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Thermal effects on effectiveness of catalysts having bidisperse pore size distributions

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Abstract

Effectiveness factor of a non-isothermal porous catalyst pellet with a bimodal pore size distribution is a strong function of the dimensionless parameter α, which is proportional to the ratio of diffusion resistances in the macro and micropores. For exothermic reactions, the maximum observed in the effectiveness factor versus particle-Thiele modulus curves shifts to lower particle-Thiele modulus values and also becomes more significant with an increase of α. In the prediction of observed rates, possible effects of four dimensionless groups, namely particle-Thiele modulus ϕ_i, α, Prater parameter β and γ should be considered for porous catalysts having bimodal pore-size distributions.

Keywords: Bidisperse catalyst; Effectiveness factor; Non-isothermal

1. Introduction

Catalysts having bidisperse pore size distributions have been frequently used in number of catalytic processes. Macroreticular resin catalysts, zeolite pellets and many of the alumina or silica based supported catalysts have bimodal pore size distributions having micro- and macropores (or mesopores). It was shown in some early publications [1,2] that erroneous diffusivities might result, if diffusion data obtained in catalysts having bidisperse pore structures were analysed with a monodisperse pore size distribution assumption. Also, predictions of observed reaction rates using a monodisperse approach may result in erroneous conclusions [2,3].

Two approaches were used in the literature for the prediction of diffusion resistance effects on the observed rates measured in bidisperse catalysts. In the first approach, the bidisperse catalyst pellet was considered as an agglomeration of microporous particles (particle–pellet models) [2,4–7]. In the second approach, bidisperse catalysts were assumed to be composed of cylindrical macropores and cylindrical micropores, which extend from the macropores into the pellet [8,9]. A review of diffusion and reaction in catalyst pellets having bidisperse pore size distributions was reported in the recent publication of Dogu [3].

In the early work of Ors and Dogu [2], it was shown that effectiveness factor of an isothermal catalyst with a bidisperse pore size distribution was a function of two dimensionless groups, namely the particle-Thiele modulus, ϕ_i and the parameter α. The dimensionless group α is proportional to the ratio of diffusion resistances in the macro- and micropore regions of the pellet.

$$\alpha = 3(1-\varepsilon_a)\frac{D_i}{D_a}\left(\frac{R_0}{r_0}\right)^2 \qquad (1)$$

$$\phi_i = r_0\left(\frac{k}{D_i}\right)^{1/2} \qquad (2)$$

It is well known that temperature gradients within catalyst pellets might have significant effects on the observed rates. There are few publications in the literature related to the heat effects in bidisperse catalysts [10,11]. Considering the temperature gradients both in the catalyst pellet and also in the microporous grains, Datar et al. [10] showed that this system may possess five stationary states in a certain parameter region. Tambe and Kulkarni [11] considered the effects of film heat transfer resistance in such systems.

Pellet to particle diameter ratios of bidisperse catalysts are usually much higher than 10^2. Also, contact resistance of heat transfer between the microporous particles is expected

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Nomenclature

C_0	reactant concentration at the external surface of the pellet
C_a	reaction concentration in the macropores
C_i	reactant concentration in the micropores
D_a	effective pellet (macropore) diffusivity
D_i	effective particle (micropore) diffusivity
k	first-order reaction rate constant
r_0	radius of microporous particles
R_0	radius of pellet
R_{obs}	observed reaction rate at a point within the pellet
T	temperature
T_0	temperature at the pellet external surface

Greek letters

α	parameter defined by Eq. (1)
β	parameter defined by Eq. (13)
ε_a	macroporosity
γ	dimensionless parameter defined by Eq. (15)
η	pellet effectiveness factor
ς_a	dimensionless radial coordinate in the pellet, R/R_0
ς_i	dimensionless radial coordinate in the particle, r/r_0
ϕ_i	particle-Thiele modulus defined by Eq. (2)
ϕ_{i0}	particle-Thiele modulus at T_0
ϕ_{a0}	pellet-Thiele modulus at T_0 (Eq. (19))
λ_a	effective thermal conductivity of the pellet
φ_i	dimensionless concentration in the micropores, C_i/C_0
φ_a	dimensionless concentration in the macropores, C_a/C_0
θ_a	dimensionless temperature in the pellet, T_a/T_0

to be high. Thermal conductivity of the microparticles is also expected to be higher than the thermal conductivity of the pellet. Considering these factors, thermal effects in bidisperse catalysts may be analyzed by assuming isothermal microparticles and a non-isothermal pellet. This is a quite acceptable assumption and simplifies the analysis of heat effects in bidisperse catalysts. Bourdin et al. [12] used a similar approach for adsorption in a non-isothermal bidisperse adsorbent. In the present study, practical predictions related to the heat effects on observed rates were obtained for a bidisperse catalyst, following a similar approach.

