Masamune, S., and J. M. Smith, "Performance of Fouled Catalyst Pellets," *AIChE J.*, **12**, 384 (1966).
Murakami, Y., et al., "Effect of Intraparticle Diffusion on Catalyst Fouling," *Ind. Eng. Chem. Fund.*, **7**, 599 (1968).
Ollis, D. F., "Diffusion Influences in Denaturable Insolubilized Enzyme Catalysts," *Biotech. Bioeng.*, **14**, 871 (1972).
Sagara, M., et al., "Effect of Nonisothermal Operation on Catalyst Fouling," *AIChE J.*, **13**, 1226 (1967).

Manuscript received January 13, 1978; revision received July 14 and accepted July 16, 1980.

Effect of External Diffusion on Deactivation Rates

S. KRISHNASWAMY
and
J. R. KITTRELL
Department of Chemical Engineering
University of Massachusetts
Amherst, MA 01003

Alteration in concentration-independent catalyst decay rates due to the presence of finite external and internal mass transfer resistances is examined. Analytical expressions for external and overall time-dependent catalytic effectiveness are developed. Analysis of diffusion-limited catalyst deactivation in flow reactors is discussed.

SCOPE

The presence of internal and external mass transfer resistances can alter the time scale of decay of solid catalysts. In another paper (Krishnaswamy and Kittrell, 1981), the interaction between internal diffusion and deactivation was examined. Analysis of the performance of reactors operating under these combined influences was discussed. In addition, the rate of diffusion-limited decay of catalysts was shown to be very different from that for diffusion-free systems. In many instances of industrial use, catalysts often operate under the combined influence of internal and external mass transport resistances. Further alternation of decay rates is likely to occur when resistances to internal as well as external transport exist.

The purpose of this paper is to extend the analysis of diffusion-limited deactivation to include the effects of external transport resistances. For illustrative purposes, the first-order reaction and deactivation model is retained.

CONCLUSIONS AND SIGNIFICANCE

A simple analytical solution can be derived for the time-dependent external catalytic effectiveness of a deactivating, nonporous particle, as well as the overall effectiveness of a deactivating porous catalyst. Extensions of this analysis to particles of nonspherical geometry and to the general case of a n-th order deactivation process are both straight-forward.

The expressions for time-dependent catalytic effectiveness can be incorporated in plug flow reactor design equations leading to analytical conversion-time relationships. Theoretical results indicate that the effect of a finite external mass transfer resistance is to further decrease the magnitude of the apparent deactivation rate constant, thereby increasing catalyst lifetime. While the lower limit on this magnitude for severe internal diffusion is $k_d/2$ for deactivation modulus $(hA) \geq 5.0$, that for a particle with severe internal and external diffusional limitations is zero. Certain analogies exist between non-deactivating and deactivating systems subject to internal and external transport resistances.

The impact of overall catalytic effectiveness on the yields of products in non-deactivating complex reaction networks has been considered by Carberry (1976). The results of this paper indicate that the concept of a time-dependent overall effectiveness will have a profound effect on such product yields, depending on the relative rates and characteristics of the diffusion and deactivation processes associated with the various reactions in any complex network.

The influence of intraparticle resistance alone on catalyst poisoning has been investigated by Masamune and Smith (1966), Chu (1968), Murakami et al. (1968), Ollis (1972), Hegedus and Petersen (1973), and Krishnaswamy and Kittrell (1981).

Hegedus (1974) studied the effects of both external and internal mass transfer resistance on porous catalysts being poisoned either by the reactant or an impurity in the feed stream. Due to the complexity of the equations, an analytical solution was not possible. His numerical results indicated that both external and internal mass transfer resistances tend to increase the lifetime of the catalyst, for impurity and reactant poisoning. Lin (1975) solved the problem of a non-isothermal deactivating enzyme catalyst, with finite mass transfer resistances, for Michaelis-

S. Krishnaswamy is presently with Gulf Research & Development Co., Harmarville, PA.

0001-1541-81-4363-0125-$02.00.

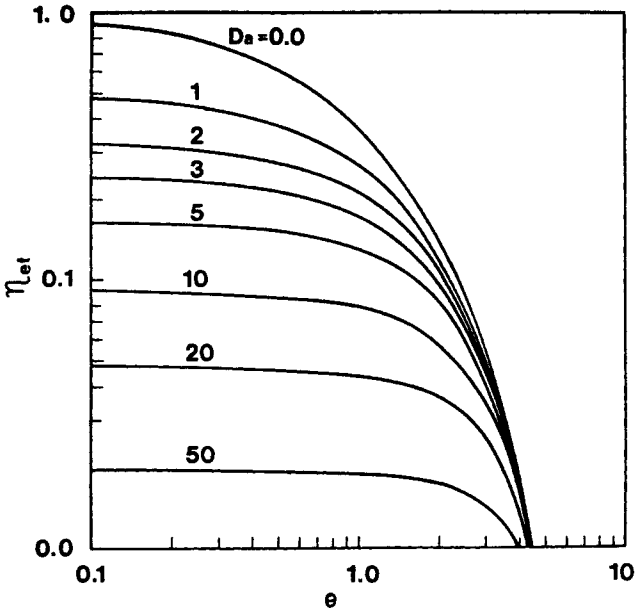

Figure 1. Initialized external effectiveness factor vs. dimensionless time.

