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NOTE

Effectiveness of Biporous Catalysts for Zero-Order Reactions[1]

Supported porous catalyst pellets with bidispersed pore structures are formed by agglomeration of porous particles. Due to the practical abundance of such micro- and macrodistributions, a large number of theoretical and experimental analyses are available in the literature (*1–5*). Örs and Dogu (*4*) have obtained analytical solutions for an effectiveness factor for a first-order reaction occurring in biporous pellets. A new parameter α has been incorporated in the analysis of Örs and Dogu (*4*) and in subsequent analyses (see Appendix). The magnitude of α is determined by the ratio of diffusion coefficients in the micro- and macropore regions and the pellet to particle radius. A wide range of values is possible for α varying from 0.1 to 100. It was found that this parameter strongly affects the pellet effectiveness factor (*4*).

Zero-order reactions occurring in a pellet are conceptually different from higher-order reactions. As the reactant can become exhausted before reaching the center, it is necessary to consider two different cases as represented by two different boundary conditions. An elegant analysis of zero-order reactions for monoporous catalysts has been presented by Weekman and Gorring (*6*). The present note is an attempt to extend this to biporous structures.

The relevant mass balance equations can be written in dimensionless form as follows.

Microspheres

$$\frac{d^2\overline{C}_i}{d\overline{x}^2} + \frac{2\,d\overline{C}_i}{\overline{x}d\overline{x}} = \phi^2 \tag{1}$$

with the conditions

$$\frac{d\overline{C}_i}{d\overline{x}} = 0 \quad \text{at } \overline{x} = 0 \tag{2}$$

$$\overline{C}_i = \overline{C}_a \quad \text{at } \overline{x} = 1. \tag{3}$$

Macrospheres

$$\frac{d^2\overline{C}_a}{d\overline{Y}^2} + \frac{2\,d\overline{C}_a}{\overline{Y}\,d\overline{y}} = \alpha\left(\frac{d\overline{C}_i}{d\overline{x}}\right)_{\overline{x}=1} \tag{4}$$

with the conditions

$$\frac{d\overline{C}_a}{d\overline{y}} = 0 \quad \text{at } \overline{y} = 0 \tag{5}$$

$$\overline{C}_a = 1 \quad \text{at } \overline{y} = 1. \tag{6}$$

Various dimensionless parameters are defined as

$$\overline{C}_i = \frac{C_i}{\text{Co}} \quad \overline{C}_a = \frac{C_a}{\text{Co}} \quad \overline{x} = \frac{x}{X} \quad \overline{y} = \frac{y}{Y}$$

$$\alpha = 3(1-\varepsilon)\frac{Y^2D_i}{X^2D_a} \tag{6a}$$

$$\phi^2 = X^2\frac{k}{D_i\text{Co}}.$$

Case 1: Reactant exhaustion. The appropriate boundary conditions for the microsphere equation for this case are

$$\overline{C}_i = \overline{C}_a \quad \text{at } \overline{x} = 1 \tag{7}$$

$$d\overline{C}_i/d\overline{x} = 0 \quad \text{at } \overline{x} = \overline{xe} \tag{8}$$

$$\overline{C}_i = 0 \quad \text{at } \overline{x} = \overline{xe}. \tag{9}$$

Integrating the microsphere equation with Eqs. (7) and (8) we obtain

$$\overline{C}_i = \overline{C}_a - (1-\overline{x})\left[\frac{\phi^2(1+\overline{x})}{6} - \frac{\overline{xe}}{\overline{x}}\left[\frac{(1+\overline{xe})\phi^2}{6} - \frac{\overline{C}_a}{1-\overline{xe}}\right]\right]. \tag{10}$$

Application of Eq. (9) to Eq. (10) yields

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$$\phi^2 = \frac{3\overline{C}_a}{(1 - \overline{xe})(((1 + \overline{xe})/2) - \overline{xe}^2)}. \quad (11)$$

The flux at the microsphere surface is given by

$$(d\overline{C}_i/d\overline{x})_{\overline{x}} = 1 = \phi^2(1 - \overline{xe}^3)/3. \quad (12)$$