2. Theoretical modeling

In the development of non-isothermal effectiveness factor, particle–pellet approach was used. It was assumed that the catalyst pellet was formed by the agglomeration of microporous particles and the pores between these agglomerated particles were considered as macropores (Fig. 1). Following the reasoning given in the Section 1, temperature gradients within the microporous particles were neglected as compared to the temperature gradients within the pellet. Considering a spherical pellet, the governing transport equations for concentration and temperature variations within the pellet and microporous particle were expressed as follows.

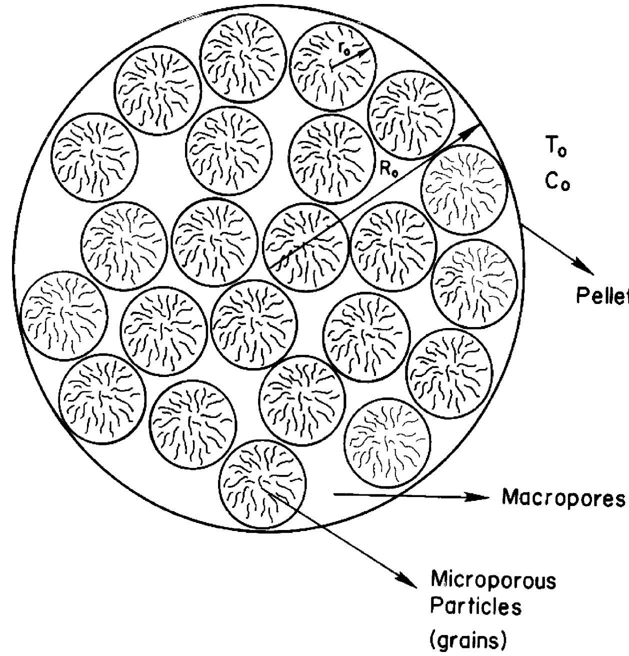

Fig. 1. Schematic diagram of a bidisperse catalyst pellet (pellet–particle model).

Microporous particle

$$\frac{D_i}{r^2}\frac{d}{dr}\left(r^2\frac{dC_i}{dr}\right) + R_i = 0 \tag{3}$$

Pellet

$$\frac{D_a}{R^2}\frac{d}{dR}\left(R^2\frac{dC_a}{dR}\right) - \frac{3(1-\varepsilon_a)}{r_0}D_i\left(\frac{dC_i}{dr}\right)_{r=r_0} = 0 \tag{4}$$

$$\frac{\lambda_a}{R^2}\frac{d}{dR}\left(R^2\frac{dT_a}{dR}\right) - (\Delta H_R)\frac{3(1-\varepsilon_a)}{r_0}D_i\left(\frac{dC_i}{dr}\right)_{r=r_0} = 0 \tag{5}$$

In this system, the observed reaction rate at an arbitrary point within pellet was expressed as

$$R_{app} = \frac{3(1-\varepsilon_a)}{r_0}D_i\left(\frac{dC_i}{dr}\right)_{r=r_0} \tag{6}$$

The boundary conditions for this set of equations are:

$$\frac{dC_i}{dr}\Big|_{r=0} = 0; \quad \frac{dC_a}{dR}\Big|_{R=0} = 0; \quad \frac{dT}{dR}\Big|_{R=0} = 0 \tag{7}$$

