Effect of Fouling on Stability of Adiabatic Packed Bed Reactors

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The effect of catalyst fouling on the stability and operation of adiabatic packed bed reactors was investigated for two poisoning mechanisms. The effect of fouling was found to be most predominant for packed beds in which nonunique pseudo steady states can exist. Fouling may cause the reactor to misbehave suddenly, with a violent temperature rise, after a long period of pacific operation.

In most industrial packed bed reactors a decay of the catalytic activity with time is observed. This decay may be caused by several mechanisms such as aging (the physical wear and tear of the pellets), poisoning (the preferential adsorption of a contaminant), or fouling (the deposition of a product formed by an undesired side reaction).

Many investigations into the causes for loss of catalytic activity in reacting systems have been published since the early work of Pease and Stewart (*16*). A review of many of these studies is found in Maxted (*13*) and Innes (*8*). Analytical studies on the effect of poisoning in a catalytic pellet have been reported by Wheeler (*18*), Carberry (*3*), and Balder and Petersen (*2*), among others. Recently Butt and Rohan (*1*) and Olsen (*15*) investigated the effect of poisoning on the conversion of packed beds.

In the last decade many investigations were concerned with the simulation of packed bed reactors. The studies of Amundson and co-workers (*10, 11, 12*) and McGuire and Lapidus (*14*) showed that these reactors may have nonunique steady states, which may cause important control and start-up problems. Wicke and co-workers (*19, 20, 21, 22*) demonstrated experimentally the occurrence of many pathological trends that have been predicted from the models.

Previous stability studies were concerned with unfouled packed beds. In this work the effect of fouling on the stability of adiabatic packed beds was investigated. It will be demonstrated that fouling may cause the occurrence of some peculiar trends that would not occur for unfouled beds.

DEVELOPMENT OF EQUATIONS

The cell model of Deans and Lapidus (*5*) was used to simulate the packed bed. This model assumes that the bed is composed of series of cells, which are connected by the interstitial fluid. The desired reaction is assumed to be first order and irreversible $A \rightarrow B$, and its rate is described by

$$r(B) = k\Psi p_p \tag{1}$$

where Ψ is the normalized activity factor. It will be assumed that the deactivation is due to fouling. Two mechanisms which might cause this fouling were investigated:

a) an undesired parallel reaction $A \rightarrow C$ for which

$$\frac{d\Psi}{d\theta} = -k_p\Psi p_p \tag{2}$$

b) an undesired consecutive reaction $B \rightarrow C$ for which

$$\frac{d\Psi}{d\theta} = -k_p\Psi p_{pB} \tag{3}$$

The mass and heat conservation equations for cell j are

$$a_1\frac{dp_j}{d\theta} = M(p_{j-1} - p_j) - (p_j - p_{pj}) \tag{4}$$

$$a_2\frac{dt_j}{d\theta} = H(t_{j-1} - t_j) - (t_j - t_{pj}) \tag{5}$$

$$a_3\frac{dp_{pj}}{d\theta} = p_j - p_{pj} - k_j\Psi_j p_{pj} \tag{6}$$

$$a_4\frac{dt_{pj}}{d\theta} = t_j - t_{pj} + \beta k_j\Psi_j p_{pj} \tag{7}$$

where

$$M = \frac{G}{P\,\overline{m}\,k_g a_v \eta D_p} = \frac{H_g}{\eta D_p},\quad k_j = \frac{D_p}{6}\,\frac{\rho_s S_g k_j'}{k_g} \tag{8a}$$

$$H = \frac{Gc_f}{h_f a_v \eta D_p} = \frac{H_T}{\eta D_p},\quad \beta = \frac{k_g}{h_f}(-\Delta H) \tag{8b}$$

$$a_1 = \frac{\epsilon\rho_f}{k_g a_v P\,\overline{m}},\quad a_2 = \frac{\epsilon\rho_f C_f}{a_v h_f} \tag{8c}$$

$$a_3 = \frac{D_p}{6}\,\frac{\alpha\rho_f}{\overline{m}\,k_g},\quad a_4 = \frac{D_p}{6}\,\frac{\rho_s c_f}{h_f} \tag{8d}$$

subject to the inlet conditions

$$t_e = t_e(\theta) \tag{9}$$

$$p_e = p_e(\theta) \tag{10}$$

and to the initial conditions

$$\left.\begin{aligned} p_j &= p_{j0} \\ t_j &= t_{j0} \\ p_{pj} &= p_{pj0} \\ t_{pj} &= t_{pj0} \\ \Psi_j &= 1 \end{aligned}\right\}\ \theta = 0,\quad j = 1, 2, \ldots, n \tag{11}$$

