has spent in the bed), the three equations take the form:

THE BALANCE EQUATIONS

$$\frac{dC_{Ab}}{dt} = -\left(k_b C_{Ab}^n\right) - K_{bc}\left(C_{Ab} - C_{Ac}\right) \qquad \text{(R12.3-36)}$$

$$K_{bc}\left(C_{Ab} - C_{Ac}\right) = k_c C_{Ac}^n + K_{ce}\left(C_{Ac} - C_{Ae}\right) \qquad \text{(R12.3-37)}$$

$$K_{ce}\left(C_{Ac} - C_{Ae}\right) = k_e C_{Ae}^n \qquad \text{(R12.3-38)}$$

Note

or only one differential equation and two algebraic equations. *In all equations, kC_A^n is the g-moles per second reacted in the particular phase per volume of bubbles.*

R12.3.5D Partitioning of the Catalyst

To solve these equations, it is necessary to have values of k_b, k_c, and k_e. Three new parameters are defined:

$$\gamma_b: \frac{\text{Volume of solid catalyst dispersed in bubbles}}{\text{Volume of bubbles}}$$

$$\gamma_c: \frac{\text{Volume of solid catalyst in clouds and wakes}}{\text{Volume of bubbles}}$$

$$\gamma_e: \frac{\text{Volume of solid catalyst in emulsion phase}}{\text{Volume of bubbles}}$$

First of all the specific reaction rate of solid catalyst , k_{cat} must be known. It is normally determined from laboratory experiments. The term $k_{cat}\ C_A^n$ is the g-moles reacted per volume of solid catalyst. Then

Relating the specific reaction rates

$$k_b = \gamma_b k_{cat}; \quad k_c = \gamma_c k_{cat}; \quad k_e = \gamma_e k_{cat} \qquad \text{(R12.3-39)}$$

$$k_{cat} = \rho_c \times k' = \frac{\text{g cat}}{\text{cm}^3\text{cat}} \times \frac{\text{cm}^3}{\text{g cat} \cdot \text{s}} \left(\frac{\text{cm}^3}{\text{mol}}\right)^{n-1} = \frac{\text{cm}^3}{\text{cat} \cdot \text{s}} \left(\frac{\text{cm}^3}{\text{mol}}\right)^{n-1}$$

The term k′ is the specific reaction rate per weight of catalyst.

Guess $\gamma_b \sim 0.01$

The value of γ_b ranges between 0.001 and 0.01, with 0.005 being the more typical number. The volume fraction of catalyst in the clouds and wakes is $(1 - \varepsilon_{mf})$. The volume of cloud and wakes per volume of bubble is

$$\frac{V_c}{V_b} = \frac{3\left(u_{mf}/\varepsilon_{mf}\right)}{u_b - \left(u_{mf}/\varepsilon_{mf}\right)}$$

so the expression for γ_c is

The volume of catalysts in the clouds is γ_c.

$$\gamma_c = \left(1-\varepsilon_{mf}\right)\left[\frac{3\left(u_{mf}/\varepsilon_{mf}\right)}{u_b-\left(u_{mf}/\varepsilon_{mf}\right)}+\alpha\right] \qquad \text{(R12.3-40)}$$

It turns out that the value of α is normally far from insignificant in this expression for γ_c and represents a weakness in the model because there does not yet exist a reliable method for determining α. The typical values of γ_c ranges from 0.3 to 0.4. The value of γ_c can be quite incorrect on occasion, in particular, a value of α=1.

The volume fraction of the solids in the emulsion phase is again $(1 - \varepsilon_{mf})$. The volume of emulsion per volume of bubble is

$$\frac{V_e}{V_b} = \frac{1-\delta}{\delta} - \left(\frac{\text{Volume of clouds and wakes}}{\text{Volume of bubbles}}\right)$$

and so the expression for γ_e is

The value of catalysts in the emulsion is γ_e.

$$\gamma_e = \left(1-\varepsilon_{mf}\right)\left(\frac{1-\delta}{\delta}\right) - \gamma_c - \gamma_b \qquad \text{(R12.3-41)}$$

Typical values of γ_b, γ_c, and γ_e are 0.005, 0.2, and 1.5, respectively. Using the expressions given above, the three balance equations become

For reactors other than first or zero order, these equations must be solved numerically.

Bubble balance	$\frac{dC_{Ab}}{dt} = -\left(\gamma_b k_{cat} C_{Ab}^n\right) - K_{bc}\left(C_{Ab} - C_{Ac}\right)$	(R12.3-42)
Cloud balance	$K_{bc}\left(C_{Ab} - C_{Ac}\right) = \gamma_c k_{cat} C_{Ac}^n + K_{ce}\left(C_{Ac} - C_{Ae}\right)$	(R12.3-43)
Emulsion balance	$K_{ce}\left(C_{Ac} - C_{Ae}\right) = \gamma_e k_{cat} C_{Ae}^n$	(R12.3-44)

R12.3.5E Solution to the Balance Equations for a First-Order Reaction

If the reaction is first order, then the C_{Ac} and C_{Ae} can be eliminated using the two algebraic equations, and the differential equation can be solved analytically for C_{Ab} as a function of t. An analogous situation would exist if the reaction were zero. Except for these two situations, solution to these two equations must be obtained numerically.

For first-order reactions, we can combine the three balance equations into one differential equation, which we can then solve to determine the conversion achieved in a fluidized-bed reactor. In addition, the closed form solution allows us to examine certain limiting situations in order to determine which operating parameters are most influential in dictating bed performance. Here we can pose and ask a number of "What if . . ." questions. To arrive at our fluidized-bed design equation for a first-order reaction, we simply express both the concentration of A in the emulsion, C_{Ae},

and in the cloud, C_{Ac}, in terms of the bubble concentration, C_{Ab}. First, we use the emulsion balance

$$K_{ce}\left(C_{Ac} - C_{Ae}\right) = \gamma_e k_{cat} C_{Ae}^n \tag{R12.3-45}$$

to solve for C_{Ae} in terms of C_{Ac}.

