Effectiveness Factors for Continuous Mixtures

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Catalyst effectiveness factors provide a quantitative estimate of diffusion resistance for chemical reactions in porous particles. The objective of this research is to develop an approach to calculate liquid-phase, porous-particle effectiveness factors, which are based on spherical reactant molecules and cylindrical pores that both have size distributions. Reactants larger than a given pore are excluded from the pore. A first-order reaction occurs when reactant molecules diffuse into pores that hinder their movement due to steric interactions with the pore wall. The reactant size distribution is described by rectangular or gamma distributions, and the pore-size distribution is modeled by continuous rectangular or discrete fractal distributions. Effectiveness factors are defined and evaluated for (a) one-size reactants in one-size pores, (b) all reactants in one-size pores, (c) one-size reactants in all pores, and (d) all reactants in all pores. Most of the discussion deals with equal-length pores, but the effect of a distribution of pore lengths is also considered.

Introduction

Effectiveness factors quantify the effect of intraparticle diffusion on chemical reactions in permeable catalyst particles. The diffusive effect can be influenced by a variety of factors, including the relative size of the pores and reactant molecules (Xiao and Wei, 1992). When reactant molecules are of size comparable to the pore size, diffusion will be restricted. Solutes larger than a pore will be excluded from that pore. Such configurational diffusion processes and their effects on chemical reactions need additional study, as stressed by Froment and Bischoff (1990).

Several studies have addressed the question of how hindered diffusion of reactants affects their catalyzed conversion. Lee et al. (1991) estimated the effect of restricted diffusion in catalytic hydroprocessing. Limbach and Wei (1990) studied restricted diffusion of porphyrins in porous particles, and showed how best to estimate average pore and molecular sizes. Rajagopalan and Luss (1979) discussed the influence of catalyst pore size on demetallation rates. Leung and Haynes (1984) included catalyst deactivation by pore plugging and reactive-size poisoning in bidisperse pores. The Fischer–Tropsch synthesis experiments of Fan et al. (1992) revealed how catalyst pore size can control the distribution of products due to diffusion effects. Catalyst reactivity is strongly influenced by diffusion control in zeolites. Karpinski et al. (1993) demonstrated that product molecules can be trapped in small-diameter pores that are filled with physisorbed reactant molecules. The resulting hindered transport has been modeled as single-file diffusion in straight, nonintersecting pores (Karger et al., 1992).

Recently, based on experimental data and simulations of aromatic hydrocracking in zeolites, Matsui et al. (1995) reported that the product distribution depended on molecular sizes of reactants *and* zeolite channels. As recognized by Spry and Sawyer (1975), the quantitative description of pore diffusion and catalytic reaction is further complicated if *both* the pores and the reactant molecules are distributed in size. Froment and Bischoff (1990) provide a discussion of the ideas of Spry and Sawyer, who considered catalytic demetallization of petroleum residuum containing asphaltenes ranging in size from 2.5 to 15 nm. As the Co/Mo catalyst pore-size distribution was in this same range, diffusive hindrance was significant. An approximate treatment of hindered diffusion was employed, and semiempirical summations over pore and molecular sizes accounted for catalyst surface area and reaction rates. This work related the key concepts: catalysts having pores in a given diameter range admit all molecules of diameter less than the maximum diameter (the cutoff size). Larger molecules, especially those with diameter approaching the cutoff, are hindered in their diffusion, and have reduced reactivity. The smallest reactants have maximum access to the catalyst sites.

The goal of the present research is to develop a systematic approach for calculating catalyst effectiveness factors based on solutes and pores that both have size distributions, and to illustrate the general principles with example calculations. A first-order reaction is considered to occur after the reactant molecule has diffused into pores that hinder its movement due to steric interactions with the pore wall (adsorption and electrical interactions are ignored). Molecules larger than a given pore are excluded from the pore, and hence cannot react unless they diffuse into a larger pore. The pores are assumed straight and unconnected, an assumption that can be compensated for with a tortuosity factor, as shown by Sahimi and Jue (1988). In addition to examples cited before that can be modeled by the present approach, the concepts may also be applicable to biological systems (Weisz, 1973) where diffusion in distributed pores can influence reactivity.

The theory of hindered diffusion was reviewed by Deen (1987). Reasonable models are available for predicting the hindered convection and diffusion of dilute rigid spheres in cylindrical pores (Bungay and Brenner, 1973). We let r_j or r, respectively, be the radius of pores that are discretely or continuously distributed. For the reactant we let x stand for the solute radius. The distance coordinate along the pore from the particle interior to its surface is z. The distribution of radii of the reactant solute is given by a frequency distribution function (FDF), which in general depends on the three independent variables as $c(x, r_j, z)$. The *concentration* of molecules in a pore of radius r_j at a position z and having a radius in the differential interval $(x, x+dx)$ is $c(x, r_j, z)dx$. The *total* lumped concentration, $C(r_j, z)$, is the integral over all x. McCoy (1995a,b) recently used these concepts for studies of size-exclusion chromatography and of membrane sieving (ultrafiltration) of a continuous polydisperse mixture through distributed pores. Principles of chemical reaction processes in both discrete and continuous multicomponent mixtures are presented in Astarita and Sandler (1991) and Sapre and Krambeck (1991).

Effectiveness Factor

The effectiveness factor is a steady-state concept that describes the effect of diffusive resistance on a chemical reaction that occurs when reactant molecules diffuse inside the particle. It is defined as the ratio of the actual reaction rate for a particle (influenced by intraparticle diffusion resistance) to the ideal reaction rate in the absence of diffusive resistance. The extreme of infinite diffusive resistance occurs when solutes are larger than the pore and thus cannot penetrate the particle at all. As the external surface is assumed catalytically inert, reactant molecules larger than *all* pores remain unreacted. Including these solutes in the ideal reaction rate would give an effectiveness factor that would not have the desired asymptotic value of unity when the pore length is very short or the reaction rate constant is very small (small Thiele modulus). In the effectiveness factor definition we will therefore not include molecules that are *totally* excluded from *all* the pores. It is of course necessary to account for reactants that are larger than some pores but smaller than others in a pore-size distribution.

