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Effect of Catalyst Fouling in Fixed-, Moving-, and Fluid-Bed Reactors*

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A quantitative means of assessing the performance of fixed-, moving-, and fluid-bed reactors under conditions of catalyst fouling is presented. The treatment covers simple reactions of general order in which the effect of different decay forms is considered, the role of axial diffusion is examined, and an expression is developed for the effect of catalyst decay on yield in a consecutive reaction. Finally the practical implications of the development are considered through an example.

NOMENCLATURE

a	$\{1 + [4B'/(\lambda + 1)\mathrm{Pe}]\}^{1/2}$
A	reactant
A_f	$F_B\rho_f/\rho_F S_F\theta_{pt}$
b	$\dfrac{1}{[(1+a)^2\exp(a\mathrm{Pe}/2) - (1-a)^2\exp(-a\mathrm{Pe}/2)]}$
B	$F_BM/\rho_F S_F$, $F_BM/\rho_L S_L$ (ml-hr/mole)
B'	$(F_BM/\rho_F S_F)\,k_{v0}$, reaction parameter
C_A	molal concentration of A (g-moles/ml)
C_{A0}	molal concentration of A at zero time (g-moles/ml)
C_R	molal concentration of intermediate R (g-moles/ml)
d	decay order
D	axial diffusion coefficient (cm²/hr)
$E_i^*(h)$	$-E_i(-h) = \int_h^t (e^{-t}/t)\,dt$ is the exponential integral
F_B	porosity of catalyst bed
G	mass velocity (g/cm² hr)
k_v	rate constant (g-moles/ml hr)
k_{v0}	rate constant at zero time (g-moles/ml hr)
k_1	rate constant (1/hr)
k_2	rate constant (1/hr)
l	axial distance in reactor (cm)
L	total length of reactor (cm)
m	order of reaction
M	molecular weight of feed
Pe	Peclet number, Lu/D
r_{vA}	instantaneous rate of reaction (g-moles/hr ml)
r_{vR}	instantaneous rate of reaction (g-moles/hr ml)
R	intermediate desired product
s	selectivity, k_1/k_2
S	undesired product
S_F	space velocity of feed (1/hr)
S_L	space velocity of liquid feed (g/hr ml) [Ref. (7)]
u	linear velocity of feed (cm/hr)
v	decay velocity constant (1/hr) for exponential decay; and [g-moles/(hr)$^{3/2}$ ml] for linear decay
x	conversion, mole fraction
y_A	instantaneous mole fraction of A
y_R	mole fraction of R
z	normalized distance, l/L

Greek Letters

θ_p	time
θ_{pt}	catalyst decay time (hr)
$\bar{\theta}_p$	normalized time, θ_p/θ_{pt}
ρ_{cat}	density of catalyst (g/ml)
ρ_f	density of fluid (g/ml)
ρ_F	density of any feed (g/ml)
ρ_L	density of liquid feed (g/ml)
λ	$v\theta_{pt}^d$, decay parameter, dimensionless for exponential decay and dimensions of k_{v0} for linear decay

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Introduction

The rational choice of a reactor for handling a time-decaying catalyst involves such considerations as reaction type and thermal behavior of the reaction; but an important consideration—one that might easily outweigh others—is the reactor type itself. For this purpose, a quantitative means of assessing the performance of fixed-, moving-, and fluid-bed reactors under conditions of catalyst fouling is desirable.

Voorhies (*1*) proposed a simple expression for the decay of a cracking catalyst as a function of time, which was later employed by Andrews (*2*) to compare the performances of various reactor types. Subsequently, although considerable work has been reported on catalyst fouling as such, no theoretical assessment was made of the behavior of different reactor types subject to catalyst fouling, until in 1968, Weekman (*3*) proposed a mathematical model for catalytic cracking (under conditions of catalyst decay) in fixed-, moving-, and fluid-bed reactors on the assumption of second-order kinetics, first-order decay, and ideal plug flow. This was followed (*4, 5*) by an analysis of cracking selectivity in a fixed-bed reactor, and it was shown that the time-averaging that is characteristic of such a reactor has a deleterious effect on gasoline yield.

In the present paper, the work of Weekman is extended to a simple reaction of general order (and also first-order), the effect of different decay forms is considered, the role of axial diffusion is examined, and an expression is developed for the effect of catalyst decay on yield in a consecutive reaction. Finally the practical implications of the development are demonstrated through an example.

Theoretical Development

The continuity equation for a plug flow reactor operating under isothermal conditions, through which a reactant [A] is passing and reacting under diffusion-free conditions is:

$$\frac{F_B\rho_f}{M}\left(\frac{\partial y_A}{\partial \theta_p}\right) + \frac{G}{M}\left(\frac{\partial y_A}{\partial l}\right) = -r_{vA}(y_A, \theta_p)F_B. \quad (1)$$

The reaction rate, r_{vA}, is a function not only of the mole fraction of A but also of the reaction time, θ_p. Making use of this basic relation the governing equations for the three reactor types can be written on the basis of the development given earlier (*3*).

