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EFFECTIVENESS FACTORS IN BIDISPERSED CATALYSTS UNDER CONDITIONS OF CATALYST FOULING

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INTRODUCTION

Catalyst pellets that are manufactured by compaction of porous particles are often characterized by a bidispersed size distribution, with micropores lying inside the porous particles and macropores between single or agglomerated particles. Considerable work on diffusion and adsorption in this type of catalyst has been reported in the literature (Hashimoto *et al.*, 1976; Uyanik, 1977; Dogu and Smith, 1975; Hashimoto and Smith, 1974), and both the micro- and macropore diffusivities can be determined experimentally (MacDonald and Habgood, 1972; Dogu and Smith, 1975; Ma and Lee, 1976; Ravi Kumar *et al.*, 1982). There are also numerous studies concerned with the effectiveness of these catalysts (Silvestra and Hashimoto, 1975; Mingle and Smith, 1961; Ors and Dogu, 1979; Jayaraman *et al.*, 1980, 1983; Namjoshi *et al.*, 1983a).

There are well known reasons why commercial catalysts are liable to lose their activity during the course of reaction. The problem of catalyst deactivation has been analyzed theoretically and good reviews and treatises covering this area are available (Butt *et al.*, 1978; Masamune and Smith, 1966). The most common mechanisms for catalyst deactivation involve fouling through either parallel or series route. In the present paper we shall study bidisperse catalysts from the specific viewpoint of catalyst poisoning.

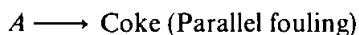
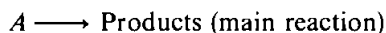
Inclusion of these effects in the analysis of the micro-macro effectiveness factor leads to a coupled two-point boundary value problem that requires trial-and-error on the micropore equations for each integration step of the macropore equation,—and the macropore equation must itself be solved by trial and error. This point has been discussed in an earlier paper (Namjoshi *et al.*, 1983b) and it suffices to state here that the conventional finite difference methods become too cumbersome and almost impossible to use for obtaining solutions to these problems. In the present work, we employ the methods of weighted residuals (Villadsen and Michelsen, 1978)—more specifically, the Galerkin method—and present comprehensive solutions to these problems with first-order main reaction. The order of the method employed is restricted to *two* to avoid

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excessive computation. This, of course, restricts the applicability of the results to moderate variations in the parameter values. For parameter values that would give very steep profile it would be necessary to employ higher-order approximation but still the present approximation order would give essentially correct results.

Parallel Fouling

Let us consider spherical catalyst particles of radius r_i which are compacted into spherical pellets of radius R as shown in Figure 1. In the micropores of the particles we shall assume that a single first order, isothermal, irreversible reaction takes place. Catalyst deactivation occurs simultaneously with the main reaction:



At time θ , the residual activity is expressed by the fraction S which is determined by

$$\frac{-\partial S(x, \theta)}{\partial \theta} = C_i S; \quad S(\theta = 0) = 1 \quad (1)$$

where C_i is the reactant concentration relative to the pellet surface reactant concentration (Eq. (3)).

The reaction rate for the main step is given by $r_A = k_0 S C_i$.

Neglecting the accumulation of reactant in the particles as well as in the pellet, we obtain the following mass balance equation for species A in the particle:

$$\nabla_x^2 C_i = k_0 S C_i r_i^2 / D_i = \phi^2 S C_i \quad (2)$$

where

$$\phi^2 = k_0 \frac{r_i^2}{D_i}; \quad x = \frac{r}{r_i}; \quad C_i = \frac{C'_i}{C'_a(y=1)} \quad (3)$$

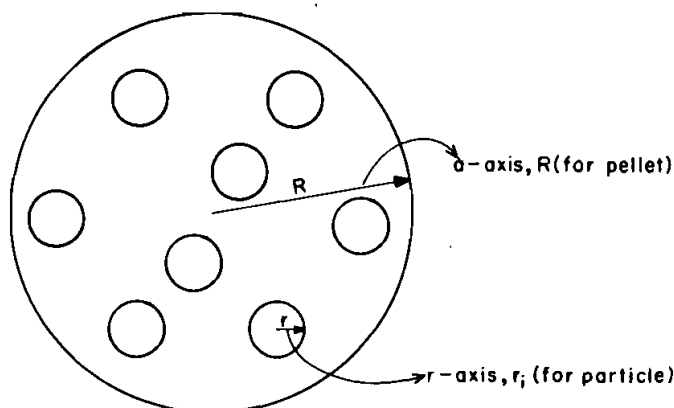


FIGURE 1 Schematic Diagram showing micro-macro particles in a pellet.

