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Effect of Particle Size Distribution on Catalyst Effectiveness

Calculations of catalyst effectiveness in heterogeneous catalysis are normally based on an average particle size. This approach is quite adequate for situations in which the catalyst particles are nearly uniform in size. In packed bed reactors, for example, the catalyst particles are usually tabletted, extruded, or formed in some other fairly consistent manner. On the other hand, there are cases in which a distribution of particle sizes must be considered. In fluidized bed catalytic cracking, the catalyst particles are typically distributed over a range of diameters from about 10 to 150 μm. Another example is catalyst microeffectiveness[1] in pilled zeolite catalysts. Synthetic zeolite crystals are typically distributed over a range of particle sizes from about 1 to 10 μm. Under such circumstances it is not clear how the average particle size should be calculated. Neither is it clear at what point the use of an average particle size becomes unacceptable and the entire distribution of sizes must be considered. These questions will be addressed in the present communication.

We will consider the case of a first-order catalytic reaction in spherical particles, but before proceeding further it is important to distinguish between several different types of particle size distribution functions. Let $f_v(r)$ be the *volume* fraction particle size distribution such that $f_v(r)dr$ is the volume fraction of particles with radii between r and $r + dr$. The volume fraction distribution is observed experimentally in particle size analyses by conductometric techniques (Coulter counter), for example. Provided that the particle density does not vary with radius, the volume fraction distribution is identical to the *weight* fraction distribution, $f_w(r)$, which is obtained in sedimentation measurements. Microscopic determinations yield a *number* fraction distribution, $f(r)$, such that $f(r)dr$ is the number fraction of particles with radii between r and $r + dr$. The two distributions, $f(r)$ and $f_v(r)$, are related according to

$$f_v(r)dr = \frac{(\frac{4}{3}\pi r^3)f(r)dr}{\int_0^\infty (\frac{4}{3}\pi r^3)f(r)dr}$$

or

$$f_v(r) = \frac{r^3}{\overline{r^3}} f(r), \qquad (1)$$

where

$$\overline{r^n} = \int_0^\infty r^n f(r)dr, \qquad (2)$$

that is, $\overline{r^n}$ is the expectation of r^n.

It is convenient to define a mean value of the effectiveness factor, η_m, applicable to a distribution of particle sizes according to

$$\eta_m = \frac{-R_{AW,\text{obs}}}{-R_{AW,S}}, \qquad (3)$$

where $-R_{AW,\text{obs}}$ is the reaction rate observed for the distribution of particle sizes and $-R_{AW,S}$ is the rate that would be obtained in the limit of infinite intraparticle mass transfer, i.e., if the reactant concentration throughout all particles was uniform at C_{AS}, the particle surface concentration.

[1] Pilled zeolites are "bidisperse structured," and the overall catalyst effectiveness will generally depend upon the rates of diffusion within the interstices between crystals (macroeffectiveness) as well as the diffusion rate within the crystals (microeffectiveness). See Ors and Dogu (*1*) for more details.

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The observed reaction rate can also be obtained by integrating over the distribution of particle sizes, i.e.,

$$\rho_p(-R_{AW,\text{obs}}) = \int_0^\infty \eta\rho_p(-R_{AW,S})f_v(r)dr,$$

and since the particle density is assumed to be independent of particle size,

$$-R_{AW,\text{obs}} = -R_{AW,S}\int_0^\infty \eta f_v(r)dr. \quad (4)$$

It is appropriate to employ the volume distribution function $f_v(r)$ in this integration since $\eta\rho_p(-R_{AW,S})$ is the observed reaction rate per unit volume in particles of radius r. From Eqs. (3) and (4) it is immediately apparent that

$$\eta_m = \int_0^\infty \eta f_v(r)dr. \quad (5)$$

We note that this result is quite general since no assumptions have been made regarding reaction rate form or shape of the particle size distribution.

For a first-order reaction in a sphere the kinetics expression on a catalyst weight basis is

$$-R_{AW} = kC_A \quad (6)$$

and the effectiveness factor is given by

$$\eta = \frac{3}{h}\left[\frac{1}{\tanh(h)} - \frac{1}{h}\right], \quad (7)$$

where h is the Thiele modulus,

$$h = r\sqrt{\frac{\rho_p k}{D_A{}^e}}. \quad (8)$$

Note that the nonsubscripted h and η are written for particles of a particular size, r.