Fixed-Bed Reactor

The catalyst decay time θ_{pt}, i.e., the reaction or on-stream time in a fixed-bed reactor, is used to normalize the time at any point during the reaction or decay cycle. Thus the governing equation in normalized coordinates is:

$$A_f\left(\frac{\partial y_A}{\partial \bar{\theta}_p}\right) + \left(\frac{\partial y_A}{\partial z}\right) = -Br_{vA}(y_A, \bar{\theta}_p), \quad (2)$$

where

$$\bar{\theta}_p = \frac{\theta_p}{\theta_p}, \; z = \frac{l}{L}, \; B = \frac{F_B M}{\rho_F S_F},$$

and

$$A_f = \frac{F_B\rho_f}{\rho_F S_F \theta_{pt}}; \quad (3)$$

G has been replaced by $\rho_F S_F L$ (or $\rho_L S_L L$ for liquid feed). A_f represents the ratio of the feed transit time through the reactor to the catalyst decay time, and is generally of negligible magnitude. Thus, assuming A_f = 0, Eq. (2) reduces to

$$\left(\frac{dy_A}{dz}\right) = -Br_{vA}(y_A, \bar{\theta}_p). \quad (4)$$

The rate of disappearance of A can be written for mth order kinetics as

$$r_{vA} = k_{v0}e^{-\lambda\bar{\theta}_p}{y_A}^m, \quad (5)$$

where k_{v0} is the rate constant at zero time, v is the decay velocity constant, and

$$\lambda = v{\theta_{pt}}^d = v\theta_{pt} \text{ (for first-order decay)}, \quad (6)$$

represents a decay group.

Substituting Eq. (5) for r_{vA} in Eq. (4)

$$\frac{dy_A}{dz} = -B'e^{-\lambda\bar{\theta}_p}{y_A}^m, \quad (7)$$

where

$$B' = Bk_{v0}, \quad (8)$$

and may be regarded as a reaction group.

The solution of Eq. (7) is

$$y_A = \left[\frac{1}{(m-1)B'e^{-\lambda\bar{\theta}_p z} + 1}\right]^{1/(m-1)}, \quad m \neq 1, \tag{9}$$

and

$$y_A = e^{-(B'e^{-\lambda\bar{\theta}_p z})}, \quad m = 1. \tag{10}$$

The average conversion obtained at the reactor outlet, i.e., at $z = 1$, is

$$(x)_{av} = 1 - \int_0^1 y_A d\bar{\theta}_p. \tag{11}$$

Introducing Eqs. (9) and (10) in (11):

mth order:

$$x = 1 - \int_0^1 \left[\frac{1}{(m-1)B'e^{-\lambda\bar{\theta}_p} + 1}\right]^{1/(m-1)} \times d\bar{\theta}_p, \; m \neq 1. \tag{12}$$

First-order:

$$x = 1 + \frac{1}{\lambda}[E_i^*(B') - E_i^*(B'e^{-\lambda})] \tag{13}$$

where

$$E_i^*(h) = -E_i(-h) = \int_h^\infty \frac{e^{-t}}{t}\,dt$$

is the exponential integral.

Similarly, equations for conversion can also be derived for the linear decay form represented by

$$k_v(\bar{\theta}_p) = k_{v0} - \lambda\bar{\theta}_p, \tag{14}$$

in which case

$$\frac{dy_A}{dz} = -B'y_A{}^m + \frac{B'}{k_{v0}}\lambda\bar{\theta}_p y_A{}^m. \tag{15}$$

The solution to Eq. (15) is

$$y_A = \left[\frac{k_{v0}}{B'z(m-1)(k_{v0} - \lambda\bar{\theta}_p) + k_{v0}}\right]^{1/(m-1)}, \quad m \neq 1, \tag{16}$$

and

$$y_A = \exp\left(-\left[B' - \frac{B'\lambda\bar{\theta}_p}{k_{v0}}\right]z\right), \; m = 1. \tag{17}$$

The conversion at $z = 1$ is then:

mth order:

$$x = 1 - \int_0^1 \left[\frac{k_{v0}}{B'(m-1)(k_{v0} - \lambda\bar{\theta}_p) + k_{v0}}\right]^{1/(m-1)} \times d\bar{\theta}_p, \; m \neq 1. \tag{18}$$

First-order:

$$x = 1 - \frac{k_{v0}}{B'\lambda} \times \left[\exp\left(-\left\{\frac{B'(k_{v0} - \lambda)}{k_{v0}}\right\}\right) - e^{-B'}\right]. \tag{19}$$

Another convenient decay form which can be adopted is

$$k_v(\bar{\theta}_p) = k_{v0} - \lambda\bar{\theta}_p{}^d. \tag{20}$$

Employing this, solutions corresponding to Eqs. (18) and (19) are given in Table 1.

