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Isothermal Fouling of Catalyst Pellets

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A study of the effects of fouling on catalyst effectiveness and activity has been made. Parallel, series and a combination of parallel/series fouling have been considered. A Langmuir–Hinshelwood model was used for the main reaction and the fouling reaction was assumed to be first order. The equations were solved using the orthogonal collocation method and the dehydration of alcohols was chosen to illustrate the method. The same procedure is capable of extension to nonisothermal systems and to other kinetics.

INTRODUCTION

The poisoning and fouling of catalysts is of great practical importance and has attracted an increasing amount of experimental and theoretical investigation. The subject has been comprehensively surveyed in a recent review by Butt (*1*). Poisoning is generally considered to be a specific phenomenon, caused very often by impurities in the feed stream; whereas fouling is nonspecific, often requires larger amounts of material for deactivation than poisoning processes and in general is a physical deposition process. Typical of fouling deposits is the "coke" produced by process streams on catalyst surfaces. Fouling may occur in parallel or in series with the main reaction or by a combination of series and parallel processes.

Wheeler (*2*) first analyzed the effect of poisoning and fouling coupled with intraparticle concentration gradients on the yield and selectivity of catalysts. He distinguished between nonselective or homogeneous poisoning and selective or "pore mouth" poisoning and determined the conditions under which these effects could occur. Most of the subsequent analytical studies of fouling have assumed integral or zero order rate expressions for the main and fouling reactions. Thus Masamune and Smith (*3*) assumed both reactions to be of first order, whereas Greco *et al.* (*4*) in a study of the dehydration of higher alcohols assumed the main reaction to be zero order and the fouling reaction to be first order. Many catalytic processes, however, obey complex kinetics and may be fitted more readily by nonintegral order rate expressions such as the Langmuir–Hinshelwood type. Chu (*5*) has modeled the fouling process using a generalized rate expression but he considered only two values of the intraparticle diffusion parameter (Thiele modulus) and did not consider the case of combined series/parallel fouling.

The present paper reports a study of the effect of fouling on deactivation using as an illustration the dehydration of alcohols over alumina. Parallel, series and series/parallel fouling have been considered for a process where the main reaction obeys Langmuir–Hinshelwood kinetics and the fouling is first order. This is considered to be more realistic than some of the models proposed hitherto.

NOMENCLATURE

a	dimensionless concentration of A
b	dimensionless concentration of B

b_0	dimensionless surface concentration of B
C_A, C_B	concentration of A and B, within pellet
C_{A_0}, C_{B_0}	surface concentrations
C_w (C_{w_0})	concentration (surface concentration) of water
D_{e_A}, D_{e_B}	effective diffusivity of A and B
D_{e_w}	effective diffusivity of water
k	rate constant for main reaction
k_{f_1}	rate constant for parallel fouling
k_{f_2}	rate constant for series fouling
K_A, K_w	adsorption constants for alcohol and water, respectively
K_A^*, K_w^*	modified adsorption constants, $K_A C_{A_0}{}^{1/2}$, $K_w C_{A_0}$ (D_{e_A}/D_{e_w}), respectively
q	$C_{w_0} D_{e_w}/C_{A_0} D_{e_A}$
r	radial position
r_A	rate of reaction of A
R	radius of pellet
S	activity of catalyst
t	time
δ	dimensionless radial coordinate
ϕ	Thiele modulus, $R(k/D_{e_A} C_{A_0})^{1/2}$
η	effectiveness factor, defined by Eq. (16)
τ	dimensionless time

GENERAL THEORY

We shall develop the analysis for the case of parallel and/or series type of fouling given by the equations

A → B + C	main reaction,
A → coke	parallel deactivation,
B → coke	series deactivation.

The rate of the main reaction is assumed to be a function of the amount of active sites available for the reaction. Isothermal conditions with no external mass transfer resistance are assumed. The mass balance for the reactant A and the product B in the catalyst pellet for an irreversible reaction can be formulated as:

$$D_{e_A} \nabla^2 C_A = \frac{\partial C_A}{\partial t} + r_A(C_A) S, \qquad (1)$$

$$D_{e_B} \nabla^2 C_B = \frac{\partial C_B}{\partial t} - r_A(C_A) S, \qquad (2)$$

where

C_A, C_B	are the concentration of the species A and B, respectively
D_{e_A}, D_{e_B}	the corresponding effective diffusivities
∇^2	denotes the Laplacian operator
t	is the time elapsed
$r_A(C_A)$	is the rate of reaction of A for a fresh (completely active) catalyst
S	is the fraction of active sites remaining unfouled at time t.