AVERAGE PARTICLE RADIUS

A convenient definition of average particle radius can be obtained by considering the asymptotic region of strong intraparticle diffusion resistance. For large h Eq. (7) is closely approximated by

$$\eta = \frac{3}{h} \quad (9)$$

Upon substituting from Eqs. (1), (8) and (9) into Eq. (5) we have

$$\eta_m = \frac{3}{\overline{r^3}\sqrt{\dfrac{\rho_p k}{D_A{}^e}}}\int_0^\infty r^2 f(r)dr.$$

and with the aid of Eq. (2)

$$\eta_m = \frac{3}{\dfrac{\overline{r^3}}{\overline{r^2}}\sqrt{\dfrac{\rho_p k}{D_A{}^e}}}$$

or

$$\eta_m = \frac{3}{h_m} \quad (10)$$

where

$$h_m = r_m\sqrt{\frac{\rho_p k}{D_A{}^e}} \quad (11)$$

and

$$r_m = \frac{\overline{r^3}}{\overline{r^2}} \quad (12)$$

is the average particle radius. Defining the average particle radius in this fashion ensures that effectiveness factor plots (η_m vs h_m) will converge to the same asymptotic curve at large values of Thiele modulus for all particle size distributions. Aris recommended using a mean radius equivalent to r_m on the basis of an argument similar to that employed here (*2*). Although Eq. (12) was obtained for a first-order reaction, it is easily shown from an analysis based on the generalized Thiele modulus (*3*) that the result is valid for any reaction rate form.

EFFECT OF PARTICLE SIZE DISTRIBUTION

The use of a mean particle size is strictly valid only in the asymptotic limit of strong intraparticle diffusion resistance (or in the trivial case where η is unity in all particles). Outside the asymptotic region calculations based on a mean particle size can only be approximate. In order to explore the magnitude of this approximation, let us consider a case in which the volume fraction particle size distribution is log-normal with parameters α and β, i.e.,

$$f_v(r) = \frac{1}{\sqrt{2\pi}\ \beta} \left(\frac{1}{r}\right) \exp\left[-\frac{(\ln r - \alpha)^2}{2\beta^2}\right], \qquad r > 0. \quad (13)$$

The log-normal distribution is very common in nature. It arises when an event can be expressed as the product of independent causative factors, and under such circumstances Eq. (13) can be derived by application of the Central Limit theorem of mathematical statistics (*4*).

To express the mean radius, r_m, in terms of the distribution parameters, α and β, we first write Eq. (2) for $n = 2$ and eliminate $f(r)$ with the aid of Eq. (1) to obtain

$$\overline{r^2} = \overline{r^3} \int_0^\infty \frac{1}{r} f_v(r) dr.$$

The integral in this expression can be evaluated after substituting from Eq. (13) for the distribution function. Upon combining these results with Eq. (12) we have

$$r_m = e^{\alpha - \beta^2/2}. \quad (14)$$

The mean effectiveness factor, η_m, is obtained by substituting for $f_v(r)$ in Eq. (5). Thus

$$\eta_m = \int_0^\infty \eta \left\{\frac{1}{\sqrt{2\pi}\ \beta} \left(\frac{1}{r}\right) \exp\left[-\frac{(\ln r - \alpha)^2}{2\beta^2}\right]\right\} dr. \quad (15)$$

This expression is written in a more convenient form by making the transformation of variables:

$$z = \frac{\ln r - \alpha}{\sqrt{2}\ \beta}. \quad (16)$$

Equation (15) can then be written as

$$\eta_m = \frac{1}{\sqrt{\pi}} \int_{-\infty}^\infty e^{-z^2} \eta \ dz. \quad (17)$$

From a rearrangement of Eq. (16) we have

$$r = e^{\alpha + \sqrt{2}\beta z}. \quad (18)$$

The Thiele modulus is obtained by substituting for r in Eq. (8),

$$h = e^{\alpha + \sqrt{2}\beta z} \sqrt{\frac{\rho_p k}{D_A^e}}$$

or

$$h = e^{\alpha - \beta^2/2} \sqrt{\frac{\rho_p k}{D_A^e}}\ e^{\sqrt{2}\beta z + \beta^2/2},$$

and upon combining this result with Eqs. (14) and (11) we have

$$h = h_m\ e^{\sqrt{2}\beta z + \beta^2/2}, \quad (19)$$

Equations (19), (7), and (17) can be solved to obtain η_m as a function of only two parameters, h_m and β. The parameter α is contained in h_m.

The integral of Eq. (17) was evaluated using the Gauss–Hermite quadrature formula (*5*) for a range of parameter values and the results are plotted in Fig. 1. For values of β less than about 0.5 an average particle size can be employed in calculations of effectiveness factor with little loss of accuracy. The maximum error in this approximation is only 9%. Errors as great as 32% can result from using an average particle size when β is unity. For values of β greater than unity it will be necessary to include the entire particle size distribution in calculations of catalyst effectiveness. Note, however, that values greater than unity will seldom be encountered in practice.