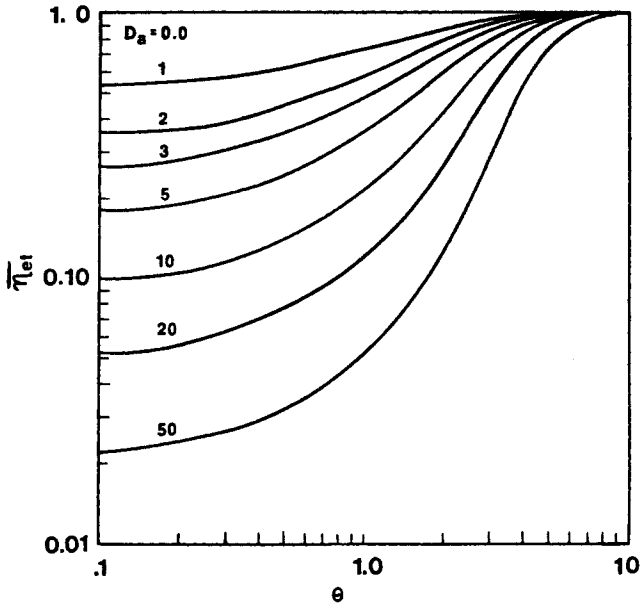

Figure 2. Instantaneous external effectiveness factor vs. dimensionless time.

Menten kinetics, but did not present time-dependent effectiveness factor plots.

In this study, the first-order reaction and deactivation model of Krishnaswamy and Kittrell (1981) is solved with finite external and internal diffusion resistances present.

EXTERNAL DIFFUSION AND DEACTIVATION

Carberry (1976) has pointed out several instances of important nonporous solid catalytic reaction systems wherein external diffusion gradients are known to be present. In addition, instances of practical interest exist, where the catalyst is restricted to a thin porous layer on the surface of the support particle. Such systems could conceivably have large external transport resistances, in the absence of any strong internal diffusion limitations. The impact of such external transport resistances alone on the deactivation of porous catalysts is, therefore, of considerable interest.

For a first-order reaction and deactivation process occurring on the surface of an isothermal, nonporous spherical particle, equating surface reaction to interphase mass transport at any instant of time, we get:

$$k\, C_R\, a = K_m\, a_s\, (C - C_R) \tag{1}$$

Rearrangement gives the surface concentration in terms of the bulk stream concentration:

$$C_R = \frac{C}{(1 + Da\, a)} \tag{2}$$

where

$$Da = \left(\frac{k}{K_m\, a_s}\right) = \text{Damköhler number}$$

The global rate, expressed in terms of the bulk concentration is given by:

$$R_G = k\, C_R\, a = \frac{k\, C\, a}{(1 + Da\, a)} \tag{3}$$

The external, Initialized effectiveness factor is then defined as the ratio of the global rate at any instant of time to the purely chemical-reaction controlled rate at zero time:

$$\eta_{et} = \frac{k\, C\, a/(1 + Da\, a)}{k\, C\, a_o}$$

or

$$\eta_{et} = \frac{a}{(1 + Da\, a)} \tag{4}$$

where a_o has been assumed to equal unity.

Assuming pseudosteady state, the catalyst activity, for concentration-independent deactivation, is given by:

$$a = \exp\,(-k_d\, t) \tag{5}$$

When the reaction step is much slower than diffusion through the external film, i.e., when $Da \to 0$;

$$\eta_{et} = a = \exp\,(-\theta) \tag{4a}$$

where θ is the dimensionless time.

At the other extreme, when external mass transport is rate controlling, i.e., when $Da \to \infty$,

$$\eta_{et} = \frac{1}{Da} \tag{4b}$$

Figure 1 shows plots of η_{et} vs. θ for several values of the Damköhler number. The shape of these curves is similar to those for internal effectiveness, with concentration-independent decay (Krishnaswamy and Kittrell, 1981) and for decay-dependent on reactant, product or impurity in feed (Masamune and Smith, 1966). It is apparent from Figure 1 that for catalysts with large external diffusion resistances (large values of Da), conversion will decrease at a slower rate than for diffusion-free catalyst particles.

Eq. 4 is a useful definition of catalytic effectiveness, but should not be interpreted as suggesting an increase in diffusional limitations with time. Intuitively, for the external diffusion-limited particle, we would expect the diffusional restrictions to become less pronounced, as the catalyst deactivates and the reaction rate decreases with time on-stream.