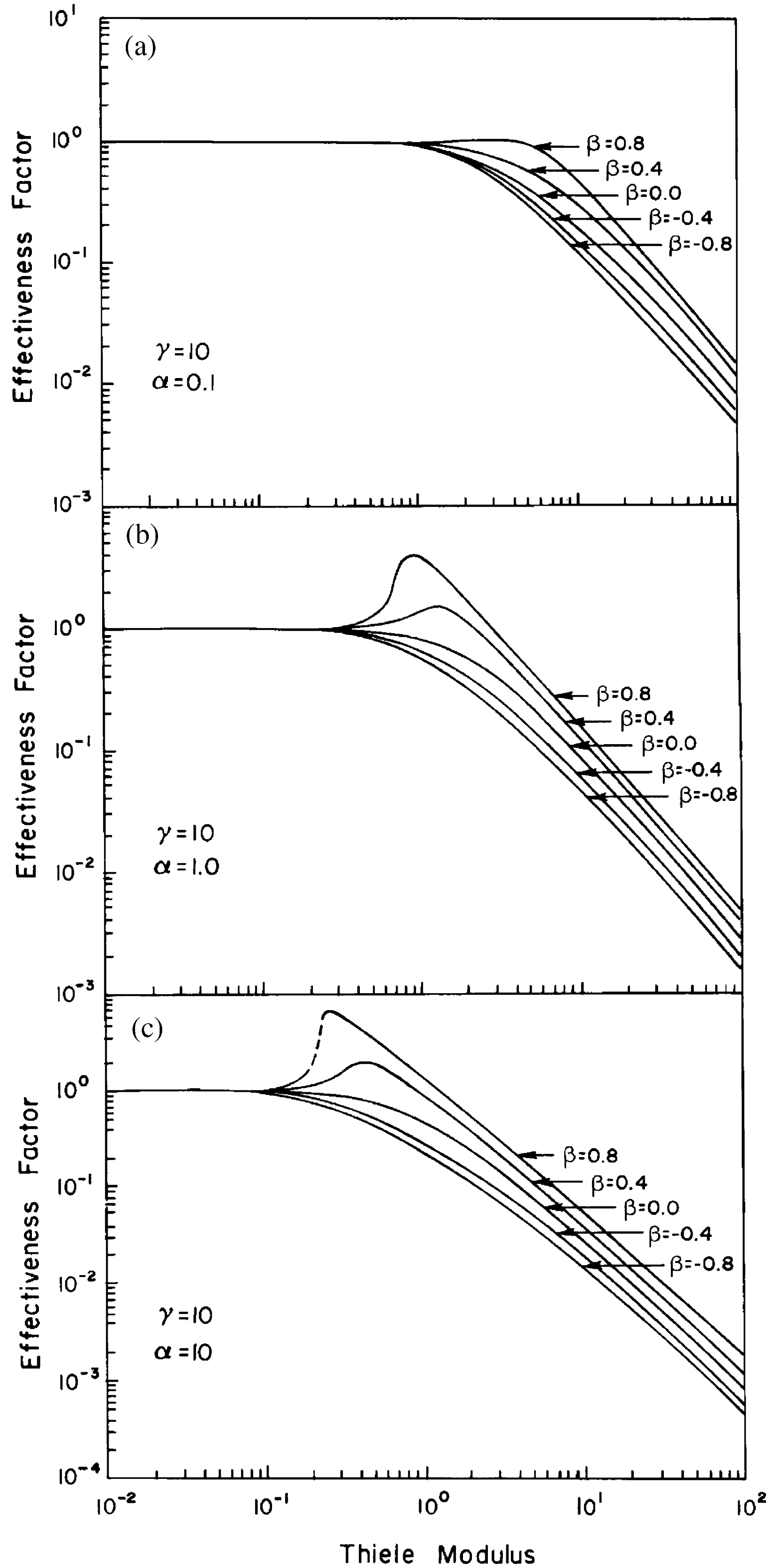

Fig. 2. Effectiveness factor of a non-isothermal bidisperse catalyst pellet at different values of β.

$$C_i = C_a \quad \text{at } r = r_0 \tag{8}$$

$$C_a = C_0; \quad T_a = T_0 \quad \text{at } R = R_0 \tag{9}$$

Four dimensionless parameters appear as a result of dimensionalisation of Eqs. (3)–(5).