The mean, μ, and variance, σ^2, of the log-normal distribution are given by the (*6*)

$$\mu = e^{\alpha + \beta^2/2}, \quad (20)$$

$$\sigma^2 = \mu^2(e^{\beta^2} - 1). \quad (21)$$

Consequently, for given α the width of the distribution varies roughly in proportion to

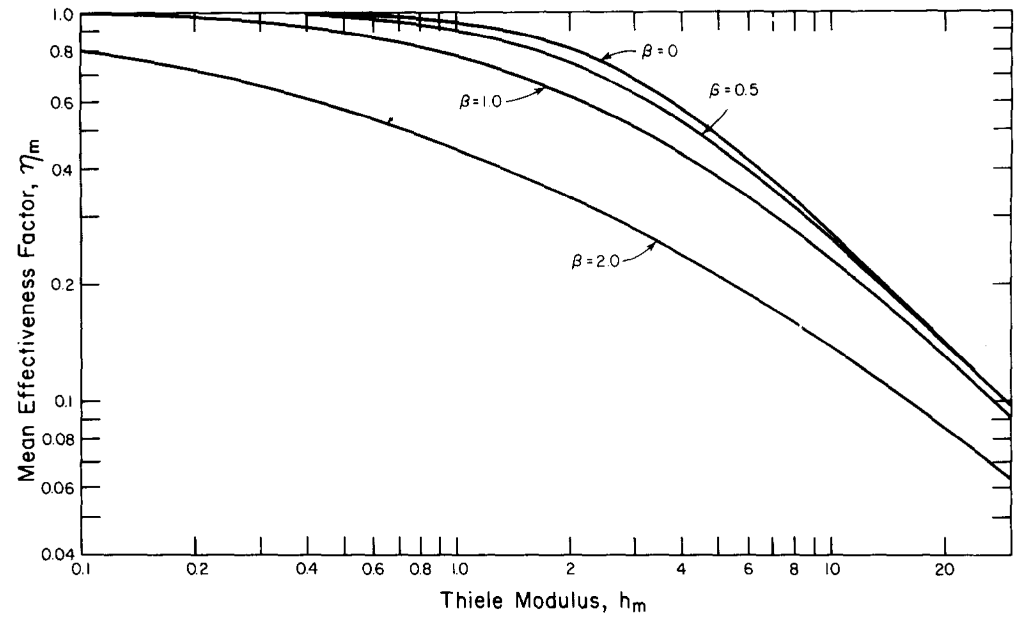

FIG. 1. Effectiveness factor plot for a first-order reaction in spherical particles having a log-normal (volume fraction) size distribution. $\beta = 0$ corresponds to particles of uniform size.

the exponential of β^2. Care must therefore be exercised in interpreting β as a measure of distribution width.

SUMMARY

When calculating the effectiveness factor for a distribution of catalyst particle sizes, the average particle radius defined by Eq. (12) should be employed. Then, in the asymptotic limit of strong intraparticle diffusion resistance all plots of effectiveness factor vs Thiele modulus, regardless of the shape of the particle size distribution, will be identical to the plot for a uniform particle size. Outside the asymptotic limit one must take into account the distribution of particle sizes, Eq. (5), for precise calculations. However, an analysis based upon the log-normal distribution indicates that the use of an average particle radius is quite reasonable for values of the parameter β less than about 0.5 (Fig. 1). If errors of the order of 32% can be tolerated, then calculations based upon the average radius can be employed for values of β less than unity.

NOMENCLATURE

C_A = Reactant concentration, mol/cm^3
D_A^e = Reactant effective diffusivity, cm^2/s
h = Thiele modulus for sphere
k = First-order rate constant, cm^3/g · s
n = Exponent in Eq. (2)
r = Particle radius, cm
$-R_{AW}$ = Reaction rate (disappearance), mol/g · s
z = Variable defined by Eq. (16)
α = Parameter in log-normal distribution, Eq. (13)
β = Parameter in log-normal distribution, Eq. (13)
η = Effectiveness factor
μ = Mean of log-normal distribution, Eq. (20), cm
ρ_p = Particle density, g/cm^3
σ^2 = Variance of log-normal distribution, Eq. (21), cm^2

Subscripts:

A = Reactant
m = Mean or average value
obs = Observed quantity
S = Quantity at external particle surface
v = Volumetric basis
w = Weight basis

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