Hence, an alternative definition of the catalytic effectiveness is one that compares the global rate at any time, to the purely chemical reaction controlled rate, at the same instant of time.

$$\eta_{et} = \frac{1}{(1 + Da\, a)} = \frac{\eta_{et}}{a} \tag{6}$$

For the extreme cases of negligible and infinite external resistances, this definition reduces to unity and $(1/Da\, a)$, respectively. Figure 2 shows that the instantaneous effectiveness factor given by Eq. 6 gradually increases from its initial value to unity for the completely poisoned pellet. Increasing the Damköhler

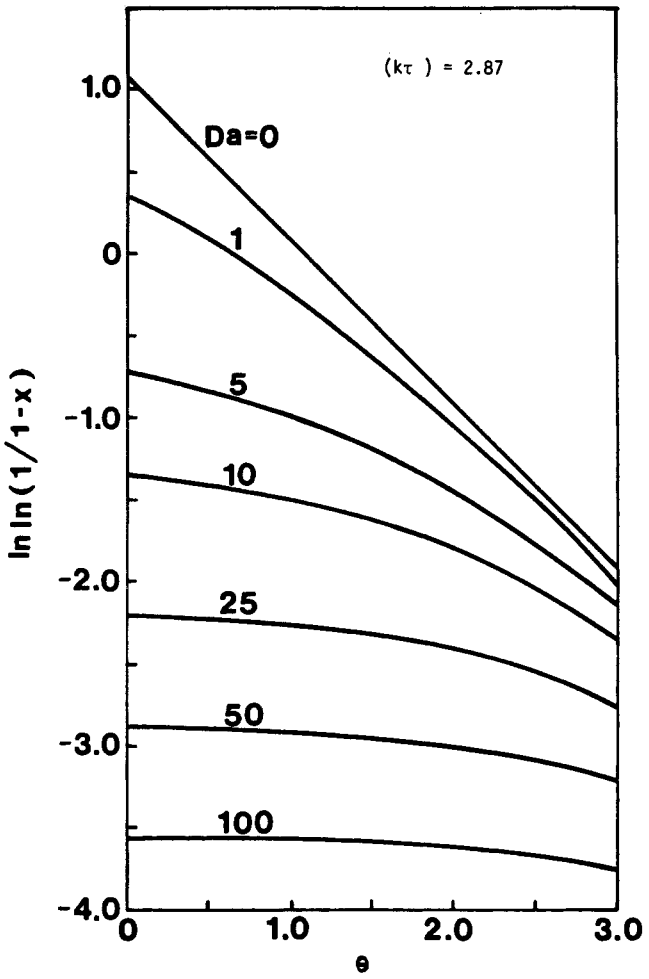

Figure 3. Conversion function vs. dimensionless time plots (Levenspiel plots).

number has a significant effect on the initial value of η_{et}, as well as its rate of change with θ.

Reactor Applications

The conversion-time relationship for an ideal plug flow reactor, obtained by incorporating the time-dependent external effectiveness factor in the reactor mass balance, is:

$$ln\ ln\left(\frac{1}{1-x}\right) = ln\ k\tau + ln\ (\eta_{et}) \tag{7}$$

Plots of this conversion function vs. time are shown in Figure 3. For a purely chemical reaction controlled system, Eq. 4a applies and Eq. 7 becomes, for $Da \rightarrow 0$,

$$ln\ ln\left(\frac{1}{1-x}\right) = ln\ k\tau - k_d\ t \tag{7a}$$

This is the equation presented by Levenspiel (1972) for diffusion-free systems.

For $Da \rightarrow \infty$, η_{et} is given by Eq. 4b; Eq. 7 now reduces to:

$$ln\ ln\left(\frac{1}{1-x}\right) = ln\ (k\tau/Da) = ln\ [(K_m\ a_s)\ \tau] \tag{7b}$$

Hence, experimental data, when plotted as $ln\ ln\ (1/1-x)$ vs. time, would be linear for the purely chemical reaction controlled system, with the slope being a valid estimate of the intrinsic deactivation constant. As the value of Da increases, the slope of the lines, and hence the magnitude of the apparent deactivation rate constant would gradually decrease, finally becoming equal to zero for the completely mass transfer controlled system. This situation is depicted in Figure 3, which suggests the extension of catalyst lifetime as the external transport limitations are increased. Note, however, that as $t \rightarrow \infty$, $\overline{\eta}_{et} \rightarrow 1$, and the slope of the lines will approach the intrinsic value.

OVERALL TIME-DEPENDENT CATALYTIC EFFECTIVENESS

Retaining the assumptions of the previous section, an overall, isothermal time-dependent effectiveness for a porous, spherical catalyst can easily be derived. The mass conservation equation for the spherical particle, assuming slow deactivation, is:

$$D\left[\frac{d^2C_r}{dr^2} + \frac{2}{r}\frac{dC_r}{dr}\right] = k_i\ C_r\ a \tag{8}$$

where a is still given by Eq. 5.