Equation (2) has boundary conditions

$$C_i = C_a; \quad x = 1 \tag{4}$$

$$\frac{\partial C_i}{\partial x} = 0; \quad x = 0 \tag{5}$$

In the same manner we can write the mass balance equation for the pellet as

$$\nabla_y^2 C_a = \frac{R^2}{D_a} (-r_A) = (1 - \epsilon) \frac{R^2}{D_a} k_0 \int_0^1 C_i S dx^3 \tag{6}$$

where $(1 - \epsilon)$ is the volume of spherical particles per unit volume of the spherical pellet; and the dimensionless variables are defined as

$$y = \frac{a}{R}; \quad C_a = \frac{C'_a}{C'_a(y=1)} \tag{7}$$

Further defining

$$\eta_i = \frac{1}{C_a} \int_0^1 C_i S dx^3 \tag{8}$$

and

$$\alpha = 3(1 - \epsilon) \frac{R^2 D_i}{r_i^2 D_a} \tag{9}$$

Equation (6) can be rewritten as

$$\nabla_y^2 C_a = \frac{\alpha}{3} \phi^2 \eta_i C_a = \alpha \frac{\partial C_i}{\partial x} \Big|_{x=1} \tag{10}$$

With the following boundary conditions

$$C_a = 1; \quad y = 1 \tag{11}$$

$$\frac{\partial C_a}{\partial y} = 0; \quad y = 0 \tag{12}$$

The time varying activity variable S can be eliminated from the micropore equations using the Legendre transformation

$$\psi_i = \int_0^\theta C_i d\theta \tag{13}$$

proposed by Del Borghi *et al.* (1976) and Dudukovic and Lamba (1978). The micropore equation can now be written as

$$\nabla_x^2 \psi_i = \phi^2 (1 - \exp(-\psi_i)) \tag{14}$$

With the transformed boundary conditions

$$\psi_i(1, \theta) = \int_0^\theta C_a d\theta = \psi_a \tag{15}$$

$$\frac{\partial \psi_i}{\partial x}(0, \theta) = 0$$

Also, employing the transformation (13) evaluated at the surface of the micropore, the macropore equation (10) can be rewritten as

$$\nabla_y^2 \psi_a = \alpha \frac{d\psi_i}{dx} \Big|_{x=1} \quad (16)$$

With the transformed boundary conditions

$$\frac{d\psi_a}{dy} = 0, \quad y = 0 \quad (17)$$

$$\psi_a = \theta, \quad y = 1 \quad (18)$$

The derivative $(d\psi_i/dx)_{x=1}$ required in Eq. (16) can be obtained by solving Eqs. (14)–(15). For this purpose we employ a single point collocation and for spherical geometry of the particles (Villadsen and Michelsen (1978), p. 234) we obtain:

$$F(\psi) = \frac{10.5}{\phi^2} (\psi - \psi_a) + 1 - \exp(-\psi) = 0 \quad (19)$$

$$F'(\psi) = \frac{10.5}{\phi^2} + \exp(-\psi) \quad (20)$$

where ψ is the value of ψ_i at the collocation point $x = \sqrt{3/7}$. It follows from these equations that $\psi = 0$ for $\psi_a = 0$ and $\psi_a - \psi \rightarrow 1/10.5$ for $\psi_a \rightarrow \infty$. Also the derivative $(d\psi_i/dx)_{x=1}$ can be obtained as

$$\frac{d\psi_i}{dx} \Big|_{x=1} = \phi^2 \left\{ \frac{7}{10} [1 - \exp(-\psi)] + \frac{3}{10} [1 - \exp(-\psi_a)] \right\} \quad (21)$$

Equations (19) and (21) together give the values of ψ and $(d\psi_i/dx)_{x=1}$ for assumed values of ψ_a which can be subsequently used in Eq. (16). This equation can now be solved using the conventional numerical methods or even by collocation. The overall effectiveness factor computed by this procedure is shown in Figures 2 and 3.