Rearranging (R12.3-45) for a first-order reaction (n = 1), we obtain

$$C_{Ae} = \frac{K_{ce}}{\gamma_e k_{cat} + K_{ce}} C_{Ac} \tag{R12.3-46}$$

We now use this equation to substitute for C_{Ae} in the cloud balance

$$K_{bc}\left(C_{Ab} - C_{Ac}\right) = C_{Ac}\gamma_c k_{cat} + K_{ce}\left(C_{Ac} - \frac{K_{ce}C_{Ac}}{\gamma_e k_{cat} + K_{ce}}\right)$$

Solving for C_{Ac} in terms of C_{Ab}

$$C_{Ac} = \frac{K_{bc}}{\gamma_c k_{cat} + \left[\frac{K_{ce}\gamma_e k_{cat}}{\gamma_c k_{cat} + K_{ce}}\right] + K_{bc}} C_{Ab} \tag{R12.3-47}$$

We now substitute for C_{ac} in the bubble balance

$$\frac{dC_{Ab}}{dt} = \gamma_b k_{cat} C_{Ab} + \left[C_{Ab} - \frac{K_{bc}C_{Ab}}{\gamma_c k_{cat} + K_{bc} + \left[\frac{K_{ce}\gamma_e k_{cat}}{\gamma_e k_{cat} + K_{ce}}\right]}\right]$$

Rearranging

$$\frac{dC_{Ab}}{dt} = k_{cat} C_{Ab}\left[\gamma_b + \frac{\gamma_e\gamma_c k_{cat}K_{bc} + \gamma_c K_{bc}K_{ce} + K_{ce}\gamma_e K_{bc}}{\gamma_e\gamma_c k_{cat}^2 + K_{ce}\gamma_c k_{cat} + K_{bc}\gamma_e k_{cat} + K_{ce}K_{bc} + K_{ce}\gamma_e k_{cat}}\right]$$

After some further rearrangement,

$$-\frac{dC_{Ab}}{dt} = k_{cat} C_{Ab}\left(\gamma_b + \frac{1}{\frac{k_{cat}}{K_{bc}} + \frac{1}{\gamma_c + \frac{1}{\frac{1}{\gamma_e} + \frac{k_{cat}}{K_{ce}}}}}\right) \tag{R12.3-48}$$

The overall transport coefficient K_R for a first-order reaction.

$$K_R = \gamma_b + \cfrac{1}{\cfrac{k_{cat}}{K_{bc}} + \cfrac{1}{\gamma_c + \cfrac{1}{\cfrac{1}{\gamma_e} + \cfrac{k_{cat}}{K_{ce}}}}} \tag{R12.3-49}$$

$$-\frac{dC_{Ab}}{dt} = k_{cat} K_R C_{Ab} \tag{R12.3-50}$$

Expressing C_{Ab} as a function of X, that is,

$$C_{Ab} = C_{A0}(1 - X)$$

We can substitute to obtain

$$\frac{dX}{dt} = k_{cat} K_R (1 - X)$$

and integrating

The design equation

$$\boxed{ln\left(\frac{1}{1-X}\right) = k_{cat} K_R t} \tag{R12.3-51}$$

The height of the bed necessary to achieve this conversion is

$$h = t u_b$$

$$\boxed{h = \frac{u_b}{k_{cat} K_R} \; ln \; \frac{1}{1-X}} \tag{R12.3-52}$$

The corresponding catalyst weight is

$$W = \rho_c A_c h (1 - \varepsilon_{mf})(1 - \delta) \tag{R12.3-53}$$

$$W = \frac{\rho_c A_c u_b (1 - \varepsilon_{mf})(1 - \delta)}{k_{cat} K_R} \; ln \; \frac{1}{1-X} \tag{R12.3-54}$$

R12.3.5F The Procedure

Unfortunately, one must use an iterative procedure to calculate the catalyst weight. This predicament is a consequence of the fact that both K_R and u_b depend upon the bubble diameter, which depends upon the bed height, Equation (R12.3-52). Consequently, one should check the estimated average bubble diameter using the value of h calculated from Equation (R12.3-52). A flow chart outlining this procedure is shown in Figure R12.3-9.

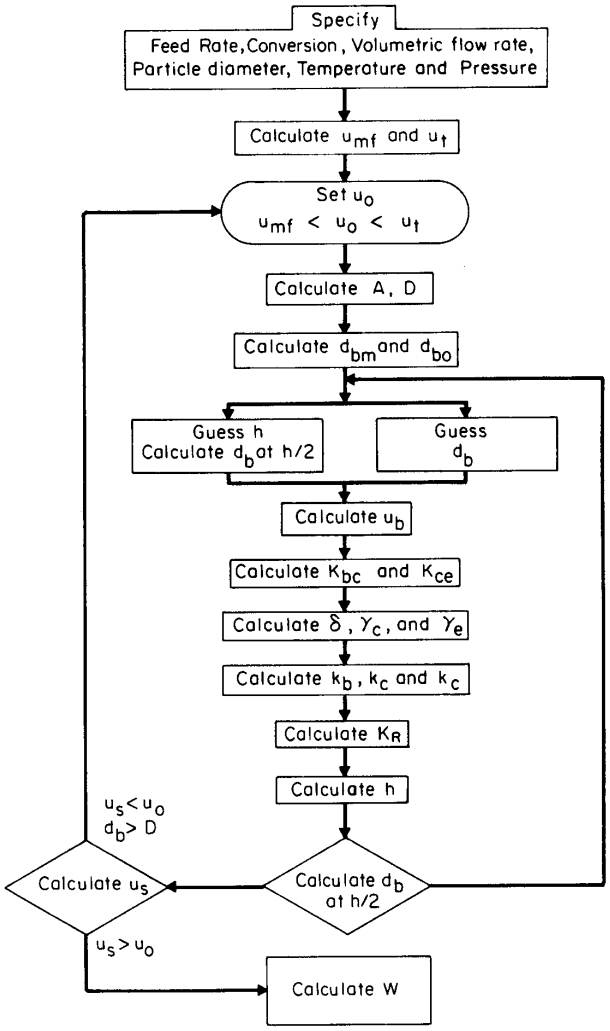

Figure R12.3-9 Computational algorithm for fluidized-bed reactor design. Reprinted with permission from Fogler and Brown, "Reaction Control and Transport," *Chemical Reactors*, ACS Symposium Series, vol. 168, 1981, H.S. Fogler, ed.