PSEUDO STEADY STATE DETERMINATION

From a rigorous mathematical point of view, a fouled bed never attains a steady state owing to the continuous variation of the activity of the catalyst. In practice, the rate of fouling is rather slow compared to the other processes occurring in the system. Hence, at any given time a pseudo steady state may be assumed in order to determine the relations between the various dependent variables. The pseudo steady state equations for cell j are

$$M(p_{j-1} - p_j) = p_j - p_{pj} \tag{12}$$

$$H(t_{j-1} - t_j) = t_j - t_{pj} \tag{13}$$

$$p_j - p_{pj} = k_j \Psi_j p_{pj} \tag{14}$$

$$t_{pj} - t_j = \beta k_j \Psi_j p_{pj} \tag{15}$$

where k_j is of the form

$$k_j = k_0 \exp\,(-\,\Delta E/Rt_{pj}) \tag{15a}$$

The techniques of Vanderveen *et al.* (*17*) are used to show that the pseudo steady state particle temperature can be determined either from the equation

$$Q_I = \frac{M(t_{pj} - t_j)}{H(t_{\max} - t_j)} = \delta_j = Q_{II} \tag{16}$$

or from

$$Q^*_I = \frac{M\,(t_{pj} - t_{j-1})}{(H+1)\,(t_{\max} - t_{j-1})} = \frac{M\delta_j}{M + \delta_j} = Q^*_{II} \tag{17}$$

where

$$\delta_j = \frac{k_j \Psi_j}{1 + k_j \Psi_j} \tag{18}$$

$$t_{\max} = t_e + \frac{\beta M p_e}{H} \tag{19}$$

A schematic description of the Q curves is shown in Figure 1. All the $Q_I(Q^*_I)$ lines pass through a common point for which $Q_I = \frac{M}{H}\left(Q^*_I = \frac{M}{H+1}\right)$ at $t_p = t_{\max}$. The intersection of the Q curves permits the determination of t_{pj}. Because the catalytic activity is usually not uniform along the bed, one has to use different $Q_{II}(Q^*_{II})$ curves at different positions in the bed.

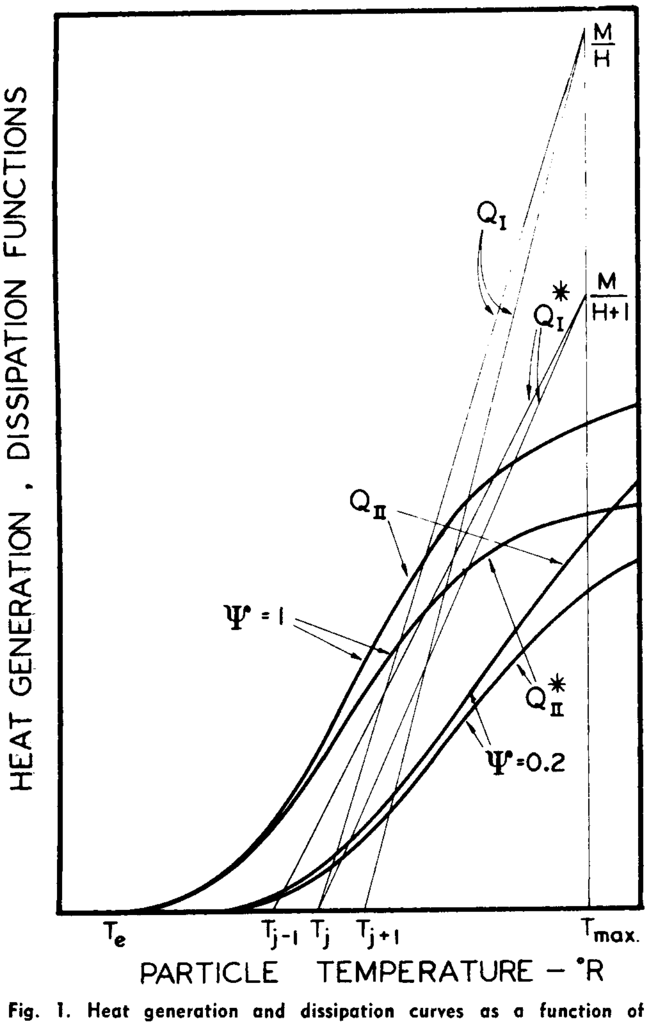

Fig. 1. Heat generation and dissipation curves as a function of activity and particle temperature.

When multiple intersections between the Q curves exist, multiple pseudo steady states can occur. In this case, transient computations are required to determine which pseudo steady state will be obtained from a given set of initial conditions.