A particular difficulty associated with the use of this procedure is the fact that the results obtained are accurate only for small values of ϕ . Also the final estimation of the effectiveness factor is very sensitive to changes in parameter values. To overcome this difficulty it was proposed to simplify the problem by invoking the approximation concerning the variation of macropore concentration with time. In view of the relatively weak dependence of C_a on θ , the boundary condition given by Eq. (15) can be approximated as shown in (22).

$$\psi_i(1, \theta) = \int_0^\theta C_a d\theta \simeq C_a \theta = \psi_a \quad (22)$$

The set of Eqs. (14)–(15) with the modified condition (22) has now been solved using Galerkins method:

We use a polynomial approximation for the ψ_i profile:

$$\psi_i = \psi_a + (1 - u) \sum_{j=1}^N a_j u^{j-1} \quad j = 1, 2, \dots, N \quad (23)$$

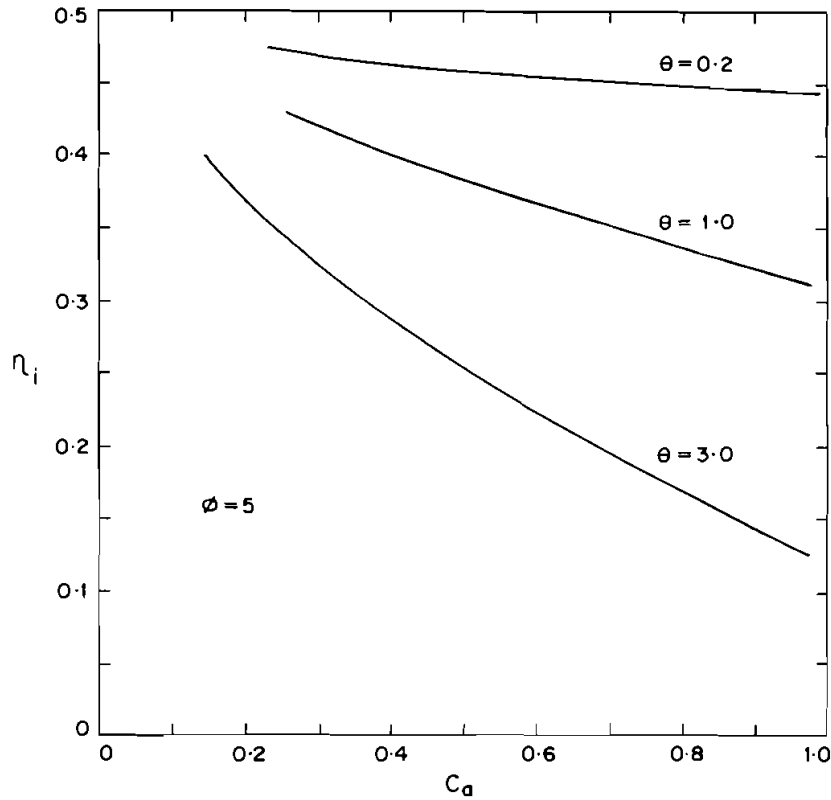


FIGURE 2 Micropore effectiveness factor as a function of macropore concentration at different dimensionless times.

and obtain the residual R_N as

$$R_N = 6(a_2 - a_1) - 20a_2u - \phi^2[1 - \exp\{-\psi_a - a_1(1 - u) - a_2u(1 - u)\}] \quad (24)$$

In Galerkin's method we make R_N orthogonal on $\partial\psi_i/\partial a_k$, $k = 1, 2, \dots, N$ over the volume of the spherical particle. The resultant equations for the case of $N = 2$ can be written as

$$\int_0^1 R_N(a, u)(1 - u)u^{1/2} du = 0, \quad k = 1 \quad (25)$$

$$\int_0^1 R_N(a, u)(1 - u)u^{3/2} \cdot du = 0, \quad k = 2 \quad (26)$$

Equations (25) and (26) are solved to obtain the constants a_1 and a_2 . Integrals in these equations cannot be evaluated analytically and they have to be solved numerically using the so-called "Galerkin by quadrature methods" (Villadsen and Michelsen, 1978).

