EFFECTIVENESS FACTORS FOR CONCENTRATION-DEPENDENT DIFFUSION

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Introduction

Studies of the effectiveness factor for reactant diffusion in a porous catalytic pellet have been of continuing interest to researchers concerned with chemical reactor design. Past investigations have been extensively surveyed by Aris.[1] A common assumption in previous investigations is that the diffusion coefficient of the reactant is a constant. In many practical situations the diffusion coefficient is not constant, but is concentration-dependent.[7] Diffusion in a molecular sieve is a typical example. In fact, concentration-dependent diffusion also appears in a variety of practical applications in other engineering and physical sciences.[5]

Ruthven[8] appears to be the first investigator to consider the effect of concentration dependence of the diffusion coefficient on the effectiveness factor. The author was particularly concerned with zeolite diffusion in molecular sieve catalysts. A first-order chemical reaction without external mass transfer resistance and with strong concentration dependence of the diffusion coefficient was examined. In more recent work, Pereira and Varma[6] investigated the problem in which external mass-transfer resistance exists. However, they restricted their consideration to the case with weak concentration dependence of the diffusion coefficient and with first-order chemical reaction. The purpose of this note is to show that by using an appropriate numerical integration method, the restrictions of previous investigations are not necessary and a wide range of problems with weak or strong concentration dependence of the diffusion coefficient and with any order of chemical reaction can be handled.

1. Physical Model

Steady-state, concentration-dependent diffusion with general-order chemical reaction can be represented by

$$\frac{1}{x^a}\frac{d}{dx}\left[D(C)x^a\frac{dC}{dx}\right]=k_0C^m \tag{1}$$

subject to

$$x=0\,; \quad \frac{dC}{dx}=0 \tag{2}$$

$$x=b\,; \quad D(C)\frac{dC}{dx}=k(C_0-C) \tag{3}$$

Different concentration-dependent functions have been used before.[2] The following two types are the most general ones:

$$D(C)=D_0\left(1+\delta\frac{C}{C_0}\right)^n \tag{4}$$

and

$$D(C)=D_0\exp\left(\delta\frac{C}{C_0}\right) \tag{5}$$

If $\delta \ll 1$, Eq. (4) reduces to that considered by Pereira and Varma.[6] Ruthven[8] used the following concentration-dependent relation:

$$D(C)=\frac{D_0C_s}{C_s-C} \tag{6}$$

Although Eq. (6) is supported by some experimental evidence, it has one major deficiency in that it becomes indefinite when C approaches its equilibrium value C_s. In fact, the concentration dependence given by Eq. (6) may well be represented by Eq. (4) with appropriate combination of the parameter δ and power n. Therefore, Eqs. (4) and (5) are sufficient to represent a wide variety of concentration dependence of the diffusion coefficient and are adopted in this study.

In terms of the dimensionless variables and parameters, Eqs. (1) to (5) can be rewritten as

$$\frac{1}{x^a}\frac{d}{dx}\left[f(\theta)x^a\frac{d\theta}{dx}\right]=\phi^2\theta^m \tag{7}$$

$$f(\theta)=(1+\delta\theta)^n \quad \text{or} \quad \exp(\delta\theta) \tag{8}$$

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subject to

$$x=0\,; \quad \frac{d\theta}{dx}=0 \tag{9}$$

$$x=1\,; \quad f(\theta)\frac{d\theta}{dx}=Sh(1-\theta) \tag{10}$$

where θ is the dimensionless concentration, C/C_0, and the Thiele modulus ϕ is defined as $(k_0 b^2 C_0^{m-1}/D_0)^{1/2}$. Eq. (7) with the boundary conditions of Eqs. (9) and (10) constitute and highly nonlinear ordinary differential equation which can be readily integrated by an interactive Runge-Kutta method.[4] To test the accuracy of the present numerical scheme, several runs were made for the special case with constant diffusion coefficient and first-order chemical reaction. **Figure 1** shows a comparison of the Thiele moduli obtained by the present numerical method with those obtained from analytic solutions.[3] It appears that the solutions are essentially identical, the difference between them being less than 10^{-3}. The following figures show some typical numerical results.