We can write the definition of η for a solute of size x in a pore of size r_j as

$$\eta(x, r_j) = \frac{\dfrac{(\text{flux into particles surface})}{(\text{area of pore openings})}}{\dfrac{(\text{reaction rate at bulk concentration})}{(\text{accessible pore volume})}}$$

$$= \frac{J(x, r_j)A_j}{R'(x, r_j)V_j} = \frac{N(x, r_j)}{R(x, r_j)}. \tag{1}$$

Our focus will be on rigid (hard sphere, hard wall) interactions between spherical solutes in cylindrical pores. A partition coefficient

$$\begin{aligned} \Phi &= (1 - x/r_j)^2 \quad &\text{for } x < r_j \\ \Phi &= 0 \quad &\text{for } x \geq r_j \end{aligned} \tag{2}$$

accounts for the annular region of thickness x at the pore surface that cannot be penetrated by the hard sphere center (Renkin, 1954; Giddings et al., 1968). We will further require, as indicated in Eq. 2, that the partition coefficient vanishes when the sphere is completely excluded from the pore. For a cylindrical pore of radius r_j and length Z,

$$\frac{A_j}{V_j} = \frac{1}{Z\Phi}, \tag{3}$$

since the *accessible* pore volume in terms of n_j, the number of pores of radius r_j, is

$$V_j = \Phi Z \pi r_j^2 n_j. \tag{4}$$

The reaction rate for a unit volume of mixture at bulk concentration is assumed to be first-order,

$$R'(x, r_j) = k(x, r_j)c_0(x), \tag{5}$$

where the rate coefficient in general can depend on molecular size x and on catalyst surface area. Since the surface area for a unit volume of cylinder is $2/r_j$, for catalytic sites uniformly distributed along the cylindrical-pore surface, we assume that

$$k(x, r_j) = k_s(x)2/r_j, \tag{6}$$

where $k_s(x)$ generally depends on the reactant size x. The maximum possible reaction rate (mol/time) for the catalyst is

$$R(x, r_j) = c_0(x)V_j k_s(x)2/r_j. \tag{7}$$

The essence of the problem is to determine the flux into the catalyst particle, that is, $J(x, r_j)$, as the other terms in the definition of $\eta(x, r_j)$ are readily calculated. The solute flux for each size pore is multiplied by the cross-sectional area, πr_j^2, and by the number of pores, n_j, to determine the diffusion rate (moles/time) into each pore of size r_j,

$$N(x, r_j) = n_j \pi r_j^2 J(x, r_j). \tag{8}$$

As shown below, the flux into the particle can be (1) summed (or integrated) over all pores for a one-size solute; (2) integrated over all solute sizes for single-size pores; or (3) summed and/or integrated over all pores and all solutes. These three rate expressions, $N_{\langle r\rangle}(x)$, $N_{\langle x\rangle}(r)$, and $N_{\langle rx\rangle}$, can be utilized to define effectiveness factors, $\eta_{\langle r\rangle}(x)$, $\eta_{\langle x\rangle}(r)$, or $\eta_{\langle rx\rangle}$, respectively, in addition to $\eta(x, r_j)$ defined in Eq. 1.

Concentration in the Pore

The governing differential equation for the steady-state diffusion-reaction process is written for the radially averaged FDF of the diffusing reactant. Since we are concerned with how the reactant is hindered in diffusing to reactive catalyst sites along the cylindrical pore, we can write

$$D_e d^2c/dz^2 = kc. \tag{9}$$

The intrapore diffusion coefficient includes the effect of hindered diffusion:

$$D_e = D_b K_d/\tau, \tag{10}$$

where D_b is the bulk-solution Brownian-motion diffusivity, and K_d is the hydrodynamic-hindrance coefficient for diffusive transport. The tortuosity, τ, accounts approximately for pores that may not be perfectly straight. In contrast to Anderson and Quinn (1974) and Limbach and Wei (1990), who analyzed effective diffusion in catalyst particles or arbitrary pore structure by means of a pseudocontinuum model, we consider diffusion exclusively in cylindrical pores of specified diameter. The present model resembles Rajagopalan and Luss's (1979) catalyst pellet as a sphere drilled with cylindrical nonintersecting pores. The porosity of the particles permeated by the cylindrical pores can be formulated as the total volume of all pores divided by the particle volume. Whatever the particle shape, however, permeation from the bulk fluid occurs only by diffusion into the cylindrical pores, whose orientation in the particle is immaterial.

To determine D_e we eliminate convection in Bungay and Brenner's (1978) formulation of hindered transport by allowing the velocity to vanish. The factor K_d for diffusion is a function of x and r_j,

$$K_d = 6\pi/K_t, \tag{11}$$

where

$$K_t = (9/4)\sqrt{2}\pi^2(1 - x/r_j)^{-5/2}\left[1 + \sum_{i=1}^{2} a_i(1 - x/r_j)^i\right] + \sum_{i=0}^{4} a_{i+3}(x/r_j)^i \tag{12}$$

and the values for a_i are given in the Notation section. Other expressions for K_d could just as easily be used.