Moving-Bed Reactor

In the moving-bed reactor, a steady state operation, the residence time of the decaying catalyst corresponds to the total decay time θ_{pt} of the fixed-bed reactor. Thus,

$$\frac{dy_A}{dz} = -B'e^{-\lambda z}y_A{}^m \tag{21}$$

The solution to Eq. (21) is

$$y_A = \left[\frac{\lambda}{(m-1)B'(1 - e^{-\lambda z}) + \lambda}\right]^{1/(m-1)}, \quad m \neq 1, \tag{22}$$

and

$$y_A = \exp\left(\frac{B'}{\lambda}[e^{-\lambda z} - 1]\right), \; m = 1. \tag{23}$$

In view of the steady state operation involved in the moving-bed reactor,

$$x = 1 - y_A \tag{24}$$

Substituting Eqs. (22) and (23) in (24), one obtains at the exit of the reactor [$z = 1$]:

mth order:

$$x = 1 - \left[\frac{\lambda}{(m-1)B'(1 - e^{-\lambda}) + \lambda}\right]^{1/(m-1)}, \quad m \neq 1. \tag{25}$$

First-order:

$$x = 1 - \exp\left[\frac{B'}{\lambda}(e^{-\lambda} - 1)\right]. \quad (26)$$

Similarly, as in the case of a fixed-bed reactor, expressions for y_A and x can also be derived using the decay forms represented by Eqs. (14) and (20). The solutions to these decay forms are included in Table 1.

Fluid-Bed Reactor

Here the fluid is in piston flow and the solid phase is assumed to be completely mixed. For a perfectly mixed catalyst system, the age distribution is given by $e^{-\bar{\theta}_a}$. The average value of the rate constant for this case has been given by Weekman (*3*) as

$$[k_v(\bar{\theta}_p)]_{av} = \frac{k_{v0}}{1 + \lambda}. \quad (27)$$

Combining this with Eqs. (4) and (8),

$$\frac{dy_A}{dz} = -\frac{B'}{1 + \lambda} y_A{}^m. \quad (28)$$

The solution to this equation is:

$$y_A = \left[\frac{\lambda + 1}{(m - 1)B'z + (\lambda + 1)}\right]^{1/(m-1)}, \quad m \neq 1, \quad (29)$$

and

$$y_A = \exp\left(-\frac{B'z}{\lambda + 1}\right), \; m = 1. \quad (30)$$

The conversion at the reactor exit, i.e., at $z = 1$, as given by Eq. (24) is then:

mth order:

$$x = 1 - \left[\frac{(\lambda + 1)}{(m - 1)B' + (\lambda + 1)}\right]^{1/(m-1)}, \quad m \neq 1. \quad (31)$$

First-order:

$$x = 1 - \exp\left(-\frac{B'}{\lambda + 1}\right). \quad (32)$$

As in the case of the other two reactors, solutions corresponding to the decay Eqs. (14) and (20) can also be found. These are included in Table 1.

TABLE 1

EXPRESSIONS FOR MOLE FRACTION AND CONVERSION OF A FOR VARIOUS DECAY FORMS

Decay form	Expression for y_A: mth order [$m \neq 1$]	Expression for y_A: 1st order
$k_v = k_{v0}e^{-\lambda\bar{\theta}_p}$		
Fixed	$\left[\frac{1}{(m-1)B'e^{-\lambda\bar{\theta}_p} + 1}\right]^{1/(m-1)}$	$e^{-[B'e^{-\lambda\bar{\theta}_p}]}$
Moving	$\left[\frac{\lambda}{(m-1)B'(1 - e^{-\lambda}) + \lambda}\right]^{1/(m-1)}$	$\exp\left(\frac{B'}{\lambda}[e^{-\lambda} - 1]\right)$
Fluid	$\left[\frac{(\lambda+1)}{(m-1)B' + (\lambda+1)}\right]^{1/(m-1)}$	$\exp\left(-\left[\frac{B'}{\lambda+1}\right]\right)$
$k_v = k_{v0} - \lambda\bar{\theta}_p$		
Fixed	$\left[\frac{k_{v0}}{B'(m-1)(k_{v0} - \lambda\bar{\theta}_p) + k_{v0}}\right]^{1/(m-1)}$	$\exp\left(-\left[B' - \frac{B'\lambda\bar{\theta}_p}{k_{v0}}\right]\right)$
Moving	$\left[\frac{2k_{v0}}{B'(m-1)(2k_{v0} - \lambda) + 2k_{v0}}\right]^{1/(m-1)}$	$\exp\left(B'\left[\frac{\lambda}{2k_{v0}} - 1\right]\right)$
Fluid	$\left[\frac{k_{v0}}{B'(k_{v0} - \lambda)(m-1) + k_{v0}}\right]^{1/(m-1)}$	$\exp\left(\left[\frac{B'}{k_{v0}}\right][k_{v0} - \lambda]\right)$
$k_v = k_{v0} - \lambda\bar{\theta}_p{}^d$		
Fixed	$\left[\frac{k_{v0}}{(B'k_{v0} - B'\lambda\bar{\theta}_p{}^d)(m-1) + k_{v0}}\right]^{1/(m-1)}$	$\exp\left(\left[\frac{B'}{k_{v0}}\lambda\bar{\theta}_p{}^d - B'\right]\right)$
Moving	$\left[\frac{(d+1)k_{v0}}{(m-1)B'[(d+1)k_{v0} - \lambda] + (d+1)k_{v0}}\right]^{1/(m-1)}$	$\exp\left(B'\left[\frac{\lambda}{k_{v0}(d+1)} - 1\right]\right)$
Fluid	$\left[\frac{k_{v0}}{k_{v0} + (m-1)B'(k_{v0} - \underline{[d}\lambda)}\right]^{1/(m-1)}$	$\exp\left(B'\left[\frac{\underline{[d}\lambda}{k_{v0}} - 1\right]\right)$

Comparison of Performances

Equations (13), (26), and (32), for fixed-, moving-, and fluid-bed reactors, respectively, can be displayed graphically as curves of conversion vs B' for different values of λ. Since the curves obtained show trends that are similar to those for a second-order reaction given by Weekman (*3*), they are not presented here.