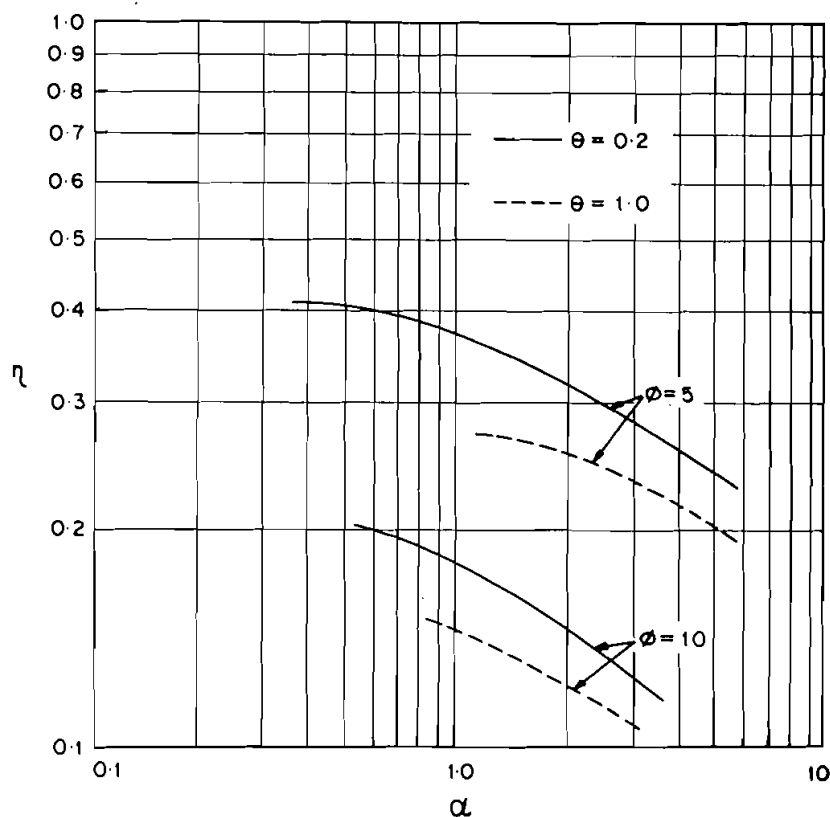


FIGURE 3 Effectiveness factor as a function of α for different values of θ and ϕ .

Equivalently Eqs. (25)–(26) can also be written as

$$\int_0^1 F_j(u)(1-u)u^{1/2} du = \sum_{k=1}^M w_k F_j(u_k) = 0 \quad (27)$$

where $F_j(u) = R_N(a, u)u^{j-1}$, $j = 1, 2, \dots, N$ (here 2) and M may have any value $\geq N$. The u_k 's are chosen to be the zeros of the Jacobi polynomial $p_2^{(1, 1/2)}$. Equation (27) is solved using the Gaussian quadratures to obtain the values of a_1 and a_2 . These values of a_1 and a_2 are utilized in the estimation of η_i which in terms of transformed variables can be written as

$$\eta_i = \frac{3}{C_a} \int_0^1 x^2 \frac{d\psi_i}{d\theta} \exp(-\psi_i) dx \quad (28)$$

It should be noted that the values of a_1 and a_2 calculated using the above mentioned procedure are specific to the values of θ , ϕ and C_a . In view of the dependence of a_1 and a_2 on θ , in the process of calculation of η_i we need to know the variations of a_1 and a_2 with θ at constant C_a and ϕ . These values ($da_1/d\theta$) have been generated by introducing an infinitesimal variation in θ keeping ϕ and C_a constant and then used to obtain the $\eta_i - C_a$ variation for one value of ϕ and several values of θ . One such typical curve for three different values of θ ($= 0.2, 1$ and 3) for one value of ϕ ($\phi = 5$) is shown in Figure 2.