The boundary conditions, at any instant of time, are:

$$\frac{dC_r}{dr} = 0\ ;\ r = 0$$
$$D\frac{dC_r}{dr} = K_m\ (C - C_r)\ ;\ r = R \tag{9}$$

Solution of Eqs. 8 and 9 yields the following relationship for the dimensionless concentration profile inside the particle, at any instant of time:

$$\psi = \left(\frac{C_r}{C_o}\right) = \frac{1}{\xi}\left(\frac{Bim}{3hA}\right)\left(\frac{1}{\coth\ (3hA) - \frac{1}{(3hA)} + \frac{Bim}{(3hA)}}\right)\left(\frac{\sinh\ (3hA\xi)}{\sinh\ (3hA)}\right) \tag{10}$$

where the various dimensionless terms are:

$$h = \frac{R}{3}\sqrt{k_i/D} = \text{Thiele modulus}$$

$$Bim = \frac{K_m\ R}{D} = \text{Mass Biot number}$$

$$A = \exp\ (-\theta/2)\ ;\ \theta = (k_d\ t)$$

and

$$\xi = (r/R)$$

As before, two choices for the definition of catalytic effectiveness exist: it can be defined as the ratio of the overall rate for the particle at any instant of time to the purely chemical reaction controlled rate, either at zero time (initialized overall effectiveness factor), or at the same instant of time (instantaneous overall effectiveness factor). The former definition results in the following relationship for the catalytic effectiveness:

$$\eta_{ot} = \left(\frac{3A^2}{\phi'}\right)\left(\frac{Bim}{\phi'}\right)\left(\frac{\coth\ \phi' - 1/\phi'}{\coth\ \phi' - 1/\phi' + Bim/\phi'}\right) \tag{11}$$

where $\phi' = (3hA)$.

For four values of the Biot number, Figure 4 shows the overall Initialized effectiveness of Eq. 11, as a function of dimensionless time, with Thiele modulus as parameter. For Bim = 1,000, the external diffusion resistance is negligible; the plots are equivalent to those of Krishnaswamy and Kittrell (1981) for internal diffusion. As the magnitude of the Biot number decreases, external diffusion influences become more pronounced. The curves for Bim = 1.0 and large values of h are flat, suggesting very slow rate of decay. Clearly, the effects of adding finite external resistances to an internal diffusion-limited particle (with $hA > 5.0$) are further reductions in overall effectiveness and rate of decay.

The alternate definition of overall catalytic effectiveness, as the ratio of global and chemical reaction controlled rates at the

