Fixed Bed with Catalyst Deactivation: On-Line Estimation of Deactivation, Control, and Design

On-line measurements of temperature and concentration and the global rate for fresh catalyst can be used to estimate a measure of catalyst deactivation. A feedback control policy is obtained from this measure of catalyst deactivation for maintaining the reactor outlet conversion constant with time at a desired level. This feedback control enables one to maintain the desired conversion without any knowledge of deactivation kinetics. These results are applicable to any type of deactivation. The optimal control can easily be taken into consideration for reactor design. This combination of process design and control with due consideration of catalyst deactivation for both is shown to result in a substantial improvement of the reactor performance.

JAN-CHEN HONG and
HONG H. LEE
Department of Chemical Engineering
University of Florida
Gainesville, FL 32611

SCOPE

An important problem in operating a fixed bed with catalyst deactivation is that of finding a means of estimating the extent of catalyst deactivation from on-line measurements, because of the uncertainty regarding the deactivation. Another problem is using a feedback scheme to control the conversion at a desired level. The optimization problem of maximizing a performance index for such a reactor has been solved as a Bolza's problem, the solution leading to very concise but powerful extremum conditions (Szepe and Levenspiel, 1968; Chou et al., 1967), and open-loop control schemes have been devised (Ogunye and Ray, 1971; Haas et al., 1974). The open-loop control, however, is much less attractive for implementation than a feedback control scheme.

The usual design practice is to specify the reactor size without any consideration for catalyst deactivation. The problem of combining process design and control with due consideration of catalyst deactivation for both is perhaps more important than the problems raised above since the reactor size limits the extent to which the best possible performance can be attained by process control. These problems are dealt with in this paper.

CONCLUSIONS AND SIGNIFICANCE

A measure of the extent of deactivation can be determined from the on-line measurements of inlet temperature and outlet concentration along with the intrinsic rate of a single reaction for an adiabatic reactor. Additional measurements of coolant temperature are required for a nonadiabatic reactor. These results can be extended to multiple reactions in a rather straightforward manner. The measure of deactivation is determined in such a way that a piecewise feedback control scheme follows directly from it. This feedback control maintains the conversion within a band about a desired level of conversion. It is shown that the bandwidth can in practice be made large enough without affecting the maximum of a performance index. These results enable one to carry out feedback control of the reactor without any knowledge of catalyst deactivation for a given desired level of converison. Further, the results are applicable to any type of deactivation, whether the deactivation is dependent or independent and whether the kinetics are separable or nonseparable.

The problem of combining process control with process design while giving due consideration of the deactivation for both can be solved in a straightforward manner using the feedback control scheme and the approach of reactor point effectiveness. However, detailed knowledge of deactivation has to be known to solve this problem. It is shown that the choice of reactor size can substantially affect the reactor performance. The solution yields the optimal reactor size and an optimal way of manipulating the inlet temperature based on on-line measurements for those reactors for which detailed knowledge of deactivation is available. Even when there is some uncertainty about the knowledge, the procedure yields approximate ranges of the optimal values and also some directions as to what to choose. These results enable one to fully account for catalyst deactivation for a substantial improvement in the reactor performance.

INTRODUCTION

The usual practice of operating a fixed bed with catalyst deactivation is to raise the reactor inlet temperature to compensate for the declining catalytic activity so as to maintain a desired conversion. The catalyst is regenerated when the required temperature becomes too high. The reactor is usually designed to yield the desired conversion without any consideration for the catalyst deactivation.

A number of questions can be raised regarding these usual practices. An immediate question is how we should control the operating conditions of a reactor designed in the usual way. This question has been the subject of many studies (Szepe and Levenspiel, 1968; Chou et al., 1967; Ogunye and Ray, 1971; Haas et al., 1974). The control policies resulting from these studies either lead to an open-loop control or require detailed knowledge of catalyst deactivation. Although considerable progress has been made in our understanding of catalyst deactivation, it is still the least understood of all facets involved in the quantitative description of a fixed bed. This uncertainty regarding the deactivation and the compounded effect of deactivation and diffusion in a fixed bed make it quite unattractive to implement an open-loop control policy. A central question, therefore, is whether a measure of catalyst deactivation can be estimated from process measurements, and, if so, how a feedback control can be realized with the measurements made. In the first part of this paper we present a method of determining a measure of catalyst deactivation and then utilize the result for a feedback control policy.

A much more important question than the one discussed above has to do with the inherent interrelationship between process controllability and process design. It is intuitively clear that the process design dictates the controllability, for the parameters involved in describing a process contain design parameters which in turn dictate the way the process can be controlled. It is also clear, therefore, that the best possible performance of the process can be attained when process design and control are combined. For the reactor under consideration, this means that the best possible performance can be attained when the catalyst deactivation is taken into consideration not only for the reactor control but also for the reactor design. The question, therefore, is what the reactor size and the feedback control should be for the best performance of the reactor. In the latter part of this paper we provide the answer to this question.

ON-LINE ESTIMATION AND A FEEDBACK CONTROL: A SINGLE REACTION

Consider a nonadiabatic reactor in which a single reaction takes place. Assuming that the radial gradients can be neglected, pseudosteady-state, one-dimensional balance equations can be written as

$$\frac{dC}{dz} = -\tau R_G;\ \tau = Z(1-\epsilon_B)/v,\ z\epsilon[0,1] \tag{1}$$

$$\frac{dT}{dz} = \left(\frac{-\Delta H}{\rho C^b}\right)\tau R_G + \frac{(mC_p)_c}{mC_p}\frac{dT_c}{dz} \tag{2}$$

$$\frac{dT_c}{dz} = -\frac{2U\pi R_t Z}{(mC_p)_c}(T - T_c) \tag{3}$$

where C and T are the concentration and temperature of the reactant, and T_c is the countercurrent coolant temperature. Here m and m_c are the reaction fluid and coolant mass rates; C_p and $(C_p)_c$ are the specific heat capacities for the reaction fluid and the coolant; Z is the reactor length; v is the superficial velocity assumed constant in the radial direction; ϵ_B is the bed porosity; U is the overall heat transfer coefficient; and R_t is the tube radius. The global rate based on pellet volume, R_G, can be expressed as

$$R_G = h(z;t)k_a f(C,K_j) \tag{4}$$

where k_a is the apparent rate constant in the form of the Arrhenius relationship and f represents the apparent dependence of the rate on concentration and equilibrium constants K_j. In the absence of diffusion and deactivation effects, the apparent rate reduces to intrinsic rate. The activity factor h (Wheeler, 1955) is defined by

$$h(z;t) \equiv \frac{(R_G)_d}{(R_G)_f} \tag{5}$$

where the subscripts d and f denote fresh and deactivated catalyst, respectively. This activity factor decreases with time due to catalyst deactivation and thus depends on time. It should be recognized in Eq. 5 that the definition of h is general, in that h can depend on the concentration C and thus is applicable to dependent deactivation. Since C is a function of z at a given time, $h(C;t)$ is a subset of $h(z;t)$. The pseudo steady state assumption is based on the fact that the time scale of catalyst deactivation is many orders of magnitude larger than that for the reactor to reach a steady state.