Similar calculations for different values of ϕ have been repeated and the data interpolated to obtain η_i for any value of C_a at constant θ and ϕ . This information has been subsequently used in the macropore equation which has been solved using Weisz and Hick's method (1962). The results are presented as $\eta - \alpha$ or $\eta - \theta$ plots for different values of (θ, ϕ) or (α, ϕ) .

Figure 4 shows a plot of $\eta - \theta$ for two values of ϕ (1 and 5), each for two values of α , (1 and 10). It is seen from this figure (curves for $\phi = 1$ or 5; $\alpha = 1$) that curves with the same α intersect. This implies that at lower times a catalyst with no significant diffusional resistance ($\phi = 1$) gives better performance while a catalyst with high diffusional resistance fares well for higher θ values. Also a catalyst with moderate diffusional resistance deactivates faster than one with higher diffusional resistance. In general, for any value of ϕ the catalyst has lower effectiveness and deactivates faster with increase in α . Also, the influence of the parameter α , is less severe for a catalyst with low diffusional resistance. That is, for low values of ϕ (say $\phi = 1$) the deviation in the η values and the final time of deactivation are less severely affected with increase in α from 1 to 10. On the other hand, for a catalyst with high diffusional resistance, the influence of an increase in α is felt more severely and both the η and the final time of deactivation get affected considerably. An alternative representation of $\eta - \alpha$ for different values of θ has already been shown in Figure 3.

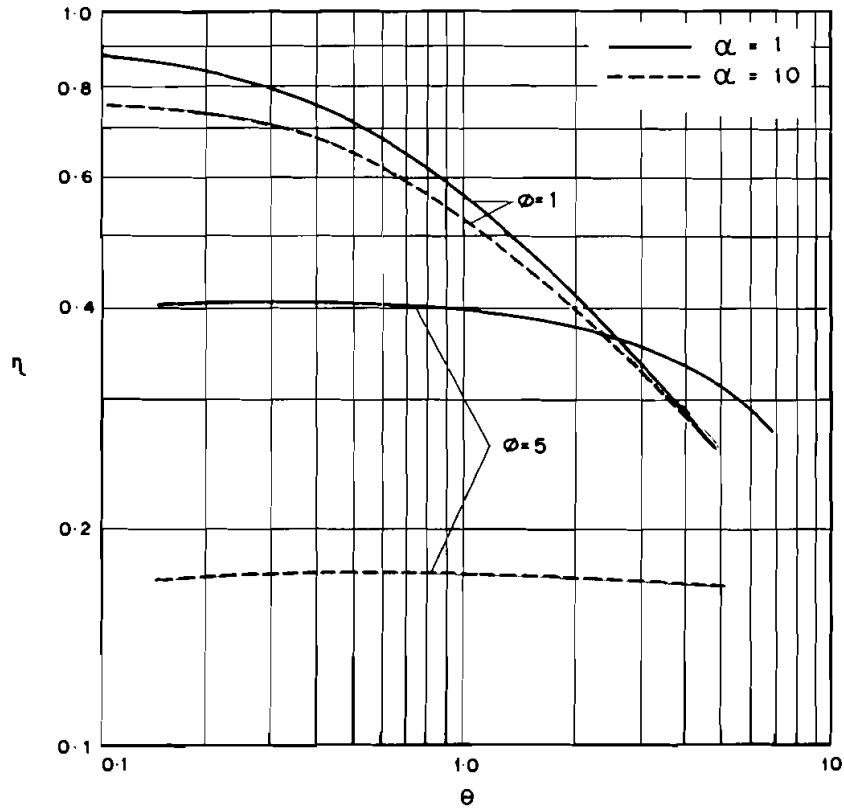


FIGURE 4 Effectiveness factor as a function of dimensionless time for different values of α and ϕ .

