Semianalytical Expression of Effectiveness Factor for Michaelis-Menten Kinetics

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To design a heterogeneous chemical reactor it is common to employ the concept of an effectiveness factor to determine whether the reactions in a catalyst particle are limited by pore diffusion. This concept can also be applied to design a biochemical reactor where the enzymes are immobilized on the internal surface of a porous support (Bailey and Ollis, 1977).

Most of the biochemical reaction systems are frequently characterized by the Michaelis-Menten type of kinetics. Due to their nonlinear nature, numerical methods in general are required to calculate the effectiveness factor of an immobilized enzyme catalyst particle, such as the orthogonal collocation method used by Ramachandran (1975), and a special numerical scheme for high Thiele moduli proposed by Chang (1982). Obviously if an approximate solution giving the desired accuracy is available, the computation effort can be drastically reduced. Some approximate solutions are available in the literature, such as the empirical solutions suggested by Atkinson (1971) and Bailey and Ollis (1977), and the weighting-factor methods proposed by Moo-Young and Kobayashi (1972), Gondo et al. (1974), and Kobayashi et al. (1976). The weighting-factor-methods employ a weighting function to weight the effectiveness factors for reactions in zeroth-and first-order regions, while the modification of Thiele modulus is required, for example, using the generalized Thiele modulus concept (Bischoff, 1965). Among those, only the model proposed by Kobayashi et al. (1976) could generate a large range of the effectiveness factors over a large range of the existing parameters with errors less than 2.0 percent. But the weighting function of this model is strictly empirical.

The purpose of this article is to propose a semianalytical expression of an effectiveness factor for the Michaelis-Menten type kinetics. This expression satisfies the asymptotic behaviors of the reaction system and is applicable over the whole range of existing parameters.

Formulation

The dimensionless mass balance of the susbtrate in a spherical catalyst particle may be written as,

$$\frac{1}{x^2}\frac{d}{dx}\left(x^2\frac{dS}{dx}\right) - \Phi^2\frac{S}{1+\beta S} = 0 \tag{1}$$

the corresponding boundary conditions are

$$\text{B.C. 1 at } x = 0, \quad \frac{dS}{dx} = 0 \tag{2}$$

$$\text{B.C. 2 at } x = 1, \quad S = 1 \tag{3}$$

Equation 1 contains two asymptotic behaviors which are:

1. Zeroth-order reaction when β is large
2. First-order reaction when β is small. The effectiveness factors at these extreme conditions are well documented in the literature (Hill, 1977 and Smith, 1971)

The real solution to Eq. 1 therefore should exist between these two asymptotic solutions, which may be expressed by

$$\eta = \frac{W}{1+W}\eta_o(\psi) + \frac{1}{1+W}\eta_1(\psi) \tag{4}$$

where η_o and η_1 are the effectiveness factors for zeroth- and first-order reactions, respectively; ψ is the modified Thiele modulus; and W is the weighting factor which is the function of Φ and β. In order to seek the suitable expressions of ψ and W, the analytical solutions at small and large Thiele moduli are first derived. This can be done by using the regular perturbation method for small Φ and the singular perturbation method for large Φ (Finlayson, 1980), which generate the following expressions:

For small, Φ,

$$\eta = 1 - \frac{\Phi^2}{15(1+\beta)^2} + \frac{2\Phi^4}{315(1+\beta)^4} + \dots \tag{5}$$

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For large Φ,

$$\eta = \frac{3\sqrt{2}}{\Phi}\frac{1+\beta}{\beta}[\beta - \ln(1+\beta)]^{1/2} \tag{6}$$

When β is large, Eq. 4 should be reduced to $\eta = \eta_0(\psi)$, and the analytical solution to the zeroth-order reaction is

$$\eta_0 = \left\{ \begin{matrix} 1.0, & \dfrac{\Phi^2}{\beta} \le 6 \\ 1 - x_c^3, & \dfrac{\Phi^2}{\beta} > 6 \end{matrix} \right\} \tag{7}$$

where

$$x_c = \frac{1}{2} + \cos\frac{A + 4\pi}{3}$$

and

$$A = \cos^{-1}\left(\frac{12\beta}{\Phi^2} - 1\right)$$

By comparing Eqs. 4 and 7, the following expression may be found,

$$\psi = \frac{\Phi}{\sqrt{\beta}} \simeq \frac{\Phi}{\sqrt{1+\beta}} \tag{8}$$

Equation 8 can also be applied to small β. When β is small the reaction becomes first-order kinetics, and it can be easily seen that ψ equals Φ from Eq. 1.

when ψ is small, we have

$$\eta_0(\psi) \simeq 1.0 \tag{9}$$

and

$$\eta_1(\psi) = 1.0 - \frac{\psi^2}{15} + \frac{2\psi^4}{315} + \dots \tag{10}$$

Equation 10 is derived by using the regular perturbation method. Substituting Eqs. 5, 9 and 10 into Eq. 4, the weighting factor W can be found as

$$W = \beta, \text{ for small } \psi \tag{11}$$

When ψ is large, we have

$$\eta_0(\psi) = \frac{3\sqrt{2}}{\psi} \tag{12}$$

and

$$\eta_1(\psi) = \frac{3}{\psi} \tag{13}$$

Substituting Eqs. 6, 12 and 13 into Eq. 4, the following expression can be obtained,

$$W = \frac{1-\gamma}{\sqrt{2}\gamma - 1}, \quad \text{for large } \psi \tag{14}$$

where

$$\gamma = \frac{\beta}{\{2(1+\beta)[\beta - \ln(1+\beta)]\}^{1/2}} \tag{15}$$

For the whole range of ψ, the following weighting factor is suggested,

$$W = \frac{\beta + a\psi^b \dfrac{1-\gamma}{\sqrt{2}\gamma - 1}}{1 + a\psi^b} \tag{16}$$

where a and b are the adjustable parameters which can be determined by minimizing the errors between this approximate as well as numerically exact solutions. With Eqs. 4, 8 and 16, the effectiveness factor for the Michaelis-Menten type kinetics can be evaluated.