The solution of the reaction-diffusion equation for the FDF in a pore is similar to the usual solution for a rectangular slab geometry (Froment and Bischoff, 1990). In terms of a dimensionless distance coordinate, $\xi = z/Z$, and reaction-diffusion modulus,

$$\phi(x, r_j) = Z(k/D_e)^{1/2} \tag{13}$$

the differential equation, Eq. 9, for the frequency distribution, $c(x, r_j, z)$, becomes

$$d^2c/d\xi^2 = \phi^2 c. \tag{14}$$

The boundary conditions are based on the coordinate oriented toward the surface of the particle:

$$dc/d\xi = 0 \quad \text{at} \quad \xi = 0 \tag{15}$$

and

$$c(x, r_j, \xi = 1) = \Phi c_0(x). \tag{16}$$

The partition coefficient Φ, defined in Eq. 2, accounts for exclusion of a sphere of radius x from an annular region of thickness x at the pore surface (Giddings et al., 1968), *and* for the complete exclusion of spheres larger than the pore radius.

The solution to the differential equation is

$$c = \Phi c_0 \cosh(\phi\xi)/\cosh(\phi). \tag{17}$$

It follows that the gradient at the particle surface is

$$dc/dz = \Phi c_0(\phi/Z)\tanh(\phi) \quad \text{at} \quad z = Z, \tag{18}$$

which is needed to calculate the rate of diffusion into the particle,

$$J(x, r_j, z) = D_e dc/dz = D_e \Phi c_0(\phi/Z)\tanh(\phi). \tag{19}$$

This diffusion rate, which equals the diffusion-affected reaction rate, depends on solute size x through $c_0(x)$, $\Phi(x, r_j)$, and $\phi(x, r_j)$. The presence of the factor Φ in Eq. 18 for dc/dz ensures that $J(x > r_j) = 0$. The influence of the pore-size distribution on the effectiveness factor is through the modulus ϕ and the partition coefficient Φ. For simple kinetics of multicomponent mixtures, the concentration FDF satisfies the same z functionality as the lumped concentration.

Fluxes and Diffusion Rates

For purposes of calculating hindered diffusion the cylindrical pores of radius r_j are assumed straight and nonintersecting. Only solutes smaller than a pore diameter are allowed to diffuse into the pore. This cutoff, as well as the hindered diffusion, reduces the reactivity of the catalyst. The discussion here is restricted to catalytic reactions in the absence of mass transfer resistances external to the particle, although such effects can be readily included in the formulation of a global effectiveness factor (Froment and Bischoff, 1990). Substituting Eqs. 7, 8 and 19 into the definition of $\eta(x, r)$ yields

$$\eta(x, r) = (1/\phi)\tanh(\phi), \tag{20}$$

the usual expression for a single catalytic pore, or for a rectangular slab particle. Note that both factors Z and Φ have canceled, except for their implicit presence in ϕ.

We next define effectiveness factors for continuous mixtures in a population of discretely distributed pores all of length Z. An effectiveness factor can be defined for a reactant of radius x in a particle having n_j pores of radii r_j ($j = 1, 2, 3, \ldots$),

$$\eta_{\langle r\rangle}(x) = N_{\langle r\rangle}(x)/R_{\langle r\rangle}(x). \tag{21}$$

For discrete pore sizes, the diffusion rate of solutes of radius x in the sum over all pore sizes,

$$N_{\langle r\rangle}(x) = \sum n_j \pi r_j^2 J(x, r_j), \tag{22}$$

and the maximum reaction rate for these pores is

$$R_{\langle r\rangle}(x) = \sum k_s(x) c_0(x) V_j 2/r_j \tag{23}$$

The distribution $c_0(x)$ cancels from the ratio, $\eta_{\langle r\rangle}(x)$. The presence of n_j in the numerator and denominator ensures that the normalization constant for n_j also cancels.

The effectiveness factor for a continuous distribution of reactants in n_j pores of radius r_j is defined as

$$\eta_{\langle x\rangle}(r_j) = N_{\langle x\rangle}(r_j)/R_{\langle x\rangle}(r_j). \tag{24}$$

This factor is expected to be useful for catalysts with a monodisperse pore-size distribution. For *all* solutes diffusing through pores of radius r_j we have

$$N_{\langle x\rangle}(r_j) = n_j \pi r_j^2 \int_0^\infty J(x, r_j)\, dx. \tag{25}$$

The ideal reaction rate for these pores is

$$R_{\langle x\rangle}(r_j) = n_j \pi r_j^2 Z \int_0^\infty \Phi k(x, r_j) c_0(x)\, dx. \tag{26}$$

The presence of Φ in Eqs. 25 and 26 ensures that the same molecules that are totally excluded in calculating $N_{\langle x\rangle}$ are excluded in $R_{\langle x\rangle}$. Also, n_j cancels from $\eta_{\langle x\rangle}(r_j)$.

The effectiveness factor for *all* solutes in *all* pores is

$$\eta_{\langle xr\rangle} = N_{\langle xr\rangle}/R_{\langle xr\rangle}. \tag{27}$$

The total transport of solute into the particle is the sum over all pore sizes and the integral over the solute radii,

$$N_{\langle xr\rangle} = \sum n_j \pi r_j^2 \int_0^\infty J(x, r_j)\, dx. \tag{28}$$

The presence of the partition coefficient in J will limit the integration interval to $x \le r_j$. The maximum possible rate of reaction in the total pore volume (barring those molecules excluded from pores) is

$$R_{\langle xr\rangle} = \sum n_j \pi r_j^2 Z \int_0^\infty \Phi k(x, r_j) c_0(x)\, dx. \tag{29}$$

We have assumed that the chemical reaction simply converts reactant molecules to product molecules that have the same size distribution but are perfectly distinguishable. The theory of cracking or addition reactions would in general require a more complicated analysis (McCoy, 1993), since products of the reaction could further react.