Example R12-2 Catalytic Oxidation of Ammonia

Massimilla and Johnstone[17] studied the catalytic oxidation of ammonia in a fluidized-bed reactor. Under their experimental conditions, the reaction was first-order, dependent only upon the ammonia concentration, and without a significant change in volumetric flow rate. In one of their runs, 4 kg of catalyst were used with a gas flow rate of 818 cm^3/s at reaction conditions. A conversion of 22% of the entering ammonia was obtained. Predict this conversion using the Kunii-Levenspiel model.

[17] L. Massimilla and R.F. Jornstone, *Chem. Eng. Sci.* 16, (105) (1961).

Other data:

Operating conditions:

$P = 840 \text{ torr} = 1.11 \text{ atm}$

$T = 523 \text{ K} \ (250°\text{C})$

Reactor:

$D_t = 11.4 \text{ cm}$

Distributor plate is porous stainless steel.

Feed:

$v_0 = 818 \text{ cm}^3/\text{s}$ @ reaction conditions

Composition: 10% NH_3, 90% O_2

Catalyst:

$d_p = 105 \ \mu m \ (0.0105 \text{ cm})$

$\psi = 0.6$ (assumed)

$\rho_p = 2.06 \ (\text{g}/\text{cm}^3)$

$h_s = 38.9 \ (\text{cm})$

Reaction rate:

$-r_A = kC_{NH_3} \left(\text{gmoles } NH_3/(\text{s})(\text{cm}^3 \text{ of catalyst})\right)$

$k_{cat} = 0.0858 \text{ s}^{-1}$ @ reaction conditions

Fluid properties:

$\rho_g = 7.85 \times 10^{-4} \text{ g}/\text{cm}^3$

$\mu_g = 2.98 \times 10^{-4} \text{ g}/\text{cm} \cdot \text{s}$

$D_{AB} = 0.618 \text{ cm}^2/\text{s}$

Solution

A. Mechanical Characteristics of Bed

Step 1. Gravitation term, η

$$\eta = g\left(\rho_c - \rho_g\right)$$

$$= 980 \ \text{cm/s}^2 \ \left(2.06 - 7.85\times10^{-4}\right)\text{g/cm}^3$$

$$= 2.02\times10^3 \ \text{g/(s)}^2\,(\text{cm})^2$$

Step 2. Porosity of bed a minimum fluidization, ε_{mf}

$$\varepsilon_{mf} = 0.586\psi^{-0.72}\left(\frac{\mu^2}{\rho_g \eta d_p^3}\right)^{0.029}\left(\frac{\rho_g}{\rho_c}\right)^{0.021} \qquad \text{(R12.3-7)}$$

$$= (0.586)(0.6)^{-0.72}\left\{\left(2.98\times10^{-4}\ \text{g/cm}\cdot\text{s}\right)^2 \Big/ \left[\left(7.85\times10^{-4}\right)^2\left(2.02\times10^3\ \text{g/cm}^2\cdot\text{s}^2\right)(0.0105\ \text{cm})^3\right]\right\}^{0.029} \times\left(7.85\ \text{g/cm}^3\times10^{-4}/2.06\ \text{g/cm}^3\right)^{0.021}$$

$\varepsilon_{mf} \sim 0.65$

$$\boxed{\varepsilon_{mf} = 0.657}$$

Step 3. Gas velocity at minimum fluidization

$$u_{mf} = \frac{\left(\psi d_p\right)^2}{150\mu}\underbrace{\left[g\left(\rho_c - \rho_g\right)\right]}_{\eta}\frac{\varepsilon_{mf}^3}{1-\varepsilon_{mf}} \qquad \text{(R12.3-5)}$$

$$= \left[(0.6)\left(0.0105\ \text{cm}^2\right)\right]^2\left(2.02\times10^{-3}\ \text{g/cm}^2\cdot\text{s}^2\right)(0.657)^3 \Big/ \left[(150)\left(2.98\times10^{-4}\ \text{g/cm}\cdot\text{s}\right)(1-0.657)\right]$$

$u_{mf} \sim 1.5$ cm/s

$$\boxed{u_{mf} = 1.48\ \text{cm/s}}$$

Step 4. Entering gas velocity u_0

$$u_0 = v_0/A_c = v_0\Big/\left(\pi D_t^2/4\right)$$

$$= 818\ \text{cm}^3/\text{s}\Big/\left[(\pi)(11.4\ \text{cm})^2/4\right]$$

$u_o \sim 8$ cm/s

$$\boxed{u_0 = 8.01 \text{ cm/s}}$$

Step 5. Is u_0 within a reasonable operating range?

Check u_t.

$$u_t = \left(1.78 \times 10^{-2}\, \eta^2 / \rho_g \mu\right)^{1/3} \left(d_p\right) \qquad \text{(R12.3-11)}$$

$$= \left[\left(1.78 \times 10^{-2}\right)\left(2.02 \times 10^{-3} \text{ g/cm}^2 \cdot \text{s}^2\right)^2 / \left(7.85 \times 10^{-4} \text{ g/cm}^3\right)\left(2.98 \times 10^4 \text{ g/cm} \cdot \text{s}\right)\right]^{1/3} (0.0105)$$

$u_t \sim 70$ cm/s

$\boxed{u_t = 71.1 \text{ cm/s}}$ Maximum fluidization gas velocity (Particle blown out of the bed)

Are N_{Re} in proper range for use of Equations (R12.3-6) and (R12.3-11)?

$$N_{Re} = \frac{d_p \rho_g u}{\mu}$$

At u_{mf}: $N_{Re} = (0.0105 \text{ cm})\left(7.85 \times 10^{-4} \text{ g/cm}^3\right)(1.48 \text{ cm/s}) / \left(2.98 \times 10^{-4} \text{ g/cm} \cdot \text{s}\right)$

$= 0.0409$ (OK, since it is < 10)

At u_t $N_{Re} = (0.0105 \text{ cm})\left(7.85 \times 10^{-4} \text{ g/cm}^3\right)(71.1 \text{ cm/s}) / \left(2.98 \times 10^{-4} \text{ g/cm} \cdot \text{s}\right)$

$= 1.97$ (OK, since $0.4 < N_{Re} < 500$)

Thus u_0 is 5.4 times u_{mf}, and well below u_t.