The effect of reaction order on conversion for the three reactor types is shown in Fig. 1. When the decay parameter is zero, the equations for all the three reactor types reduce to

$$x = 1 - \left[\frac{1}{B'(m-1)z + 1}\right]^{1/(m-1)}, \quad m \neq 1, \tag{33}$$

$$x = 1 - e^{-B'z}, \; m = 1, \tag{34}$$

regardless of the decay form employed. Thus, the nature of catalyst present, whether in fixed, moving, or fluidized form, mixed or unmixed, is of no consequence as long as it is ensured that the catalyst exhibits a fixed time-independent activity and the fluid is in plug flow. This is shown by the single line obtained for all reactor types at $\lambda = 0$ in Fig. 1. On the other hand, for different finite values of the decay group λ, different curves are obtained for fixed, moving, and fluid-bed reactors. In Fig. 1, curves are presented for $\lambda = 6$, and for $\lambda = 10$ (i.e., for a higher value of the fouling group). It is clearly shown that the effect of fouling is far less severe for reactions of higher order in a moving or fluid-bed reactor than in a fixed-bed reactor. In fact, in fixed-bed reactors, the effect is practically negligible. The conclusion follows, therefore, that the moving and fluid-bed reactors, which are in general (but not always) superior to the fixed-bed reactor for a fouling catalyst, are to be preferred for reactions of higher order under conditions of severe fouling.

Effect of Axial Dispersion

In the treatment so far, the fluid in all the three types of reactors was assumed to be in

TABLE 1 (*Continued*)

Expression for conversion	
mth order $[m \neq 1]$	1st order
$1 - \int_0^1 \left\{\frac{1}{(m-1)B'e^{-\lambda\bar{\theta}_p} + 1}\right\}^{1/(m-1)} d\bar{\theta}_p$	$\left[1 + \frac{1}{\lambda}E_i^*(B') - E_i^*(B'e^{-\lambda})\right]$
$1 - \left[\frac{\lambda}{(m-1)B'(1-e^{-\lambda}) + \lambda}\right]^{1/(m-1)}$	$1 - \exp\left(\frac{B'}{\lambda}[e^{-\lambda} - 1]\right)$
$1 - \left[\frac{(\lambda+1)}{(m-1)B' + (\lambda+1)}\right]^{1/(m-1)}$	$1 - \exp\left(-\left[\frac{B'}{\lambda+1}\right]\right)$
$1 - \int_0^1 \left\{\frac{k_{v0}}{B'(m-1)(k_{v0} - \lambda\bar{\theta}_p) + k_{v0}}\right\}^{1/(m-1)} d\bar{\theta}_p$	$1 - \int_0^1 \exp\left(-\left[B' - \frac{B'\lambda\bar{\theta}_p}{k_{v0}}\right]\right)d\bar{\theta}_p$
$1 - \left[\frac{2k_{v0}}{(m-1)B'(2k_{v0} - \lambda) + 2k_{v0}}\right]^{1/(m-1)}$	$1 - \exp\left(B'\left[\frac{\lambda}{2k_{v0}} - 1\right]\right)$
$1 - \left[\frac{k_{v0}}{B'(k_{v0} - \lambda)(m-1) + k_{v0}}\right]^{1/(m-1)}$	$1 - \exp\left[\left(-\frac{B'}{k_{v0}}\right)(k_{v0} - \lambda)\right]$
$1 - \int_0^1 \left[\frac{k_{v0}}{(B'k_{v0} - B'\lambda\bar{\theta}_p{}^d)(m-1) + k_{v0}}\right]^{1/(m-1)} d\bar{\theta}_p$	$1 - \int_0^1 \exp\left[\frac{B'}{k_{v0}}\lambda\bar{\theta}_p{}^d - B'\right]d\bar{\theta}_p$
$1 - \left[\frac{(d+1)k_{v0}}{(m-1)B'[(d+1)k_{v0} - \lambda] + (d+1)k_{v0}}\right]^{1/(m-1)}$	$1 - \exp\left(B'\left[\frac{\lambda}{k_{v0}(d+1)} - 1\right]\right)$
$1 - \left[\frac{k_{v0}}{k_{v0} + (m-1)B'(k_{v0} - \lfloor d\lambda)}\right]^{1/(m-1)}$	$1 - \exp\left(B'\left[\frac{\lfloor d\lambda}{k_{v0}} - 1\right]\right)$