One of the functions selected to represent the bulk continuous-mixture distribution of solute sizes is a gamma distribution (Abramowitz and Stegun, 1968) in terms of $y = (x - x_0)/\beta$,

$$c_0(x) = (C_0/\beta\Gamma(\alpha)) y^{\alpha-1} \exp(-y) \quad \text{for} \quad x \ge x_0$$

and

$$c_0(x) = 0 \quad \text{for} \quad x < x_0. \tag{30}$$

The zero moment with respect to x is C_0, the first moment is $x_{\text{avg}} = x_0 + \alpha\beta$, and the variance is $\alpha\beta^2$. Depending on the magnitude of α, the gamma distribution can represent a spectrum of shapes between exponential ($\alpha = 1$) and gaussian ($\alpha \gg 1$). If $\alpha = 1$ and $y \ll 1$, Eq. 30 is approximated by a rectangular distribution. Increasing β when α is constant broadens the distribution. According to the gamma distribution, Eq. 30, the continuous mixture has a minimum solute radius, x_0, which is convenient for scaling x and r as x/x_0 and r/x_0.

If the pore sizes are distributed continuously, then the summations in the preceding equations are replaced by integrals over a pore-size distribution, $n(r)$, where the number of pores in the size range $(r, r + dr)$ is $n(r)\,dr$. Then instead of the summation in Eq. 22 the diffusion rate of solutes of radius x is the integral over $n(r)$,

$$N_{\langle r\rangle}(x) = \int_0^\infty dr\, n(r) \pi r^2 J(x, r) \tag{31}$$

and the ideal reaction rate is

$$R_{\langle r\rangle}(x) = \int_0^\infty dr\, k(x, r) c_0(x) Z n(r) \pi r^2 \Phi. \tag{32}$$

For $N_{\langle x\rangle}(r)$, Eq. 25 is unchanged except that the discrete variable r_j becomes the continuous variable r. The advantage of the continuous distributions is that integrations are usually more readily evaluated and manipulated algebraically than summations.

Calculations for *rectangular* distributions of solutes and pores provide illustrative results. The rectangular distributions of solute and pore sizes are given, respectively, by $c(x) = c_{rt}$ for $x_0 \le x \le x_m$ and zero for other values of x, and $n(r) = n_{rt}$ for $x_0 \le r \le x_m$ and zero for other values of r. The maximum value of r is taken to be the largest solute size to avoid the effect of totally excluded solutes, which cannot react and are thus effectively inert. Cancellation causes effectiveness factors to be independent of either c_{rt} or n_{rt}.

In the special case that the mixture consists of only one component of size x_1 and the particle has only one pore size r_1, then both distributions are Dirac delta functions, that is, $c_0(x) = C_{01}\delta(x - x_1)$, and $n(r) = n_1\delta(r - r_1)$. It follows when $r_1 > x_1$ that $N_1 = n_1\pi r_1^2 J(x_1, r_1)$, and the effectiveness factors are therefore all equivalent, that is, $\eta = \eta_{\langle r\rangle} = \eta_{\langle x\rangle} = \eta_{\langle rx\rangle}$. For a discrete number of solute species of size x_i the concentration is the summation over the species.

If pores are distributed according to the number distribution, $n_p(Z, r)$, rather than assumed of equal length, then the total volume of pores is

$$V_p = \int_0^\infty \int_0^\infty drdZ\pi r^2 n_p(Z, r). \tag{33}$$

The flux into all pores and the ideal reaction rate are readily formulated as integral expressions.

Fractal Pore-Size Distributions

Certain pore-size distributions can be represented by power-law relations of the kind

$$V_p/Za^2 = A^D(r/a)^{2-D}, \tag{34}$$

where a is the edge length of a square section of the external catalyst surface (Adler, 1992). McCoy (1995a) showed how such relations can be used to represent pore-size distributions in a membrane, including discrete fractal distributions. A deterministic fractal distribution of pores is developed by a conceptual process of making holes according to a repetitive formula relating size and number of pores. A similar construction was used by Adler (1989) for flow in a porous slab. Adler (1989) suggested that such fractals could be applied to diffusion and conduction (thermal or electrical), but did not introduce mixtures of different-sized molecules. Sernetz et al. (1989) recognized the importance of the diffusion of a mixture of different-sized molecules in fractal porous media for chromatographic separations. The benefit of the fractal approach is that simple mathematical formulas describe the fractal properties, for example, the pore-size distribution.

Following McCoy (1995a,b) we first consider a pore distribution based on the fractal known as the Sierpinski carpet (Mandelbrot, 1977), and then generalize the concept to consider holes of different numbers, shapes, and sizes. The steps $j = 1, 2, 3, \ldots$ in the construction from a unit square of area a^2 are as follows: at step 1 a square hole of edge $a/3$ is formed perpendicular to the slab. In each of the remaining eight squares a hole of size $(a/3^2)^2$ is formed. This process is repeated indefinitely for every square. The edge length of a square at step j is $r_j = a/3^j$ and its cross section has area $a^2/9^j$. The number and volume, respectively, of pores formed at the jth step are

$$n_j = 8^{j-1} \quad \text{and} \quad V_{pj} = Z(8/9)^j a^2/8. \tag{35}$$

The cumulative pore-volume distribution up to the jth step is $Za^2[1-(8/9)^j]$, which becomes Za^2 if $j \to \infty$, meaning that all mass is eventually removed by making square holes in the slab. The discrete pore-volume distribution has the fractal property (Mandelbrot, 1977) that it can be represented by a noninteger power, or fractal dimension, $D = \ln 8/\ln 3$. The coefficient A in Eq. 34 is given by $A = (1/8)^{1/D}$.