Pellet

$$\frac{1}{\varsigma_a^2}\frac{d}{\varsigma_a}\left(\varsigma_a^2\frac{d\varphi_a}{d\varsigma_a}\right) - \alpha\left(\frac{d\varphi_i}{d\varsigma_i}\right)_{\varsigma_i=1} = 0 \tag{10}$$

$$\frac{1}{\varsigma_a^2}\frac{d}{d\varsigma_a}\left(\varsigma_a^2\frac{d\theta_a}{d\varsigma_a}\right) + \alpha\beta\left(\frac{d\varphi_i}{d\varsigma_i}\right)_{\varsigma_i=1} = 0 \tag{11}$$

Particle (first-order reaction)

$$\frac{1}{\varsigma_i^2}\frac{d}{d\varsigma_i}\left(\varsigma_i^2\frac{d\varphi_i}{d\varsigma_i}\right) - \phi_i^2\phi_i = 0 \tag{12}$$

Here, β corresponds to the Prater parameter:

$$\beta = \frac{(-\Delta H)D_a C_0}{T_0\lambda_a} \tag{13}$$

Due to temperature gradients within the pellet, particle-Thiele modulus, ϕ_i, is also expected to vary with respect to the radial position, R:

$$\phi_i = \phi_{i0}\exp\left(-\frac{\gamma}{2}\left(\frac{1-\theta_a}{\theta_a}\right)\right) \tag{14}$$

where

$$\gamma = \frac{E_a}{R_g T_0} \tag{15}$$

Here ϕ_{i0} is the particle-Thiele modulus evaluated at the surface temperature T_0.

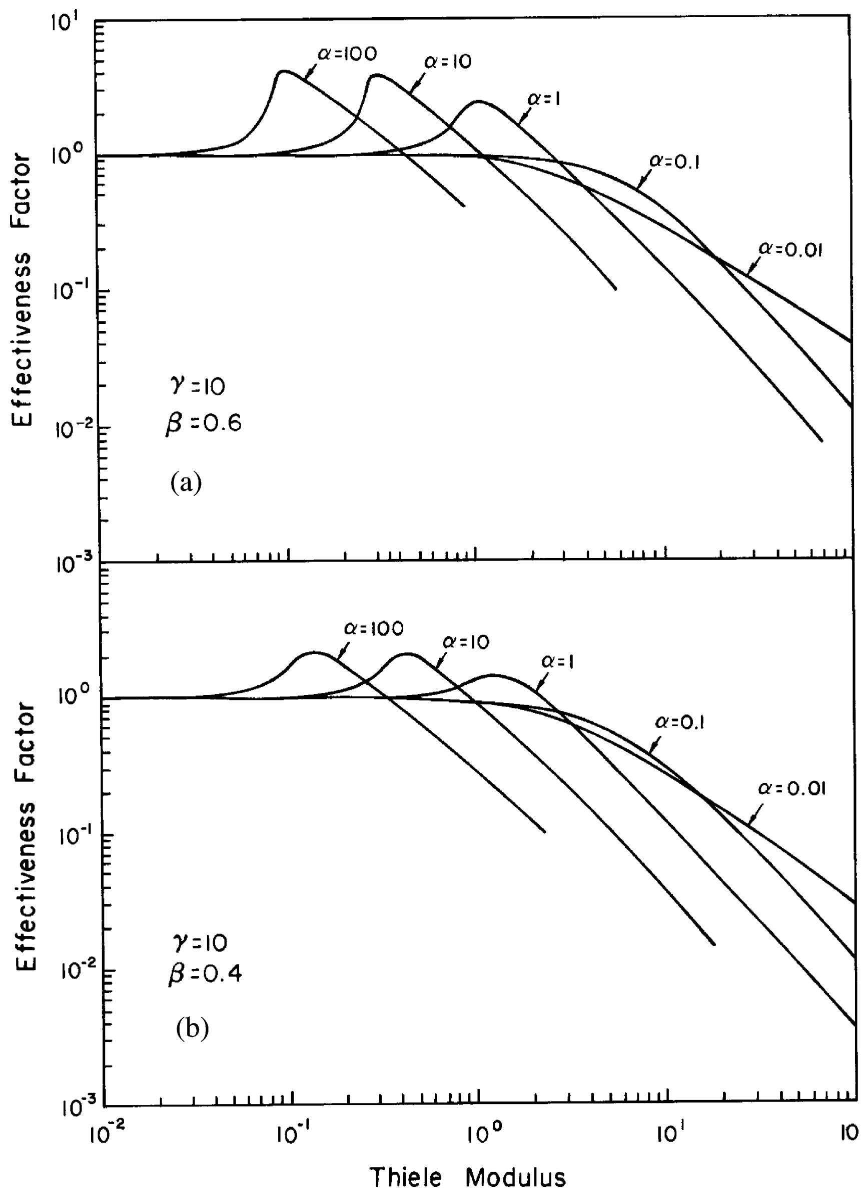

Fig. 3. Effect of α on non-isothermal effectiveness factor for an exothermic reaction. (a) $\beta = 0.6$; (b) β=0.4.