Series Fouling

The governing equations for the micro-macro pore system where a reaction leading to series fouling proceeds ($A \rightarrow v_1 B \rightarrow \text{coke}$) can be written as

$$\begin{aligned} \nabla_x^2 C_{iA} &= \phi^2 C_{iA} S; & C_{iA} &= C_a, & x &= 1; \\ \frac{dC_{iA}}{dx} &= 0, & x &= 0 \end{aligned} \quad (29)$$

$$\nabla_x^2 C_{iB} = -v\phi^2 C_{iA} S; \quad C_{iB} = b_0, \quad x = 1; \quad \frac{dC_{iB}}{dx} = 0, \quad x = 0 \quad (30)$$

$$-\frac{\partial S}{\partial \theta} = C_{iB} S, \quad S = 1, \quad \theta = 0 \quad (31)$$

Combining Eqs. (29) and (30), C_{iB} can be eliminated in terms of C_{iA} as

$$C_{iB} = v(C_a - C_{iA}) + b_0 \quad (32)$$

Employing Eq. (32) in Eq. (31) and using the definition of ψ_i [Eq. (13)], on integration we obtain

$$S = \exp[-\{b_0\theta + v(\psi_a - \psi_i)\}] \quad (33)$$

Further, presuming a weak dependence of C_a on θ , this equation can be written as

$$S = \exp[-(b_0 + vC_a)\theta + v\psi_i] \quad (34)$$

Employing this definition of S in Eq. (29) the micropore equation can be rewritten in terms of the transformed variable as

$$\nabla_x^2 \psi_i = \int_0^\theta \phi^2 \frac{d\psi_i}{d\theta} \exp[-(b_0 + vC_a)\theta + v\psi_i] d\theta \quad (35)$$

By using single point collocation this equation can be rewritten as

$$B_{11}\psi + B_{12}C_a\theta = \int_0^\theta \phi^2 \frac{d\psi}{d\theta} \exp[-(b_0 + vC_a)\theta + v\psi] d\theta \quad (36)$$

Differentiating Eq. (36) and rearranging we obtain

$$\frac{d\psi}{d\theta} = C_a \left[1 + \frac{\phi^2}{B_{12}} \exp[-(b_0 + vC_a)\theta + v\psi] \right]^{-1} \quad (37)$$

which on subsequent integration subject to condition $\psi = 0$ for $\theta = 0$ yields

$$\begin{aligned} \theta &= \frac{1}{b_0} \ln \left[\frac{\{ (b_0 + vC_a)\phi^2/B_{12} \}}{\{ b_0 + (b_0 + vC_a)\phi^2/B_{12} \}} \right] / \left[\frac{\{ (b_0 + vC_a)\phi^2 Z/B_{12} \}}{\{ b_0 + (b_0 + vC_a)\phi^2 Z/B_{12} \}} \right] \\ &+ \frac{1}{(b_0 + vC_a)} \ln \left[\frac{b_0 B_{12}/\phi^2 + b_0 + vC_a}{b_0 B_{12}/\phi^2 + (b_0 + vC_a)Z} \right] \end{aligned} \quad (38)$$

where

$$Z = \exp[-(b_0 + vC_a)\theta + v\psi]$$

The derivative $d\psi/d\theta$ and θ given by Eqs. (37) and (38) are required in the estimation of micropore effectiveness factor which can be written as

$$\eta_i = \frac{(1+s)}{C_a} \int_0^1 x^s \frac{d\psi_i}{d\theta} \exp[-(b_0 + vC_a)\theta + v\psi_i] dx \quad (39)$$

or equivalently as

$$\eta_i = 3 \left[\frac{w_1 \exp[-(b_0 + C_a v)\theta + v\psi]}{1 + \phi^2/B_{12} \exp[-(b_0 + C_a v)\theta + v\psi]} + w_2 \exp(-b_0\theta) \right] \quad (40)$$

In these equations w_1 and w_2 refer to the weight factors and B_{12} the coefficient matrix. It is important to note that b_0 appearing in the equation for η_i is also dependent on C_a , the corresponding concentration in the macropore. As such this equation will have to be simultaneously solved along with the macropore equations.