For the purpose of deriving an expression for a measure of the extent of deactivation, we rewrite Eq. 1 with the aid of Eq. 4 as

$$\frac{dC}{dz} = -\tau h(z;t)k_a f(C,K_j) \tag{6}$$

Here again, one can write h as $h(C;t)$ in place of $h(z;t)$ for dependent deactivation. This equation can be integrated from the reactor inlet to the outlet to give

$$-\int_{C_{in}}^{C_e} \frac{dC}{\tau k_a(T) f(C,K_j)} = \int_0^1 h(z;t)dz \equiv H(1;t) \qquad (7)$$

where C_e and C_{in} are the concentrations at the outlet and the inlet respectively at any given time. By definition, $H(1,0) = 1$ since at time zero the activity factor h is uniform at unity throughout the reactor. The quantity H is a measure of the extent of catalyst deactivation which represents the activity for the reactor and thus may be termed "reactor activity factor." The value of H decreases as the outlet conversion decreases due to the catalyst deactivation for a given inlet temperature.

The temperature appearing in Eq. 7 needs to be related to concentration for the integration. Integrating Eq. 2 from the reactor inlet to z, we obtain

$$T = T_{\text{in}} + \left(\frac{-\Delta H}{\rho C_p}\right)(C_{\text{in}} - C) - \frac{(mC_p)_c}{mC_p}(T_{c_{\text{out}}} - T_c) \qquad (8)$$

where $T_{c_{\text{out}}}$ is the coolant temperature at $z = 0$ and T_{in} is the reactor inlet temperature. Consider first an adiabatic reactor for which Eq. 8 reduces to

$$T = T_{\text{in}} + \left(\frac{-\Delta H}{\rho C_p}\right)(C_{\text{in}} - C) \qquad (9)$$

Now that T is expressed in terms of C and readily measurable inlet conditions, the value of H can be calculated by simply carrying out the integration numerically with respect to C in Eq. 7 with the measured outlet concentration. For instance, the apparent rate constant $k_a(T)$ for an adiabatic reactor can be expressed as

$$k_a = k_{a_0} \exp\left\{\frac{-E_a/R_g}{T_{\text{in}} + \left(\frac{-\Delta H}{\rho C_p}\right)(C_{\text{in}} - C)}\right\} \qquad (10)$$

where k_{a_0} is the apparent preexponential factor and E_a is the apparent activation energy. The equilibrium constants K_j can be expressed in a similar manner. For a nonadiabatic reactor to which Eq. 8 applies, the calculation of H requires measurement of coolant temperature along the reactor length. This measurement can be used in Eq. 3 for the calculation of T as a function of z. With these T and T_c the corresponding change in C for a selected interval of Δz can be obtained from Eq. 8 which in turn can be used in Eq. 7 for the calculation of H.

An immediate use of the reactor activity factor calculable from the temperature and concentration measurements is in the manipulation of the reactor inlet temperature for the purpose of maintaining the desired conversion. Suppose that the inlet temperature is adjusted intermittently, as in the usual operation of a reactor, to compensate for the declining activity. Consider an adiabatic reactor for clarity. If we let the subscript c denote the current quantities and n the new quantities resulting from a change in the reaction inlet temperature, Eq. 7 can be written twice to give

$$H_c = \int_0^1 h_c(z;t)dz = -\int_{C_{\text{in}}}^{C_e} \frac{dC}{\tau k_a[T;(T_{\text{in}})_c]f(C,K_j)} \qquad (11)$$

$$H_n = \int_0^1 h_n(z;t)dz = -\int_{C_{\text{in}}}^{C_d} \frac{dC}{\tau k_a[T;(T_{\text{in}})_n]f(C,K_j)} \qquad (12)$$

where C_d is the desired concentration which will be attained by changing the current inlet temperature $(T_{\text{in}})_c$ to the new inlet temperature $(T_{\text{in}})_n$. As we shall see in the next section, the activity factors h_c and h_n depend mainly on the fraction of catalyst deactivated and slightly on the temperature difference between bulk fluid and pellet surface. If we neglect this change in the temperature difference for the time being, we can set

$$h_c(z;t) = h_n(z;t) \qquad (13)$$

for the purpose of calculating the new inlet temperature that yields the desired outlet concentration. The justification here is that the fraction of catalyst deactivated changes negligibly for all points along the reactor while the inlet temperature is adjusted from the current value to a new value. Note that the justification is still valid for reactant-dependent deactivation; i.e., $h_c\{C(z);t\} = h_n\{C(z);t\}$. Equations 11 through 13 together with Eq. 10 can be used to obtain

$$-\int_{C_{\text{in}}}^{C_d} \frac{dC}{\tau k_{a_0} \exp\left[\frac{-E_a/R_g}{(T_{\text{in}})_n + \left(\frac{-\Delta H}{\rho C_p}\right)(C_{\text{in}} - C)}\right] f(C,K_j)} = H_c \qquad (14)$$

where H_c is the known, current reactor activity factor calculated from Eq. 11 just prior to the change in the inlet temperature, based on the measured current outlet concentration C_e and inlet temperature $(T_{\text{in}})_c$. Equation 14 can now be solved for $(T_{\text{in}})_n$ by a numerical technique such as Newton's method or bisection method since the left hand side of the equation can be evaluated, given a value of $(T_{\text{in}})_n$. The value of $(T_{\text{in}})_n$ that satisfies Eq. 14 will yield the desired conversion, and therefore the inlet temperature can be changed to $(T_{\text{in}})_n$ to maintain the conversion at the desired level.

The control policy of Eq. 14 is a piecewise algorithm for the manipulation of the inlet temperature. Therefore, it will maintain the conversion at the desired level only for a short period of time after a change in the inlet temperature, and the conversion thereafter will gradually decrease with time until the inlet temperature is raised again. A bandwidth for the allowed decrease in conversion can be used to trigger the adjustment of the reactor inlet temperature. The control algorithm for a nonadiabatic reactor can be obtained in a similar manner. The equation corresponding to Eq. 14 is

$$-\int_{C_{\text{in}}}^{C_d} \frac{dC}{\tau k_a[T;(T_{\text{in}})_n]f(C,K_j)} = H_c \qquad (15)$$

This equation, however, needs to be solved in conjunction with Eqs. 3 and 10 for $(T_{\text{in}})_n$ along with the measured T_c profile.

As indicated earlier, we assumed that the heat transfer resistance across the interface between bulk fluid and pellet surface is negligible in arriving at the control policies of Eqs. 14 and 15. If there exists a significant temperature difference between bulk fluid and pellet surface, Eqs. 13 through 15 no longer hold. The discrepancy between h_c and h_n caused by the temperature difference can be compensated by adjusting C_d as follows:

$$\tilde{C}_{d_i} = C_d + \beta(\tilde{C}_{d_{i-1}} - C_{e_{i-1}}) \quad i = 1,2,\ldots$$
$$C_{d_0} = C_d \qquad (16)$$

where $\tilde{C}_{d_i}$ is the adjusted C_d when a step change in the inlet temperature, which is triggered by the bandwidth constraint, made at the ith step and β is a proportionality constant with a value between zero and unity. Thus, for a given maximum decrease in the outlet concentration from the desired value, the piecewise feedback control algorithm can be stated as follows:

$$-\int_{C_{\text{in}}}^{\tilde{C}_{d_i}} \frac{dC}{\tau k_a[T;(T_{\text{in}})_i]f(C,K_j)} = (H_c)_{i-1} \quad i = 1,2,\ldots \qquad (17)$$

where $(H_c)_{i-1}$ is calculated from

$$(H_c)_{i-1} = -\int_{C_{\text{in}}}^{C_{e_{i-1}}} \frac{dC}{\tau k_a[T;(T_{\text{in}})_{i-1}]f(C,K_j)} \quad i = 1,2,\ldots \qquad (18)$$

$$(H_c)_0 = 1$$

with the measured outlet concentration and inlet temperature, and C_{d_i} is given by Eq. 16. Each time the outlet concentration reaches the allowed bandwidth, the new inlet temperature $(T_{\text{in}})_i$ is calculated for the manipulation of the inlet temperature. All that is required for the feedback control is the global rate for fresh catalyst.