The fractal pore distribution can be generalized by considering pores of cross-sectional area Ωr_j^2, where $\Omega = 1$ for squares, π for circles, or other constants for other cross-section shapes. For diffusion into catalyst pores the placement and orientation of the pores is immaterial if the cross sections do not overlap and the bulk fluid is well-stirred. The relative size (e.g., radius) of the pores formed at two subsequent steps is defined as the constant,

$$\sigma = (\text{size of pore formed at step } j)/(\text{size of pore formed at step } j+1). \tag{36}$$

The relative number of pores formed at subsequent steps is also a constant,

$$h = (\text{no. of pores formed at step } j+1)/(\text{no. of pores formed at step } j). \tag{37}$$

A similar generalization of the Sierpinski carpet was suggested by Pfeifer and Obert (1989). The unit square of area a^2 can be replicated side-by-side to form the total catalyst surface area as a spatially periodic porous medium. Consideration of the unit square is sufficient to calculate the effectiveness factor for a catalyst. The size of pores removed at step j is $r_j = a/\sigma^j$ and the volume of a pore is $Z\Omega(a/\sigma^j)^2$. The volume removed at the jth step is $Z(\Omega a^2/h)(h/\sigma^2)^j$, and the cumulative volume removed is $[Z\Omega a^2/(\sigma^2 - h)][1 - (h/\sigma^2)^j]$. For a slab all the catalyst mass is removed if the cumulative volume of pores at the jth step is Za^2. Such a structure possesses fractal properties in a finite range of pore sizes. The fractal dimension D and the premultiplier in Eq. 40 are

$$D = \frac{\ln h}{\ln \sigma} \quad \text{and} \quad A = \left(\frac{\Omega}{h}\right)^{1/D}. \tag{38}$$

The fractal dimension D depends on σ and h, but not on the shape factor Ω; the premultiplier A depends on h and Ω but not on σ. For the Sierpinski carpet, which is fractal over the entire range of pore sizes, $\Omega = 1$, $\sigma = 3$, and $h = 8$. If $h = \sigma^2$, then the distribution is rectangular. Examples of fractal constructions are plotted in McCoy (1995a,b). The Sierpinski carpet has square holes ($\Omega = 1$) of size ratio $\sigma = 3$ and number ratio $h = 8$. Random positioning of pores does not affect the reaction-diffusion process. Table 1 shows the

Table 1. Pore Size and Pore Volume for Fractal Distribution of Pores ($\sigma = 1.5$, $\Omega = \pi$, $a = 10x_0$)

j	r_j/a	V_{pj}/Za^2 ($h = 2$)	V_{pj}/Za^2 ($h = 3$)	V_{pj}/Za^2 ($h = 5$)
1	0.6667	1.158	1.356	1.977
2	0.4444	1.029	1.808	4.393
3	0.2963	0.915	2.411	9.762
4	0.1975	0.813	3.215	21.69
5	0.1317	0.723	4.286	48.21
6	0.0978	0.622	5.715	107.1

discrete pore-volume distribution for $\sigma = 1.5$ and $h = 2$, 3, and 5. Since the pores are ordered by size, there is no problem in summing (or integrating in the case of continuous distributions) over the deterministic pore-size distributions.

Results and Discussion

The dimensionless modulus for unrestricted diffusion,

$$\phi_0 = Z(\tau k_s 2/x_0 D_b)^{1/2} \tag{39}$$

is independent of variables x and r, but otherwise contains key parameters that influence the reaction-diffusion process. The usual Thiele modulus $\phi(x,r)$ is related to ϕ_0 by

$$\phi = \phi_0 (x_0/rK_d)^{1/2}. \tag{40}$$

Representative calculations of the effectiveness factors defined earlier illustrate the dependence on key parameters. In these calculations we assume k_s and D_b to be independent of x. Values selected for the calculations are $D_b = 0.00001$ cm²/s, $k_s = 1.0 \times 10^{-12}$/s, $\tau = 1$, and $x_0 = 1.0 \times 10^{-7}$ cm, so that $\phi_0 = 1.414$ when $Z = 1.0$ cm. Figure 1 shows how $\eta(x,r)$ varies with the pore size. Since reactant molecules are increasingly restricted as the reactant radius approaches the pore radius, the effectiveness factor tends to zero as $x \to r$. At the other extreme, η will increase with smaller r, and if ϕ is small, $\eta \approx 1$ for $x \ll r$, since small reactants easily diffuse into the pore.

Whereas $\eta(x,r_j)$ is independent of the bulk FDF, $c_0(x)$, as shown in Eq. 20, the reaction rates $R(x,r_j)$ and $N(x,r_j)$ depend on $c_0(x)$. In Figure 2 we show how changing β in the gamma FDF for $c_0(x)$ influences the ideal and diffusion-affected rates. As β increases, R decreases since more molecules in the tail of the distribution are excluded from the pore. It follows that for a larger pore size, R will be larger as shown in Figure 2, where N and R are plotted for $r/x_0 = 4.0$ and 8.0.

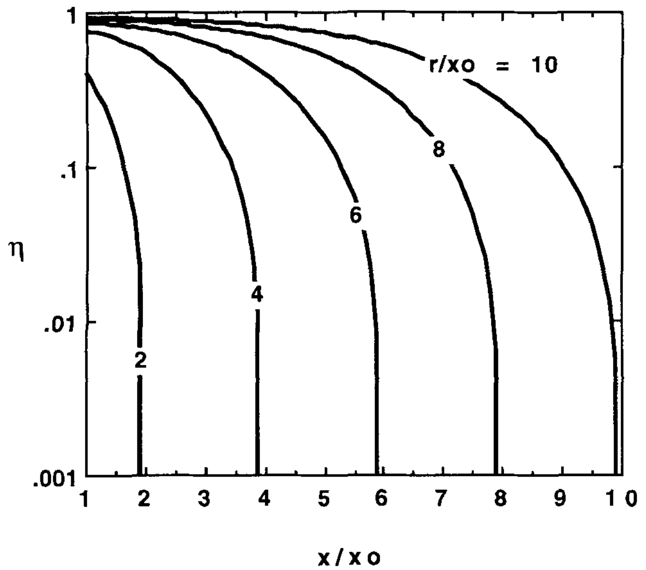

Figure 1. Effectiveness factor $\eta(x,r)$ for hindered diffusion in cylindrical pores ($\phi_0 = 1.414$).