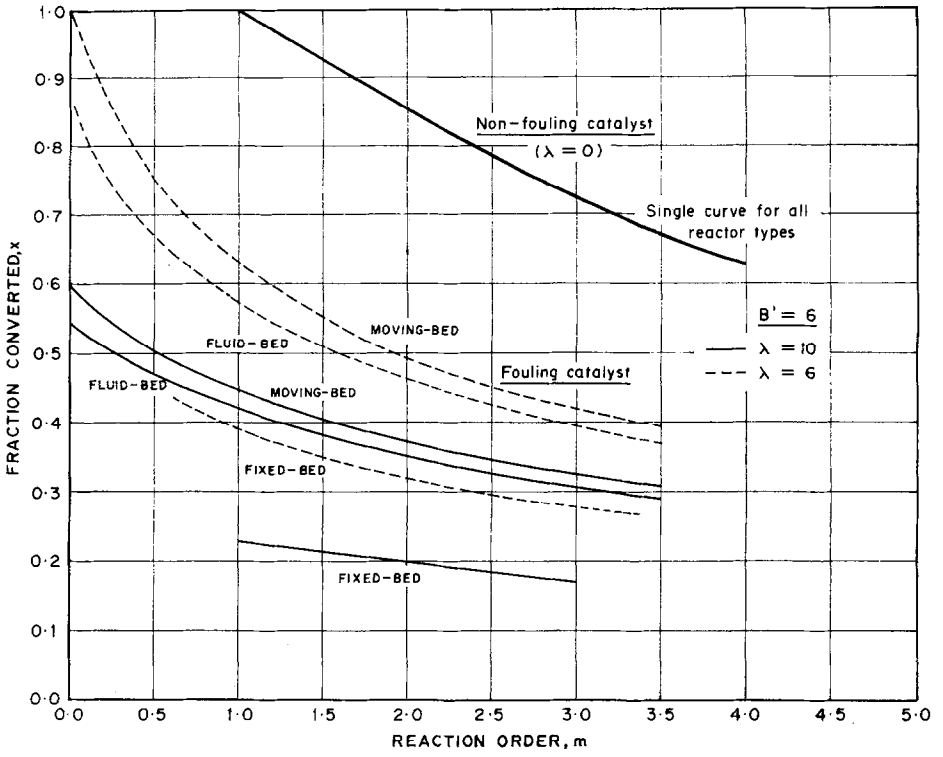

FIG. 1. Fractional conversion as a function of the reaction order for the three reactor types at a relatively low and high value of the fouling factor.

piston flow—an ideal case. The effect of axial diffusion can be readily included by adopting the axial dispersion model. Considering a fluid-bed reactor, Eq. (30) becomes (for a first-order reaction):

$$\frac{dy_A}{dz} - \frac{1}{\mathrm{Pe}}\frac{d^2y_A}{dz^2} = -\left(\frac{B'}{\lambda+1}\right)y_A. \quad (35)$$

Using the Danckwerts boundary condition (6),

$$\frac{dy_A}{dz} = 0 \text{ at } z = 1.0,$$

and

$$y_A - \frac{1}{\mathrm{Pe}}\frac{dy_A}{dz} = 1.0 \text{ at } z = 0,$$

the solution to Eq. (35) is

$$y_A = 4ab\exp\left(\frac{\mathrm{Pe}z}{2}\right), \quad (36)$$

where

$$a = \left[1 + \frac{4B'}{(\lambda+1)\mathrm{Pe}}\right]^{1/2}, \quad (37)$$

and

$$b = \frac{1}{[(1+a)^2\exp(a\mathrm{Pe}/2) - (1-a)^2\exp(-a\mathrm{Pe}/2)]}. \quad (38)$$

The conversion, x, at the reactor exit is

$$x = 1 - 4ab\exp\left(\frac{\mathrm{Pe}}{2}\right). \quad (39)$$

If $\mathrm{Pe} \to \infty$, Eq. (39) reduces to (32) for plug flow. For $\mathrm{Pe} \to 0$, Eq. (39) reduces to

$$\left(\frac{B'}{\lambda+1}\right)\Big/\left[1 + \left(\frac{B'}{\lambda+1}\right)\right].$$

For a reaction of mth order, Eq. (35) becomes nonlinear and is to be solved by iterative or linearization methods of solution.

