A Note on Generalization of Effectiveness Factor for Bidispersed Porous Catalysts

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Although many porous catalysts have a bidispersed pore structure, in many cases they are treated as monodispersed catalysts and a single effective diffusion coefficient is used to describe the diffusion process. In the catalyst pellets that are formed by compacting fine porous particles, macropores are formed between the agglomorated particles; the fine pores within the particles are called micropores. The macroporosity and the average radius of macropores are significantly affected by the compacting pressure, while the micropore structure is essentially unchanged. In such catalysts the surface area of micropores is usually much greater than the macropore surface area and most of the active sites lie within the microporous region. In such catalysts, both macro and micropore diffusion resistances might have significant effect on the observed rates. The relative importance of macro- and micropore diffusion limitations on the observed rates can be tested by using the criterion suggested by Doğu and Doğu (1980). The objective of the present study is to generalize the effectiveness factor for bidispersed porous catalysts with respect to the parameter α, which represents the ratio of diffusion resistances in the macro- and micropores and with respect to pellet geometry.

One approach to analyzing diffusion and reaction processes in such catalysts involves the assumption that macropores are cylindrical tubes, and that branched cylindrical micropores extend from the macropores into the pellet. A more realistic approach is to consider the catalyst pellet as an agglomeration of microporous particles. The particles that are agglomerated to form the catalyst pellet are generally present in powder or granular form and their shape can be approximated as spheres. Considering that the ratio of the pellet radius to particle radius is quite large for many of the catalysts, the major assumption of this model, which states that the concentration profiles in the particles are symmetrical, is generally accepted to be reasonable.

Some of the earlier papers on the effectiveness of bidispersed porous catalysts were reported by Mingle and Smith (1961), Carberry (1962), and Wakao and Smith (1964). It was shown by Örs and Doğu (1979) that the effectiveness factor of such systems depends on a dimensionless parameter, α, in addition to the Thiele modulus. The magnitude of α is determined by the ratio of diffusion times in the macro- and microporous regions. As it was reported by Örs and Doğu (1979), use of a single effective diffusion coefficient and prediction of the effectiveness factors from conventional expressions derived for monodispersed systems give overestimated values. Consequently, the bidispersed pellet approach was recommended for better design of reactors in which such catalysts are used.

Kulkarni et al. (1981) and Jayaraman et al. (1983) extended the approach reported by Örs and Doğu to nonlinear rate forms covering power law. They presented numerical and asymptotic solutions of effectiveness factor. Neogi and Ruckenstein (1980) derived ensemble averaged transport equations and showed that the point sink approximation is valid if the ratio of radius of the microporous particle to pellet radius is less than 1/20. Hashimoto et al. (1976) presented a method to predict the effective diffusivities both in the macro- and micropore regions. Hashimoto and Smith (1973, 1974), and Furusawa and Smith (1973) showed that both macro- and micropore diffusion coefficients can be determined from the chromatographic experiments. Uyanik and Doğu (1977) and Doğu and Ercan (1983) applied the single pellet technique that was originally derived by Doğu and Smith (1975, 1976) to study diffusion and adsorption in bidisperse systems.

Considering an nth order reaction, the dimensionless mass conservation equations for the macroporous pellet and the microporous particle are written, respectively, as

$$\frac{1}{\lambda^b}\frac{d}{d\lambda}\left(\lambda^b\frac{d\psi_a}{d\lambda}\right) - \alpha\left(\frac{d\psi_i}{d\xi}\right)_{\xi=a+1} = 0 \qquad (1)$$

$$\frac{1}{\xi^a}\frac{d}{d\xi}\left(\xi^a\frac{d\psi_i}{d\xi}\right) - \phi_i^2\psi_i^n = 0 \qquad (2)$$

where $b = 2,1,0$ for spherical, cylindrical, and slab pellet geometries, respectively ($a = 2,1,0$ for the particle), and λ and ξ are defined as

$$\lambda = R/(V_p/A_e)_{\text{pellet}} \qquad (3)$$

$$\xi = r/(V_p/A_e)_{\text{particle}} \qquad (4)$$

The shape generalized dimensionless parameters α and ϕ_i are defined as

$$\alpha = (1-\epsilon_a)\frac{D_i}{D_a}\frac{(V_p/A_e)^2_{\text{pellet}}}{(V_p/A_e)^2_{\text{particle}}} \qquad (5)$$

$$\phi_i = \left(\frac{V_p}{A_e}\right)_{\text{particle}}\left(\frac{\rho_p' S_g k_s C_o^{n-1}}{D_i}\right)^{1/2} \text{ (particle Thiele modulus)} \qquad (6)$$

Following a similar procedure to that of Örs andDoğu (1979), the effectiveness factor expressions are derived for different pellet geometries using the following boundary conditions:

TABLE 1. EFFECTIVENESS FACTOR EXPRESSIONS FOR A BIDISPERSED CATALYST (FIRST-ORDER REACTION)