Step 6. Bubble sizes, d_{bo}, d_{bm}, and d_b

$$d_{b0} = 0.00376\left(u_o - u_{mf}\right)^2, \text{ cm} \qquad \text{(R12.3-17)}$$

$$= 0.00376\ (8.01 \text{ cm/s} - 1.48 \text{ cm/s})^2$$

$d_b = 0.160$ cm

$$d_m = 0.652\ \left[A_c\left(u_0 - u_{mf}\right)\right]^{0.4} \qquad \text{(R12.3-18)}$$

$$= 0.652\left\{\left[\pi(11.4)^2/4\right](8.01\ \text{cm/s} - 1.48\ \text{cm/s})\right\}^{0.4}\ \text{cm}$$

d_{bm} = 08.8 cm

$\boxed{d_{bm} = 8.79\ \text{cm}}$ (Since this is smaller than column diameter, slugging will not occur.)

Step 7. Bubble sizes, d_{bo}, d_{bm}, and d_b

The unexpanded bed height is 38.9 cm. The expanded bed height will probably be 40 to 50% greater, say ~ 60 cm. We therefore will assume the average bubble size will be taken as the one calculated for (h/2) = 30 cm.

Step 8. Average bubble diameter

$$d_b = d_{bm} - (d_{bm} - d_{b0})e^{-0.3h/D_t} \quad \text{(From Equation R12.3-15)}$$

$$= 8.79 - (8.79 - 0.160)e^{-(0.3)(30)/11.4}$$

d_b ~ 5 cm

$\boxed{d_b = 4.87\ \text{cm}}$

Step 9. Rise velocity of single bubble

$$u_{br} = (0.71)(gd_b)^{1/2} = (0.71)\left[(980\ \text{cm/s}^2)(4.87\ \text{cm})\right]^{1/2} = 49.0\ \text{cm/s} \qquad \text{(R12.3-13)}$$

Step 10. Rise velocity of a bubble when many bubbles are present

$$u_b = u_0 - u_{mf} + (0.71)(gd_b)^{1/2} \qquad \text{(R12.3-14)}$$

$$= 8.01 - 1.48 + 49.0 = 55.6\ \text{cm/s}$$

u_b ~ 55 cm

$u_b = 55.6\ \text{cm/s}$

From Figure (R12.3-5) for glass spheres with d_p = 0.105 mm, then $\alpha = 0.4$

Step 11. Fraction of bed in bubble phase

$$\delta = (u_o - u_{mf})/\left[u_b - u_{mf}(1+\alpha)\right] \qquad \text{(R12.3-23)}$$

$$= (8.01 - 1.48)/\left[55.6 - 1.48(1+0.4)\right]$$

δ ~ 0.12

$\boxed{\delta = 0.122}$

Step 12. Bed height

$$\underbrace{(h\,A_c)}_{\text{Volume of bed}}\ \underbrace{(1-\delta)}_{\substack{\text{Volume in emulsion,}\\ \text{clouds, and wakes}}}\ \underbrace{(1-\varepsilon_{mf})}_{\substack{\text{Volume of solids in emulsion,}\\ \text{clouds, and wakes}}}\quad \rho_p = \text{mass of catalyst in bed}$$

$$h = \frac{W}{A_c(1-\delta)\left(1-\varepsilon_{mf}\right)\rho_c}$$

$$= \frac{4000\ \text{g}}{\left[\pi(11.4\ \text{cm})^2/4\right](1-0.122)(1-0.657)\left(2.06\ \text{gm}/\text{cm}^3\right)} = 63.2\ \text{cm}$$

Good Guess of h = 60 cm

Since the estimated bed height of 60 cm is sufficiently close to the calculated value of 63.2 cm, one can proceed further in the calculations without making a new estimate of *h*.

C. Mass Transfer and Reaction Parameters:

Step 1. Bubble-cloud mass transfer coefficient

Order of magnitude parameters

$$K_{bc} = 4.5\left(u_{mf}/d_b\right) + 5.85\left(D^{1/2}\, g^{1/4}/d_b^{5/4}\right) \qquad \text{(R12.3-30)}$$

$$= 4.5\left(1.48\text{cm/s}\right)/(4.87\text{cm}) + 5.85\left(0.61\text{cm}^2/\text{s}\right)^{1/2}\left(980\text{cm}/\text{s}^2\right)^{1/4}/(4.87\text{cm})^{5/4}$$

$$= 1.37\ \text{s}^{-1} + 3.54\ \text{s}^{-1}$$

$K_{bc} \sim 5\ \text{s}^{-1}$

$$\boxed{K_{bc} = 4.92\ \text{s}^{-1}}$$

Step 2. Cloud-emulsion mass-transfer coefficient

$$K_{ce} = 6.78\left(\varepsilon_{mf} D u_b/d_b^3\right)^{1/2} \qquad \text{(R12.3-32)}$$

$$= 6.78\left[(0.657)\left(0.61\text{cm}^2/\text{s}\right)(55.6\text{cm/s})/(4.87\text{cm})^3\right]^{1/2}$$

$K_{ce} \sim 3\ \text{s}^{-1}$

$$\boxed{K_{ce} = 3.00\ \text{s}^{-1}}$$

Step 3. Volume of catalysts in the bubble per volume of bubble.

$$\boxed{\gamma_b = 0.01 \text{ (assumed)}}$$

Step 4. Volume of catalyst in clouds and wakes/cm^3 of bubbles

$$\gamma_c = \left(1-\varepsilon_{mf}\right)\left\{3\left(u_{mf}/\varepsilon_{mf}\right)/u_b - \left(u_{mf}/\varepsilon_{mf}\right)\right] + \alpha\right\}$$

$$= (1-0.657)\left\{(3)(1.48/0.657)/\left[49.0 - (1.48/0.657)\right] + 0.4\right\} \qquad \text{(R12.3-40)}$$

$\gamma_c \sim 0.2$

$$\boxed{\gamma_c = 0.187}$$

Step 5. Volume of catalyst in emulsion/cm^3 of bubbles

$$\gamma_e = \left(1-\varepsilon_{mf}\right)\left[(1-\delta)/\delta\right] - \gamma_c - \gamma_b$$

$$= (1-0.657)\left[\left(1-0.122/0.122\right)\right]-0.187-0.005 \qquad \text{(R12.3-41)}$$