NATURE OF REACTOR ACTIVITY FACTOR

Before we proceed to illustrate the calculation of the reactor activity factor and its use for the manipulation of the reactor inlet temperature, let us examine the nature of the reactor activity factor. By definition, it is an integrated value of local activity factor (Eq. 7). The local activity factor, which is the activity factor at a point in the reactor, can be obtained by solving pellet conservation equations. Instead of solving the conservation equations, we utilize the global rate obtained by Lee and Butt (1982) for a reaction affected by uniform deactivation and diffusion to get a clear picture of the local activity factor. The global rate for this case is

$$(R_G)_d = \frac{(1-\gamma)^{1/2}}{\dfrac{L}{[2D_ekI(C)]^{1/2}} - q} \tag{19}$$

where

$$I = \int_0^C g(\alpha)d\alpha \tag{20}$$

$$q = \frac{1.2E_a(-\Delta H)[2D_ekI]^{1/2}}{2h_mR_gT^2} \tag{21}$$

Here, γ is the fraction of catalyst deactivated, $g(C)$ the concentration dependence of the intrinsic rate of reaction, k the intrinsic rate constant, D_e the effective diffusivity, L the characteristic pellet length, and h_m the film heat transfer coefficient. The local activity factor can be obtained from the definition of Eq. 5:

$$h = \frac{(R_G)_d}{(R_G)_f} = \frac{(R_G)_d}{(R_G)_{d|\gamma=1}} = (1-\gamma)^{1/2}\left[\frac{1-q}{1-(1-\gamma)^{1/2}q}\right] \tag{22}$$

The same results hold (Lee and Ruckenstein, 1982) for nonuniform deactivation if γ is replaced with $\overline{\gamma}$, which is γ at the pellet surface, as long as $\overline{\gamma}$ is less than, say, 0.5.

It is clear from Eq. 22 that the local activity factor depends on γ and the quantity q which represents the heat transfer resistance across the bulk fluid-pellet surface interface. Since γ changes very little while the inlet temperature is raised to a new value, the magnitude of q determines whether h_c can be set to h_n. Therefore, the proportionality constant β in Eq. 16 can be chosen in accordance with the magnitude of q: for q much smaller than unity, the value of β can be set to zero, its value increasing with increasing q. Although the conclusion is made from the result for independent deactivation, the same should be valid for dependent deactivation since the factor causing the discrepancy between h_c and h_n is still the same, i.e., the heat transfer resistance across the interface, which q represents.

AN ILLUSTRATION

For an illustration of the calculation of H and its use for the reactor control, we consider the reaction system studied earlier (Lee and Butt, 1982), which is summarized in Table 1. For the reaction taking place in an adiabatic reactor, which is affected by diffusion and uniform, independent poisoning, the intrinsic rate of deactivation r_p is given (Lee and Butt, 1982a) by

$$r_p = k_{p_s}(1-\gamma)N$$

where k_{p_s} is the rate constant evaluated at the pellet surface temperature and N is the concentration of poisoning species. With the use of reactor point effectiveness (Lee and Butt, 1982), the reactor behavior can be simulated in a straightforward manner. The simulation results are used here as the process output for the purpose of illustrating the feedback control given by Eqs. 16 through 18. The control problem is how the inlet temperature should be manipulated whenever the outlet conversion decreases to a certain level from the desired conversion (bandwidth). Note that the intrinsic rate of deactivation r_p is used here only to generate the process response. In the feedback control, r_p is treated as an unknown and only the on-line measurements (simulated temperature and concentration) are used to manipulate the inlet temperature. The constraints are the maximum reactor temperature allowed and the final time at which the catalyst is regenerated as the time when the final bandwidth becomes one-tenth of the initial bandwidth. These constraints are also given in Table 1 along with the desired outlet concentration (conversion) and the reactor size. The initial inlet temperature for fresh catalyst is the one corresponding to the specified reactor size (τ) and outlet conversion, which is 691.8K. Since the film heat transfer coefficient is quite small for the example problem and thus the value of q is relatively large, the proportionality factor β in Eq. 16 was set at 0.95.

TABLE 1. PARAMETERS FOR THE MODEL REACTION SYSTEM

$$r(C,T) = kg(C) = k\left(\frac{C}{1+\xi}\right)$$

$$k = \exp\left(-\frac{12{,}000}{T} + 14.6\right)(1/s);$$

$$E_a = 23.76 \text{ kcal/mol } (99.55 \text{ kJ/mol})$$

$$\xi = \exp\left(\frac{3{,}600}{T} + 3.86\right)(\text{cm}^3/\text{mol})$$

$$C_{\text{in}} = 1.81 \times 10^{-5} \text{ mol/cm}^3$$

$$\left(\frac{-\Delta H}{\rho C_p}\right) = 4 \times 10^7 \text{ K cm}^3/\text{mol};$$

$$-\Delta H = 5.04 \text{ kcal/mol } (21.12 \text{ kJ/mol})$$

$$h_{\text{m}} = 3.245 \times 10^{-4} \text{ cal/s}\cdot\text{cm}^2\cdot\text{K}$$

$$N_{\text{in}} = 5 \times 10^{-3} \text{ mol/cm}^3$$

$$Q = 10^{-4} \text{ mol/cm}^3 \text{ cat. pellet}$$

$$k_p = \exp\left(-\frac{7{,}000}{T} + 3.27\right);$$

$$E_p = 13.86 \text{ kcal/mol } (58.07 \text{ kJ/mol})$$

$$D_p = 10^{-3} \text{ cm}^2/\text{s}$$

$$T_{\text{max}} = 1{,}280\text{K}$$

$$y = 70\% \quad \Delta y = 10\%$$

$$\tau = 20\text{s}$$

$$T_{\text{in},o} = 691.8\text{K}$$

The behavior of the model reactor resulting from the feedback control is shown in Figure 1. Initially, the inlet temperature is at its initial value and the outlet temperature, which is the maximum reactor temperature in this case, is well below the maximum temperature allowed. Due to the deactivation, however, both the conversion and the outlet temperature decrease with time and the conversion eventually reaches the lower bound given by the bandwidth, triggering an adjustment of the inlet temperature. The new inlet temperature $(T_{\text{in}})_1$ calculated by the algorithm of Eqs. 16 through 18 is seen to bring the conversion back to the desired level, the actual value being 69.96% as opposed to the desired value of 70%. A bisection method was used for the calculation of $(T_{\text{in}})_j$. When the outlet temperature reaches the allowed maximum, which occurs at around $t = 2 \times 10^4$s, it can no longer be brought back to the desired level due to the temperature constraint. Consequently the bandwidth decreases as time increases and eventually the bandwidth becomes less than one-tenth of the original bandwidth, resulting in the reactor shut-down for catalyst regeneration according to the constraint imposed. In practice, however, the conversion may be allowed to decrease below 60% when the maximum temperature is reached. In the example, the average conversion is essentially maintained at the middle of the bandwidth, which is 65%.

A few comments are in order here. The feedback control policy considered is a piecewise rather than a continuous control. The piecewise control necessitated by the pseudo steady state nature of deactivation with respect to the reactor response time allows us to avoid one problem in any feedback control involving dead time due to sampling and another one associated with reactor transients.