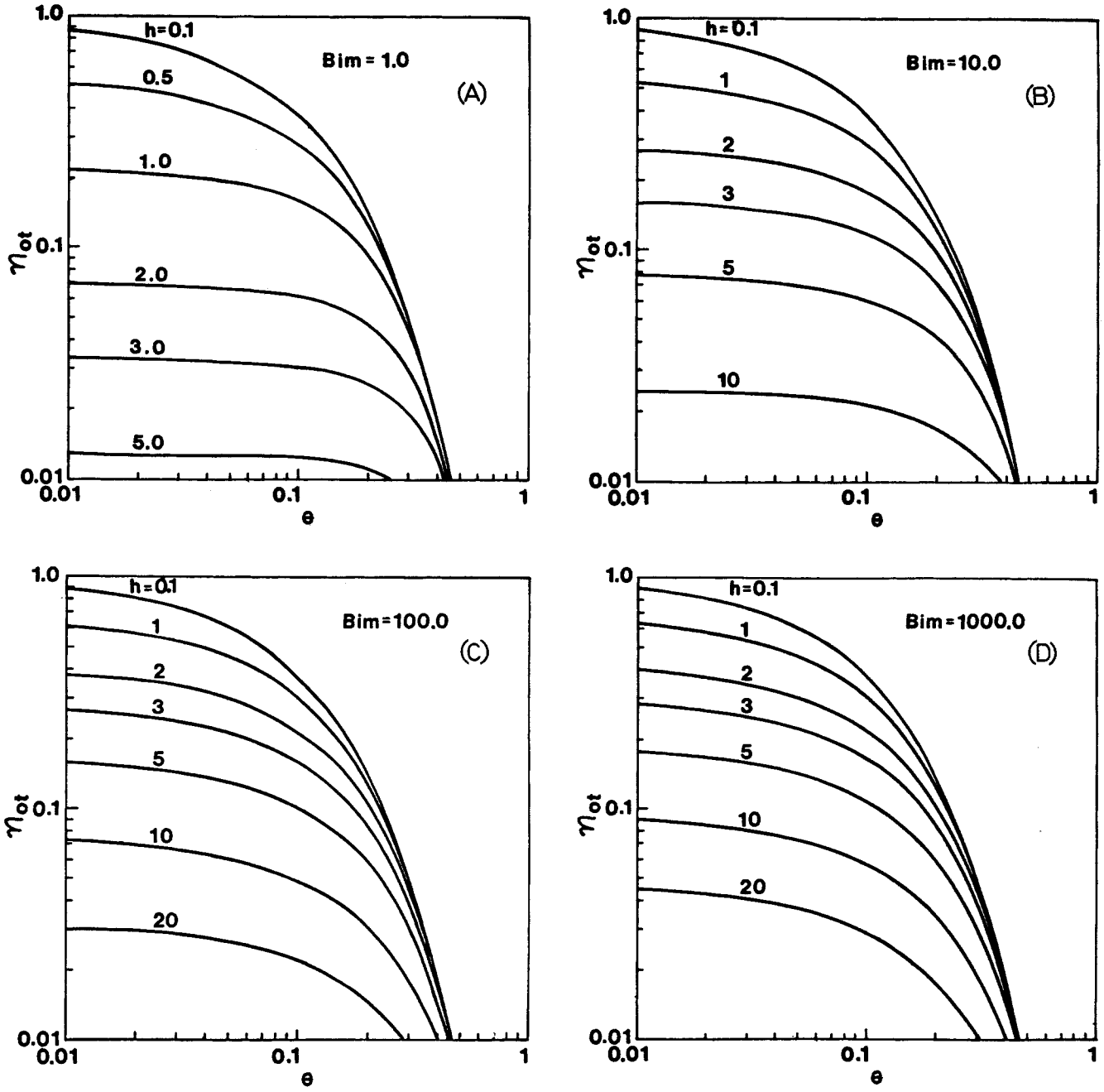

Figure 4. Initialized overall effectiveness factor vs. dimensionless time.

same instant of time, leads to the following representation:

$$\overline{\eta}_{ot} = \frac{\eta_{ot}}{a} = \left(\frac{3}{\phi'}\right)\left(\frac{Bim}{\phi'}\right)\left[\frac{\coth\phi' - 1/\phi'}{\coth\phi' - 1/\phi' + Bim/\phi'}\right] \quad (12)$$

The behavior of $\overline{\eta}_{ot}$ vs. θ curves of Figure 5 is in accordance with intuitive expectations. Diffusional limitations decrease and $\overline{\eta}_{ot}$ increases from its initial value to unity, as time proceeds. Again, severe internal diffusion limitations (large values of h) and strong external diffusion resistances (low values of Bim) tend to decrease the overall instantaneous effectiveness and at the same time, slow down the rate of loss of conversion.

Limiting Cases

Negligible External Diffusion ($Bim \to \infty$). Eq. 11 can be rewritten as:

$$\eta_{ot} = \frac{3A^2}{\phi'}\left(\coth\phi' - \frac{1}{\phi'}\right)\left[\frac{Bim/\phi'}{\coth\phi' - 1/\phi' + Bim/\phi'}\right] \quad (13)$$

Upon application of L'Hospital's rule, the term within the square brackets becomes unity and

$$\eta_{ot} = \frac{A}{h}\left(\coth\phi' - \frac{1}{\phi'}\right) \quad (13a)$$

For the case of no deactivation, i.e., when $t = 0$, this further reduces to the conventional isothermal effectiveness factor form:

$$\eta = \frac{1}{h}\left(\coth\phi - \frac{1}{\phi}\right) \quad (13b)$$

Severe Internal Diffusion ($\phi' \geq 15$, *Finite Bim*). For $\phi' \geq 3.0$, Eq. 13 reduces to:

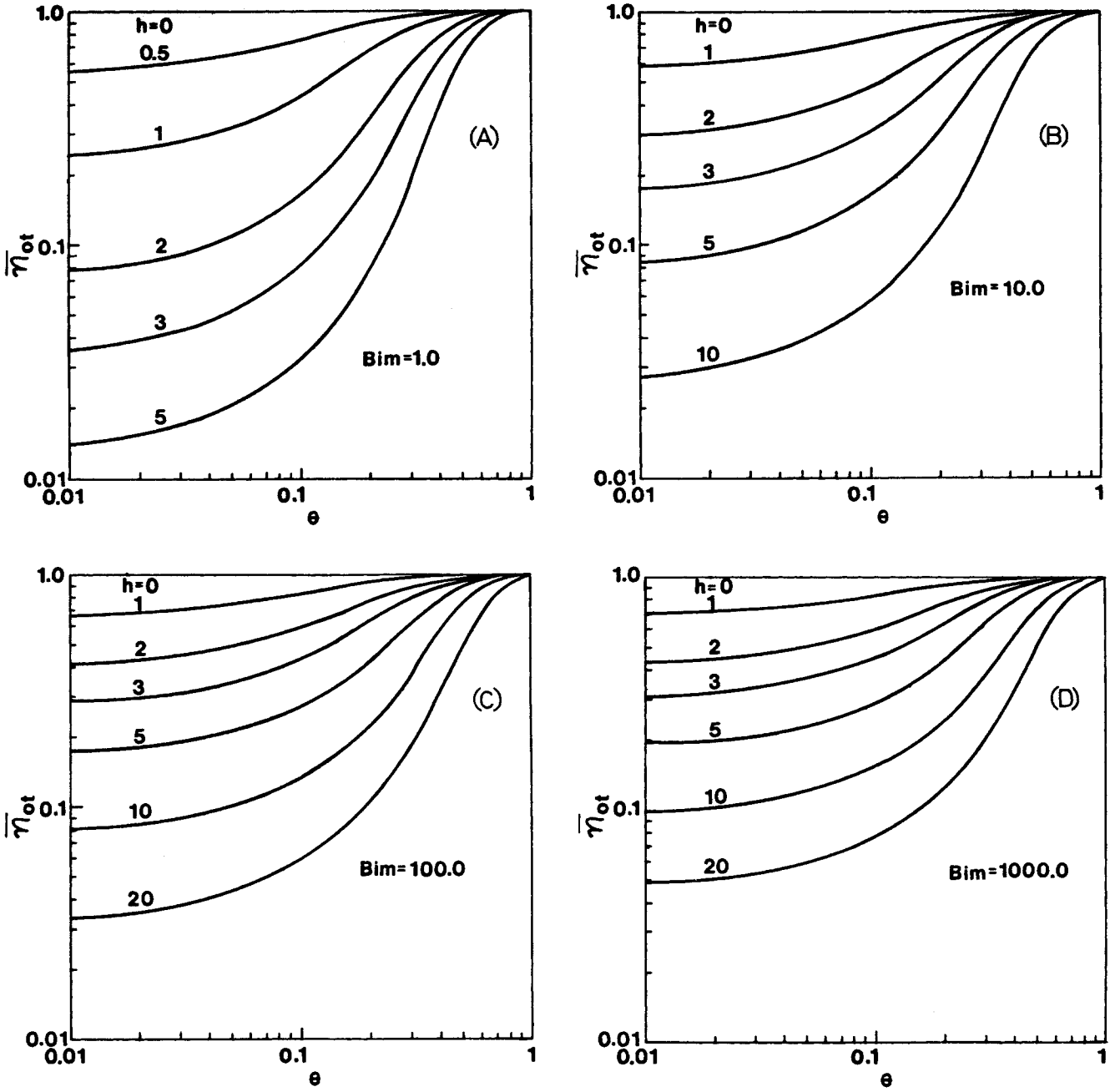

Figure 5. Instantaneous overall effectiveness factor vs. dimensionless time.

$$\eta_{ot} = \frac{3A^2}{\phi'}\left(\frac{Bim}{\phi'}\right)\left(\frac{\phi' - 1}{\phi' - 1 + Bim}\right) \tag{13c}$$

For $\phi' \geq 15.0$, the above equation further reduces to:

$$\eta_{ot} = \frac{3A^2}{\phi'}\left(\frac{Bim}{\phi' + Bim}\right) \tag{13d}$$

Severe Internal Diffusion with Negligible External Diffusion ($\phi' \geq 15$, $Bim \to \infty$). Under these conditions, Eq. 13d becomes, upon application of L'Hospital's rule,

$$\eta_{ot} = \frac{A}{h} \tag{13e}$$

Large Da (large h, low Bim). For this case, Eq. 13d simplifies to:

$$\eta_{ot} = \frac{3A^2}{\phi'}\left(\frac{Bim}{\phi'}\right) = \frac{Bim}{3h^2} = \frac{K_m}{k_i}\cdot\frac{3}{R} = \frac{K_m}{k}\cdot a_s$$

i.e.,

$$\eta_{ot} = \frac{1}{Da} \tag{13f}$$

which is the result presented in the previous section (Eq. 4b).

Interpretation of Reactor Data

In the presence of external and internal diffusion limitations, the conversion-time relationship for a plug flow reactor, analogous to Eq. 7, is:

$$ln\ ln\left(\frac{1}{1-x}\right) = ln\ (k\tau) + ln\ (\eta_{ot}) \tag{14}$$

where η_{ot} is a function of dimensionless time, Thiele molulus and Biot number, as given by Eq. 11. Plots of $ln\ ln\ (1/1-x)$ vs. θ (Levenspiel Plots), with h as parameter, for four values of Bim, are shown in Figure 6.

TABLE 1. ANALOGOUS CHARACTERISTICS OF DIFFUSION FOR DEACTIVATING AND NONDEACTIVATING SYSTEMS

Condition	Kinetic Analysis	Deactivation Analysis
Slope without Diffusion	E	k_d
Slope with Severe Internal Diffusion ($hA \geq 5.0$)	$E/2$	$k_d/2$
Slope with Severe External Diffusion ($Da\ a >> 1.0$)	$\rightarrow 0$	$\rightarrow 0$
Dependence on Particle Size	Reciprocal	Reciprocal