In Fig. 2 conversion is plotted against

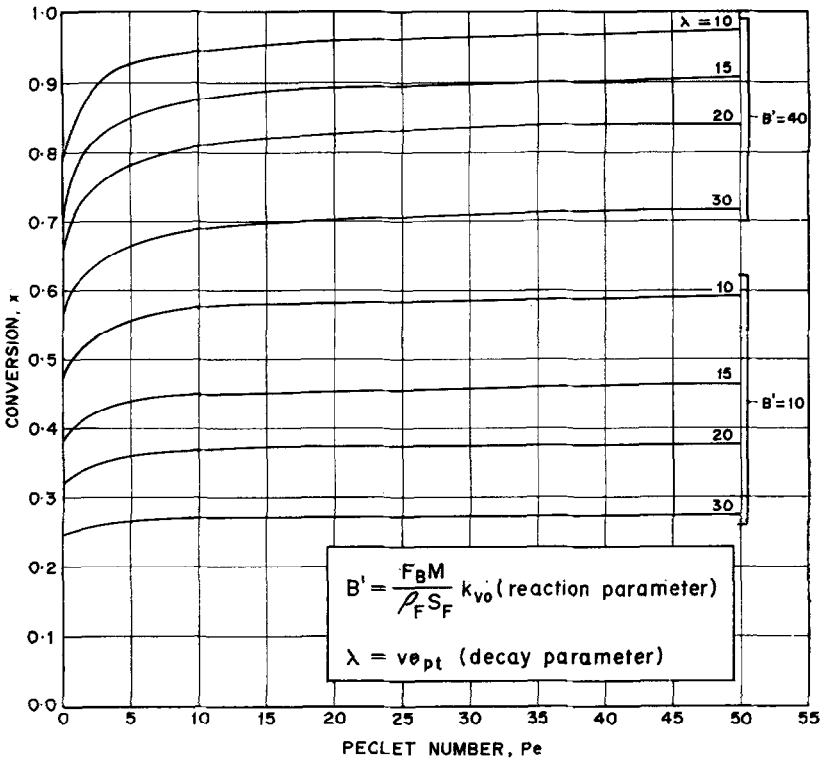

FIG. 2. Effect of axial mixing on the performance of a fluid-bed reactor subject to catalyst fouling.

Peclet number for different values of the decay parameter λ and two values of the reaction group B'. Notice that, at relatively low values of the reaction group, the increased conversion due to plug flow practically vanishes as the decay parameter is increased.

Similar equations for the fixed- and moving-bed reactors can be written for first-order kinetics.

Fixed-bed:

$$\frac{dy_A}{dz} - \frac{1}{\mathrm{Pe}}\frac{d^2y_A}{dz^2} = -B'e^{-\lambda\bar{\theta}_p}y_A. \qquad (40)$$

Moving-bed:

$$\frac{dy_A}{dz} - \frac{1}{\mathrm{Pe}}\frac{d^2y_A}{dz^2} = -B'e^{-\lambda z}y_A. \qquad (41)$$

The boundary conditions are the same as for the fluid-bed reactor. However, no analytical solutions to Eqs. (40) and (41) are possible.

Extension to a Consecutive Reaction System

So far the effect of different decay forms on a simple reaction in an isothermal reactor was considered. Now, the effect of the decay parameter λ on the intermediate product R in a consecutive reaction $A \rightarrow R \rightarrow S$ will be examined, first in fluidized and moving-bed reactors, and then in a fixed-bed reactor.

Fluidized and Moving-Bed Reactors

The first-order rate equations for the consecutive reaction system mentioned above are:

$$r_{vA} = -k_1C_A, \qquad (42)$$

and

$$r_{vR} = k_1C_A - k_2C_R. \qquad (43)$$

If it is assumed that the reaction is carried out under isothermal conditions with no axial diffusion in the fluid phase, the following set of equations result (at constant density):

$$\frac{dy_A}{dz} = -\left(\frac{B'}{\lambda+1}\right) y_A, \tag{44}$$

$$\frac{dy_R}{dz} = \left(\frac{B'}{\lambda+1}\right) y_A - \frac{1}{s}\left(\frac{B'}{\lambda+1}\right) y_A, \tag{45}$$

where s is the selectivity k_1/k_2. Simultaneous solution of these equations under the boundary conditions,

$$\left.\begin{aligned} &z = 0, \quad y_A = 1 \text{ and } y_R = 0 \\ &z = 1, \quad \frac{dy_A}{dz} = \frac{dy_R}{dz} = 0 \end{aligned}\right\} \tag{46}$$

leads to

$$y_R = \frac{s}{1-s}\left[\exp\left(-\left(\frac{B'}{\lambda+1}\right)\right) - \exp\left(-\frac{1}{s}\left(\frac{B'}{\lambda+1}\right)\right)\right] \tag{47}$$

Restricting our attention now to a fluid-bed reactor, Eq. (47) can be combined with (30) for $z = 1$ (reactor exit) to give

$$y_R = \frac{s}{1-s}\left(y_A - y_A^{1/s}\right). \tag{48}$$

Notice that this solution is independent of B' and λ, and a knowledge of the selectivity ratio s alone is required. Also Eq. (48) is identical with that derived by Wheeler (7) for a consecutive reaction under diffusion-free conditions for a nonfouling catalyst. The effect of fouling is shown up in the present case through Eq. (30) for y_A.