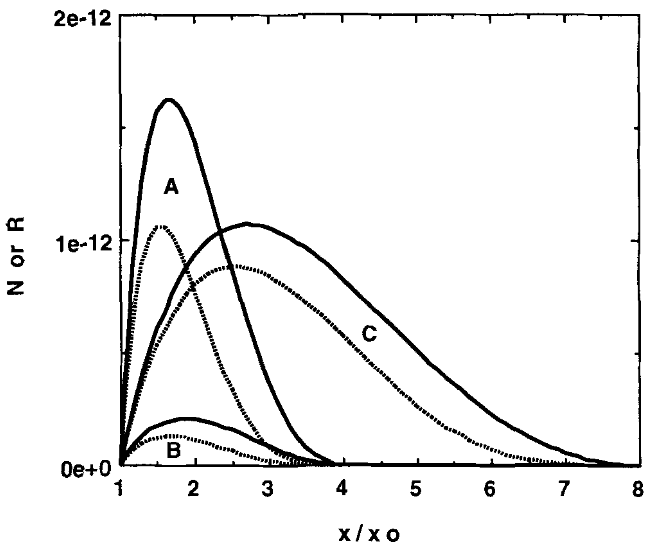

Figure 2. Maximum and diffusion-affected rates of reaction, $R(x,r)$ (solid line) and $N(x,r)$ (dashed line) for values of the pore radius r/x_0 and width parameter β/x_0 in the gamma distribution ($\phi_0 = 1.414$): A ($\beta/x_0 = 1.5$, $r/x_0 = 4$); B ($\beta/x_0 = 0.5$, $r/x_0 = 4$); C ($\beta/x_0 = 0.5$, $r/x_0 = 8$).

Spry and Sawyer (1975), as reported by Froment and Bischoff (1990), demonstrated that a catalyst can have an optimum catalyst pore size. We can define the "relative activity" as $\eta(x,r)x_0/r$ to account for the increase of the rate coefficient as pore radius decreases. This relative activity peaks at values of r/x_0 that increase with x/x_0. Small pores restrict diffusion on reactant molecules but provide a greater reactive surface area, thus causing the maximum for each value of x.

For a catalyst with a known pore-size distribution, the quantity $\eta_{\langle r\rangle}(x)$ is useful for calculating the steady-state conversion for each size of reactant, given the bulk FDF, $c_0(x)$. Based on calculations for rectangular distributions for $n(r)$, Figure 3 shows that $\eta_{\langle r\rangle}$ decreases with x, approaching zero as x nears the maximum pore size. The behavior is similar to that of $\eta(x,r_j)$ for both large- and small-x asymptotes. This general behavior is unchanged for other continuous unimodal forms of $n(r)$.

Figure 3 also shows the effect of a discontinuity in the pore-size distribution. The dashed line is for

$$\begin{aligned} n(r) &= 1 && \text{for } r \geq r_d \\ n(r) &= 10^5 && \text{for } r < r_d, \end{aligned} \tag{41}$$

where $r_d/x_0 = 5.0$. As x decreases, the number of pores jumps at $x/x_0 = 5$, causing a sharp decrease in $\eta_{\langle r\rangle}(x)$ due to the increased surface area of reaction. A very large number of pores that were inaccessible suddenly become available for catalysis, but with hindered access. Understanding this behavior helps to explain $\eta_{\langle r\rangle}(x)$ for the discrete fractal pore distribution (see below). The actual reaction rate is the product of the effectiveness factor η and the ideal reaction rate R, where R would be quite small for $r > r_d$.

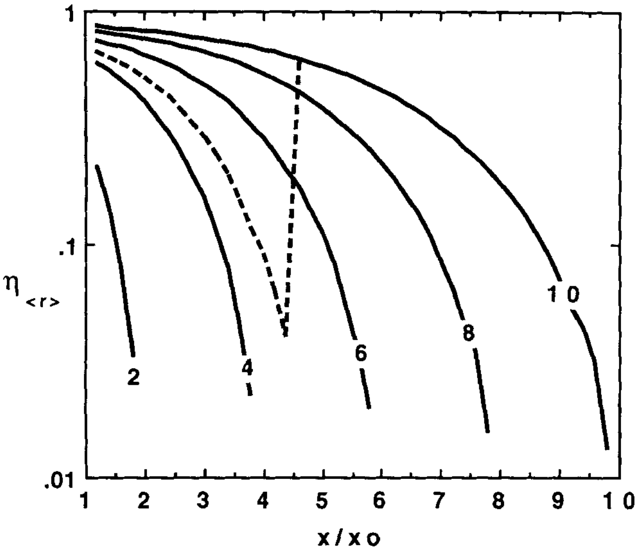

Figure 3. Effectiveness factor $\eta_{\langle r\rangle}(x)$ for $\phi_0 = 1.414$ and as a function of reactant radius, x/x_0, for several maximum values, r_m/x_0, of a rectangular pore-size distribution.