Sufficient Conditions for Uniqueness

It is of interest to determine the conditions under which a unique pseudo steady state exists. Using simple algebra, we can rewrite Equation (15) as

$$t_{pj} - t_{j-1} = A k_j \psi_j (D - t_{pj}) = f(t_{pj}) \tag{20}$$

where

$$A = \frac{M+1}{M}, \quad D = \frac{H+1}{M+1}\,t_{\max} - \frac{H-M}{M+1}\,t_{j-1}$$

If multiple solutions exist, topological arguments (*9*) may be used to prove the existence of a bifurcation solution v which satisfies the equation

$$v = \frac{df(t_{pj})}{dt_{pj}}\,v \tag{21}$$

If we multiply Equation (20) by v and Equation (21) by $t_{pj} - t_{j-1}$ and subtract, we obtain

$$\left[\, f(t_{pj}) - (t_{pj} - t_{j-1})\,\frac{df(t_{pj})}{dt_{pj}} \right] v = H(t_{pj})\,v = 0 \tag{22}$$

If $H(t_{pj})$ is positive for all possible values of t_{pj}, there can be no nontrivial solution which satisfies Equation (22) and, hence, no bifurcation solution. Thus, uniqueness is assured if for all possible t_{pj}

$$f(t_{pj}) \geqq (t_{pj} - t_{j-1})\,\frac{df(t_{pj})}{dt_{pj}} \tag{23}$$

which can be rewritten as

$$\frac{E}{R} < \frac{(D - t_{j-1})\,t^2_{pj}}{(t_{pj} - t_{j-1})\,(D - t_{pj})} \qquad t_e < t_{pj} < D \tag{24}$$

The minimum for the RHS of Equation (24) occurs for

$$t_{pj} = \frac{2D\,t_{j-1}}{t_{j-1} + D} \tag{25}$$

Thus, the system will have a unique steady state solution if

$$\frac{E}{Rt_e} < 4\left(1 + \frac{(M+1)t_e}{(t_{\max} - t_e)\,(H+1)}\right) \tag{26}$$

If the condition in Equation (26) is not satisfied, the technique developed by Aris (*23*) can be used to show that any cell for which either

$$\mathop{Sup}_{t_{j-1} < t_{pj} < D} \frac{df}{dt_{pj}} = \mathop{Sup}_{t_{j-1} < t_{pj} < D} \frac{M+1}{M}\,k_j\psi_j \left[\frac{E}{Rt^2_{pj}}\,(D - t_{pj}) - 1\right] < 1 \tag{27}$$

or

$$\left.\frac{df}{dt_{pj}}\right|_{t_{pj} = t_{j-1}} = \frac{M+1}{M}\,k_j\psi_j \left[\, \frac{E}{Rt^2_{j-1}}\,\frac{H+1}{M+1}\right.$$

$$(t_{\max} - t_{j-1}) - 1 \Big] > 1 \quad (28)$$

has a unique steady state solution.

Stability Analysis

A pseudo steady state will be defined to be asymptotically stable if any small disturbance will decay with time. The stability will be determined by linearizing the transient Equations (4 to 7) and checking the conditions for which all of the eigenvalues of the linearized matrix have negative real parts. Obtained by the method of Vanderveen *et al.* (*17*) are the following necessary and sufficient conditions for asymptotic stability:

$$\left.\begin{array}{l} b_{j1} > 0 \\ b_{j2} > 0 \\ b_{j1}b_{j2}b_{j3} > b^2{}_{j1}b_{j4} + b^2{}_{j3} \\ b_{j4} > 0 \end{array}\right\} j = 1, 2, \ldots, n \quad (29)$$

where

$$b_{j1} = \frac{1+M}{a_1} + \frac{1+H}{a_2} + \frac{1}{a_3} + \frac{1}{a_4} \left(1 + \frac{a_4}{a_3} k_j\Psi_j - \beta\gamma_j k_j\Psi_j\right) \quad (30)$$

$$b_{j2} = \frac{1 + k_j - \beta\gamma_j k_j\Psi_j}{a_3a_4} + \frac{1+M}{a_1a_3} \left[\left(1 + k_j\Psi_j - \frac{a_3}{a_4}\beta\gamma_j k_j\Psi_j\right) \cdot \left(1 + \frac{(1+H)a_1}{(1+M)a_2}\right) - \frac{1}{1+M} + \frac{a_3}{a_4} + \frac{(1+H)a_3}{a_2}\right] + \frac{H}{a_2a_4} \quad (31)$$