The solution of Eqs. (10)–(12) reduces to the following differential equation for the dimensionless concentration within the macropores of the pellet:

$$\frac{1}{\varsigma_a^2}\frac{d}{d\varsigma_a}\left(\varsigma_a^2\frac{d\varphi_a}{d\varsigma_a}\right) -\alpha\left[\frac{\phi_{i0}\exp(-\gamma/2(\beta(\varphi_a-1)/(\beta(1-\varphi_a)+1))}{\tanh(\phi_{i0}\exp(-\gamma/2(\beta(\varphi_a-1)/(\beta(1-\varphi_a)+1))))}\right]\varphi_a=0 \qquad (16)$$

The effectiveness factor for a bidisperse catalyst may be obtained using the following expression [3]:

$$\eta=\frac{9}{\phi_i^2\alpha}\frac{d\varphi_a}{d\varsigma_a}|\varsigma_a=1 \qquad (17)$$

By the numerical solution of Eq. (16), for different sets of dimensionless parameters α, ϕ_{i0}, β and γ, effectiveness factor values are predicted from Eq. (17), and the results are discussed in the Section 3.

3. Results and discussions

The dimensionless parameter α signifies the importance of macropore diffusion resistance as compared to the micropore diffusion resistance. Effectiveness factor curves obtained for three α values, namely for $\alpha = 0.1$, 1.0 and 10 are illustrated in Fig. 2a–c, respectively. In these figures, the value of γ was taken as 10 and β values were varied between −0.8 and 0.8. Same as for a monodisperse catalyst pellet, for exothermic reactions (positive β values) effectiveness