The dashed line is for a discontinuous pore-size distribution: $n(r \geq r_d) = 1$ and $n(r < r_d) = 10^5$ where $r_d/x_0 = 5.0$.

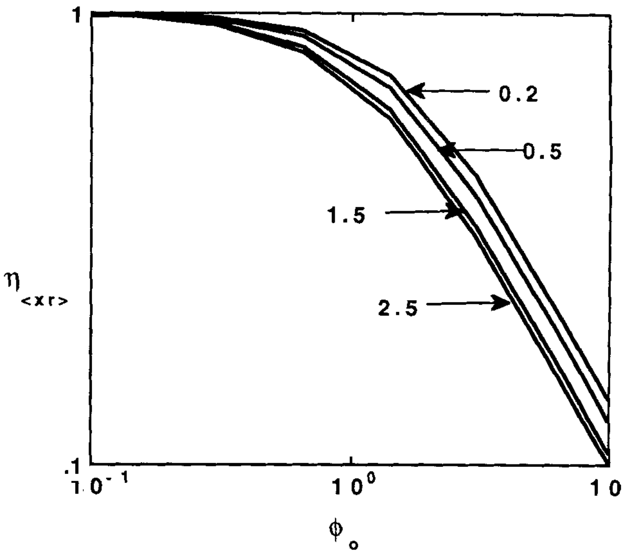

Figure 5. Effectiveness factor $\eta_{\langle xr\rangle}$ vs. ϕ_0 for a rectangular distribution of pores and a gamma distribution of reactants with $\beta/x_0 = 0.2, 0.5, 1.5, 2.5$.

The effectiveness factor, $\eta_{\langle rx\rangle}$, defined to incorporate the influence of all solutes in all pores, is pictured in Figures 4 and 5 with ϕ_0 as the horizontal coordinate ranging over several decades. Figure 4 indicates the effect of equal widths of rectangular distributions of reactant and pore radii. The general features of Figure 4 are not different if a gamma distribution is used instead of the rectangular distribution for the reactants and pores; thus, wider distributions contribute to a larger reaction rate. Figure 5 shows how changing *one* parameter β for the reactant-size distribution alters $\eta_{\langle rx\rangle}$. As the distribution broadens, the effectiveness factor decreases in the diffusion-influenced region, due to increased hindrance of diffusion of larger reactants.

Figures 6 and 7 present results for the effectiveness factors, $\eta_{\langle r\rangle}(x)$ and $\eta_{\langle rx\rangle}$, respectively, for a fractal distribution of cylindrical pores (Table 1). The discrete pore-size distribution causes local maxima and minima to appear in $\eta_{\langle r\rangle}(x)$. As the fractal parameter h increases, the number of smaller

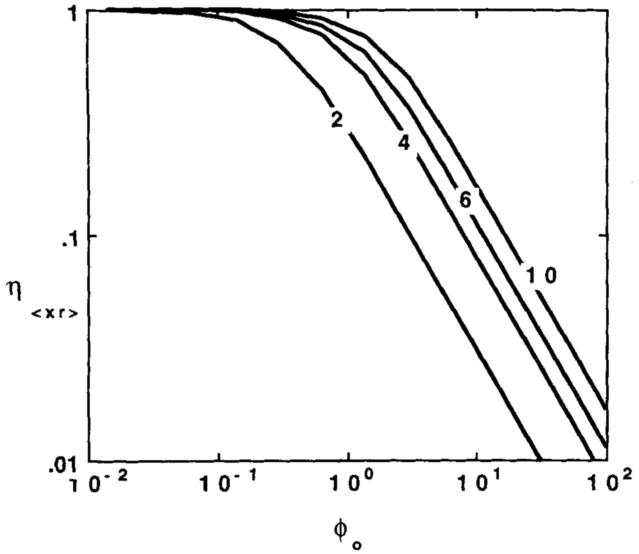

Figure 4. Effectiveness factor $\eta_{\langle xr\rangle}$ vs. ϕ_0 for rectangular distributions of reactants and pores with $x_m/x_0 = r_m/x_0$ as the parameter.

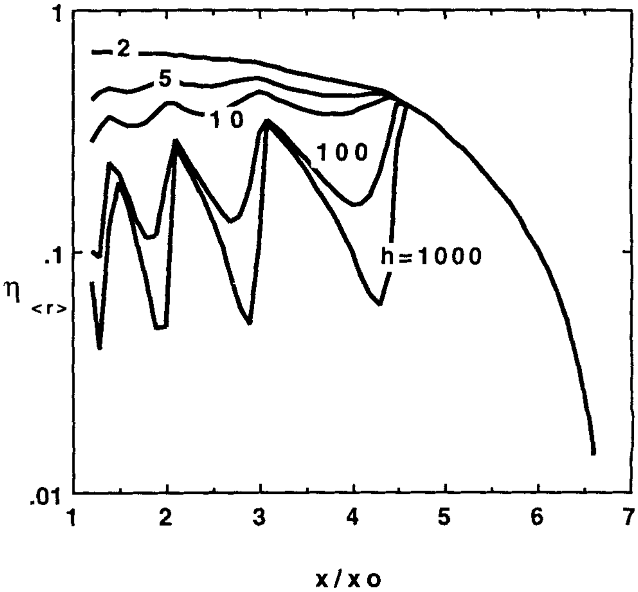

Figure 6. Effectiveness factor $\eta_{\langle r\rangle}(x)$ as a function of reactant radius, x/x_0, for discrete fractal distributions of pore sizes ($\sigma = 1.5$, $\Omega = \pi$) and with $\phi_0 = 1.414$.

As the parameter h increases, the number of smaller pores increases.