The fouling reaction results in the destruction of the active sites available for the reaction. For the purpose of modeling, a suitable rate equation has to be postulated for the fouling reaction, which is generally a function of the concentration of the species involved in the deactivation reaction and also the number of active sites present at any given time. Thus, without loss of generality, we can express the decrease in the fraction of the active sites by a relation of the following form:

$$-\frac{\partial S}{\partial t} = k_{f_1} f_1(C_A) f_2(S) + k_{f_2} f_1'(C_B) f_2'(S), \qquad (3)$$

where k_{f_1}, k_{f_2} are the rate constants for the parallel and series type of fouling reactions, respectively.

Solution of Eqs. (1), (2) and (3) simultaneously gives the concentration and catalyst activity profiles in the pellet as a function of time. Knowing the concentration profiles, we can evaluate the overall rate of reaction and the catalyst effectiveness factor at any given time. The boundary conditions required are:

$$\text{at } r = 0, \quad \frac{\partial C_A}{\partial r} = \frac{\partial C_B}{\partial r} = 0, \tag{4}$$

$$\text{at } r = R, \quad C_A = C_{A_0}, C_B = C_{B_0} \quad \text{for any given } t, \tag{5}$$

where

R is the radius of the pellet

C_{A_0}, C_{B_0} are the external (or bulk) gas phase concentrations.

$$\text{At } t = 0, \quad S = 1. \tag{6}$$

An assumption implicitly made in Eq. (1) is that the fouling reaction rate is very small in comparison with the main reaction and hence the amount of A consumed in the deactivation reaction does not appear in the mass balance equation for A. Under these conditions, a quasi-steady state assumption can be made for the main reaction and the transient terms in Eqs. (1) and (2) can be neglected.

The equation can be nondimensionalized by the introduction of the following variables:

$$a = \frac{C_A}{C_{A_0}}, \quad b = \frac{C_B}{C_{A_0}}, \quad \delta = \frac{r}{R}.$$

Equation (1) becomes:

$$\nabla^2 a = \frac{R^2}{D_{e_A} C_{A_0}} r_A(a) S, \tag{7}$$

where the Laplacian operator is now with respect to δ.

Equation (2) becomes:

$$\nabla^2 b = -\frac{D_{e_A}}{D_{e_B}} \cdot \frac{R^2}{D_{e_A} C_{A_0}} r_A(a) S. \tag{8}$$

Equation (3) becomes:

$$-\frac{dS}{d\tau} = f_1(a) f_2(S) + \frac{k_{f_2}}{k_{f_1}} f_1'(b) f_2'(S), \tag{9}$$

where τ is a suitably defined dimensionless time.

The boundary conditions become:

$$\text{at } \delta = 0, \quad \frac{da}{d\delta} = \frac{db}{d\delta} = 0, \tag{10a}$$

$$\text{at } \delta = 1, \quad a = 1,\ b = b_0\ (= C_{B_0}/C_{A_0}). \tag{10b}$$

The initial condition is:

$$\text{at } \tau = 0, \quad S = 1. \tag{11}$$

The Eqs. (7) and (8) can be combined to eliminate the rate terms and the concentration of b can be expressed in terms of the concentration of a. Thus, we have:

$$b = b_0 + \frac{D_{e_A}}{D_{e_B}} (1 - a). \tag{12}$$

The problem then consists of solving Eqs. (7) and (9) simultaneously to evaluate the concentration profile of A and the catalyst activity profile in the pellet.

METHOD OF SOLUTION

The orthogonal collocation method suggested by Villadsen and Stewart (*6*) was employed in solving the differential equation [Eq. (7)]. The method consists of expressing the Laplacian as a function of the concentrations at the selected collocation points and solving the resulting algebraic equations. Thus, the Laplacian at a point δ_i is expressed as:

$$(\nabla^2 a)\delta = \delta_i = \sum_{j=1}^{N} B_{ij} a_j, \tag{13}$$

where

N is the number of collocation points including the point $\delta = 1$

a_j concentration at the point δ_j.

The collocation matrix B_{ij} can be calculated by a straightforward procedure given in App. C of Ref. (*6*).

Equation (7) then becomes:

$$\sum_{j=1}^{N} B_{ij} a_j = \frac{R^2}{D_{e_A} C_{A_0}} r_A(a_i) S_i, \tag{14}$$

$$i = 1 \text{ to } N - 1,$$

where S_i is the catalyst activity at point δ_i. Equation (9) becomes

$$-\frac{dS_i}{d\tau}=f_1(a)f_2(S_i)+f_1'(a_i)f_2'(S_i), \quad (15)$$

$$i=1 \text{ to } N.$$

The value of S_i at $\tau=0$ is unity for all δ_i. Further the value of a_N (surface concentration) is unity for any given τ. Thus, Eq. (14) can be solved at $\tau=0$ to obtain the concentration profile. Once the concentration profiles are known, Eq. (15) can be integrated for a small increment of time, $\Delta\tau$, to obtain the active sites of the catalyst at different radial positions δ_i at time $\tau=\Delta\tau$. Using these values of S_i, Eq. (14) can once again be solved and the procedure repeated.