Results and Discussions

In order to assess the accuracy of the proposed method, Eqs. 1 to 3 were solved by the orthogonal collocation method (Villadsen and Michelsen, 1978). The numbers of the collocation point varied with Φ. At least six collocation points were used even when Φ was small. The numerical solutions were compared with those given by Ramachandran (1975) and Chang (1982). The agreement was excellent.

The parameters a and b in Eq. 16 were found to be 0.22 and 4.3, respectively, by minimizing the errors between the numerical solution and the approximate solution to the proposed model. With these two determined parameters, Figure 1 shows that

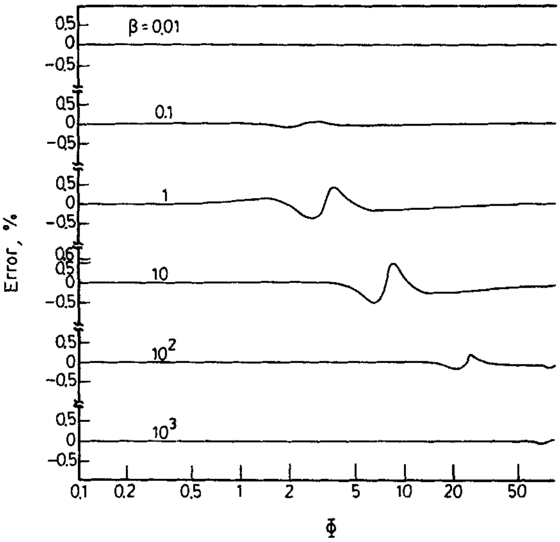

Figure 1. Relative error for the effectiveness factor calculated by the proposed method.

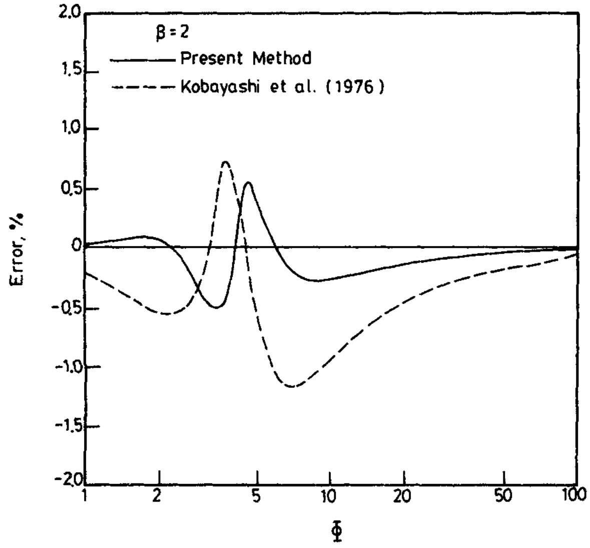

Figure 2. Comparison of the effectiveness factors by the proposed method and the method of Kobayashi et al. (1976).

the errors were very small for a large range of Φ and β, especially for β smaller than 0.1 and larger than 100. The error in Figure 1 is defined as

$$\text{Error} = \frac{\eta - \eta_{num}}{\eta_{num}} \tag{17}$$

The largest error was observed to be no more than ± 0.7% in the region of β about 2.0. Figure 2 shows that the present method generated more accurate solutions than the model of Kobayashi et al. (1976) when β equaled 2.0. This illustrates the applicability of the present method.

When the interphase mass transfer resistance is considered, the mass balance can still be represented by Eq. 1, but the boundary condition at the outer surface of the immobilized enzyme catalyst (Eq. 3) should be replaced by

$$\frac{dS}{dx} = (Bi)(1 - S) \tag{18}$$

where the dimensionless variables S is normalized by the bulk-phase concentration rather than the surface concentration.

Under this condition, the presently developed method can still be applied, but it should be accompanied by the trial and error method. The calculation procedures include:

1. Estimate surface concentration,
2. Use of the proposed method to evaluate effectiveness factor,
3. Using Eq. 18 to check the surface concentration until the convergence is reached

With these procedures the convergence was usually achieved within 1–3 times. Comparing these approximate solutions with the numerically exact solutions, it was found that the errors were also within the ranges shown in Figure 1. This indicates that the proposed method can be extended without difficulty to the conditions existing with interphase mass transfer resistance.

Notation

a, b = parameters in Eq. 16
B_i = Biot number, defined as kR/D_e
D_e = effective diffusivity in catalyst particle
K_m = parameter in Michaelis-Menten type kinetics $v_m s/(K_m + s)$
k = interphase mass transfer resistance
R = radius of catalyst particle
S = dimensionless substrate concentration, $S = s/s_i$
s = substrate concentration
s_i = substrate concentration at outer surface of catalyst particle
x = dimensionless radial position
W = weighting factor

Greek letters

β = parameter in Eq. 1, defined as s_i/K_m
η = effectiveness factor for Michaelis-Menten type
η_0, η_1 = effectiveness factors for zeroth- and first-order reactions, respectively
η_{num} = numerically calculated effectiveness factor
Φ = Thiele modulus, defined as $R\sqrt{v_m/D_e K_m}$
ψ = modified Thiele modulus

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