Short Communication

Catalyst deactivation in finite hollow cylindrical pellets

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1. INTRODUCTION

Diffusional resistance can significantly reduce the observed rates in catalytic reactions and various methods have been recommended for reducing these diffusional effects. One method which has found commercial application is the use of hollow cylindrical pellets which has the same effect as reducing the size of the catalyst pellet but without the disadvantage of a higher pressure drop. Gunn [1] derived analytical expressions for the effectiveness factors for solid and hollow cylindrical pellets of finite length. Partially impregnated catalysts can be treated as close-ended hollow pellets and Aris [2] has considered this case in detail.

Generally, the effectiveness of catalysts in promoting reactions decreases with time as a result of deactivation caused by impurity poisoning, fouling or sintering. To design and optimize reactors, the variation of the catalyst activity with time must be known. In their classical paper, Masamune and Smith [3] investigated the deactivation of catalyst pellets by numerically integrating the sets of governing equations. Peterson [4] examined the error involved when limiting approximations are made for parallel, series and impurity fouling. However, except for the study of Do and Weiland [5], all the work previously reported on catalyst deactivation is restricted to pellets in which the system can be described in terms of a single spatial coordinate and time. Do and Weiland [5] used a generalized two-timing technique and finite Sturm–Liouville integral transforms to derive theoretical expressions for the time-dependent effectiveness factors of finite-length cylindrical solid catalyst pellets of various aspect ratios. Their study showed that in some cases the effectiveness factors could be significantly underestimated if the finite length of the pellet was not accounted for. Lee [6] analysed the pore-mouth impurity poisoning of an infinite hollow slab-like pellet. As a result of the simplified geometry, the thickness of the inside and outside poisoned layers were equal at any time and as such analytical expressions could be obtained for the activity and performance factors.

The purpose of this study was to calculate the variation in the effectiveness factors with time for finite hollow cylindrical pellets which are being poisoned as a result of the presence of an impurity in the feed stream. The effects of the Thiele modulus of the reactant and impurity, the inner-to-outer radius ratio and the aspect ratio have been investigated. No analysis for deactivation in finite hollow cylindrical pellets appears to be available in the literature.

2. MATHEMATICAL FORMULATION

Let us consider the following reactions taking place on an isothermal hollow cylindrical catalyst pellet of finite length:

$$A \xrightarrow{k_A} B \text{ (main reaction)} \qquad (1)$$

$$I \xrightarrow{k_{PI}} P \text{ (deactivating reaction)} \qquad (2)$$

where I is the poison in the reaction mixture. The main reaction is assumed to be first order and the catalyst is poisoned by species P

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which results from an irreversible single-site reaction of I with an unpoisoned catalytic site. Moreover, the external mass transfer resistances are assumed to be negligible.

With the pseudo steady state assumption, the continuity equations for the reactant and impurity are respectively

$$D_A \frac{\partial^2 C_A}{\partial z^2} + D_A \frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C_A}{\partial r}\right) - k_A C_A a = 0 \quad (3)$$

$$D_I \frac{\partial^2 C_I}{\partial z^2} + D_I \frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C_I}{\partial r}\right) - $$

$$- k_{PI} C_I (C_{P0} - C_P) = 0 \quad (4)$$

A balance for P gives

$$\frac{\partial C_P}{\partial t} = k_{PI} C_I (C_{P0} - C_P) \quad (5)$$

Equations (3) - (5) can be made dimensionless by the following definitions

$$\psi_A = \frac{C_A}{C_{A0}}$$

$$\psi_I = \frac{C_I}{C_{I0}}$$

$$f = \frac{C_{P0} - C_P}{C_{P0}}$$

$$\alpha = \frac{z}{L_0}$$

$$\beta = \frac{r}{R_0} \quad (6)$$

$$\lambda = \frac{R_0}{L_0}$$

$$\gamma = \frac{R_i}{R_0}$$

$$\theta_I = k_{PI} C_{I0} t \quad (6)$$

$$\phi_A = R_0 \left(\frac{k_A}{D_A}\right)^{1/2}$$

$$\phi_I = R_0 \left(\frac{k_{PI} C_{P0}}{D_I}\right)^{1/2}$$

Substituting eqn. (6) into eqns. (3) - (5) yields

$$\lambda^2 \frac{\partial^2 \psi_A}{\partial \alpha^2} + \frac{1}{\beta} \frac{\partial}{\partial \beta}\left(\beta \frac{\partial \psi_A}{\partial \beta}\right) - \phi_A^2 \psi_A a = 0 \quad (7)$$