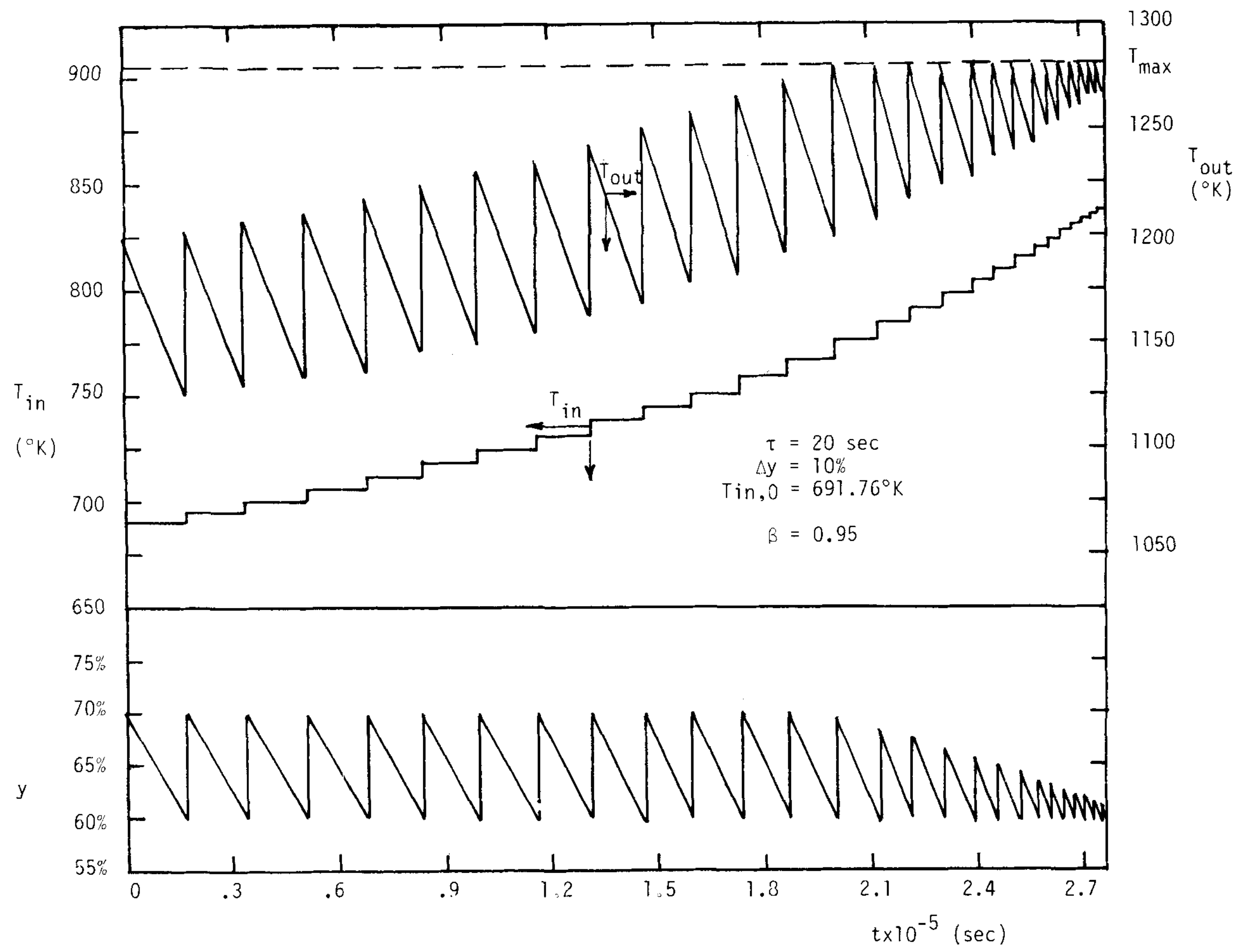

Figure 1. Temperature and conversion behavior of a fixed-bed subject to inlet temperature manipulation.

Inherent in the pseudo steady state assumption is the fact that the rate of deactivation is much slower than the rate of reaction. In terms of time, the deactivation is of the order of months for the majority of reactions carried out in a fixed bed, where the transients reach the steady state in a few residence times of the order of seconds. Therefore, the problem associated with "wrong way" transients (e.g., Crider and Foss, 1966) can be avoided since by the time a control action is to be taken, the reactor reaches a new, stable steady state. Further, the effect of dead time, which is of the order of minutes, on deactivation can be neglected since the extent of deactivation changes little in minutes.

MULTIPLE REACTIONS

For simple parallel reactions, we can write

$$A \rightarrow b_1 B$$

$$A \rightarrow b_2 C$$

where b_1 and b_2 are the ratios of stoichiometric coefficients. We restrict our attention here to an adiabatic reactor for brevity since a nonadiabatic reactor can be treated in the same manner as shown for a single reaction. Assuming that the same active sites are responsible for both reactions such that the local activity factor h is the same for both, the reactor conservation equations are

$$\frac{dC_A}{dz} = -\tau h(z;t)\{k_{a_1} f_1(C_A,C_B) + k_{a_2}(C_A,C_B)\} \tag{23}$$

$$\frac{dC_B}{dz} = b_1 \tau h(z;t) k_{a_1} f_1(C_A,C_B) \tag{24}$$

$$T = T_{in} + a_1(C_{A_{in}} - C_A) + a_2(C_B - C_{B_{in}}) \tag{25}$$

where $a_1 = -\Delta H_2/\rho C_p$ and $a_2 = -\Delta H_1(1 - \Delta H_2/\Delta H_1)\rho C_p b_1$. Equation 25 results when the heat balance equations are combined with the mass balance equations. Here the global rates for the first and second reactions are expressed as $hk_{a_1} f_1(C_A,C_B)$ and $hk_{a_2}(C_A,C_B)$.

The reactor activity factor can be obtained in the same manner as for a single reaction:

$$H = -\int_{C_{A_{in}}}^{C_{A_e}} \frac{dC_A}{k_{a_1}(T) f_1(C_A,C_B) + k_{a_2}(T) f_2(C_A,C_B)} \tag{26}$$

where C_{A_e} is the outlet concentration of species A. As Eq. 25 indicates, the temperature can be expressed in terms of C_A and C_B for the calculation of H, but C_B has to be related to C_A to carry out the integration. Combining Eqs. 23 and 24, we have

$$\frac{dC_B}{dC_A} = \frac{-b_1 k_{a_1} f_1(C_A,C_B)}{k_{a_1} f_1(C_A,C_B) + k_{a_2} f_2(C_A,C_b)}$$

which can be rewritten in a discrete form as

$$\Delta C_B = \left[\frac{-b_1 k_{a_1} f_1(C_A,C_B)}{k_{a_1} f_1(C_A,C_B) + k_{a_2} f_2(C_A,C_B)}\right]_{\text{present}} \Delta C_A \tag{27}$$

Although a more rigorous numerical scheme can be used, the simple Euler method is given here for illustration purpose. With a chosen step size ΔC_A for the integration in Eq. 26, we can start with $C_{A_{in}}$ and $C_{B_{in}}$ to obtain C_A and C_B at the next interval from Eq. 27 and ΔC_A, which in turn can be used in Eq. 26 for the integration up to the next interval. These procedures can be repeated to obtain the value of H. If species B is the desired species such that $(C_B)_d$ is the desired outlet concentration, the control policy similar to Eq. 14 can be written as

$$H_c = \int_{C_{B_{in}}}^{(C_B)_d} \frac{dC_B}{b_1 \tau k_{a_{10}} \exp\left[\dfrac{-E_a/R_g}{(T_{in})_n + a_1(C_{A_{in}} - C_A) + a_2(C_B - C_{B_{in}})}\right] f_1(C_A, C_B)} \tag{28}$$

which follows from Eq. 24. Here again, H_c is the reactor activity factor calculated just prior to a change in the inlet temperature. Equation 28 can be solved for $(T_{in})_n$ with the aid of Eq. 27. It is noted that $(T_{in})_n$ should also be used in Eq. 27 in the calculation.