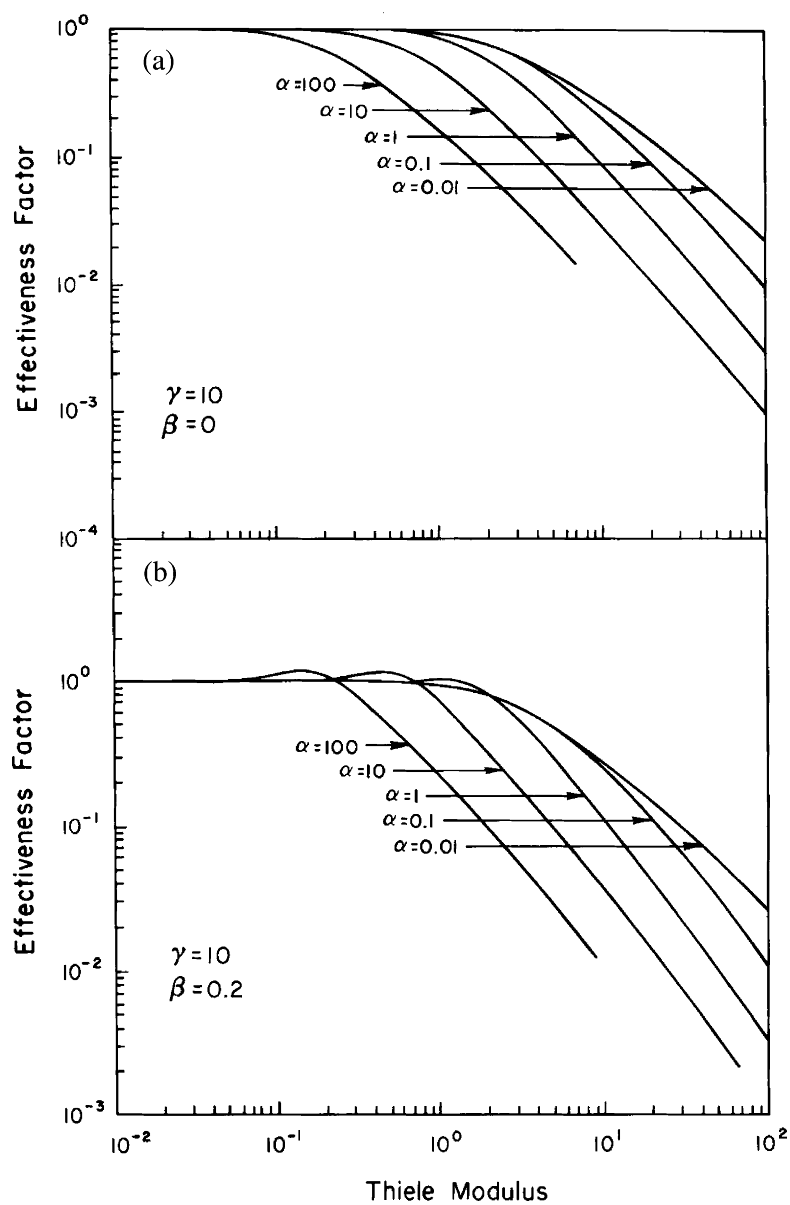

Fig. 4. Effectiveness factor of a bidisperse catalyst for (a) $\beta = 0$ (isothermal pellet; after Ors and Dogu, 1979), and (b) $\beta = 0.2$.

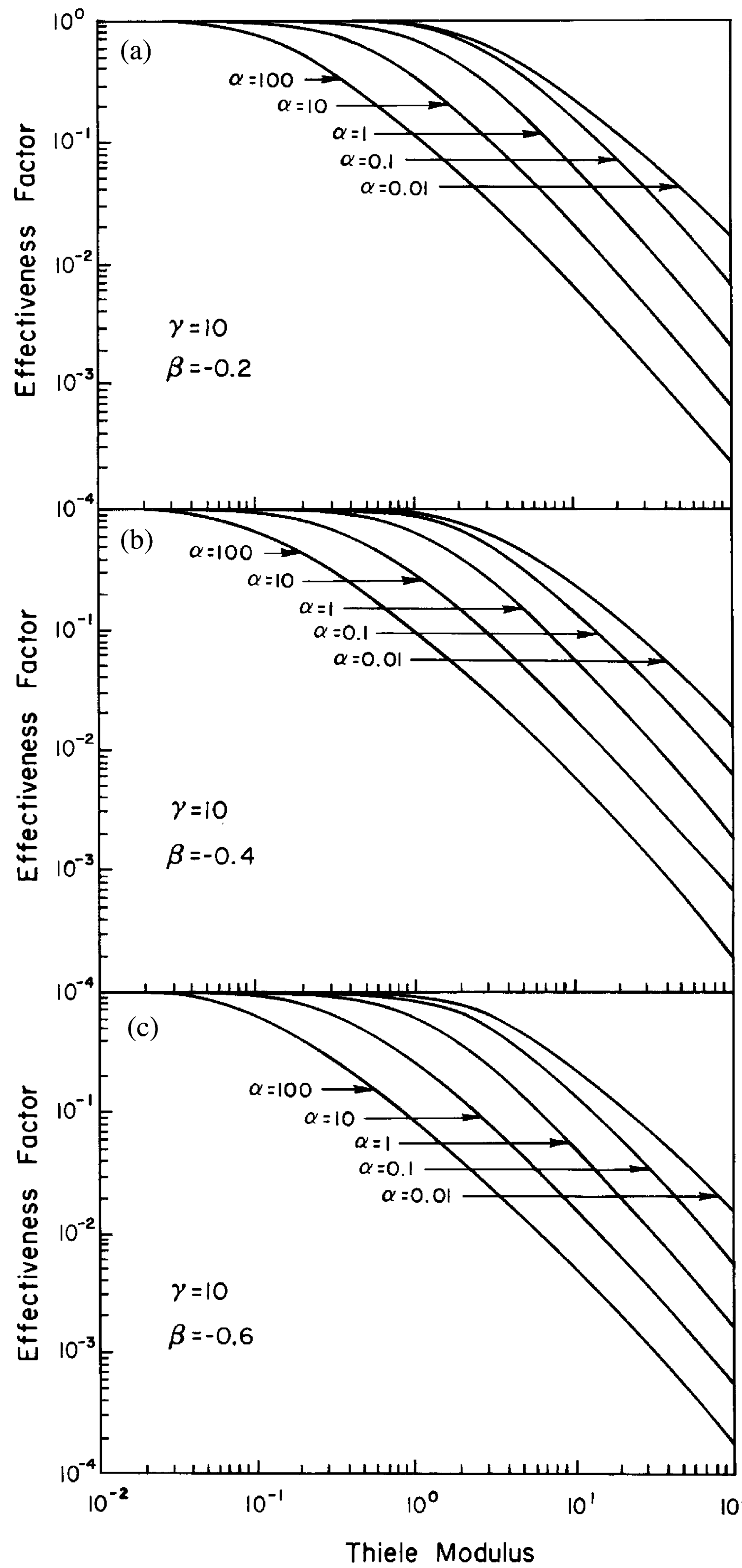

Fig. 5. Effect of α on non-isothermal effectiveness factor for an endothermic reaction.