$$\lambda^2 \frac{\partial^2 \psi_I}{\partial \alpha^2} + \frac{1}{\beta} \frac{\partial}{\partial \beta}\left(\beta \frac{\partial \psi_I}{\partial \beta}\right) - \phi_I^2 \psi_I f = 0 \quad (8)$$

$$\frac{\partial f}{\partial \theta_I} = - \psi_I f \quad (9)$$

To solve the set of equations (7) - (9), the activity a must be related to f. For this analysis, it will be assumed that $a = f$ as implicitly assumed by Masamune and Smith [3]. The boundary conditions and initial conditions for eqns. (7) - (9) are

$\theta_I = 0$	$a = f = 1$	for all α and β	(10a)
$\alpha = 0$	$\psi_A = 1, \psi_I = 1$	for all β	(10b)
$\alpha = 1$	$\psi_A = 1, \psi_I = 1$	for all β	(10c)
$\beta = 1$	$\psi_A = 1, \psi_I = 1$	for all α	(10d)
$\beta = \gamma$	$\psi_A = 1, \psi_I = 1$	for all α	(10e)

3. RESULTS AND DISCUSSION

Equations (7) - (9) together with the initial condition and boundary conditions given by eqns. (10) were solved using the finite element method. The details of the finite element method formulation are not presented here but are available elsewhere [7].

The effectiveness factor η and global or residual activity a of the catalyst can be defined as

$$\eta = \frac{\text{rate of reaction of the pellet at } \theta_I}{\text{rate of reaction with uniform concentration } C_{A0} \text{ inside the pellet and } \theta_I = 0} \quad (11)$$

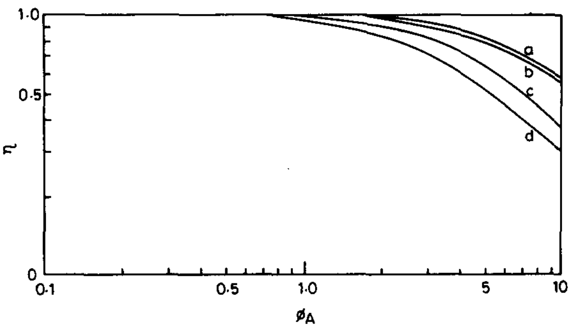
and

$$a = \frac{\text{rate of reaction of the pellet at } \theta_I}{\text{rate of reaction of the pellet at } \theta_I = 0} \quad (12)$$

3.1. Effectiveness factor for the unpoisoned pellet

The variation in the initial effectiveness factor of hollow cylindrical pellets for different values of the Thiele modulus, λ and γ is shown in Fig. 1. These results are in very close agreement with the results of Gunn [1] who analytically solved the case of finite hollow cylinders. For infinite hollow cylinders ($\lambda = 0$), an expression for η can be derived by the usual methods and is

$$\eta = \frac{2}{\phi_A(1-\gamma^2)}\left[\frac{\{I_0(\phi_A) - I_0(\phi_A\gamma)\}K_1(\phi_A) + \{K_0(\phi_A) - K_0(\phi_A\gamma)\}I_1(\phi_A)}{I_0(\phi_A\gamma)K_0(\phi_A) - I_0(\phi_A)K_0(\phi_A\gamma)} - \right.$$
$$\left. -\gamma\frac{\{I_0(\phi_A) - I_0(\phi_A\gamma)\}K_1(\phi_A\gamma) + \{K_0(\phi_A) - K_0(\phi_A\gamma)\}I_1(\phi_A\gamma)}{I_0(\phi_A\gamma)K_0(\phi_A) - I_0(\phi_A)K_0(\phi_A\gamma)}\right] \quad (13)$$



Curve	γ	λ
a	0.6	1.0
b	0.6	0.0
c	0.2	1.0
d	0.2	0.0

Fig. 1. Effectiveness factor *vs.* Thiele modulus for finite hollow cylindrical pellets.

The results shown in Fig. 1 for $\lambda = 0$ compare very well with those calculated using eqn. (13). As can be seen from Fig. 1, for a fixed value of ϕ_A and γ, increasing the length of the cylinder (decreasing λ) decreases the effectiveness factor. This is because for short cylindrical pellets, mass transfer of the reactant to the interior of the pellets by axial diffusion is also significant. For a fixed value of ϕ_A and λ, the effectiveness factor increases with an increase in γ as a result of the greater accessibility of catalyst sites to reacting molecules since diffusion time is less. At high values of γ ($\gamma > 0.8$), the effect of λ is insignificant and the hollow pellet can be assumed to be infinitely long without any loss in accuracy.