Consider now consecutive reactions, for which we have

$$A \rightarrow b_1 B \rightarrow b_2 C$$

With the same assumptions made for the parallel reactions, the conservation equations for an adiabatic reactor are

$$\frac{dC_A}{dz} = -\tau h(z;t) k_{a_1} f_1(C_A, C_B) \tag{29}$$

$$\frac{dC_B}{dz} = -\tau h(z;t)\{k_{a_2} f_2(C_A, C_B) - b_1 k_{a_1} f_1(C_A, C_B)\} \tag{30}$$

$$T = T_{in} + a_3(C_{A_{in}} - C_A) - a_4(C_B - C_{B_{in}}) \tag{31}$$

where $a_3 = (-\Delta H_1 - b\Delta H_2)/\rho C_p$ and $a_4 = -\Delta H_2/\rho C_p$. If we follow the same procedures as for the parallel reactions, we have for the reactor activity factor:

$$H = -\int_{C_{A_{in}}}^{C_{A_e}} \frac{dC_A}{\tau k_{a_1}(T) f_1(C_A, C_B)} \tag{32}$$

The relationship between C_A and C_B resulting from Eqs. 29 and 30, when cast in a discrete form, is

$$\Delta C_B = \left[-b_1 + \frac{k_{a_2} f_2(C_A, C_B)}{k_{a_1} f_1(C_A, C_B)}\right]_{\text{present}} \Delta C_A \tag{33}$$

The same procedures as for the parallel reactions can be used to calculate H from Eq. 32 with the aid of Eqs. 31 and 33.

The control policy for maintaining the desired outlet concentration of species B follows directly from Eq. 30 and the definition of H:

$$H_c = -\int_{C_{b_{in}}}^{(C_B)_d} \times \frac{dC_B}{\tau\{k_{a_2}[(T_{in})_n] f_2(C_A, C_B) - b_1 k_{a_1}[(T_{in})_n] f_1(C_A, C_B)\}} \tag{34}$$

This can be solved for $(T_{in})_n$ with the aid of Eqs. 31 and 33. If, however, the control objective is to have the maximum C_B at the outlet, it is more convenient to work with Eq. 29. The control policy then is

$$H_c = -\int_{C_{A_{in}}}^{(C_A)_d} \frac{dC_A}{\tau k_{a_{10}} \exp\left[\dfrac{-E_a/R_g}{(T_{in})_n + a_3(C_{A_{in}} - C_A) - a_2(C_B - C_{B_{in}})}\right] f_1(C_A, C_B)} \tag{35}$$

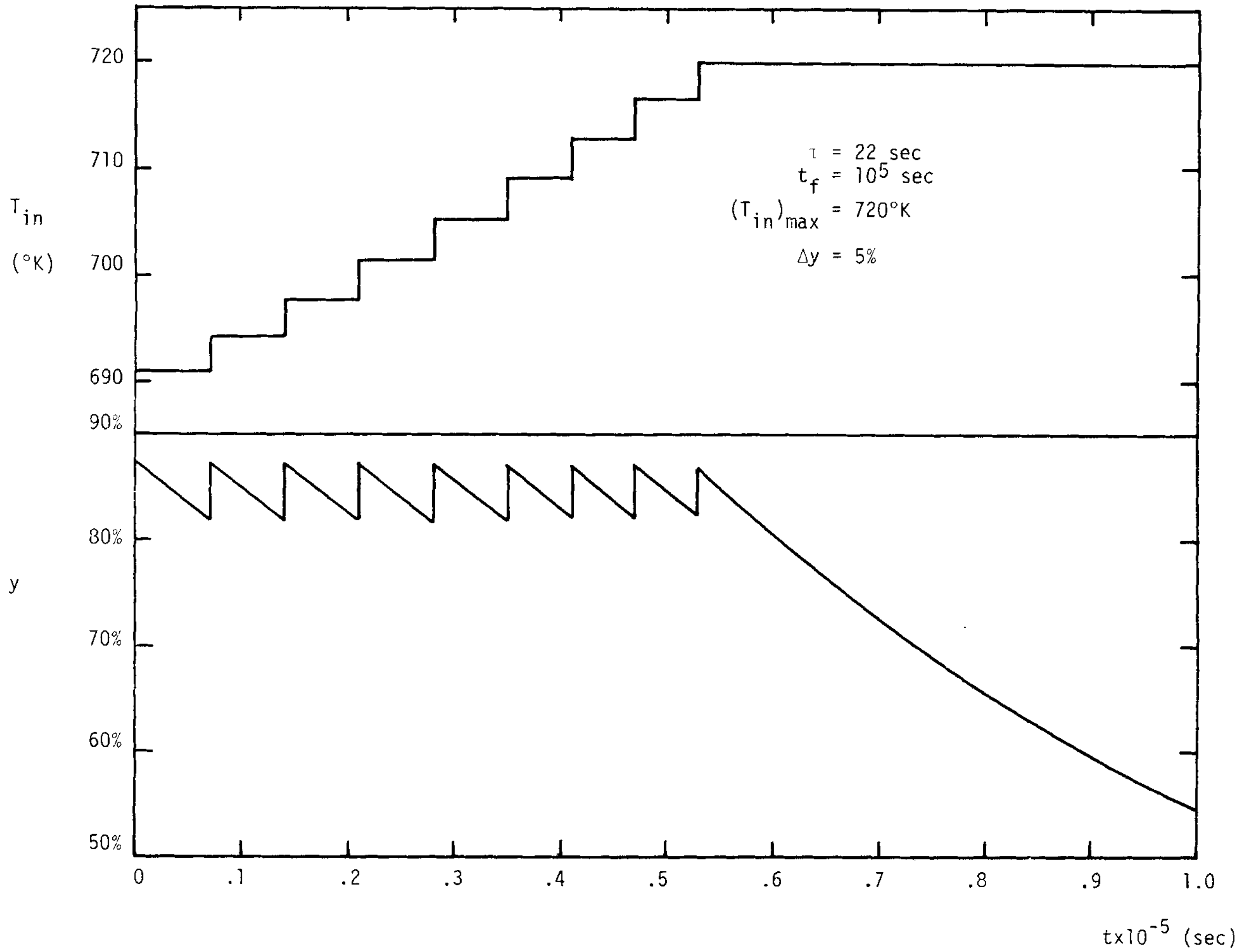

Figure 2. Inlet temperature and conversion behavior for an optimal control with bandwidth of 0.05.