$\gamma_e \sim 2$

$$\boxed{\gamma_e = 2.28}$$

Step 6. Calculate K_R and X from Equations (R12.3-49) and (R12.3-51)

$$X = 1-\exp\left[-\frac{K_R k_{cat} h}{u_b}\right]$$

where

$$K_R = \gamma_b + \cfrac{1}{\cfrac{k_{cat}}{K_{bc}} + \cfrac{1}{\cfrac{1}{\cfrac{1}{\gamma_e} + \cfrac{k_{cat}}{K_{ce}}} + \gamma_c}} \qquad \text{(R12.3-49)}$$

$$K_R = 0.01 + \cfrac{1}{\cfrac{0.0858/\text{s}}{4.92/\text{s}} + \cfrac{1}{\cfrac{1}{\cfrac{1}{2.28} + \cfrac{0.0858/\text{s}}{3.0/\text{s}}} + .187}}$$

$K_R \sim 2$

$$K_R = 0.01 + \cfrac{1}{0.0174 + \cfrac{1}{.187 + 2.14}} = 2.23$$

$$\boxed{K_R = 2.23}$$

$$ln\left(\frac{1}{1-X}\right) = k_{cat} K_R t$$

$$= k_{cat} K_R \frac{h}{u_b}$$

Solving for X

$$X = 1-\exp\left[-\frac{(2.23)\left(0.0858\ \text{s}^{-1}\right)(63.2\ \text{cm})}{55.6\ \text{cm/s}}\right]$$

$$X = 0.20$$

This is close to the observed value of 22% conversion.

R12.3.6 Limiting Situations

As engineers, it is important to deduce how a bed will operate if one were to change operating conditions such as gas flow rate or catalyst particle size. To give

some general guides as to how changes will affect bed behavior, we shall consider the two limiting circumstances of reaction control and transport control.

In the K-L bubbling bed model, reaction occurs within the three phases of the bed, and material is continuously transferred between the phases. Two limiting situations thus arise. In one, the interphase transport is relatively fast, and transport equilibrium is maintained, causing the system performance to be controlled by the rate of reaction. In the other, the reaction rate is relatively fast, and the performance is controlled by interphase transport between the bubbles, clouds, and emulsions. It will be shown that the ammonia oxidation example used earlier is essentially a reaction-limited system.

The overall reaction rate in the bed is proportional to K_R, so the reciprocal of K_R can be viewed as an overall resistance to the reaction. The different terms and groups on the right-hand side of Equation (R12.3-49) can be viewed as individual resistances,zs which can be arranged in series or parallel to give the overall resistance.

$$R_0 = \frac{1}{K_R} = \frac{1}{\dfrac{1}{\dfrac{1}{\gamma_b}} + \dfrac{1}{\dfrac{k_{cat}}{K_{bc}} + \dfrac{1}{\dfrac{1}{\dfrac{1}{\gamma_c}} + \dfrac{1}{\dfrac{1}{\gamma_e} + \dfrac{k_{cat}}{K_{ce}}}}}} \qquad \text{(R12.3-55)}$$

$$R_0 = \frac{1}{\dfrac{1}{R_{rb}} + \dfrac{1}{R_{tbc} + \dfrac{1}{\dfrac{1}{R_{rc}} + \dfrac{1}{R_{re} + R_{tce}}}}} \qquad \text{(R12.3-56)}$$

in which:

$R_{rb} = \dfrac{1}{\gamma_b}$ = Resistance to reaction in the bubble

$R_{tbc} = \dfrac{k_{cat}}{K_{bc}}$ = Resistance to transfer between bubble and cloud

$R_{rc} = \dfrac{1}{\gamma_c}$ = Resistance to reaction in cloud

$R_{re} = \dfrac{1}{\gamma_e}$ = Resistance to reaction in the emulsion

$R_{tce} = \dfrac{k_{cat}}{K_{ce}}$ = Resistance to transfer between cloud and emulsion

Example R12-3 Calculation of Resistances

Calculate each of the resistances to reaction and transfer, and the relationship between C_{Ab}, C_{Ac} and C_{Ae} for the ammonia oxidation reaction described in Example R12-2. Assume $\gamma_b = 0.01$.

Solution

$$R_{rb} = \frac{1}{\gamma_b} = \frac{1}{0.01} = 100$$

$$R_{tbc} = \frac{k_{cat}}{K_{bc}} = \frac{0.0858}{4.92} = 0.0174$$

$$R_{re} = \frac{1}{\gamma_e} = \frac{1}{2.28} = 0.439$$

$$R_{rc} = \frac{1}{\gamma_c} = \frac{1}{0.187} = 5.35$$

$$R_{tcb} = \frac{k_{cat}}{K_{ce}} = \frac{0.0858}{3.0} = 0.0286$$

To relate C_{Ae} and C_{Ac}, we rearrange Equation (R12-67) for a first-order reaction as

$$C_{Ae} = \left(\frac{K_{ce}}{\gamma_e + k_{cat} + K_{ce}}\right) C_{Ac} = \frac{3.00}{(2.28)(0.0858) + 3.00}\ C_{Ac}$$

$$C_{Ae} = 0.939\ C_{Ac}$$

The analog electrical resistance for the system is shown in Figure R12.3-10 along with the corresponding resistances for this reaction. As with its electrical analog, the reaction will pursue the path of least resistance, which in this case is along the right hand-side branch of Figure R12.3-10. If the major resistance in this side, the resistance to reaction in the emulsion R_{re}, could be reduced, a greater conversion could be achieved for a specific catalyst weight. To reduce R_{re}, one needs to look for ways of increasing γ_e.

Electrical Analog

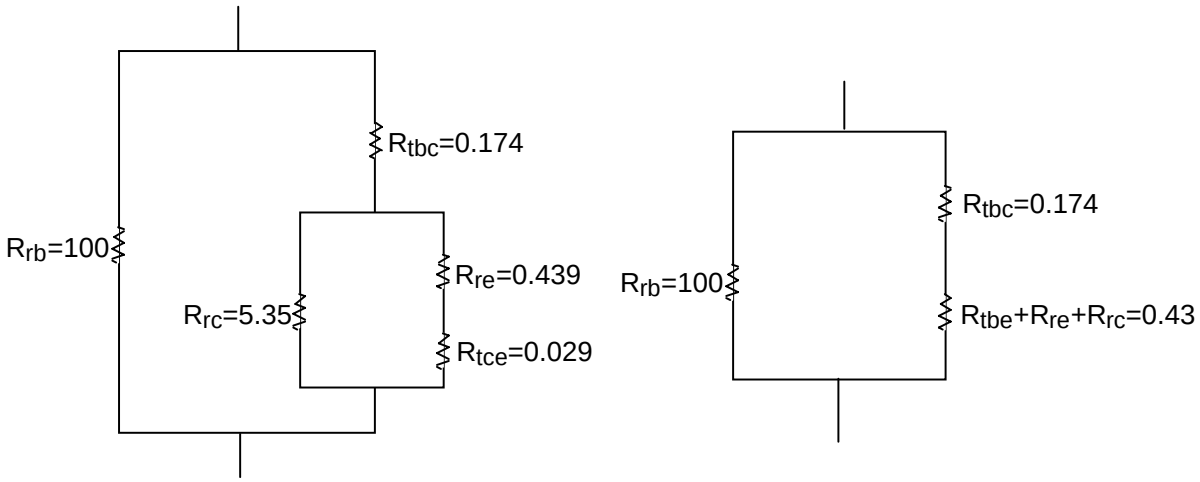

Figure R12.3-10 Electrical analog.