Once the concentration profiles are known, the effectiveness factors can be calculated. For spherical geometry the relation is:

$$\eta(\tau)=\frac{3\int_0^1 \delta^2 r_A(a_i)S_i}{r_A(1)}$$

$$=\frac{3}{r_A(1)}\sum_{i=1}^{N} w_i r_A(a_i)S_i, \quad (16)$$

where

w_i	are the statistical weights and may be calculated by a method given in App. C of Ref. (*6*)
$\eta(\tau)$	is the effectiveness factor for the main reaction at a time τ.

Application to Dehydration of Alcohols

The solution procedure discussed in the preceding section is valid for any general kinetics. We shall illustrate the method of solution by considering the case of dehydration of alcohols where a kinetic equation of the following form is likely to be applicable.

$$r_A(C_A)=\frac{kC_A^{1/2}}{1+K_AC_A^{1/2}+K_WC_W}, \quad (17)$$

where

C_A	concentration of alcohol
C_W	concentration of the product (water)
k	rate constant
K_A, K_W	adsorption constants for alcohol and water, respectively.

The above rate expression has been found to be valid for this system (*7*). The case of zero order reaction considered by Greco *et al.* (*4*) reduces to a special case of the above or similar nonlinear kinetics.

The dimensionless product concentration can be related to the reactant concentration with the use of Eq. (12) and hence the term C_W in Eq. (17) can be eliminated. Using the resulting value of r_A in Eq. (14) yields:

$$\sum_{i=1}^{N} B_{ij}a_j - \frac{\phi^2 a_i^{1/2} S_i}{1+K_A^* a_i^{1/2}+K_W^*(1+q-a_i)}=0, \quad (18)$$

$$i=1 \text{ to } N-1,$$

where

$$\phi^2=\frac{kR^2}{D_{e_A}C_{A_0}^{1/2}}, \qquad K_A^*=K_AC_{A_0}^{1/2},$$

$$K_W^*=K_WC_{A_0}\frac{D_{e_A}}{D_{e_W}}, \qquad q=\frac{C_{W_0}}{C_{A_0}}\frac{D_{e_W}}{D_{e_A}},$$

where

D_{e_W}	diffusivity of water vapor in the pellet
C_{W_0}	bulk concentration of water
ϕ	refers to the main reaction with no fouling present.

For the purpose of illustration, we shall assume that the decrease in catalyst activity is first order with respect to concentration of alcohol (component A) for parallel fouling and first order with respect to the concentration of olefin (component B) for series fouling. Further, both series and parallel fouling will be assumed to be first order with respect to the number of active sites. Thus Eq. (15) becomes:

$$-\frac{dS_i}{d\tau}=a_iS_i+\frac{k_{f_2}}{k_{f_1}}b_iS_i, \quad (19)$$

where τ is defined as $k_{f_1} C_{A_0} t$.

Using the value of b_i from Eq. (12), Eq. (19) becomes:

$$-\frac{dS_i}{d\tau} = a_i S_i + \frac{k_{f_2}}{k_{f_1}} S_i \left[b_0 + \frac{D_{e_A}}{D_{e_B}} (1 - a_i) \right], \qquad (20)$$
$$i = 1 \text{ to } N.$$

The sequential solution of Eqs. (18) and (20) gives the effectiveness factor of the catalyst as a function of time. The nonlinear Eq. (18) can be solved by Newton–Raphson type of iteration. For all the computations reported here, six collocation points were used.

RESULTS AND DISCUSSION

Parallel Fouling

A plot of the effectiveness factor of the catalyst pellet as a function of the Thiele modulus was constructed by solving the corresponding equations for parallel fouling. The results are shown in Fig. 1. The variation of the catalyst activity, S, with time at various radial positions in the pellet is shown in Fig. 2 for three Thiele moduli. The extent of fouling and the resulting distribution of the active sites at any given time depends on the Thiele modulus. For small values of the Thiele modulus, the reaction of A takes place in the entire volume of the pellet and the effectiveness factor, η, tends to unity at zero time because of the lack of diffusional restrictions. For parallel fouling, the fouling is directly related to the concentration of reactant, A, and consequently the fouling is also uniform throughout the pellet as evidenced by the virtual horizontal lines in Fig. 2 (top). At large values of the Thiele modulus, the reaction of A occurs over a small region near the surface of the pellet. This results in the poisioning being confined to this same small region near the surface while the catalyst in the interior of the pellet still retains the original activity. This situation, illustrated in Fig. 2 (bottom), corresponds to the pore mouth poisoning of Wheeler (2). With increase of time the deactivated zone moves into the interior of the pellet. For intermediate values of the Thiele modulus fouling occurs within the center of the pellet but is greater near the surface [Fig. 2 (middle)]. Analogous behavior is observed when the effectiveness factor is plotted against the Thiele modulus as in Fig. 1. For small