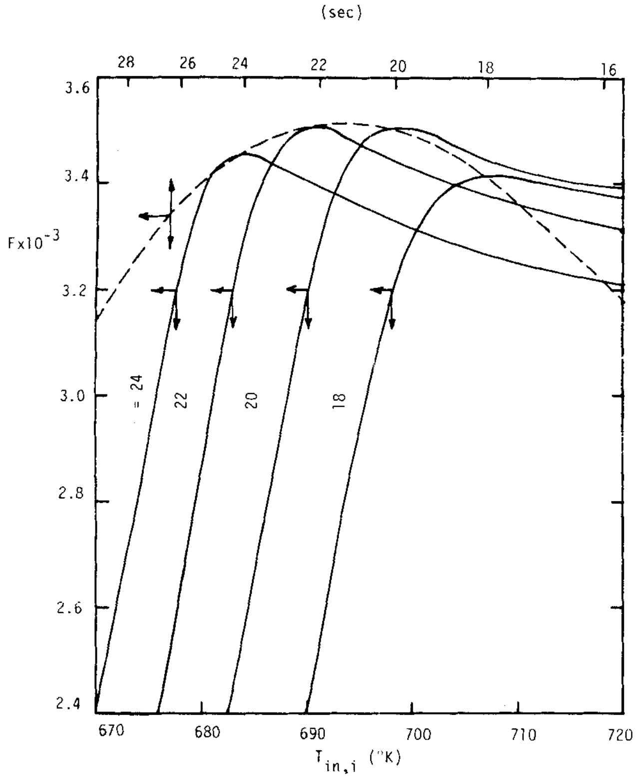

Figure 3. Performance index of Eq. 38 as a function of τ and initial inlet temperature. The dotted line shows the locus of the maximum values of F.

The value of $(C_A)_d$ that corresponds to the maximum C_B at the outlet can be found by plotting $C_{A_{out}}$ vs. $C_{B_{out}}$ for the maximum with the aid of Eq. 30 and the condition $dC_B/dz|_{z=1} = 0$:

$$k_{a_2}(T_{out})f_2(C_{A_{out}}, C_{B_{out}}) = b_1 k_{a_1}(T_{out})f_1(C_{A_{out}}, C_{B_{out}}) \tag{36}$$

with

$$T_{out} - T_{in} = a_3(C_{A_{in}} - C_{A_{out}}) - a_4(C_{B_{out}} - C_{B_{in}}) \tag{37}$$

The control policies of Eqs. 28, 34, and 35 can be modified using Eq. 16 to obtain the piecewise algorithms similar to Eqs. 17 and 18.

OPTIMAL CONTROL AND DESIGN

We address in this section the problem of how a fixed bed with catalyst deactivation should be designed to obtain the best possible performance when it is controlled optimally. In particular, we ask what the size of the reactor is that maximizes a certain performance index when the inlet temperature is also manipulated to maximize the performance index. This is a design practice in which process control is taken into consideration. In order to clearly demonstrate the interrelationship between design and control and the advantage that can be gained by utilizing this interrelationship, we assume for the time being that the detailed knowledge of deactivation is available. We restrict our attention here to a single reaction taking place in an adiabatic reactor.

Consider an optimization problem given by

$$\max_{\{\tau, T_{in}(t)\}} F = \frac{1}{\tau} \int_0^{t_f} y\,dt \tag{38}$$

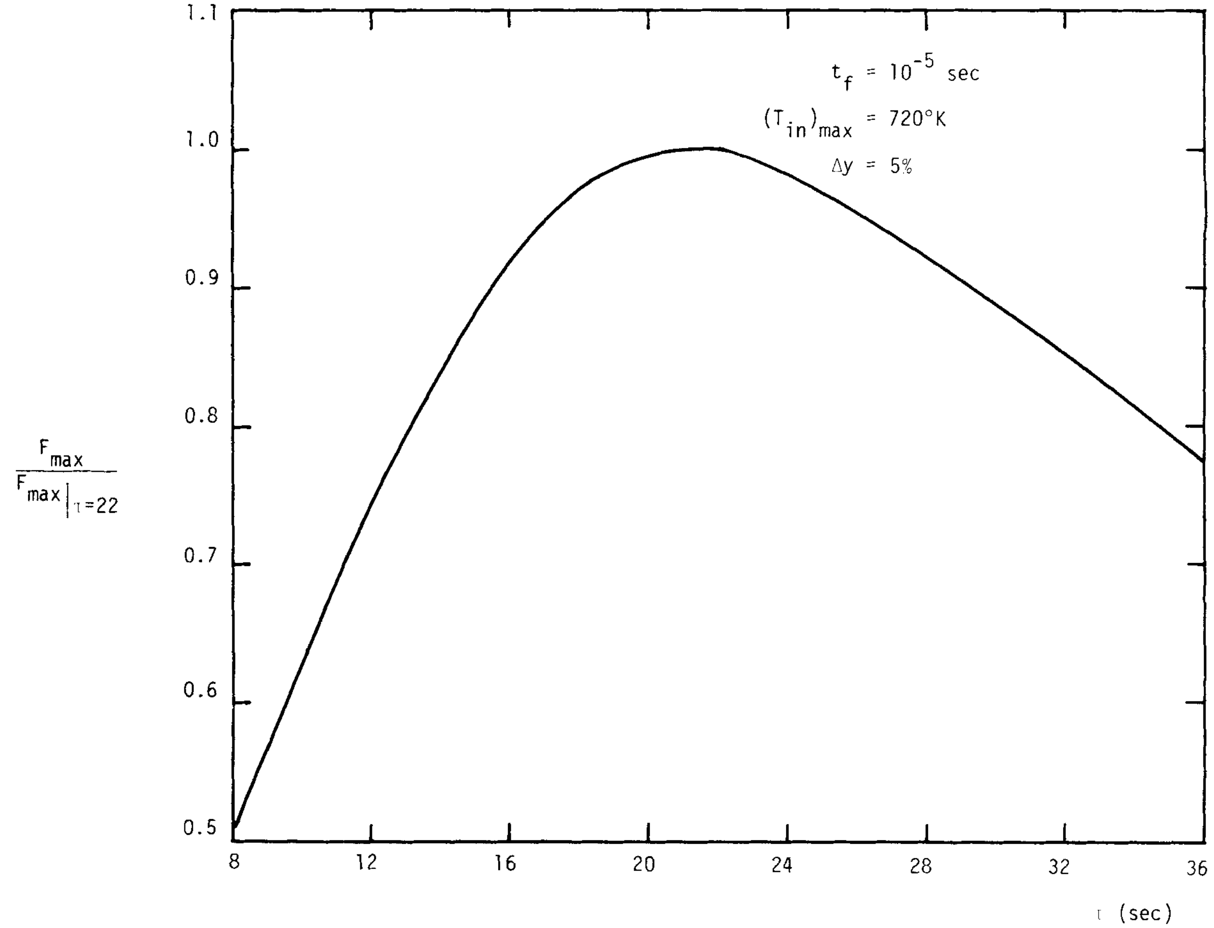

Figure 4. Maximum values of performance index of Eq. 38 for various τ values.