We now turn to macropore equations for species A and B which can be written as

$$\begin{aligned} \nabla_y^2 C_a &= \alpha \frac{dC_{iA}}{dx} \Big|_{x=1} = \frac{\alpha}{(s+1)} \phi^2 \eta_i C_a, & C_a &= 1, \\ y &= 1; \quad \frac{dC_a}{dy} = 0, & y &= 0 \end{aligned} \quad (41)$$

$$\nabla_y^2 C_b = -v\alpha \frac{dC_{iA}}{dx} \Big|_{x=1}, \quad C_b = B_0, \quad y = 1; \quad \frac{dC_b}{dy} = 0, \quad y = 0 \quad (42)$$

Eliminating C_b in terms of C_a from these equations we obtain the following relation between the concentration of species B at the surface of the micropore (b_0) to the concentration at the surface of the pellet (B_0)

$$b_0 = v(1 - C_a) + B_0 \quad (43)$$

Note that b_0 is required in Eq. (40) for estimation of micropore effectiveness factor.

The macropore equation for the species A has now been solved using the polynomial approximation method. The profile for C_a is defined as

$$C_a = 1 + b_1(1 - T) + b_2 T(1 - T); \quad T = y^2 \quad (44)$$

Substituting Eq. (44) in (41) we obtain the residual R_N as

$$R_N = -2b_2 T + 1.5(-b_1 + b_2 - 2b_2 T) - \frac{0.25\alpha\phi^2}{(s+1)} \eta_i C_a \quad (45)$$

The residual R_N is minimized over the volume of the pellet so as to get the best approximation profile. For $N = 2$, this leads to Eqs. (25) and (26) where R_N is now defined by Eq. (45). The η_i and C_a required in Eq. (45) are given by Eqs. (40) and (44). Once b_1 and b_2 are known the overall effectiveness factor is simply obtained as $\eta_i = -18(b_1 + b_2)/\alpha\phi^2$. The results calculated in terms of the overall effectiveness factor as a function of time θ for different values of ϕ and α are presented in Figure 5.

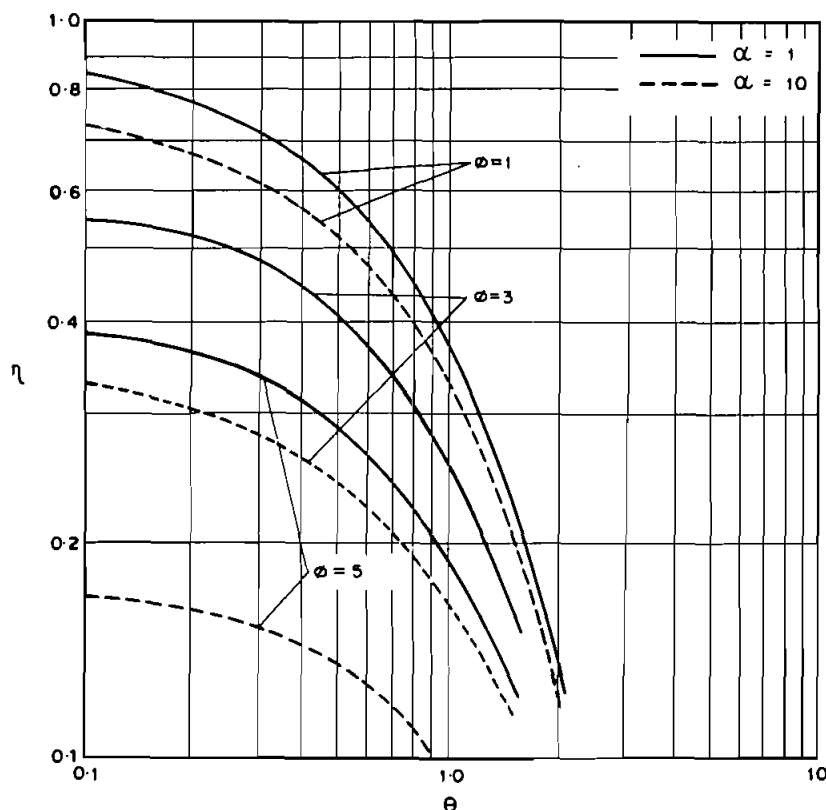


FIGURE 5 Effectiveness factor as a function of θ for different values of α and ϕ .