3.2. Impurity poisoning

The effect of impurity poisoning on the catalyst activity of finite hollow cylindrical pellets was studied for various values of θ_A, θ_I, γ and λ. The variation of activity with dimensionless time θ_I for different aspect ratios at otherwise identical conditions is shown in Fig. 2. Since the poison can be transported more easily to the interior of the pellet, the activity decreases at a faster rate for shorter cylinders resulting in a lower catalyst life. The effect of changing the ratio of the inner-to-outer catalyst radius on activity is shown in Fig. 3. Pellets of a higher γ deactivate faster because as γ increases the total volume (or mass) of the pellet decreases, whereas the surface area for mass transfer increases resulting in a faster rate of deactivation. It should be mentioned that for very porous pellets, the difference between the finite and infinite cylindrical pellet effectiveness factors is negligible. For a proper choice of γ and λ, a balance has to be made between the initial effectiveness factor and the deactivation rate. For example, if the process time is relatively short, then the time-average effectiveness factor would be higher for higher γ and λ values. The optimal choice of γ and λ

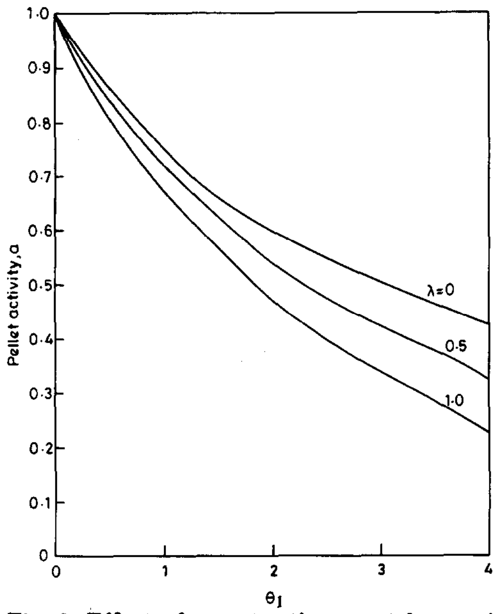


Fig. 2. Effect of aspect ratio on catalyst activity. ($\phi_A = 5$, $\phi_I = 10$ and $\gamma = 0.2$.)

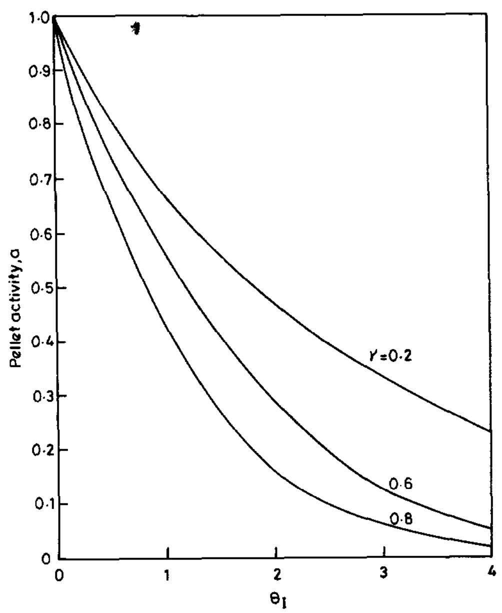


Fig. 3. Effect of γ on catalyst activity. ($\phi_A = 5$, $\phi_I = 10$ and $\lambda = 1.0$.)

will depend on the extent of diffusional limitation, catalyst cost and life of the catalyst.

The variation of catalyst activity with ϕ_A and θ_I for three different values of ϕ_I is shown in Figs. 4 and 5. Impurity poisoning of spherical pellets has been discussed by Peterson [4] and these trends are similar to those obtained for spherical pellets. At low values