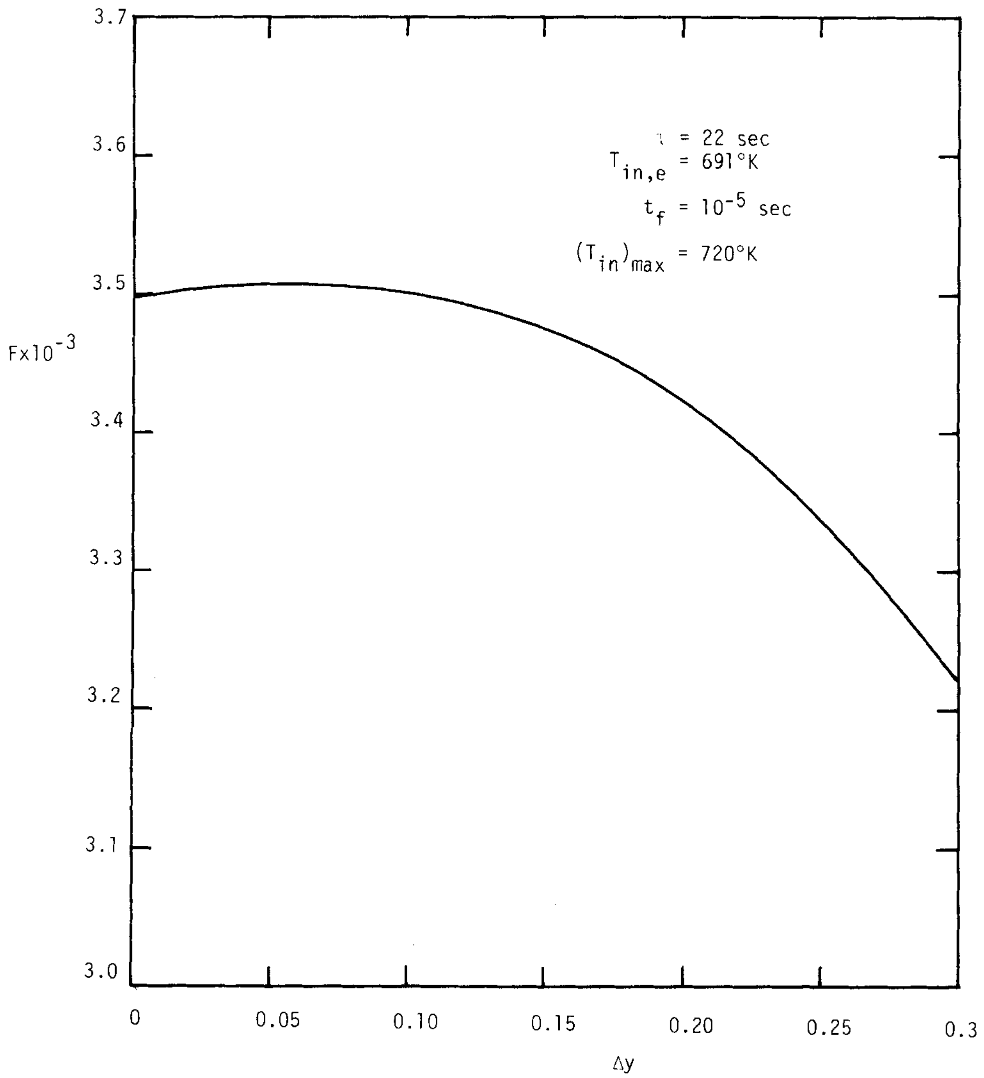

Figure 5. Effect of bandwidth Δy on performance index of Eq. 38.

subject to the system equations of Eqs. 1 and 2 with $(mC_p)_c = 0$ for the adiabatic reactor under consideration and subject to $T_{in} \leq (T_{in})_{max}$ with a fixed t_f. The problem is to maximize the performance index F, which is the conversion (y) integrated over the catalyst life t_f per unit reactor volume, by properly choosing τ and $T_{in}(t)$. This two-parameter optimization problem can be solved one at a time by first searching for the maximum for a given τ and then finding the value of τ that yields the maximum. For a fixed τ, it is a Bolza's problem (Bliss, 1961) and the extremum condition obtained by Chou et al. (1967) and Ogunye and Ray (1971) is to maintain the conversion at a constant level until the maximum allowed temperature is reached, and then to remain at the maximum if one rate constant is involved. For the deactivation problem under consideration, however, the policy is not directly applicable since the rate constant cannot be separated out. Examples of independent deactivation are sintering (Lee, 1981) and independent poisoning. Since the feedback control policy obtained earlier is for maintaining a constant conversion level, the problem is simply that of finding an initial value of T_{in} (or the desired conversion level) if we use the control policy, for T_{in} can be set at $(T_{in})_{max}$ once $(T_{in})_{max}$ is reached. The bandwidth Δy can be chosen small for continuous manipulation, for the control policy will become continuous as Δy approaches zero.

The optimization problem was solved for the reaction system in Table 1 using the control algorithms of Eqs. 16 through 18 with the constraints of $t_f = 10^5$ and $(T_{in})_{max} = 750$K. The typical behavior of $T_{in}(t)$ and the outlet conversion is shown in Figure 2 for the bandwidth Δy of 5% and the initial inlet temperature of 691K (or conversion of 87.2%). In accordance with the constraint on t_f and the extremum condition, T_{in} stays at the maximum allowed temperature once it reaches the maximum and the conversion decreases with time, eventually reaching a conversion of 54.5% at $t = t_f$, at which time the catalyst is regenerated. As indicated earlier, the optimization problem for a chosen τ is that of finding an initial conversion (or initial inlet temperature) that yields a maximum. The solutions obtained for various τ are shown in Figure 3 for a bandwidth of 0.05. The reason for this choice of the bandwidth is given below. A few observations can be made from the figure. The results show that for a given τ, the extremum condition does yield a maximum. Furthermore, the value of the performance index is much more sensitive to a choice of the initial inlet temperature (or the initial conversion) at relatively lower values of the inlet temperature than at higher values. The locus of the maximum values of F for various τ is given by the dotted line in Figure 3. As apparent from the figure, there exists a maximum at around $\tau = 22$ s. The performance index normalized with respect to the index corresponding to $\tau = 22$ s, when the reactor is operated optimally, is shown in Figure 4 as a function of the reactor size τ. It is seen that the performance index (Eq. 38) doubles (τ of 8 vs. τ of 22 s) when the reactor is sized optimally. This result confirms the intuitive reasoning that the best possible reactor performance obtainable by process control is inherently dictated by process design. It also confirms the fact that a significant improvement can be made by combining process design with process control.

The choice of 0.05 for the bandwidth Δy used in Figures 3 and 4 needs further comment. Undoubtedly, the choice of Δy for the feedback control affects the value of the performance index. This effect is shown in Figure 5 for $\tau = 22$ s. Since the continuous control corresponds to Δy of zero, it is seen that the stepwise control is at least as good as the continuous control for $\Delta y < 10\%$.

We have so far assumed that detailed knowledge of catalyst deactivation is available. The same optimal control and design can still be carried out if some knowledge of deactivation is available, however uncertain it may be, since what is sought in such a case would be approximate values of the optimal size and inlet temperature and some directions as to what to choose. In the example considered, for example, one would choose a relatively high initial conversion (or a high inlet temperature) rather than a low initial conversion in view of the sensitivity discussed earlier.

CONCLUSION

A method of estimating a measure of the extent of catalyst deactivation is developed. It is based on the global rate for fresh catalyst and on process measurements. This measure of deactivation leads directly to a piecewise feedback control algorithm for maintaining a desired conversion. Since a necessary condition for maximizing a performance index is that the conversion stay constant in time, the feedback control policy developed here is also an optimal control policy with respect to the performance index of Eq. 38, at least for a single irreversible reaction that proceeds at the intrinsic rate. This control policy, when taken into consideration for the specification of reactor size, leads to an optimal set of reactor size and $T_{\text{in}}(t)$ which yields a far superior reactor performance than possible with the optimal control alone. The practice of combining optimal design with optimal control is shown to be rather straightforward with the aid of the feedback control scheme and the approach of reactor point effectiveness (Lee and Butt, 1982).

ACKNOWLEDGMENT

This is based upon work supported by National Science Foundation under Grant No. CPE-8104713.