2. Discussion of Results

Figure 2 shows the effectiveness factor vs the Thiele modulus in a spherical catalyst for a linearly concentration-dependent diffusion. The bottom curve for $\delta=0$ corresponds to diffusion with constant diffusion coefficient. It is apparent that the effect of the variable diffusion coefficient on the effectiveness factor is quite significant even when the diffusion coefficient has only a linear concentration dependence. Such an effect will be considerably amplified if a higher power is used in Eq. (8).

The effectiveness factors vs the Thiele modulus and the Sherwood number are displayed in **Figs. 3** and **4**, respectively, for varions geometries. It is of interest to note in Fig. 4 that the effectiveness factor asymptotically approaches a constant as the Sherwood number increases. In fact, the effect of the Sherwood number on the effectiveness factor is negligible for Sh> 100. This is due to the fact at such a large Sherwood number the external mass transfer resistance is almost nonexistent. It is obvious from this figure that the effectiveness factor increases rapidly for Sherwood numbers less than 50. This figure also indicates that the curves of the precicted effectiveness factors for linear and exponential concentration dependences are close, primarily because of the small δ value chosen here. For larger δ, they are expected to be quite different.

The effect of the order of chemical reaction on the effectiveness factor is demonstrated in **Fig. 5.** At low Thiele modulus, less than 2, the influence of the reaction order is relatively small. The curves for the onehalf and second-order chemical reactions, how-

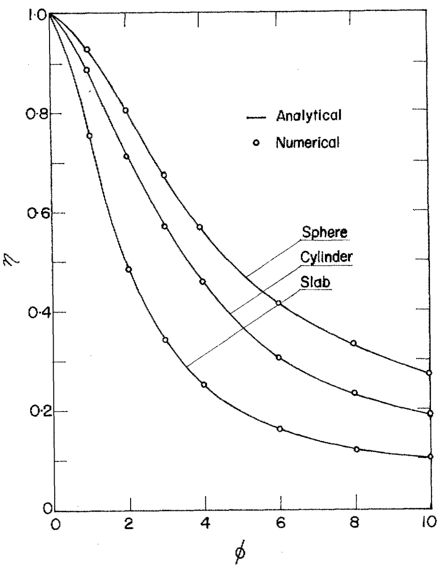

Fig. 1. Comparison of numerical and analytical solutions with constant diffusion coefficient and first-order chemical reaction

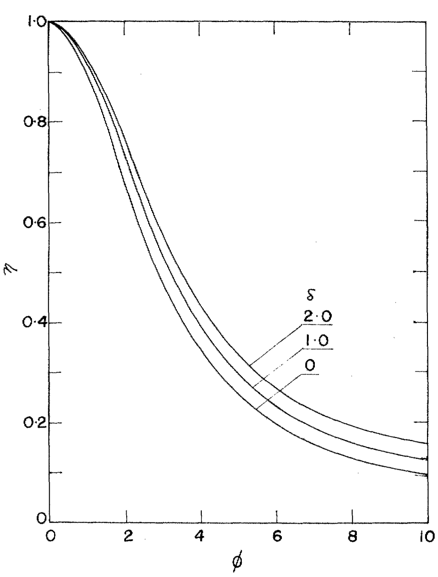

Fig. 2. Effectiveness factor vs Thiele modulus in a sphere with $Sh=5.0$, $m=1$ and $f(\theta)=(1+\delta\theta)$

ever, depart considerably from that of the first-order chemical reaction for large Thiele modulus.

Conclusions

A numerical procedure is presented in this note for computing the effectiveness factor for concentration-dependent diffusion in various geometries. Because of the versatility of the numerical integration scheme employed here, practically no restrictions need be imposed on the form of concentration dependence of diffusion coefficient or the order of chemical reaction. According to the numerical results obtained here, the external mass transfer resistance can be neglected for Sherwood numbers larger than 100. It is also shown