$$\gamma_e = \left(1-\varepsilon_{mf}\right)\left[\frac{1-\delta}{\delta} - \frac{3u_{mf}/\varepsilon_{mf}}{\left(0.71\,d_b g\right)^{1/2} - \left(u_{mf}/\varepsilon_{mf}\right)} - \alpha\right] \qquad \text{(R12.3-57)}$$

Examination of Equation (R12.3-57) shows that decreasing the bubble fraction, δ, and the minimum fluidization velocity would increase γ_e and hence the conversion. The minimum fluidization velocity could be decreased by decreasing the particle size. We now will investigate how the various parameters will affect the conversion for different limiting situations.

R12.3.6A The Slow Reaction

In addition to the obvious way of increasing the temperature to increase the conversion, and perhaps some unwanted side reactions, there are other ways the conversion may be increased when the reaction is slow. From Equation (R12.3-31) we know the conversion depends upon h, k_{cat}, u_b, and K_R. We will first determine K_R under this situation. For a slow reaction, k_{cat} is small when compared to K_{bc} and K_{ce} so that resistance to transport is essentially zero, that is,

$$\frac{k_{cat}}{K_{bc}} \approx 0 \qquad \text{(R12.3-58)}$$

and

$$\frac{k_{cat}}{K_{ce}} \approx 0 \qquad \text{(R12.3-59)}$$

then

$$K_R = \gamma_b + \cfrac{1}{0 + \cfrac{1}{\gamma_c + \cfrac{1}{\cfrac{1}{\gamma_e} + 0}}} = \gamma_b + \gamma_c + \gamma_e \qquad \text{(R12.3-60)}$$

Using Equation (R12-64) to substitute for γ_e, we have

$$K_R = \gamma_b + \left(1-\varepsilon_{mf}\right)\left(\frac{1-\delta}{\delta}\right) \tag{R12.3-61}$$

neglecting γ_b, with respect of the second term yields

$$K_R = \left(1-\varepsilon_{mf}\right)\left(\frac{1-\delta}{\delta}\right) \tag{R12.3-62}$$

Consequently, we see that K_R can be increased by decreasing δ the volume fraction of bubbles. For the ammonia oxidation example, this would give

$$K_R \approx 2.47$$

or about 11% higher than the value obtained by the more elaborate calculations which included the transport. This would predict a conversion of 21.4%, very close to the 20% given by the method which includes the transport limitations. Thus the ammonia oxidation system of Massimilla and Johnstone is essentially a reaction-limited system. The conversion and catalyst weight are related by

$$W = A_c h \rho_c \left(1-\varepsilon_{mf}\right)(1-\delta) = \frac{A_c u_b \rho_c \left(1-\varepsilon_{mf}\right)(1-\delta)}{k_{cat} K_R} ln\frac{1}{1-X} \tag{R12.3-63}$$

Substituting for K_R,

$$W = \frac{A_c \rho_c u_b \delta}{k_{cat}} ln\left(\frac{1}{1-X}\right) \tag{R12.3-64}$$

Recalling Equation (R12.3-23),

$$\delta = \frac{u_o - u_{mf}}{u_b - u_{mf}(1+\alpha)} \tag{R12.3-23}$$

In almost all instances, u_b is significantly greater than u_{mf} (1+α) so that Equation (R12.3-45) is approximately

$$\delta = \frac{u_0 - u_{mf}}{u_b} \tag{R12.3-65}$$

Combining Equations (R12.3-64) and (R12.3-65) gives

Approximate catalyst weight for slow reactions

$$\boxed{W = \frac{A_c \rho_c \left(u_o - u_{mf}\right)}{k_{cat}} ln\frac{1}{1-X}} \tag{R12.3-66}$$

Therefore one observes that to reduce the catalyst weight for a specified conversion, u_0 and u_{mf} should be as close as possible. One can now ask in what ways the catalyst weight may be reduced for a specified conversion. The answer to this question is the

"What if . . ." questions

same as to the question, "How may one increase the conversion for a fixed catalyst weight?"

Example R12-4 Effect of Particle Size on Catalyst Weight for a Slow Reaction

Suppose you are operating at five times the minimum fluidization velocity, $u_0 = 5u_{mf}$. What would be the effect of doubling the particle diameter on the catalyst weight for the same throughput and conversion?

Solution

Substitution for u_0, into Equation (R12.3-66) gives

Case 1

$$W_1 = \frac{A_c \rho_c 4u_{mf1}}{k_{cat1}} ln \frac{1}{1-X_1} \tag{RE12-7.1}$$

Case 2

$$W_2 = \frac{\rho_c A_c \left(u_{o2} - u_{mf2}\right)}{k_{cat2}} ln \frac{1}{1-X_2} \tag{RE12-7.2}$$

Since the temperature remains constant and there are no inter- and intra-particle resistances, $k_{cat1} = k_{cat2}$, the throughput ($u_{01} = u_{02}$), and conversion ($X_1 = X_2$) are the same for Cases 1 and 2. The ratio of Equation (E4-1) and (E4-2) yields

$$\frac{W_2}{W_1} = \frac{u_{o1} - u_{mf2}}{4u_{mf1}} = \frac{5u_{mf1} - u_{mf2}}{4u_{mf1}} \tag{RE12-7.3}$$