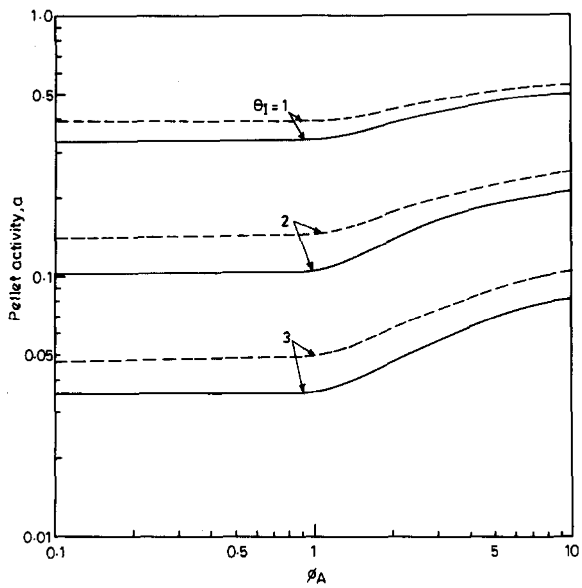


Fig. 4. Pellet activity *vs.* reactant Thiele modulus for low and intermediate values of ϕ_I: ——, $\phi_I = 0.1$; – – –, $\phi_I = 3$. ($\lambda = 1$ and $\gamma = 0.2$.)

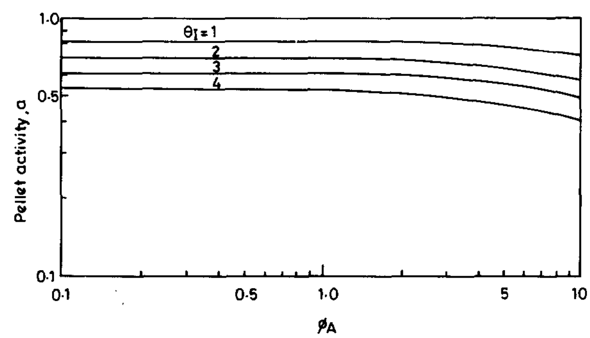


Fig. 5. Pellet activity *vs.* reactant Thiele modulus for $\phi_I = 20$. ($\lambda = 1$ and $\gamma = 0.2$.)

of ϕ_I, uniform poisoning is approached and the activity is uniform throughout the pellet. For uniform poisoning, as Peterson [4] has shown, the activity a can be expressed as

$$a = \frac{e^{-\theta_I}\eta'}{\eta} \tag{14}$$

where η' is a modified effectiveness factor based on ϕ_A' defined as

$$\phi_A' = \phi_A a^{1/2} = e^{-(\theta_I/2)}\phi_A \tag{15}$$

For low and intermediate values of ϕ_I, as shown in Fig. 4, the activity increases with increasing ϕ_A. This effect is well known for uniform poisoning. For large values of ϕ_I, pore-mouth poisoning is approached and the pellet activity decreases slightly with increasing ϕ_A (Fig. 5).

4. CONCLUSIONS

From the above discussion it can be concluded that both γ and λ have an effect on the pellet activity as well as the initial effectiveness factor. Compared with solid cylindrical catalysts, hollow pellets have a higher effectiveness factor but the decline in activity is faster. Similarly, if the hollow cylindrical pellets are assumed to be infinitely long, then the effectiveness factor would be underestimated and the catalyst life overestimated. The actual magnitude of the difference will depend on the Thiele moduli of the reactant and poison, the ratio of the inner-to-outer catalyst radii and the aspect ratio.

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APPENDIX A: NOMENCLATURE

a catalyst activity
C_A concentration of reactant A in the pellet
C_{A0} concentration of A at the external surface of the catalyst
C_I concentration of poison in the reaction mixture
C_{I0} concentration of poison at the external surface of the catalyst
C_P foulant concentration on catalyst surface
C_{P0} foulant concentration on catalyst surface at saturation
D_A effective diffusivity of reactant
D_I effective diffusivity of poison
f non-dimensional foulant concentration, defined in eqn. (6)
I_0, I_1 modified Bessel functions of first kind
k_A rate constant for main reaction
k_{PI} rate constant for poisoning reaction
K_0, K_1 modified Bessel functions of second kind
L_0 length of the catalyst pellet
r radial coordinate
R_i inner radius of hollow pellet
R_0 outer radius of hollow pellet
t time
z axial coordinate

Greek Symbols

α non-dimensional axial coordinate
β non-dimensional radial coordinate
γ R_i/R_0
η effectiveness factor
η' modified effectiveness factor
θ_I non-dimensional time
λ R_0/L_0, aspect ratio of pellet
ϕ_A Thiele modulus of reactant
ϕ_A' modified Thiele modulus of reactant, defined in eqn. (15)
ϕ_I Thiele modulus of poison
ψ_A non-dimensional reactant concentration
ψ_I non-dimensional poison concentration