$$b_{j3} = (1 + k_j\Psi_j - \gamma_j\beta k_j\Psi_j)\left(\frac{H}{a_2a_3a_4} + \frac{M}{a_1a_3a_4}\right) + \frac{k_j\Psi_j}{a_1a_3a_4} - \frac{\beta\gamma_j k_j\Psi_j}{a_2a_3a_4} + \frac{M(1+H) - \frac{a_3}{a_4}(1+M)}{a_1a_2a_3} + \frac{(1+M)(1+H)}{a_1a_2a_4}\left(1 + \frac{a_4}{a_3}k_j\Psi_j - \beta\gamma_j k_j\Psi_j\right) \quad (32)$$

$$b_{j4} = \frac{1}{a_1a_2a_3a_4}\{H[(1 + k_j\Psi_j)M + k_j\Psi_j] - (H+1)\,M\beta\gamma_j k_j\Psi_j\} \quad (33)$$

The fourth condition in Equation (29) can be rewritten as

$$M + (M+1)k_j\Psi > \frac{\beta M p_{pj}(H+1)k_j\Psi_j\,\Delta E}{H\,Rt^2{}_{pj}} \quad (34)$$

According to Equation (14),

$$p_{pj} = p_j/(1 + k_j\Psi_j) \quad (35)$$

and an overall enthalpy balance on the packed bed yields

$$\beta M p_j = H\,(t_{\max} - t_j) \quad (36)$$

Substitution of Equations (35) and (36) in (34) yields

$$M + (M+1)k_j\Psi_j > \frac{(H+1)(t_{\max} - t_j)k_j\Psi_j}{(1 + k_j\Psi_j)}\,\frac{\Delta E}{Rt_{pj}^2} \quad (37)$$

The enthalpy balance Equation (36) for two adjacent cells is used to obtain

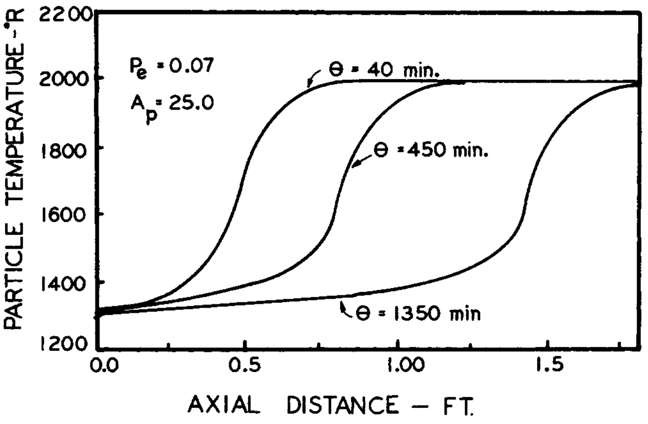

Fig. 2. Transient temperature profiles for fouling by a parallel reaction for a case where each particle has a unique pseudo steady state.

$$\frac{t_{\max} - t_j}{t_{\max} - t_{j-1}} = \frac{p_j}{p_{j-1}} = \frac{M(1 + k_j\Psi_j)}{M + (M+1)k_j\Psi_j} \quad (38)$$

Substitution of Equation (38) into (37) yields the condition

$$\frac{M}{(H+1)}\,\frac{1}{(t_{\max} - t_{j-1})} > \frac{M^2k_j\Psi_j}{(M + (M+1)k_j\Psi_j)^2}\,\frac{\Delta E}{Rt_{pj}^2} \quad (39)$$

which can be rewritten as

$$\frac{dQ^*{}_I}{dt_{pj}} > \frac{dQ^*{}_{II}}{dt_{pj}} \quad (40)$$

Thus, if a total of $2n + 1$ steady states exist, n of them will violate the slope condition, Equation (40) and will be unstable. Gavalas (7) offers topological arguments to show that, in general, at least n out of $2n + 1$ steady states must be unstable.

The $n + 1$ steady states which satisfy the slope condition are not necessarily stable unless all the stability conditions are satisfied. For gas-solid systems $a_4/a_3 >> 1$, and it can be shown that the first two stability conditions in Equation (29) are implied by the slope condition. The third condition in Equation (29), however, is very complicated and has no obvious physical meaning. Thus, only if each cell satisfies that third stability condition as well as the slope condition in Equation (40) will a steady state be asymptotically stable.