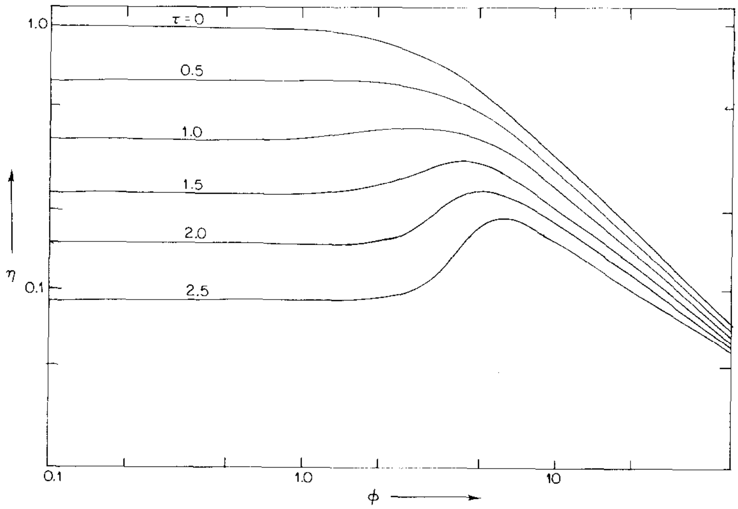

FIG. 1. Effectiveness factor vs Thiele modulus for parallel fouling.

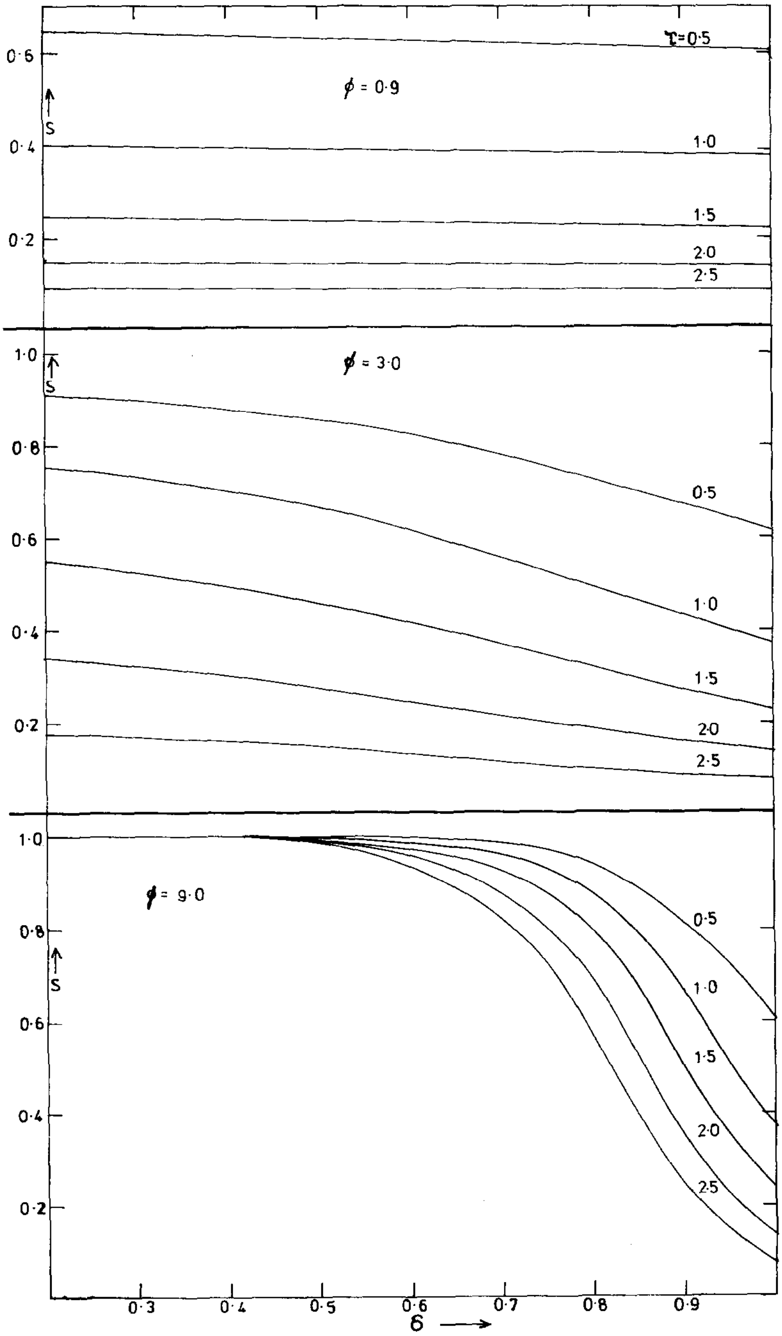

FIG. 2. Variation of surface activity with radial position for parallel fouling.