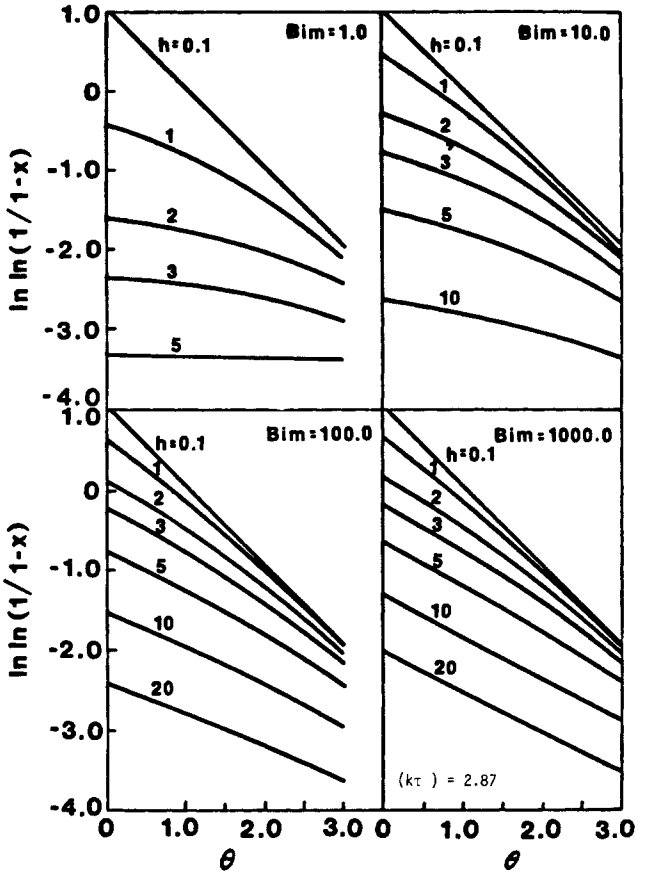

Figure 6. Conversion function vs. dimensionless time plots (Levenspiel plots).

With severe external diffusion, the slope of the Levenspiel plots approaches zero, as does the slope of Arrhenius plots (except for the temperature dependence of the mass transfer coefficient) in classical kinetic analysis. Table 1 summarizes this diffusional analogy.

To illustrate this analogy further, $\ln(\eta_{ot})$ in Eq. 14 can be linearized using Taylor expansion about zero time. For the case of severe internal diffusion limitation with finite external resistances, η_{ot} is given by Eq. 13d. Linearization for this case results in the following conversion-time relationship:

$$\ln\ln(1/1-x) = \ln(k_p \cdot \tau) - k_{dp} \cdot t \qquad (16)$$

where the apparent reaction and deactivation rate constants are given by:

$$k_p = \left(\frac{k}{h}\right)\left[\frac{1}{1+\left(\frac{3h}{Bim}\right)}\right] \qquad (17)$$

$$k_{dp} = \left(\frac{k_d}{2}\right)\left[\frac{1}{1+\left(\frac{3h}{Bim}\right)}\right] \qquad (18)$$

These relationships give an indication of how intrinsic reaction and deactivation rate constants are altered in an analogous manner by the presence of internal and external diffusion resistances. Since the term in brackets in the above equations is always less than unity, the effect of adding finite external transport resistances to a severely internal diffusion-limited system ($hA \geq 5.0$) is to further reduce the magnitude of the apparent rate constants. In the extreme limit of severe internal and external transport limitations, k_p and k_{dp} will approach zero values and rates of reaction and deactivation will be negligible. Even under these circumstances, however, as $t \rightarrow \infty$, $\overline{\eta}_{ot}$ will approach unity (Figure 5) corresponding to a completely deactivated particle, and the slope of the Levenspiel plots will eventually increase to its intrinsic value.

In Conclusion

Under the presence of severe internal and external diffusional limitations, theory predicts that the apparent deactivation rate constant can decrease below the one-half value limit for internal diffusion alone, and even approach zero asymptotically. However, similar effects on the rate of apparent decay could also be caused by other reaction and deactivation rate forms. At the present time, the state-of-the-art has not developed enough to distinguish between such kinetic and diffusional effects.

NOTATION

A = $\exp(-k_d\, t/2)$
a = fractional catalyst activity
a_s = external specific surface area of particle, cm²/g
Bim = Mass Biot number = $(K_m \cdot R/D)$
C_r = concentration of reactant inside spherical particle, g-mol/cc
C_R = concentration of reactant at the surface of spherical particle, g-mol/cc
C = bulk stream concentration of reactant, g-mol/cc
D = effective diffusivity within spherical particle, cm²/s
Da = Damköhler number = $(k/K_m \cdot a_s)$
h = Thiele modulus = $\frac{R}{3}\sqrt{k_i/D}$
k_i = intrinsic reaction rate constant, s^{-1}
k = reaction rate constant = (k_i/ρ_p), cc/(s)(g cat.)
k_p = apparent reaction rate constant, cc/(s)(g cat.)
k_d = deactivation rate constant, h^{-1}
k_{dp} = apparent deactivation rate constant, h^{-1}
K_m = mass transfer coefficient, cm/s
R_G = global rate of reaction, g-mol/(cc)(s)
R = radius of spherical particle, cm
r = radial position, cm
t = process time, h
x = fractional conversion of reactant

Greek Letters

η_{et} = initialized external effectiveness factor given by Eq. 4
$\overline{\eta}_{et}$ = instantaneous external effectiveness factor given by Eq. 6
η_{ot} = initialized overall effectiveness factor given by Eq. 11