NUMERICAL SOLUTION OF TRANSIENT EQUATIONS

The transient behavior of the bed was simulated by the numerical solution of Equations (2 to 7). A reactor composed of 80 cells was used for the computations. The poisoning rate was such that the time required to foul the bed was very long compared to that of the transients in the bed, but not so long as to make the computation time prohibitive. In all cases, the frequency factor of the poisoning rate constant was assigned values that caused the bed to be fouled after about 1,350 min. Although not a long operation time, it is long compared to the time (order of 10 min.) needed for the reactor to reach a steady state from start-up. Time of computation was about forty times faster than real time on the SDS Sigma 7 computer. For comparison, the same values of the dimensionless groups considered by Liu and Amundson (*10*) were chosen, as follows:

$H = 2.352$ $\qquad M = 3.919$
$\beta = 6000°\text{F./atm.}$ $\qquad a_4 = 1/5.45\ \text{min.}$
$k_j = \exp\,(12.98 - 22{,}000/t_{pj})$ $\qquad k_p = A_p \exp(-10{,}000/t_{pj})$

Temperature and Activity Profiles

Unique Pseudo Steady State Cases. Figure 2 presents temperature profiles for a case with deactivation due to a parallel reaction. This reactor would operate with a constant conversion for a long period of time. The reaction zone is continuously moving downstream. As the reaction zone eventually moves out of the reactor, however, a rather sudden decrease in conversion will occur. The corresponding activity profiles in Figure 3 show that most of the deactivation occurs in the same region as the original reaction zone. Although the activity profiles flatten with time, the end of the bed is still practically unpoisoned even after 1,350 min. The case of fouling by a consecutive reaction is shown in Figure 4. The temperature profile ahead of the reaction zone is constantly moving downwards and tends to flatten out. At $\theta = 1{,}350$ min., the temperature profile is almost linear while the conversion has dropped to 80% of the initial value. Figure 5 shows the corresponding activity profiles. As expected, poisoning is predominant in the region after the reaction zone where the temperature and concentration of B are high. The rate of fouling decreases with time owing to the deactivation of the pellets.

Nonunique Pseudo Steady State Cases. When the partial pressure of reactant A in the feed is increased from 0.07 to 0.15 atm., nonunique steady states may occur. Profiles for the pseudo steady state profiles will depend upon the initial as well as operational conditions. The initial catalyst temperature was 1500°R. in all the examples (Figures 6 through 10). In these cases fouling had a much more important effect than for cases with a unique pseudo steady state.

Figures 6 and 7 portray the temperature and activity profiles for fouling by a parallel reaction. The temperature profiles do not level out as in the case of a unique steady state (Figure 2). Instead, the reaction zone is confined to a few cells for all times as it is moving downstream. The deactivation occurs ahead of the reaction zone, because

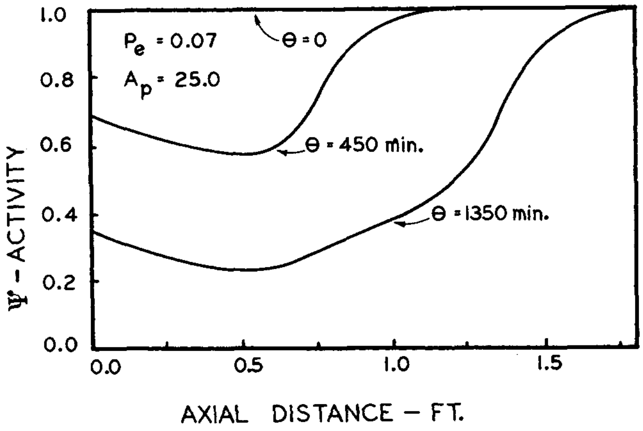

Fig. 3. Activity profiles for the case shown in Fig. 2.

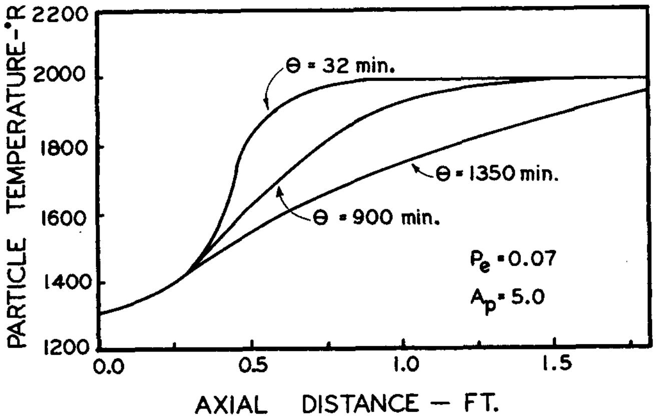

Fig. 4. Transient temperature profiles for fouling by a consecutive reaction for a case where each has a unique pseudo steady state.