Case 2: Finite reactant concentration. As the concentration is finite throughout the microsphere, the extinction radius $\overline{xe}$ must be equal to zero. Equation (10) reduces to

$$\overline{C}_i = \overline{C}_a - \phi^2(1 - \overline{x}^2)/6 \quad (13)$$

and

$$(d\overline{C}_i/d\overline{x})_{\overline{x}=1} = \phi^2/3. \quad (14)$$

The corresponding macropore profile is given by

$$\overline{C}_a = \frac{\alpha\phi^2}{18}(\overline{y}^2 - 1) + 1 \quad (15)$$

and

$$(d\overline{C}_a/d\overline{Y})_{\overline{Y}=1} = \alpha\phi^2/9$$

$$\therefore \eta = 9(d\overline{C}_a/d\overline{Y})_{\overline{Y}=1}/\phi^2\alpha = 1, \quad (16)$$

which gives the well-known result of the effectiveness factor being unity for this case. The critical value of the parameters for which the center concentration of the microsphere becomes zero is given by

$$\phi^2 = \frac{6}{(1 - \alpha(\overline{y}^2 - 1)/3)}. \quad (17)$$

The above analysis indicates that, if the reactant remains finite throughout the pellet, the effectiveness factor is unity. This result is in concurrence with the results obtained earlier by Weekman and Gorring (*6*). The reactant exhaustion phenomenon in biporous pellets exhibits certain interesting features. The position at which the reactant gets depleted is different for microspheres at different locations in the pellet. Inspection of Eq. (11) further reveals that the extinction radius is a nonlinear function of macropore concentration, and the Thiele modulus. Macropore equations cannot be solved analytically and numerical methods must be used. From the numerical results,

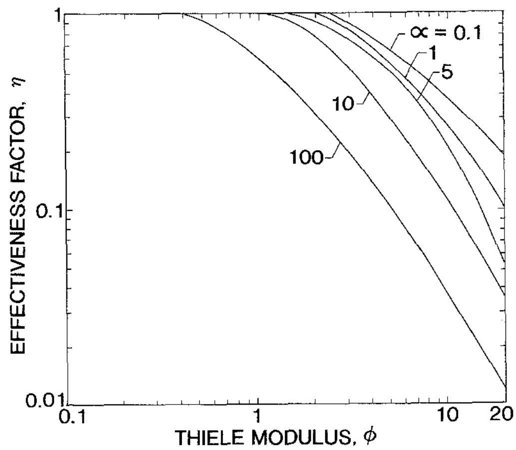

FIG. 1. Effectiveness as a function of Thiele modulus.

it was found that for any given value of α and ϕ the dead zone thickness in the micropores ($\overline{xe}$), increases progressively with decrease in the macropore length coordinate $\overline{y}$. For a given value of α with increase in ϕ the dead zone thickness profiles ($\overline{y}$ vs $\overline{xe}$), become steeper. This effect is enhanced with increase in α and is exhibited even at a relatively lower value of Thiele modulus. In case of monoporous pellet the Thiele modulus, at which the concentration at the center of the pellet becomes zero, is constant and was found to be equal to $\sqrt{6}$. From Eq. (17) it can be concluded that there exists a critical Thiele modulus profile in the pellet and this profile is a function of α; e.g., for $\alpha = 3$ extinction occurs above the critical Thiele modulus of $\sqrt{6}$ for microspheres situated at the surface. This value gradually decreases for the interior microspheres and reaches a magnitude of $\sqrt{3}$ for those located at the pellet center. Thus for this value of α if $\phi^2 < 3$ there would be a finite concentration of reactant in the pellet. It is also evident from Eq. (17) that this critical value of ϕ, below which a finite reactant concentration exists throughout the pellet, is strongly dependant on α.

Effectiveness factors were also calculated by numerical integration of macropore equations along with Eqs. (11)–(12). The results are shown in Fig. 1 for values of α

ranging from 0.1 to 100. It can be seen from the figure that for fixed values of α the effectiveness decreases with an increase in ϕ. This decrease is more pronounced as α increases.

It can be concluded from the above study that the behavior of zero-order reactions in biporous structures is strongly governed by the parameter α. Analytical solutions are not possible for the reactant exhaustion case as the extinction radius and the surface flux at the micropores are nonlinearly related to the system parameters.

APPENDIX: NOMENCLATURE

- C_a Macropore concentration
- C_i Micropore concentration
- $\bar{C}_a$ Dimensionless macropore concentration
- $\bar{C}_i$ Dimensionless micropore concentration
- Co Concentration at the pellet surface
- D_a Macropore diffusion coefficient
- D_i Micropore diffusion coefficient
- k Rate constant
- x Micropore length variable
- X Micropore length
- $\bar{x}$ Dimensionless micropore length variable
- $\overline{xe}$ Dimensionless extinction radius
- y Macropore length variable
- Y Macropore length
- $\bar{y}$ Dimensionless macropore length variable

Greek Symbols

- α Parameter defined by Eq. (6a)
- ε Macropore porosity
- η Effectiveness factor
- ϕ Thiele modulus

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