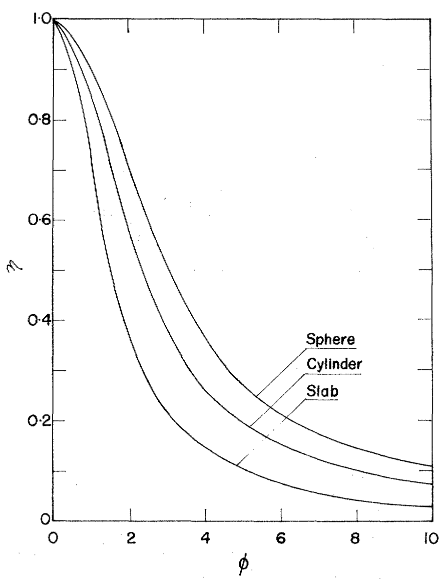

Fig. 3. Effectiveness factor vs Thiele modulus for various geometries with linear concentration dependence of diffusion coefficient and with $\delta=0.5$, $Sh=5.0$ and $m=1$

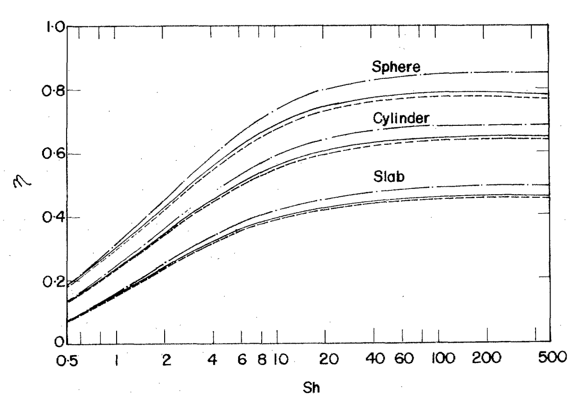

Fig. 4. Effectiveness factor vs Sherwood number for different geometries and concentration-dependent functions with $\delta=0.5$, $m=1$ and $\phi=2.5$ ——, Exponential concentration dependence, $f(\theta)=\exp(0.5\,\theta)$; ------, Linear concentration dependence, $f(\theta)=1+0.5\,\theta$; —·—·—·, Power concentration dependence, $f(\theta)=(1+0.5\theta)^4$

that the effect of the order of chemical reaction and the form of concentration dependence on the effectiveness factor are very strong in most cases.

Nomenclature

a	=	geometrical parameter (0 for slab, 1 for cylinder and 3 for sphere)
b	=	characteristic dimension of the catalytic pellet
C	=	reactant concentration inside the catalytic pellet
C_0	=	reactant concentration in the bulk phase
C_s	=	saturated zeolite concentration
$D(C)$	=	concentration-dependent diffusion coefficient
D_0	=	reference diffusion coefficient
k	=	external mass transfer coefficient
k_0	=	reaction rate constant
m	=	order of chemical reaction
n	=	power in the concentration dependent function
Sh	=	Sherwood number, kb/D_0
x	=	axial coordinate
x	=	dimensionless axial coordinate, x/b
δ	=	parameter in the concentration-dependent function
θ	=	dimensionless reactant concentration, C/C_0
ϕ	=	Thiele modulus, $(k_0 b^2 C_0^{m-1}/D_0)$
η	=	effectiveness factor

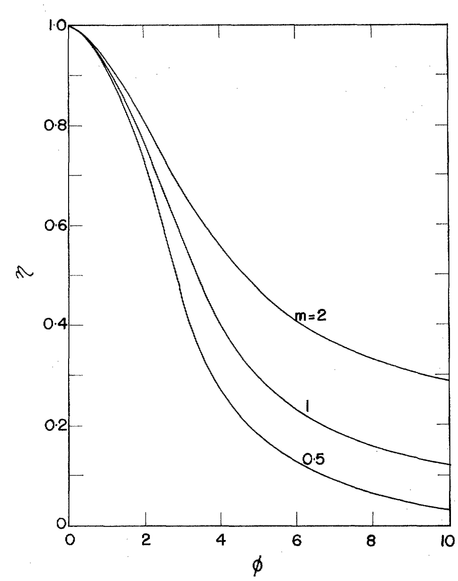

Fig. 5. Effectiveness factor vs Thiele modulus in a sphere for different reaction orders with $f(\theta)=(1+0.5\theta)$ and $Sh=5.0$

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