Pellet Geometry	V_p/Ae	b	Effectiveness Factor $\eta(\alpha,\phi_i)$	Effectiveness Factor $\eta(\eta_i,\phi_a)$
Spherical	$R_o/3$	2	$\frac{1}{\phi_i^2\alpha}\left\{\frac{\left[\alpha\left(\frac{\phi_i}{\tanh 3\phi_i}-\frac{1}{3}\right)\right]^{1/2}}{\tanh\left\{3\left[\alpha\left(\frac{\phi_i}{\tanh 3\phi_i}-\frac{1}{3}\right)\right]^{1/2}\right\}}-\frac{1}{3}\right\}$	$\frac{\eta_i^{1/2}}{\phi_a}\left[\frac{1}{\tanh(3\phi_a\eta_i^{1/2})}-\frac{1}{3\phi_a\eta_i^{1/2}}\right]$
Cylindrical	$R_o/2$	1	$\frac{\left[\alpha\left(\frac{\phi_i}{\tanh 3\phi_i}-\frac{1}{3}\right)\right]^{1/2} I_1\left\{2\left[\alpha\left(\frac{\phi_i}{\tanh 3\phi_i}-\frac{1}{3}\right)\right]^{1/2}\right\}}{\phi_i^2\alpha\, I_o\left\{2\left[\alpha\left(\frac{\phi_i}{\tanh 3\phi_i}-\frac{1}{3}\right)\right]^{1/2}\right\}}$	$\frac{\eta_i^{1/2}}{\phi_a}\frac{I_1[2\phi_a\eta_i^{1/2}]}{I_o[2\phi_a\eta_i^{1/2}]}$
Slab	R_o	0	$\frac{\left[\alpha\left(\frac{\phi_i}{\tanh 3\phi_i}-\frac{1}{3}\right)\right]^{1/2}}{\phi_i^2\alpha}\tanh\left[\alpha\left(\frac{\phi_i}{\tanh 3\phi_i}-\frac{1}{3}\right)\right]^{1/2}$	$\frac{\eta_i^{1/2}}{\phi_a}\tanh\{\phi_a\eta_i^{1/2}\}$

$$\left(\frac{d\psi_i}{d\xi}\right)_{\xi=0}=0 \tag{7}$$

$$\left(\frac{d\psi_a}{d\lambda}\right)_{\lambda=0}=0 \tag{8}$$

$$(\psi_i)_{\xi=a+1}=\psi_a \tag{9}$$

$$(\psi_a)_{\lambda=b+1}=1 \tag{10}$$

The effectiveness factor expressions derived for a first-order reaction with different pellet geometries and spherical particle geometry are summarized in Table 1. For all pellet geometries, for large values of ϕ_i the limiting form of the effectiveness factor expression approaches

$$\lim_{\phi_i\to\infty}\eta=\frac{1}{\phi_i^{3/2}\alpha^{1/2}} \tag{11}$$

The variation of the effectiveness factor with respect to shape generalized $\phi_i^{3/2}\alpha^{1/2}$ for spherical, cylindrical, and slab geometries is shown in Figure 1. As illustrated in this figure, the effectiveness factor curves get very close to each other and approach the same limits if plotted against $\phi_i^{3/2}\alpha^{1/2}$ instead of ϕ_i. It has also been shown that the effect of the value of the α on the η vs. $\phi_i^{3/2}\alpha^{1/2}$ curves is negligibly small for the practically important ranges of α. As illustrated in Figure 2, for $0.5 < \alpha < 50$, η is practically only a function of $\phi_i^{3/2}\alpha^{1/2}$, instead of two independent dimensionless groups α and ϕ_i. The magnitude of α is determined by the ratio of diffusion times in the macro- and micropore regions. Using the data reported by Hashimoto and Smith (1974) for the diffusion of n-butane in alumina pellets, α values are evaluated to be in the range of 0.7 to 4.0. Again, the experimental macro- and micropore diffusivities reported by Ercan and Doǧu (1983) for ethylene in α-alumina pellets yield an α value of 36. For many of the bidispersed catalysts, the value of α falls into the $0.5 < \alpha < 50$ range.

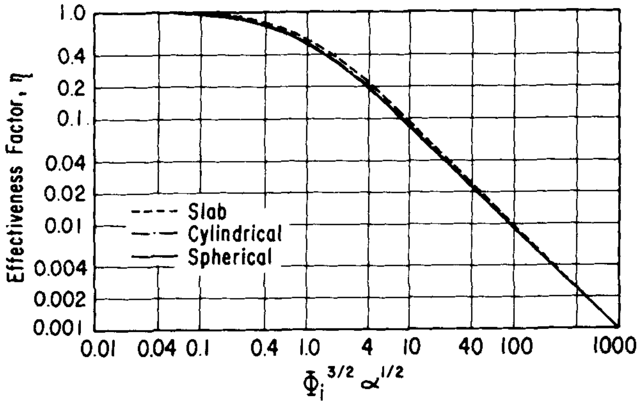

Figure 1. Dependence of effectiveness factor on $\phi_i^{3/2}\alpha^{1/2}$ for different pellet geometries (α = 1.0).