An equation similar to (47) can also be derived for a moving-bed reactor under identical boundary and fluid flow conditions. Thus:

$$y_R = \frac{s}{1-s}\left[\exp\left(-\frac{B'}{\lambda}(1-e^{-\lambda})\right) - \exp\left(-\frac{B'}{s\lambda}(1-e^{-\lambda})\right)\right]. \tag{49}$$

Combining this with Eq. (23) for $z = 1$ gives

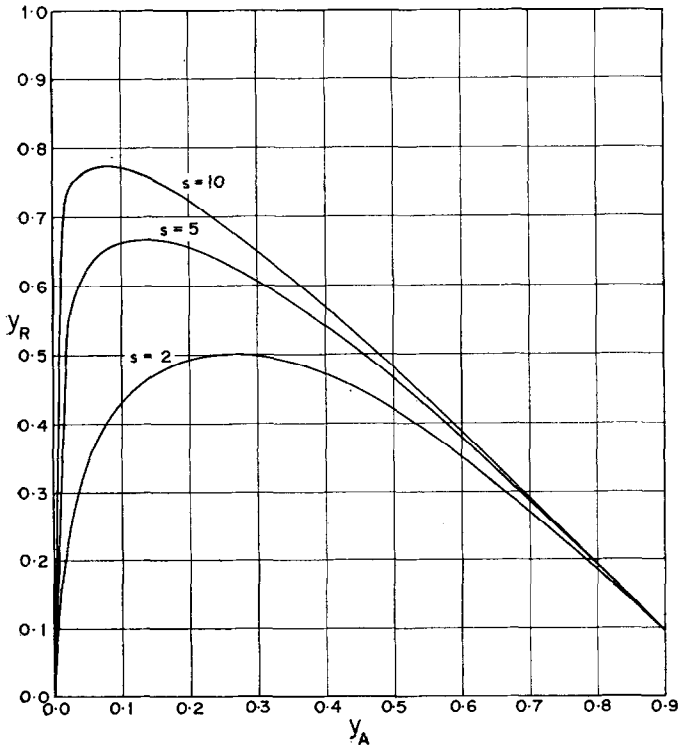

FIG. 3. Plot of Eq. (48).

an expression exactly identical with Eq. (48) for the fluid-bed reactor.

It can therefore be concluded that Eq. (48) completely describes the selectivity behavior of both fluid- and moving-bed reactors [for a first-order consecutive reaction system] under conditions of catalyst fouling. A plot of y_R vs y_A for different values of s is shown in Fig. 3. Clearly the same maximum values will be obtained for identical s for both fluid- and moving-bed reactors. The dependence of y_A on λ and B' is however different for the two reactor types, being determined by Eq. (30) for the fluid-bed reactor and (23) for the moving-bed reactor.

Fixed-Bed Reactor

The governing equations for this reactor are:

$$\frac{dy_A}{dz} = -B'e^{-\lambda\bar{\theta}_p}y_A, \tag{50}$$

$$\frac{dy_R}{dz} = B'e^{-\lambda\bar{\theta}_p}y_A - \frac{B'}{s}e^{-\lambda\bar{\theta}_p}y_R \tag{51}$$

The solution under boundary conditions similar to (46) is

$$y_R = \left(\frac{s}{1-s}\right)\left[e^{-B'e^{-\lambda\bar{\theta}_p}} - \exp\left(-\frac{B'}{s}e^{-\lambda\bar{\theta}_p}\right)\right]. \tag{52}$$

By combining this with Eq. (12) at $z = 1$, it can be seen that the solution is identical with Eq. (47); but in the case of a fixed-bed reactor, as pointed out by Nace and Weekman (*5*), time-averaged (ta) values of the mole fraction should be used. Thus

$$(y_R)_{ta} = \frac{s}{1-s}\int_0^1 (y_A - y_A^{1/s})d\bar{\theta}_p, \tag{53}$$

where y_A is given by Eq. (10) at $z = 1$. To solve this equation: for given values of B' and λ obtain y_A from Eq. (10) by setting $z = 1$; then introduce this value in (53) and solve for $(y_R)_{ta}$.

Effect of Decay Model

As already explained (see Fig. 3), for a given selectivity ratio the same maximum y_R is obtained regardless of the values of the reaction group B' and the decay group λ for all but time-averaged cases. Clearly, then, the nature of the decay model used has no influence on the maximum y_R at given s. This is brought out in a striking manner in Fig. 4 in which y_R is plotted as a function of the decay parameter λ for a fixed value of B' for three different selectivity ratios both for the exponential and linear decay forms. In the case of the linear model, a knowledge of k_{v0} is necessary in preparing the plots, and accordingly a value of 20 has been arbitrarily assumed. Notice that the maximum values of y_R are 0.375 at $s = 1$, 0.510 at $s = 2$, and 0.780 at $s = 10$, irrespective of the decay model (although different combinations of B' and λ are involved). This situation does not hold for fixed-bed reactors which are characterized by time-averaged results.

Practical Implications

Although the theoretical developments presented above are of maximum utility in the choice of petroleum cracking reactors, they are also valid for other reactions which involve catalyst fouling. Doraiswamy and Pai (*7*) examined the decay patterns of a variety of active carbons in the dehydrochlorination of ethylene dichloride to vinyl

$$CH_2Cl{\cdot}CH_2Cl = CH_2{=}CHCl + HCl,$$

chloride, and based on their results the following equation can be written for the reaction rate constant as a function of process time for each of the carbons studied:

$$k_v(\theta_p) = k_{v0} - v(\theta_p)^{1/2}. \tag{54}$$

As shown, the rate constant falls linearly with the square root of reaction (or decay) time. Equation (54) can be recast into the form

$$k_v(\bar{\theta}_p) = k_{v0} - \lambda(\bar{\theta}_p)^{1/2}, \tag{55}$$

where

$$\lambda = v(\theta_{pt})^{1/2} \tag{56}$$

Using Eq. (55) for $k_v(\bar{\theta}_p)$ in Eq. (9) and combining the result with Eq. (8), assuming the reaction to be first-order and solving, the following expressions are obtained for conversion for the three reactor types (which can also be written directly from Table 1) by