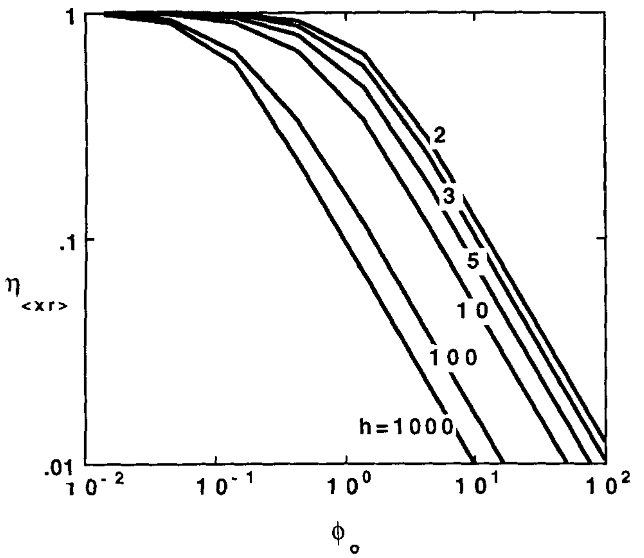

Figure 7. Effectiveness factor $\eta_{\langle xr \rangle}$ for fractal distributions of pore sizes ($\sigma = 1.5$, $\Omega = \pi$).

pores increases, amplifying the peaking. When the flux and ideal reaction expressions of Figure 6 are integrated to get $\eta_{\langle rx \rangle}$, we find the expected dependence of the overall effectiveness factor on ϕ_0.

Concluding Remarks

The general approach using FDFs to treat distributed parameters is illustrated in this work for catalyst effectiveness factors. For simple chemical reaction kinetics, averaging by summation or integration (for discrete or continuous FDFs) is required to calculate the fluxes and reaction rates. An apparently complex multicomponent, distributed pore-size system with statistical randomness is thus made amenable to quantitative analysis.

The concepts in the current study of diffusion-affected catalytic reactions in porous particles are similar to those in membrane sieving (McCoy, 1995a). Both are steady-state systems of continuous polydisperse mixtures diffusing through pores distributed in size. Hindered transport in the pores, described by available hydrodynamic analysis of spheres at the centerlines of pores, reduces the magnitude of the bulk diffusion coefficient. Solutes larger than a pore are excluded from that pore altogether. Moreover, an annular region near the pore surface cannot be penetrated by the center of rigid spherical solutes in rigid-wall cylindrical pores. Similar ideas apply to size-exclusion chromatography, which is not a steady-state process (McCoy, 1995b). To determine the cumulative effect of different sizes of solutes and pores requires a generalization of the usual effectiveness factor for monodisperse pore and reactant distributions. The necessary summations or integrations over the frequency distributions of solutes and pores give rise to definitions of effectiveness factors that apply for (a) one-size solute in one-size pore, (b) all solutes in one-size pore, (c) one-size solute in all pores, or (d) all solutes in all pores. The relationships between these definitions reflect the hindered transport and exclusion effects that are crucial to understanding the reaction-diffusion phenomena.

The approach is relevant to the understanding of the catalytic chemical reaction engineering of complex mixtures. The effectiveness factors presented in this work can be utilized for steady-state reactor calculations to estimate chemical-reaction conversions of lumped and distributed mixtures. For a CSTR with feed $c_0(x)$ and average residence time τ_0, the outlet FDF of reaction products can be written as

$$c(x) = c_0(x) - \tau_0 \eta_{\langle r \rangle}(x) R_{\langle r \rangle}(x) \tag{42}$$

and the outlet lumped concentration as

$$C = C_0 - \tau_0 \eta_{\langle rx \rangle} R_{\langle rx \rangle}. \tag{43}$$

The effectiveness factors averaged over all pore sizes, that is, $\eta_{\langle r \rangle}(x)$ and $\eta_{\langle rx \rangle}$, are thus most useful for engineering purposes.

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Notation

a_i = coefficients in expression for hindered diffusion ($i = 1$–7)
$a_1 = -73/60$
$a_2 = 77{,}293/50{,}400$
$a_3 = -22.5083$
$a_4 = 5.6117$
$a_5 = -0.3363$
$a_6 = -1.216$
$a_7 = 1.647$
A = coefficient in fractal expression for particle pore volume V_j
A_j = cross-sectional area of pores of radius r_j
C_0 = lumped concentration of solutes
h = parameter in fractal distribution of pore sizes
$\eta(x,r)$ = effectiveness factor for solute of radius x in pores of radius r
$k(x,r_j)$ = rate coefficient
$k_s(x)$ = rate coefficient for a unit area of catalyst surface
$N_{\langle x \rangle}(r)$ = diffusion rate of all solutes through pores of radius r
$N_{\langle r \rangle}(x)$ = diffusion rate of solute of radius x through all pores
$N_{\langle xr \rangle}$ = total diffusion rate of all solute sizes through all pores
$R_{\langle x \rangle}(r)$ = ideal reaction rate of all solutes in pores of radius r
$R_{\langle xr \rangle}$ = total ideal reaction rate of all solute sizes in all pores
r_m = maximum pore radius
$V_j = \Phi V_{pj}$, volume of pores of radius r_j accessible by molecules of radius x
x_m = maximum solute radius in a distribution
x_i = discrete values of reactant radius ($i = 1, 2, 3, \ldots$)

Greek letters

α = parameter in the gamma distribution
β = parameter in the gamma distribution
$\phi_0 = Z(2\tau k_s/x_0 D_b)^{1/2}$, reaction-diffusion modulus for unrestricted diffusion
σ = parameter in fractal distribution of pore sizes
$\Gamma(\alpha)$ = gamma function [$=(\alpha - 1)!$ if α is an integer]
Ω = shape factor for pore
τ_0 = reactor average residence time

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