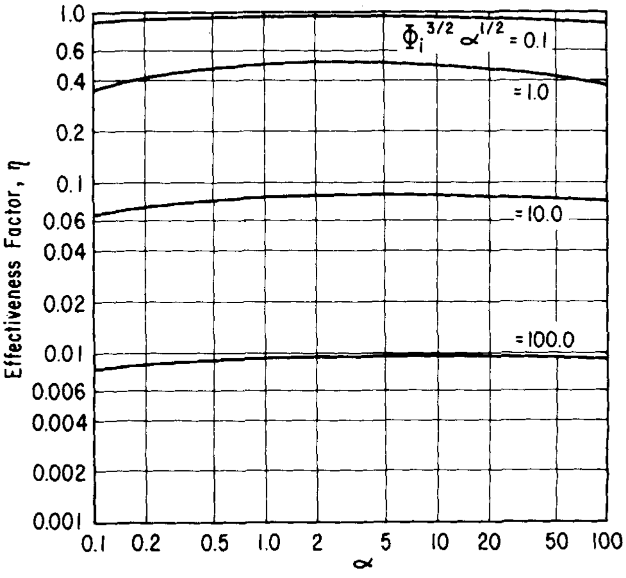

Figure 2. Dependence of effectiveness factor on α for different values of $\phi_i^{3/2}\alpha^{1/2}$ (spherical pellet).

The parameter α can also be defined as

$$\alpha = \left(\frac{\phi_a}{\phi_i}\right)^2 \qquad (12)$$

where

$$\phi_a = \left(\frac{V_p}{A_e}\right)_{\text{pellet}} \left(\frac{\rho_p Sg k_s}{D_a}\right)^{1/2} \text{(pellet Thiele modulus)} \qquad (13)$$

Using this definition of α, the effectiveness factor expressions for different geometries are obtained in terms of ϕ_a and the particle effectiveness factor η_i.

$$\eta_i = \frac{1}{\phi_i}\left(\frac{1}{\tanh 3\phi_i} - \frac{1}{3\phi_i}\right) \qquad (14)$$

These expressions are also given in Table 1. The two limiting forms of the pellet effectiveness factor for large (macropore diffusion controlling) and for small values of ϕ_a are

$$\lim_{\phi_a \to \infty} \eta = \frac{\eta_i^{1/2}}{\phi_a} \qquad (15)$$

$$\lim_{\phi_a \to 0} \eta = \eta_i \qquad (16)$$

Considering the definition of α given in Eq. 12, as $\phi_a \to 0$, the parameter α also goes to zero for finite values of ϕ_i, and the pellet effectiveness factor becomes equal to the particle effectiveness factor.

As a result of this analysis it has been shown that shape generalization and generalization with respect to α is possible by expressing η as a function of $\alpha^{1/2}\phi_i^{3/2}$. All the derivations are made for a first-order reaction to illustrate the generalization procedure. A similar generalization can be made for higher order reactions that might require numerical solution. This generalization would be helpful in the design of reactors and also in the modeling of deactivation of such catalysts.

NOTATION

A_e = external area of pellet or particle
a = geometric constant for the particle $a = 2$ (sphere), $= 1$ (cylinder), $= 0$ (slab)
b = geometric constant for the pellet $b = 2$ (sphere), $= 1$ (cylinder), $= 0$ (slab)
C_a = concentration of reactant A in the macropores
C_i = concentration of reactant A in the micropores
C_o = external surface concentration of A
D_a = effective macropore diffusion coefficient
D_i = effective micropore diffusion coefficient
k_s = surface reaction rate constant
R = diffusion coordinate for the pellet
R_o = pellet radius (spherical), radius of the cylinder (cylindrical) half-thickness (slab)
r = diffusion coordinate in the particle
r_o = radius of the particle
Sg = surface area per unit mass of catalyst
V_p = pellet or particle volume

Greek Letters

α = defined by Eq. 5
ϵ_a = macroporosity of the pellet
η = pellet effectiveness factor
η_i = particle effectiveness factor
ρ_p = $\rho_p'(1 - \epsilon_a)$, pellet density
ρ_p' = particle density
ϕ_i = particle Thiele modulus defined by Eq. 6
ϕ_a = pellet Thiele modulus defined by Eq. 13
ψ_a = dimensionless concentration in the macropores, C_a/C_o
ψ_i = dimensionless concentration in the micropores, C_i/C_o
ξ = dimensionless coordinate in the particlet, $r/(V_p/Ae)_{\text{particle}}$
λ = dimensionless coordinate in the pellet, $R/(V_p/Ae)_{\text{pellet}}$

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