factor values higher than unity are possible. As it is shown in Fig. 2, this becomes more significant as α gets larger. For α values much smaller than unity, the maximum observed in the effectiveness factor versus particle-Thiele modulus curves disappears. For very small values of α, diffusion resistance within the microporous grains becomes much more significant than the diffusion resistance in the macropores. This case corresponds to a catalyst with significant diffusion resistance in the microporous grains (for large values of ϕ_{i0}) and significant temperature gradients within the pellet. For large positive values of β, multiple steady-state values of the temperature within the pellet and the corresponding effectiveness factor values are possible especially for higher values of γ and α.

With an increase of α, the maximum observed in the effectiveness factor versus particle-Thiele modulus curves shifts to lower Thiele modulus values. This is clearly seen in Figs. 3a and b, and 4b. These figures were prepared for positive values of β, namely for $\beta = 0.6$, 0.4 and 0.2. As α gets larger, diffusion resistance in the macropores becomes more and more significant. For particle-Thiele modulus values of about 10^{-1}, effect of micropore diffusion resistance on the observed rate becomes very small. However, for $\phi_i = 10^{-1}$ and $\alpha = 100$ macropore diffusion resistance becomes the controlling factor.

The parameter α is actually proportional to the square of the ratio of pellet and particle-Thiele modulus expressions:

$$\alpha = 3\left(\frac{\phi_{a0}}{\phi_{i0}}\right)^2 \tag{18}$$

where

$$\phi_{a0} = R_0\left(\frac{k(1-\varepsilon_a)}{D_a}\right)^{1/2} \tag{19}$$

For many of the industrially important reactions, the value of α may vary between 10^{-2} and 10^2 [3]. Significance of α in the prediction of effectiveness factor values can be illustrated by evaluating the ratio of effectiveness factors calculated from the conventional monodisperse model and the bidisperse model. For instance, for a set of intermediate values of β and γ ($\beta = 0.4$, $\gamma = 10$), the ratio of effectiveness factors evaluated from the conventional monodisperse approach and from the bidisperse model becomes about 5 for a particle-Thiele modulus (ϕ_{i0}) of 2 at $\alpha = 100$. For smaller values of α, this ratio becomes even larger. As α becomes smaller micropore diffusion resistance becomes more significant as compared to macropore diffusion resistance. Prediction of the effectiveness factor from the conventional monodisperse approach would generally give overestimated values.

For a β value of zero, the solution of Eqs. (16) and (17) reduces to the analytical solution reported in the early work of Ors and Dogu [2], (Fig. 4a). For this case, the analytical solution for the effectiveness factor is

$$\eta = \frac{9}{\phi_i^2\alpha}\left[\frac{(\alpha(\phi_i/\tanh\phi_i - 1))^{1/2}}{\tanh(\alpha(\phi_i/\tanh\phi_i - 1))^{1/2}} - 1\right] \tag{20}$$

In Fig. 5a–c, effectiveness factor curves obtained for an endothermic reaction are shown (for $\beta = -0.2$, -0.4 and -0.6, respectively). Effect of α on the observed rate is also quite significant in endothermic reactions. With an increase of α, the decrease of effectiveness factor to values lower than unity starts at much lower particle-Thiele modulus values. This effect becomes more significant as the absolute value of β gets larger.

4. Concluding remarks

In the design of reactors involving bidisperse catalysts, effects of four dimensionless groups, namely α, β, γ and the particle-Thiele modulus ϕ_{i0} should be taken into account. Dimensionless group α, which corresponds to the ratio of diffusion resistances in the macro- and micropores, has a very significant effect on the effectiveness factor of a non-isothermal bidisperse catalyst pellet. The maximum observed in the effectiveness factor versus particle-Thiele modulus curves in exothermic reactions shifts to lower particle-Thiele modulus values and also becomes more significant with an increase of α.

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