$\overline{\eta}_{ot}$ = instantaneous overall effectiveness factor given by Eq. 12
θ = dimensionless time = $(k_d \cdot t)$
ξ = dimensionless radial position = r/R
ρ_p = density of catalyst particle, g/cc
τ = space time, (s)(g cat.)/(cc)
ϕ = dimensionless group = $(3h)$
ϕ' = dimensionless group = $(3hA) = (\phi \cdot A)$
ψ = dimensionless concentration = (C_r/C_R)

LITERATURE CITED

Carberry, J. J., "Chemical and Catalytic Reaction Engineering," McGraw Hill (1976).
Chu, C., "Effect of Adsorption on the Fouling of Catalyst Pellets," *Ind. Eng. Chem. Fund.*, **7**, 509 (1968).
Hegedus, L. L., and E. E. Petersen, "Study of the Mechanism and Kinetics of Poisoning Phenomena in a Diffusion-influenced Single Catalyst Pellet," *Chem. Eng. Sci.*, **28**, 69 (1973).
Krishnaswamy, S., and J. R. Kittrell, "Diffusional Influences on Deactivation Rates," *AIChE J.* (1981).
Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed., John Wiley & Sons, Inc. (1972).
Lin, S. H., "Nonisothermal Heterogeneous Reaction in a Denaturable Immobilized Enzyme Catalyst," *Biotech. Bioeng.*, **17**, 1237 (1975).
Masamune, S., and J. M. Smith, "Performance of Fouled Catalyst Pellets," *AIChE J.*, **12**, 384 (1966).
Murakami, Y., et al., "Effect of Intraparticle Diffusion on Catalyst Fouling," *Ind. Eng. Chem. Fund.*, **7**, 599 (1968).
Ollis, D. F., "Diffusion Influences in Denaturable Insolubilized Enzyme Catalysts," *Biotech. Bioeng.*, **14**, 871 (1972).

Manuscript received January 13, 1978; revision received July 14, and accepted July 16, 1980.

Design and Experimental Evaluation of Controllers for Process Undisturbability

Selected state and/or output variables can be made undisturbable, i.e., invariant, to arbitrary, unmeasured changes in specific input variables by properly designed feedback and feedforward controllers. Simulation and experimental applications to a computer-controlled, pilot plant evaporator gave results superior to conventional controllers.

Necessary and sufficient conditions for undisturbability are expressed in terms of the structure of the coefficient matrices of the state space model and equivalently of the corresponding eigenvector matrix. The design procedure normally includes arbitrary specification of all closed-loop eigenvalues and up to r elements of each eigenvector, where r is the number of control (manipulated) variables.

S. L. SHAH
D. G. FISHER
and
D. E. SEBORG

Department of Chemical Engineering
University of Alberta
Edmonton, Alberta, Canada

SCOPE

This paper describes a design procedure for process controllers that makes selected state and/or output variables *undisturbable*, i.e., invariant, to arbitrary changes in specified input variables. Note that if all process outputs are made undisturbable, the process can be said to exhibit "perfect" regulatory control. Thus, this approach should be of interest in a wide variety of process applications.

The first step was to derive the necessary and sufficient conditions to make selected state or output variables undisturbable with respect to specified input variable(s). The next step was to determine what systems can be made undisturbable by the use of *constant* feedforward and/or feedback controllers. The final step was to develop a practical design procedure and to evaluate the resulting controllers experimentally.

Other authors have dealt with *rejection* of disturbances before they reach the system outputs; *invariance* to external disturbances; and *localization* of the disturbances so they do not affect the system outputs. These concepts are similar to *undisturbability* as discussed in this paper, but are less rigorously defined and include significant differences. For example, disturbance localization is used in the context of a geometric interpretation. Therefore, this work includes a precise definition of *undisturbability* and points out some of the parallels and differences with familiar concepts such as *uncontrollability* and *unobservability*.

Necessary and sufficient conditions, in geometric terms, for the existence of state feedback controllers that localize disturbances from the system outputs have been presented by Wonham and Morse (1970), Bhattacharyya (1974), and the authors (Shah et al. 1974, 1977). Necessary and sufficient conditions for simultaneous disturbance localization plus setpoint/output decoupling have been reported by Fabian and Wonham (1975) and Chang and Rhodes (1975). Since the necessary and sufficient conditions were already known, this work focused on developing equivalent conditions in state-space terms that could be more easily applied, and which would lead to a practical, easily implementable design procedure. In contrast to the synthesis results of Wonham and Morse (1970), the emphasis here is on the use and application of structural results of Shah et al. (1977) to design controllers for undisturbability. New theoretical results on the design for undisturbability using proportional plus integral feedback are also included.

Also since to the best of the author's knowledge this design approach has never been evaluated *experimentally*, one of the prime objectives was to apply it to the computer-controlled, pilot-plant evaporator at the University of Alberta.

D. E. Seborg is presently at Department of Chemical and Nuclear Engineering, University of California, Santa Barbara, CA.