values of the Thiele modulus (<2.0) the value of the effectiveness factor decreases with time. At higher values of the Thiele modulus the reduction in the effectiveness factor may be much less pronounced with increase in fouling time. This arises because under these conditions the deactivation approaches pore mouth poisoning behavior which results in the bulk of the catalyst in the pellet interior having a high residual activity. This point may be demonstrated from Fig. 1 by considering values of ϕ equal to 1 and 5. When the pore diffusion resistance is very small ($\phi = 1$), the effectiveness factor values for times $t = 0$ and $\tau = 2$ are 1.0 and 0.15, respectively. When the Thiele modulus in the catalyst pellet has a value of 5, the initial effectiveness factor is 0.58 because of pore diffusion restrictions. However, at a time $\tau = 2$, the effectiveness factor at this same Thiele modulus has decreased to only 0.25, which is greater than that for the catalyst pellet which had little or no pore diffusion resistance initially ($\phi = 1$). The activity of the catalyst remaining after a given process time may be obtained from the area under the curve of S vs δ for the appropriate value of τ chosen. For a poisoning time $\tau = 2$, the areas are 0.4 for the ϕ value of 1 and 0.85 for the ϕ value of 5. This explains the higher value of the effectiveness factor at $\phi = 5$ compared with $\phi = 1$ under conditions of catalyst fouling. The extreme case is for values of the Thiele modulus in excess of about 30. All the curves in Fig. 1 are now very close together and the effect of increased time of fouling is now minimal. Under these conditions the diffusional restriction is extremely severe and fouling effects are now of secondary importance.

Series Fouling

The results of series fouling are shown in Fig. 3 in the form of a plot of η against ϕ for various values of the dimensionless time τ for the case of $b_0 = 0$ and equal diffusivities of A and B. The dimensionless time for this case in the absence of parallel fouling is defined as $k_{f_2}C_{A_0}t$. The effectiveness factor plots in Fig. 3 show only a slight decrease in particle effectiveness with fouling at ϕ values greater than unity and there is very little difference in relative effectiveness between fresh and deactivated catalyst with increasing Thiele modulus. For a series mechanism, fouling is proportional to the concentration of product while the rate of reaction is proportional to the reactant concentration. Thus the fouling effect is greatest for high values of the Thiele modulus. This is because the reactant concentration drops to zero in the pellet interior under these conditions, whereas the product concentration becomes very large. The activity plots within the catalyst pellet are shown in Fig. 4. At low values of the Thiele modulus the

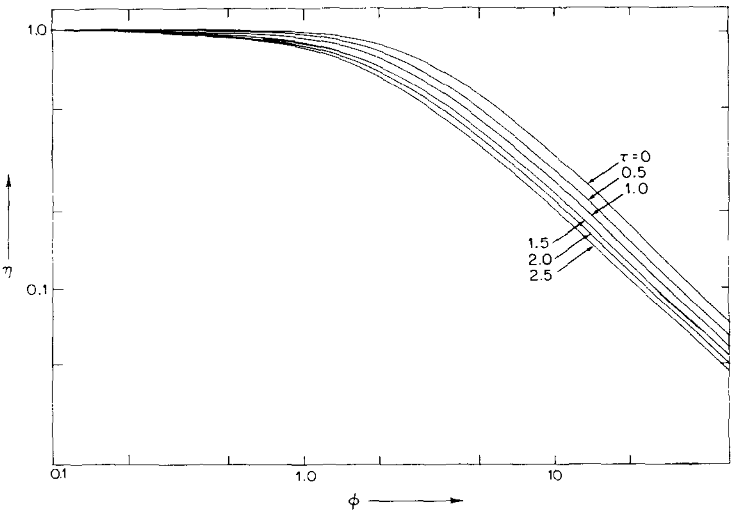

FIG. 3. Effectiveness factor vs Thiele modulus for series fouling.