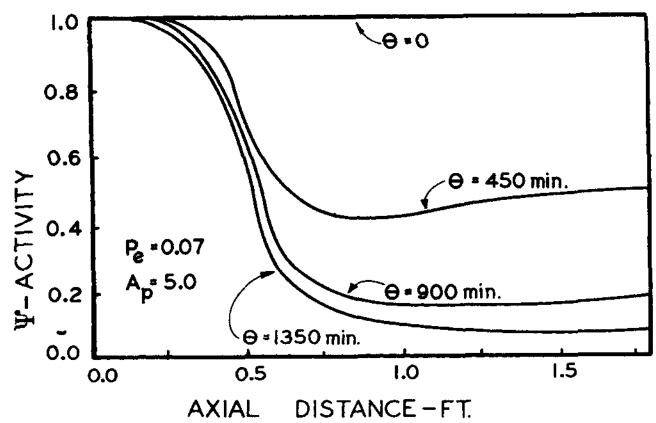

Fig. 5. Activity profiles for the case shown in Fig. 4.

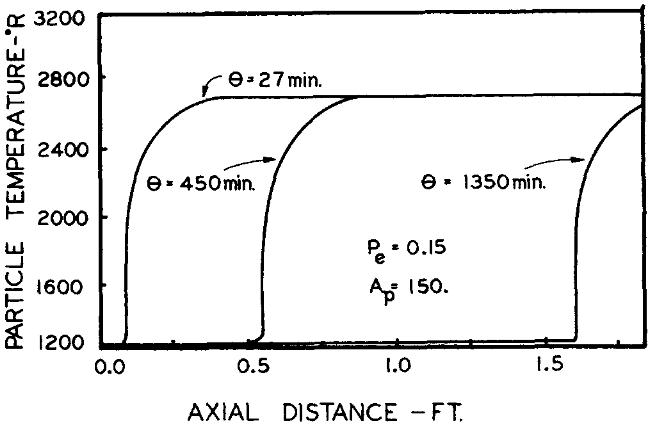

Fig. 6. Transient temperature profiles for fouling by a parallel reaction for a case where some particles have nonunique pseudo steady states.

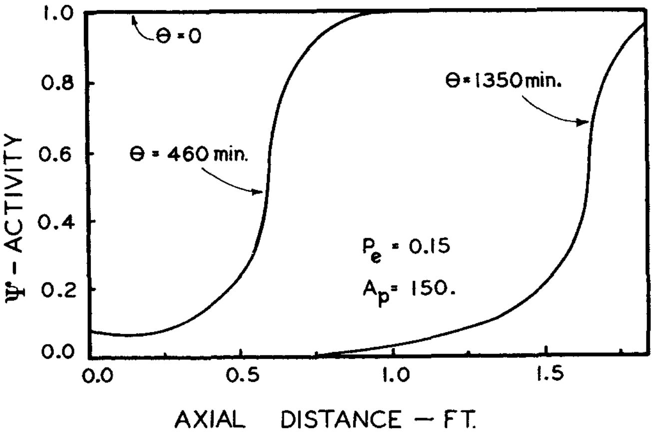

Fig. 7. Activity profiles for the case shown in Fig. 6.

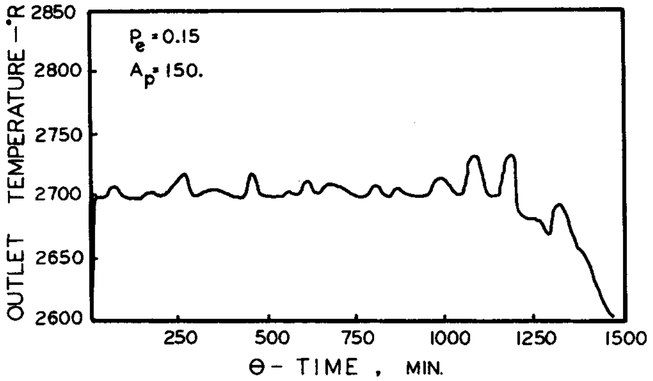

Fig. 8. The fluctuation in the outlet temperature for the case shown in Fig. 6.

in this region the concentration of A is high. The plug progression of the fouling (Figure 7) is responsible for the downstream movement of the reaction zone.

During the computations the reaction zone appeared to move not continuously but in a series of jumps. As it moved, the heat contained in the deactivated cells was carried downstream by the gas. Thus the temperature of the gas was raised above the adiabatic temperature for complete conversion. The abrupt movement of the reaction zone caused oscillations in the exit temperature of the gas (Figure 8). Similar behavior was found for other examples (*6*) in which the bed has multiple steady states but was never encountered for beds with a unique steady state.