Recalling Equation (R12.3-5),

$$u_{mf} = \frac{\left(\psi d_p\right)^2}{150\mu} \underbrace{\left[g\left(\rho_c - \rho_g\right)\right]}_{\eta} \frac{\varepsilon_{mf}^3}{1-\varepsilon_{mf}} \tag{R12.3-5}$$

and neglecting the dependence of ε_{mf} on d_p we see that the only parameters that vary between Case 1 (d_p) and Case 2 ($d_{p2} = 2d_{p1}$) are u_{mf} and W. Taking the ratio of u_{mf2} to u_{mf1} and substituting for d_{p2} in terms of d_{p1} we obtain

$$\frac{u_{mf2}}{u_{mf1}} = \left(\frac{d_{p2}}{d_{p1}}\right)^2 = \left(\frac{2d_{p1}}{d_{p1}}\right)^2 = 4 \tag{RE12-7.4}$$

and therefore

$$\frac{W_2}{W_1} = \frac{5u_{mf1} - 4u_{mf1}}{4u_{mf1}} = 0.25 \tag{RE12-7.5}$$

Thus in the situation we have postulated, with a first-order reaction and reaction limiting the bed behavior, doubling the particle size will reduce the catalyst by approximately 75% and still maintain the same conversion.

R12.3.6B The Rapid Reaction

To analyze this limiting situation, we shall assume the particles are sufficiently small so that the effectiveness factor is essentially one and that the rate of transfer from the bulk fluid to the individual catalyst particles is rapid in comparison with the rate of transfer between the fluidization phases. For the case of rapid reaction,

$$\frac{k_{cat}}{K_{bc}} \text{ and } \frac{k_{cat}}{K_{ce}} >> 1$$

Using these approximations in the equation for K_R, which is

$$K_R = \gamma_b + \cfrac{1}{\cfrac{k_{cat}}{K_{cb}} + \cfrac{1}{\gamma_c + \cfrac{1}{\cfrac{k_{cat}}{K_{ce}} + \cfrac{1}{\gamma_e}}}}$$

one observes the first term to be neglected is γ_b, and we also note that because the reaction is rapid k_{cat}/K_{ce} is a large number.

$$K_R = \cfrac{1}{\cfrac{k_{cat}}{K_{ce}} + \cfrac{1}{\gamma_c + \cfrac{1}{(\text{Large No.}) + \cfrac{1}{\gamma_e}}}}$$

Then neglecting the reciprocal of γ_e with respect to k_{cat}/K_{cb}, K_R becomes

$$K_R = \gamma_b + \cfrac{1}{\cfrac{k_{cat}}{K_{cb}} + \cfrac{1}{\gamma_c}} \approx \gamma_b + \frac{K_{cb}}{k_{cat}} \qquad \text{(R12.3-67)}$$

There are two situations one can analyze here

Situation 1: $\gamma_b << \dfrac{K_{bc}}{k_{cat}}$ Resistance to transport small wrt resistance to reaction inside the bubble

Situation 2: $\gamma_b >> \dfrac{K_{bc}}{k_{cat}}$ Resistance to transport large wrt resistance to reaction inside the bubble

Only situation 1 will be analyzed in the text; the analysis of situation 2 is left as an exercise.

Assuming very few particles are present in the bubble phase

$$K_R \cong \frac{K_{bc}}{k_{cat}} \tag{R12.3-68}$$

The catalyst weight is given by combining Equations (R12.3-54) and (R12.3-68)

$$W = \frac{A_c u_b \rho_c (1-\delta)(1-\varepsilon_{mf})}{K_{bc}} ln\left(\frac{1}{1-X}\right) \tag{R12.3-69}$$

Neglecting δ with respect to 1 in the numerator

Approximate catalyst rate for a rapid reaction

$$\boxed{W = \frac{A_c u_b \rho_p (1-\varepsilon_{mf})}{k_{cat} K_{bc}} ln\left(\frac{1}{1-X}\right)} \tag{R12.3-70}$$

On observing that the equation for K_{bc}, Equation (R12.3-30), is the sum of two terms A_0 and B_0

$$K_{bc} = 4.5\left(\frac{u_{mf}}{d_b}\right) + 5.85\left(\frac{D_{AB}^{1/2} g^{1/4}}{d_b^{5/4}}\right) \tag{R12.3-30}$$

$$K_{bc} = A_0 + B_0$$

one finds the problem can be further divided.

Case A: $A_0 >> B_0$

Case B: $B_0 >> A_0$

Only Case A will be considered here; Case B again will be left as an exercise.

For Case A

$$K_{bc} \cong 4.5\frac{u_{mf}}{d_b} \tag{R12.3-71}$$

Then

$$W = \frac{u_b d_b}{4.5 u_{mf}} \rho_c A_c (1-\varepsilon_{mf}) ln\left(\frac{1}{1-X}\right) \tag{R12.3-72}$$

Recalling the equation for u_b and neglecting other terms in the equation with respect to the velocity of rise of a single bubble, that is,

$$u_b \approx u_{br}$$

and

$$u_{br} = 0.71 g^{1/2} d_b^{1/2}$$

$$W = \frac{0.71 g^{1/2} d_b^{3/2}}{4.5 u_{mf}} A_c \rho_c (1-\varepsilon_{mf}) \ln\left(\frac{1}{1-X}\right)$$

$$W = 4.9 \frac{d_b^{3/2}}{u_{mf}} A_c \rho_c (1-\varepsilon_{mf}) \ln\left(\frac{1}{1-X}\right) \qquad \text{(R12.3-73)}$$

The average bubble diameter is a function of the tower diameter (thus the tower cross-sectional area A_c), height, u_0, and u_{mf}. As a first approximation, we assume the average bubble diameter is some fraction, (say 0.75) of the maximum bubble diameter.

$$d_b = 0.75\, d_{bm} \qquad \text{(R12.3-74)}$$

Then, from Equation (R12.3-16), we have

$$d_{bm} = (0.75)(0.652)\left[A_c (u_o - u_{mf})\right]^{0.4} \qquad \text{(R12.3-75)}$$

One Approximation for fast reactions

which is substituted into Equation (R12.3-73) to give

$$W = 1.69 \frac{A_c^{1.6} (u_o - u_{mf})^{0.6}}{u_{mf}} \rho_c (1-\varepsilon_{mf}) \ln\left(\frac{1}{1-X}\right) \qquad \text{(R12.3-76)}$$

Example R12-5 Effect of Catalyst Weight on Particle Size for a Rapid Reaction

We again consider the effect of doubling particle size while keeping all other variables the same. Case 1: $d_{p1} = d_{p1}$, Case 2: $d_{p2} = 2\, d_{p1}$.