NOTATION

a_1 $= -\Delta H_2/\rho C_p$
a_2 $= -\Delta H(1 - \Delta H_2/\Delta H_1)/\rho C_p b_1$
a_3 $= (-\Delta H_1 - b\Delta H_2)/\rho C_p$
a_4 $= -\Delta H_2/\rho C_p$
b_1, b_2 = ratios of stoichiometric coefficients
C = concentration of main reactant
C_A = concentration of species A
C_B = concentration of species B
C_d = desired outlet concentration of main reactant
C_d = modified C_d given by Eq. 16
C_{d_e} = initial value of C_d
C_{in} = inlet concentration of main reactant
C_p = specific heat of reaction fluid
$(C_p)_c$ = specific heat of coolant
D_e = effective diffusivity
E_a = activation energy
f = apparent concentration dependence of rate of main reaction
f_1 $= f$ for reaction path 1
f_2 $= f$ for reaction path 2
F = performance index given by Eq. 38
g = concentration dependence of intrinsic rate of reaction
h = local activity factor defined by Eq. 5
h_c = current value of h
h_m = film heat transfer coefficient
h_n = new value of h
H = reactor activity factor defined by Eq. 7
H_c = current value of H
H_n = new value of H
$(-\Delta H)$ = heat of reaction
$(-\Delta H_1)$ = heat of reaction for reaction path 1
$(-\Delta H_2)$ = heat of reaction for reaction path 2
I = integral defined by Eq. 20
k = intrinsic rate constant
k_a = apparent rate constant
k_{a_e} = preexponential factor
k_{a_1} $= k_a$ for reaction path 1
k_{a_2} $= k_a$ for reaction path 2
k_{p_s} = rate cosntant for poisoning reaction evaluated at pellet surface temperature
K_j = equilibrium constant
m = mass rate of reaction fluid
m_c = mass rate of coolant
N = concentration of poisoning species
q = quantity defined by Eq. 21
r_p = intrinsic rate of poisoning reaction
R_g = gas constant
R_G = global rate of main reaction
R_t = tube radius
t = time
t_f = time at which catalyst is regenerated
T = temperature of reaction fluid
T_c = coolant temperature
T_{in} = reactor inlet temperature
$T_{c_{\text{out}}}$ $= T_c$ at $z = 0$
U = overall heat transfer coefficient
v = superficial velocity
y = conversion
Δy = bandwidth of concentration allowed before an adjustment T_{in} is made
z = axial reactor coordinate
Z = reactor length

Greek Letters

β = proportionality constant defined in Eq. 16
γ = fraction of catalyst deactivated
ϵ_B = bed porosity
τ = holding time given in Eq. 1
ρ = reaction fluid density

Subscripts

c = coolant; current value
d = deactivated
e = reactor outlet
f = fresh catalyst
i = index for a step change in inlet temperature
in = inlet
max = the maximum value
o = at $t = 0$

LITERATURE CITED

Bliss, G. A., *Lectures on the Calculus of Variations*, Univ. Chicago Press (1961).

Chou, A., W. H. Ray, and R. Aris, "Simple Control Policies for Reactors with Catalyst Decay," *Trans. Inst. Chem. Engrs.*, **45**, T153 (1967).

Crider and Foss, *AIChE J.*, **12**, 514 (May, 1966).

Haas, W. R., L. L. Tavlarides, and W. J. Wnek, "Optimal Temperature Policy for Reversible Reactions with Deactivation: Applied to Enzyme Reactors," *AIChE J.*, **20**, 707 (1974).

Lee, H. H., and J. B. Butt, "Heterogeneous Catalytic Reactors Undergoing

Chemical Deactivation. Part I: Deactivation Kinetics and Pellet Effectiveness," *AIChE J.*, **28**, 405 (1982).

———, "Heterogeneous Catalytic Reactors Undergoing Chemical Deactivation. Part II: Design and Analysis: Approach of Reactor Point Effectiveness," *AIChE J.*, **28**, 410 (1982a).

Lee, H. H., "Catalyst Sintering and Pellet Effectiveness," *Chem. Eng. Sci.*, **36**, 950 (1981).

Lee, H. H., and E. Ruckenstein, "Catalyst Sintering and Reactor Design," to appear in *Cat. Rev.*

Ogunye, A. F., and W. H. Ray, "Optimal Control Policies for Tubular Reactors Experiencing Catalyst Decay," *AIChE J.*, **17**, 43 (1971).

Szepe, S., and O. Levenspiel, "Optimal Temperature Policies for Reactors Subject to Catalyst Deactivation. I: Batch Reactor," *Chem. Eng. Sci.*, **23**, 881 (1968).

Wheeler, A., "Reaction Rates and Selectivity in Catalyst Pores," *Adv. in Cat.*, **2**, 249 (1955).

Manuscript received February 23, 1983; revision received October 17, and accepted October 20, 1983.

Carrier-Mediated Transport Across Phospholipid-Composite Membranes Containing Valinomycin

Artificial membranes containing a phospholipid and valinomycin were prepared. Valinomycin in these membranes acts as an ionophore (a mobile carrier for potassium ions) at a temperature above the phase transition point of the phospholipid. Experimental data were explained by the theory of carrier-mediated transport accompanying formation of a carrier-ion pair complex.

EIZO SADA, SHIGEO KATOH,
MASAAKI TERASHIMA and
YOSHIHIRO TAKADA

Chemical Engineering Department
Kyoto University
Kyoto 606, Japan

SCOPE

The objects of the present work are to prepare phospholipid-composite membranes containing a carrier for potassium ions and to clarify the mechanism of carrier-mediated transport for potassium ions in these membranes.

Among the unique functions of biomembrane, the carrier-mediated transport of solutes is the most interesting one. Although the mechanism of carrier-mediated transport of various ions has been widely studied with liquid membranes (Ward III, 1970; Reusch and Cussler, 1973), bilayer membranes, and liposomes (Szabo et al., 1969), on account of their mechanical unstability it is desirable to prepare more stable membranes containing carriers.

In previous work (Sada et al., 1983), we have reported that the phospholipid-composite membrane prepared from a hydrophobic polymer and a phospholipid shows similar permeability characteristics to those reported with biomembrane models such as liposomes and bilayer membranes. In the present work we intended to incorporate valinomycin, a carrier for potassium ions in biomembranes into those phospholipid-composite membranes, which are far more stable than liposomes and liquid membranes. At the temperature above the phase transition point of the phospholipid, valinomycin is expected to act as a carrier for potassium ions in a similar manner as in biomembranes.

These membranes are useful for studying transport phenomena in living systems and for the selective separation of solutes on an industrial scale by selecting suitable carriers. They further may be suitable for reconstitution or immobilization of hydrophobic enzymes which are active only in the phospholipid bilayer of biomembranes.

CONCLUSION AND SIGNIFICANCE

Valinomycin was incorporated into the stable phospholipid-composite membranes. The fluxes of potassium ions through these membranes increased steeply with potassium concentration and reached a plateau at high salt concentration above the phase transition temperature of the phospholipid. They also increased in proportion to carrier concentration. So it was presumed that valinomycin acted as a mobile carrier. The behavior of valinomycin was analyzed by the theory of mobile-carrier mechanism, in which valinomycin makes a carrier-ion pair complex at one side of the membrane, diffuses across the membrane, and releases ions at the other side.

From these results we concluded that valinomycin in the phospholipid-composite membranes acted as the mobile carrier for potassium ions at a temperature above the phase transition point of the phospholipid. The experimental data agreed well with the predictions based on the theory of carrier-mediated transport accompanying formation of a carrier-ion pair complex. Further, these membranes could be used stably at least for four weeks.

By selecting and designing suitable carriers, these types of composite membranes may make important contributions to industrial processes for selective separation of solutes.