An interesting type of behavior (Figure 9) was observed when the fouling occurred by an undesired consecutive reaction. The reaction zone did not move until $\theta = 1{,}500$ min. After this period, however, the reaction zone started to move very rapidly downstream, and the temperature of the bed greatly exceeded the adiabatic temperature. At $\theta = 1{,}570$ min., the reaction zone was completely blown out of the reactor. This violent behavior, which could severely damage the catalyst pellets, can be better understood by an examination of Figure 10. The activity profiles show that the region downstream of the reaction zone is initially fouled, and as the reaction zone moves downstream, the reactor is already fouled, causing a rapid blowout.

Several industrial reactors behave in a manner similar to that shown in Figure 9. For example, napthalene oxidation reactors (*4*) are known to misbehave suddenly, with a violent temperature rise, after months of peaceful operation. The reason may be a fouling effect similar to that shown in Figures 9 and 10.

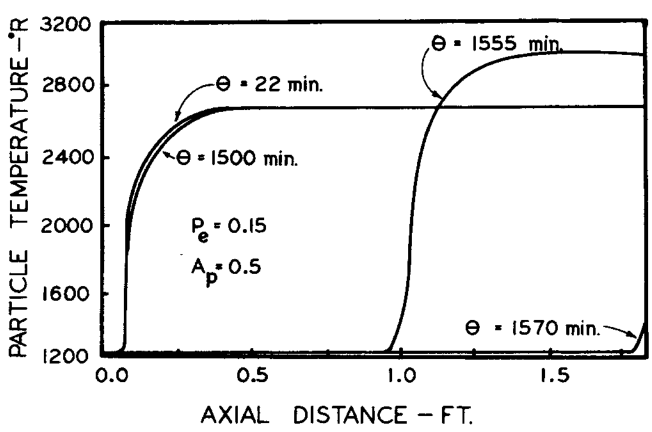

Fig. 9. Transient temperature profiles for fouling by a consecutive reaction for a case where some particles have a nonunique pseudo steady state.

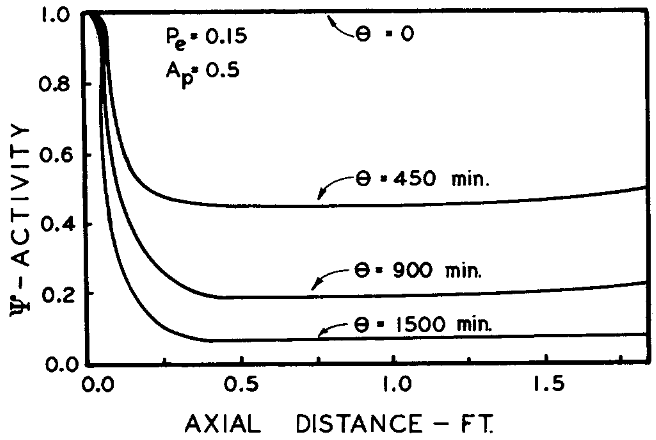

Fig. 10. Activity profiles for the case shown in Fig. 9.

Sensitivity to Variations in Gas Velocity. Vanderveen *et al.* (*17*) showed that, if some particles have a nonunique steady state, velocity changes may cause pathological behavior of the reaction zone. A case was described in which the reaction zone moves upstream with a decrease in velocity but does not move downstream with an increase in velocity. This case (*17*) is used in this work to determine the effect of fouling. Changes in the velocity are defined by the resulting change in the value of H, which is proportional to $U^{0.4}$.

Figure 11 shows the effect of fouling by a parallel reaction. The bed was initially fouled for 900 min., after which the velocity was changed. A decrease in H from 2.352 to 2 did not move the reaction zone upstream as would have happened for an unfouled bed; an increase in the velocity caused only a minor shift in the position of the reaction zone. In this case the fouling actually stabilized the position of the reaction zone and made it less sensitive to velocity fluctuations.

A completely different behavior (Figure 12) was observed when the fouling was caused by a consecutive reaction. The bed was fouled for 800 min. and then subjected to velocity perturbations. A velocity decrease caused