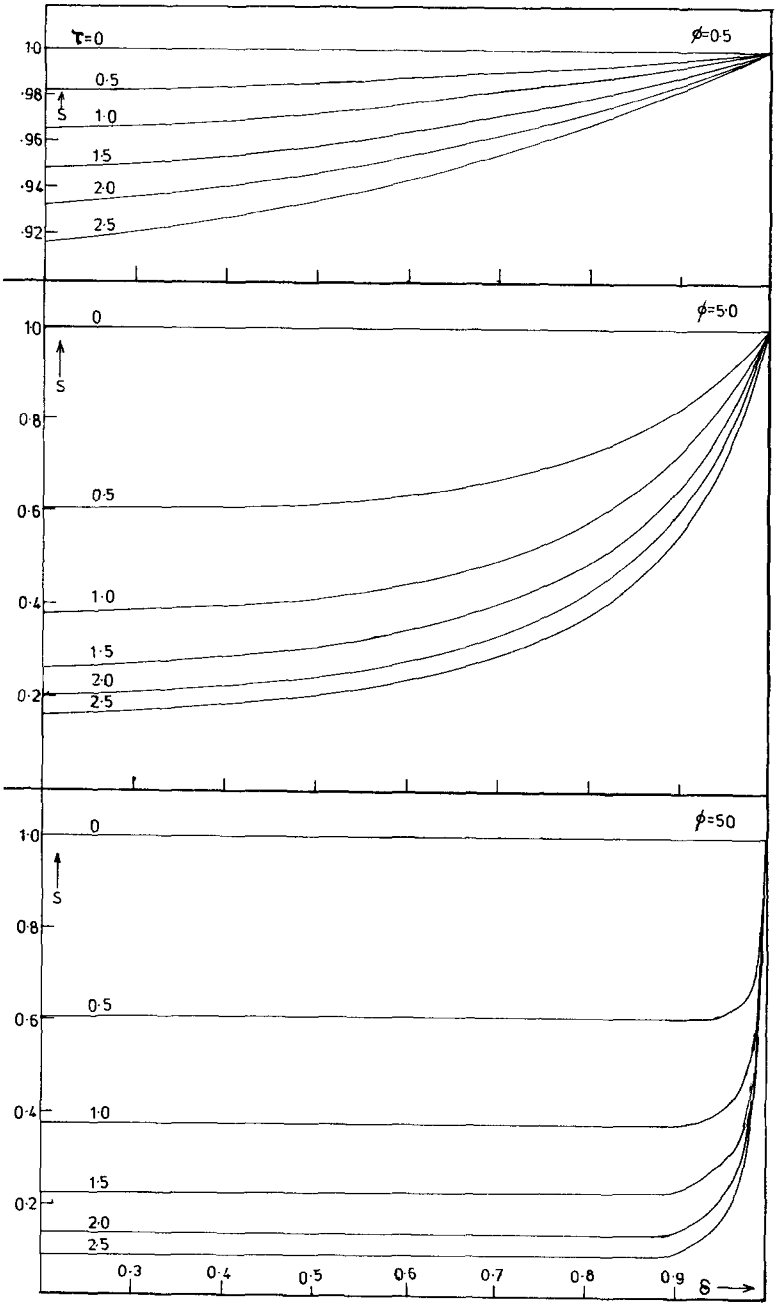

FIG. 4. Variation of surface activity with radial position for series fouling.

decrease in activity towards the pellet center is quite small [Fig. 4 (top)] but for larger values of ϕ the fouling is more pronounced [Fig. 4 (middle) for $\phi = 5.0$] and ultimately results in uniform fouling over a large portion of the interior volume of the catalyst while the activity at the surface of the pellet is unity [Fig. 4 (bottom)]. A comparison of Fig. 4 (top) and (middle) with similar plots for low ϕ values in parallel fouling [Fig. 2 (top) and (middle)] shows that under these conditions fouling is much less pronounced by a series mechanism than for a parallel process. The large

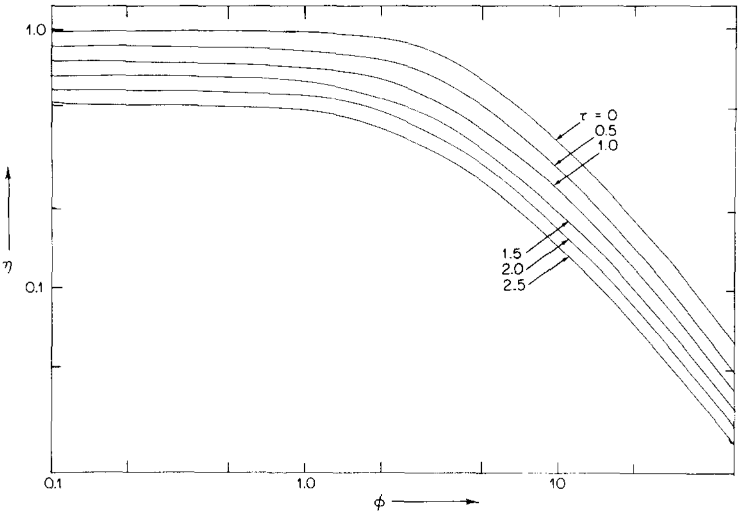

FIG. 5. Effectiveness factor vs Thiele modulus for series fouling with initial product concentration of B (0.25) in bulk gas.

decrease in activity for series fouling at $\phi = 5.0$ is obscured by the decreased effectiveness due to pore diffusion limitations (Fig. 3) so that the net effect is minimized.