Typical variations of η as a function of time θ for three different values of ϕ ($\phi = 1, 3$ and 5) for $\alpha = 1$ and 10 are shown in Figure 5. It is seen that for a given value of ϕ the difference between the effectiveness of the catalyst for $\alpha = 1$ and 10 is highest for the catalyst at shorter times. Also, this difference at any time θ is higher for higher value of ϕ . As time θ increases the differences in general decrease. This decrease in the value of η for $\alpha = 1$ and 10 with θ is more significant for low ϕ than for high ϕ .

The results of this investigation suggest that where series type of fouling occurs, it is preferable to have a catalyst with low diffusional resistance and also low values of α . Thus it is preferable to operate with as small size of catalyst as possible at low temperatures. In the limiting case of $\alpha \rightarrow 0$, the results obtained here correspond to the case of series fouling in a monopore system.

To summarize, in systems where catalyst deactivation occurs, due to either parallel or series fouling, the study leads to the following conclusions:

- (1) For parallel fouling, a catalyst with low ϕ gives better performance at shorter times, while a catalyst with high ϕ fares better at longer times. This also implies that a catalyst with low ϕ deactivates faster than a catalyst with high ϕ at any value of α .
- (2) The catalyst shows lower effectiveness and deactivates faster with increase in α for any value of ϕ .

(3) The parameter α affects the overall value of η and the time for complete deactivation of the catalyst more severely for catalysts with high ϕ than for those with low ϕ . In other words, the effect of bimodal pore dispersion increases with increasing diffusional resistance.

(4) In series fouling, the greatest influence of the parameter α is felt at shorter times. With increase of time, the influence of α diminishes for the same values of ϕ . This is particularly so for catalysts with low ϕ .

(5) In general, large values of the parameter α (characterizing the micro-macro pore system) has a detrimental effect on the effectiveness factor η . It is preferable therefore to operate the system with as low values of α as possible. This clearly suggests the use of small size of catalyst. In fact, for $\alpha = 0$, all the results derived here degenerate to the corresponding monopore case.

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NOMENCLATURE

$a_i (i = 1, 2 \dots N)$	polynomial constants
a	radial coordinate in catalyst pellet
b_1, b_2	polynomial constants
b_0	concentration of species at the surface of the particle at position a in pellet defined by Eq. (43)
B_0	concentration of species B in the bulk defined by Eq. (42)
B_{12}	coefficient matrix for single point collocation
C_i	dimensionless particle concentration
C'_i	concentration of reactant A in particle
C_{iA}	dimensionless micropore concentration for species A
C_{iB}	dimensionless micropore concentration for species B
C_a	dimensionless macropore concentration
C'_a	macropore concentration
C_b	dimensionless macropore concentration for species B
D_i	micropore effective diffusivity
D_a	macropore effective diffusivity
D_{eA}	micropore effective diffusivity of species A
D_{eB}	micropore effective diffusivity of species B
F_j	defined by Eq. (27)
$F(\psi)$	defined by Eq. (19)

$F'(\psi)$	defined by Eq. (20)
k_0	rate constant for the main reaction
k_f	rate constant for fouling reaction
r	radial coordinate in catalyst particle
r_i	radius of the catalyst particle (see Figure 1)
r_A	rate expression for the main reaction
\bar{r}_A	average rate of the main reaction on a particle at position a in the pellet
R	radius of the catalyst pellet (see Figure 1)
R_N	residual
s	geometry of the pellet
S	activity of particle at position x and at time θ . $S(x, 0) = 1$.
T	defined as y^2
u	defined as x^2
w_k	weights in a quadrature [Eq. (22)]
x	dimensionless distance variable used in micropore
y	dimensionless distance variable used in macropore
Z	defined by Eq. (38)

Greek Letters

α	parameter defined as $3(1 - \epsilon)(D_i/D_a)(R^2/r_i^2)$
η_i	micropore effectiveness factor
η	macropore effectiveness factor
θ	dimensionless time defined as $k_f C_{as} t$
ν	parameter defined as $[D_{eA}/D_{eB}]^{\nu_1}$
ν_1	stoichiometric coefficient
ϕ	Thiele modulus
ψ_i	cumulative gas concentration defined by Eq. (13)
ψ_a	cumulative gas concentration defined by Eq. (15)
ψ	value of parameter ψ_i at the collocation point

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