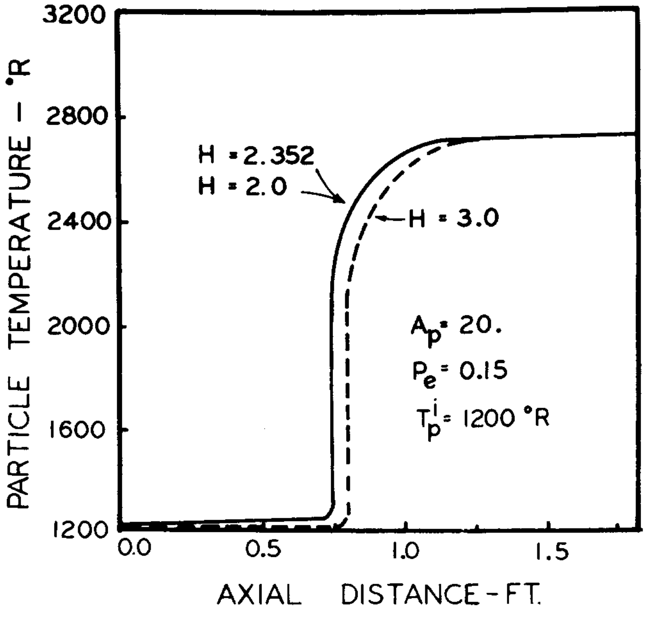

Fig. 11. The effect of a variation in gas velocity on the behavior of a reactor fouled by a parallel reaction.

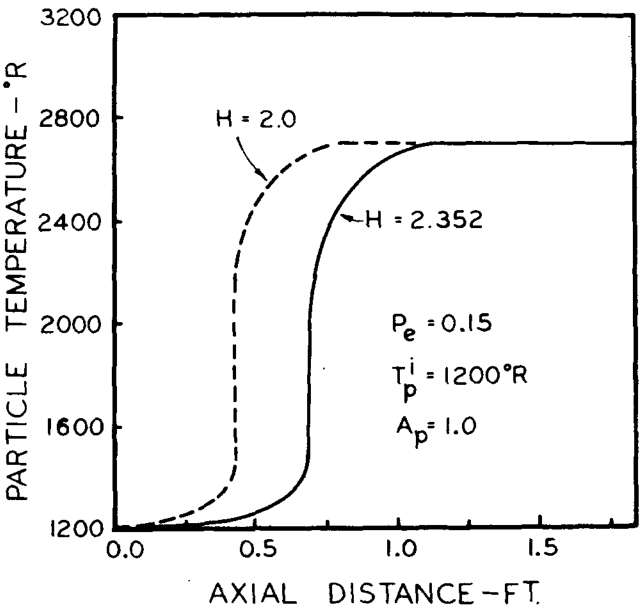

Fig. 12. The effect of variation in gas velocity on the behavior of a reactor fouled by a consecutive reaction.

the reaction zone to move upstream while a velocity increase caused the reaction zone to move rapidly and completely out of the reactor. In this case the reactor is more sensitive to velocity fluctuations than it was with no fouling.

CONCLUSIONS

Fouling can have an important effect on the behavior and stability of adiabatic packed beds. The effects were found to be more predominant in reactors for which multiple steady states can occur and strongly dependent on the fouling mechanism.

Under certain conditions fouling caused the reactor to behave in a more stable fashion than did the unfouled reactor. On the other hand, fouling may cause a violent behavior that would not occur if the activity of the catalytic pellets remained constant.

ACKNOWLEDGMENT

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NOTATION

A_p = pre-exponential factor in fouling rate equation
a_1, a_2, a_3, a_4 = capacity terms defined by Equations (8*c*) and (8*d*)
a_v = surface area of particles per unit volume of bed
c_f = specific heat of gas mixture
c_s = specific heat of particle
D_p = particle diameter
ΔE = activation energy of desirable reaction
ΔE_p = activation energy of fouling reaction
G = fluid mass velocity
H = parameter defined by Equation (8*b*)
$H(t_{pj})$ = function defined by Equation (22)
ΔH = heat of reaction
h_f = film heat transfer coefficient
k = dimensionless reaction rate for main reaction
k' = reaction rate coefficient for main reaction
k_g = film mass transfer coefficient
k_p = reaction rate for fouling reaction
M = parameter defined in Equation (8a)
$\overline{m}$ = average molecular weight of gas mixture
P = total pressure (atm.)
p = partial pressure of reactant A in gas
p_p = partial pressure of reactant A in catalyst
p_{pB} = partial pressure of reactant B in catalyst
Q_I, Q^*_I = heat dissipation functions
Q_{II}, Q^*_{II} = heat generation functions
R = ideal gas law constant
$r(B)$ = rate of formation of B
Sg = surface area of catalyst per unit mass of catalyst
t = gas temperature
t_p = particle temperature

Greek Letters

α = void fraction of particles
β = $(-\Delta H)k_g/h_f$
γ = $\Delta Ep_p/Rt_p{}^2$
δ = heat generation function $k\Psi/(1 + k\Psi)$
ϵ = void volume of bed
η = height of cell/D_p
θ = time
ρ_f = density of fluid
ρ_s = density of solid
Ψ = normalized catalyst activity

Subscripts

e = influent conditions
i = initial conditions
j = cell number

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