All the results quoted above have assumed a feed of 100% of reactant A with no product B present in the gas phase. In practice, some product would be expected to occur either from recycle or towards the

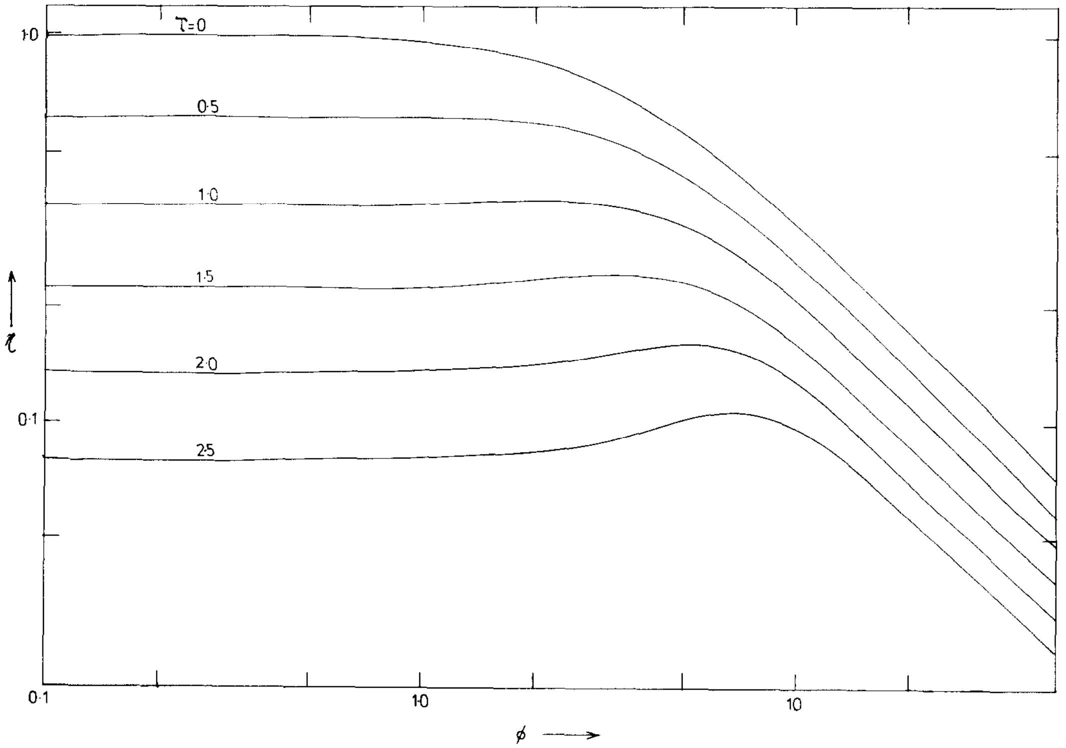

FIG. 6. Effectiveness factor vs Thiele modulus for parallel/series fouling, $2k_{f_2} = k_{f_1}$.