Solution

Using Equation (R12.3-76) and taking the ratio of Case 1 to Case 2

$$\frac{W_2}{W_1} = \frac{(u_{02} - u_{mf2})^{0.6}}{(u_{01} - u_{mf1})^{0.6}} \frac{u_{mf1}}{u_{mf2}} \qquad \text{(RE12-6.1)}$$

Recalling from previous examples

$$u_{o2} = u_{o1} = 5u_{mf1}$$

$$u_{mf2} = 4u_{mf1}$$

then

$$\frac{W_2}{W_1} = \left(\frac{5u_{mf1} - 4u_{mf1}}{5u_{mf1} - u_{mf1}}\right)^{0.6} \frac{u_{mf1}}{4u_{mf1}} = \left(\frac{1}{4}\right)^{0.6} \frac{1}{4} \qquad \text{(RE12-6.2)}$$

or

$$\frac{W_2}{W_1} = 0.11 \qquad \text{(RE12-6.3)}$$

In this case, we see that doubling the particle diameter decreases the catalyst weight by 89% while maintaining the same conversion. However, for a fast reaction, a significant decrease in effectiveness factor could offset this advantage.

SUMMARY

1. Minimum fluidization velocity

$$u_{mf} = \frac{\left(\psi d_p\right)^2 \eta\, \varepsilon_{mf}^3}{150\ \mu \left(1-\varepsilon_{mf}\right)} \tag{S12.3-1}$$

2. Porosity at minimum fluidization

$$\varepsilon_{mf} = \frac{0.586}{\psi^{0.72}} \left[\frac{\mu^2}{\rho_g \eta d_p^3}\right]^{0.029} \left[\frac{\rho_g}{\rho_c}\right]^{0.021} \tag{S12.3-2}$$

or

$$\varepsilon_{mf} = \frac{0.415}{\psi^{0.33}} \tag{S12.3-3}$$

3. Bubble size

$$d_b = d_{bm} - \left(d_{bm} - d_{bo}\right) e^{-0.3\ h/D_t} \tag{S12.3-4}$$

where

$$d_{bm} = 0.652\left[A_c\left(u_o - u_{mf}\right)\right]^{0.4},\ cm \tag{S12.3-5}$$

For porous plates

$$d_{b0} = 0.00376\left(u_o - u_{mf}\right)^2,\ cm \tag{S12.3-6}$$

4. Velocity of bubble rise

$$u_b = u_0 - u_{mf} + 0.71\left(g d_b\right)^{1/2} \tag{S12.3-7}$$

5. Bed height - conversion in first order reaction

$$h = \frac{u_b}{k_{cat} K_R}\ \ln\ \frac{1}{1-X} \tag{S12.3-8}$$

$$K_R = \gamma_b + \cfrac{1}{\cfrac{k_{cat}}{k_{bc}} + \cfrac{1}{\gamma_c + \cfrac{1}{\cfrac{1}{\gamma_e} + \cfrac{k_{cat}}{K_{ce}}}}} \tag{S12.3-9}$$

6. Mass Transfer Parameters

   a. Between the bubble and the cloud

$$K_{bc} = 4.5\left[\frac{u_{mf}}{d_b}\right] + 5.85\frac{D^{1/2} g^{1/4}}{d_b^{5/4}} \tag{S12.3-10}$$

   b. Between the cloud and the emulsion

$$K_{ce} = 6.78\left[\frac{\varepsilon_{mf} D u_b}{d_b^3}\right]^{1/2} \quad \text{(S12.3-11)}$$

7. The reaction rate parameters

$$k_{cat} = \rho_p k \quad \text{(S12.3-12)}$$

a. Bubble

$$0.001 < \gamma_b < 0.01 \quad \text{(S12.3-13)}$$

b. Cloud

$$\gamma_c = \left(1-\varepsilon_{mf}\right)\left[\frac{3\left(u_{mf}/\varepsilon_{mf}\right)}{u_{br}-\frac{u_{mf}}{\varepsilon_{mf}}}+\alpha\right] \quad \text{(S12.3-14)}$$

c. Emulsion

$$\gamma_e = \left(1-\varepsilon_{mf}\right)\frac{(1-\delta)}{\delta} - \gamma_c \quad \text{(S12.3-15)}$$

$$\delta = \frac{u_0 - u_{mf}}{u_b - u_{mf}\left(1+\alpha\right)} \quad \text{(S12.3-16)}$$

where α is given by Figure 12.3-5.

8. Procedure

See flow chart in Figure R12.3-9.

Supplementary Reading

1. Anonymous, *Chem. Eng. Prog*., 53 (10), 50 (1957).

2. Blanding, F. H., *Ind. Eng. Chem*., 45, 1186 (1953).

3. Carlsmith, L. E., and F. B. Johnson, *Ind. Eng. Chem*., 37, 451 (1945).

4. Davidson, J. F., and D. L. Keairns, *Fluidization*. Proceedings of the Second Engineering Foundation Conference, Cambridge: Cambridge University Press, 1978.

5. Grace, J. R., and J. M. Matsen, *Fluidization*. New York: Plenum Press, 1980.

6. Keavins, D. L., ed. *Fluidization Technology*, vol. I and II. Washington, D.C.: Hemisphere Publishing Co. in association with McGraw-Hill I(1975), II(1976).

7. Kunii, D., and O. Levenspiel, *Ind. Eng. Chem. Process Design Devel*., 7, 481 (1968).

8. Kunii, D., and O. Levenspiel, *Fluidization Engineering*, 2nd Ed., (Boston: Butterworth, 1991).

9. Mathur, R. B., and N. Epstein, *Spouted Beds*, (New York: Academic Press, 1974).

10. Weekman, V. W., Jr., *Ind. Eng. Chem. Process Design Devel*. 7, 91 (1968).

11. Wen, C. Y., and Y. H. Yu, *AIChE J*., 12, 610 (1966).

12. Zenz, F. A., *Ind. Eng. Chem. Fund*., 3, 65 (1964).

13. Zenz, F. A., *Ind. Chem. E. Symposium Series*, No. 30, 136 (1968).

14. Zenz, F. A., and N. A. Weil, *AIChE J*., 4, 472 (1958).