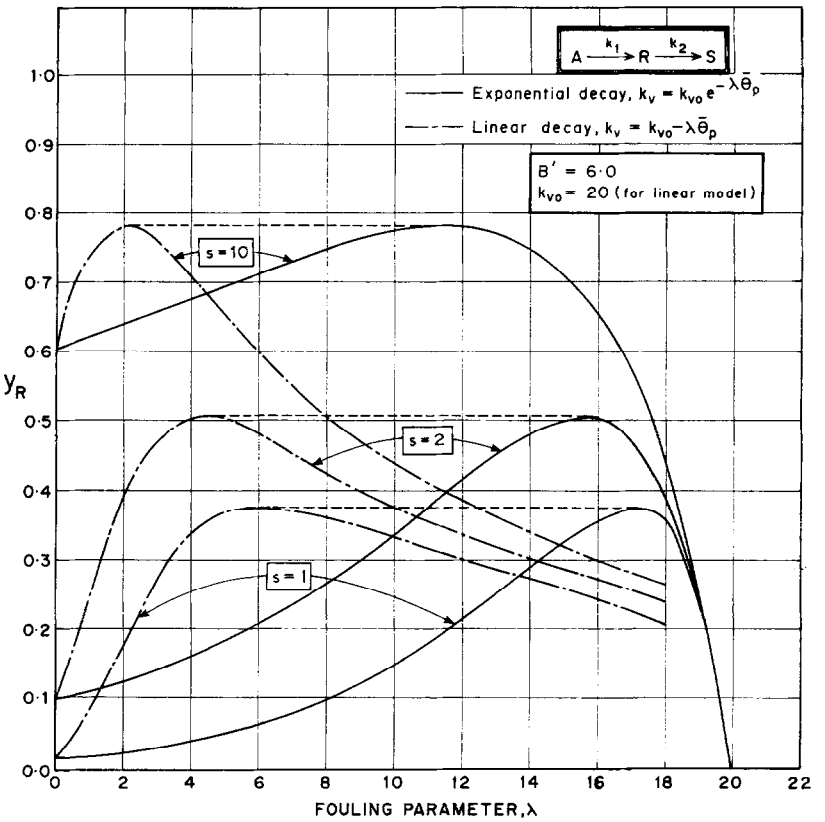

FIG. 4. Effect of decay model on the yield of intermediate.

substituting $d = \frac{1}{2}$ in the equations corresponding to the general decay form $[k_v(\bar{\theta}_p) = k_{v0} - \lambda\bar{\theta}_p{}^d]$.

Fixed-bed:

$$x = 1 - \int_0^1 \exp\left(\frac{B'}{k_{v0}}\lambda\bar{\theta}_p{}^{1/2} - B'\right) d\bar{\theta}_p. \quad (57)$$

Moving-bed:

$$x = 1 - \exp\left[B'\left(\frac{\lambda}{1.5\,k_{v0}} - 1\right)\right]. \quad (58)$$

Fluid-bed:

$$x = 1 - \exp\left[B'\left(\frac{\frac{1}{2}\lambda}{k_{v0}} - 1\right)\right]. \quad (59)$$

For the present problem, we restrict our attention to a single catalyst [catalyst (*8*) at 435°C]. The value of the total reaction time (which is the same as the catalyst residence time in a moving-bed reactor and average catalyst residence time in a fluid-bed reactor) may be conveniently fixed at 1.5 hr. From the unpublished experimental data for catalyst (*8*), and assuming first-order kinetics, the following values of k_{v0} and v have been obtained:

$$k_{v0} = 0.112 \text{ g-moles/hr ml}$$
$$v = 0.041 \text{ g-moles/(hr)}^{3/2} \text{ ml}$$

The other basic data required are:

$$S_1 = 4 \text{ g/hr ml}$$
$$\rho_l = 1.2 \text{ g/ml}$$
$$F_B = 0.5 \text{ (assumed)}$$
$$\rho_F = 1.73 \times 10^{-2} \text{ g/ml at 435°C}$$

Therefore

$$\lambda = 0.041\ (1.5)^{1/2}$$
$$= 0.0502$$
$$S_L = \frac{4}{\rho_{\text{cat}}} \simeq 4 \cdot \frac{1}{\text{hr}},$$

and

$$B' = \frac{0.112 \times 0.5 \times 99}{1.2 \times 4}$$
$$= 1.155.$$

Substituting these values of λ and B' in Eqs. (57), (58), and (59) for the three reactor types, the following results are obtained for the conversion at the reactor exit bed reactor:

Fixed	Moving	Fluid
0.553	0.556	0.501

The fluid-bed reactor was shown to be the least efficient, while the fixed- and moving-bed reactors are almost equally efficient. Since all three reactor types give conversions in the range 0.50 to 0.56, the choice should be dictated by considerations other than those of catalyst fouling.

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