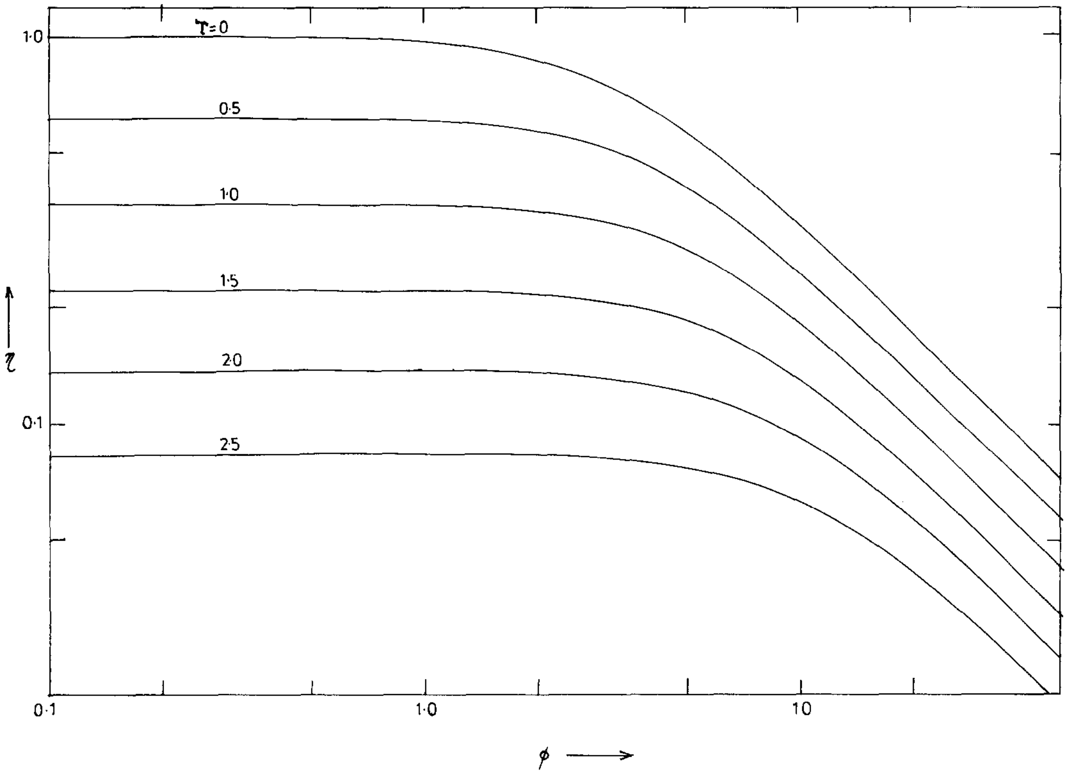

FIG. 7. Effectiveness factor vs Thiele modulus for parallel/series fouling, $k_{f_2} = k_{f_1}$.

exit of the bed in a packed bed reactor. The effect of a finite concentration of product (b_0) on the fouling characteristics for a series mechanism is shown in Fig. 5 for a b_0 value of 0.25. For this case there is an almost uniform drop in catalyst activity irrespective of the Thiele modulus. This is because the activity at the surface is no longer unity as for series fouling with no product in the gas phase. The finite concentration of the product at the surface causes considerable fouling in the regions of the pellet close to the surface and causes a loss in activity even when the Thiele modulus is less than unity.

Series and Parallel Fouling

Where fouling occurs by a combination of series and parallel processes the deactivation depends on the relative magnitude of the series and parallel fouling rate constants k_{f_2} and k_{f_1}, respectively, [Eqs. (3), (9), (20)]. Results for series/parallel fouling are given in Fig. 6 (parallel fouling rate constant twice that for series) and Fig. 7 (equal rate constants). In each case the concentration of product is assumed to be zero at the surface of the pellet (i.e., $b_0 = 0$). When $k_{f_2}/k_{f_1} = 0.5$ (Fig. 6) the effectiveness factor curves are similar in shape to those for parallel fouling, as might be expected, but the magnitude of the maxima at large values of the fouling time, τ, are much reduced. At values of the Thiele modulus greater than about 10, series fouling has a greater effect than for parallel fouling alone (Fig. 1). The case of equal rate constants, $k_{f_2}/k_{f_1} = 1$, $b_0 = 1$ and equal diffusivities of the two components is interesting. In this situation the effect of reactant and product concentration is such that the rate becomes independent of concentration and depends solely on the surface activity of the catalyst. This is because the rate is proportional [Eq. (20)] to the product $S(a + b_0 + 1 - a)$, which is constant for $b_0 = 0$. Thus, this leads to uniform fouling of the catalyst with time, independent of the Thiele modulus of the catalyst pellet.

Comparison of Fouling Processes

From the results presented it is clear that parallel fouling is more important than series fouling, for comparable values of k_{f_1} and k_{f_2}. This is because the parallel process being dependent on the reactant concentration usually has a much greater driving force than series fouling. For low concentrations of product, series fouling only becomes important at high values of the Thiele modulus where the diffusion restriction is already of major importance. The only exception is when appreciable concentrations of product are present in the gas phase. This could occur when there is large recycle fraction or in a packed bed operating at high conversion when the product concentration could reach high values near the exit of the bed. Relative deactivation by fouling may also be less in the parallel case if the main reaction is operating with some degree of diffusion control.

In general the effects of combined parallel and series fouling depend on the relative magnitudes of the individual rate constants for series and parallel deactivation. If the parallel fouling rate constant is much greater than that for series fouling, then the system tends to reproduce parallel behavior but on a reduced scale. Series/parallel fouling can, however, show considerable deactivation compared to series fouling alone when the rate constants are almost equal as is demonstrated in Fig. 7.

The effect of the introduction of Langmuir–Hinshelwood kinetics into the rate expression for the main reaction is to increase the importance of fouling and this has been confirmed in a recent study by Wolf and Petersen (*8*).

The numerical method used in this paper is relatively simple and may be extended to more complex (and realistic) situations. Thus nonisothermal behavior may be readily incorporated by inclusion of the heat balances and external mass transfer, which has been assumed to be negligible in this work, may also be accounted for.

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