procedure masks the amount of actual drag reduction, relative to the pure solvent, which occurs.

The salt and low *p*H solutions show low levels of drag reduction at small Reynolds number due to their collapsed conformations. At high Reynolds numbers, however, coil expansion should occur, with solution behavior approaching that of the deionized water or high *p*H solutions. This clearly is the case for the salt solution, and the fact that it does not occur with the low *p*H solution implies the presence of storing intramolecular interactions between nonadjacent sections of the polymer coil, most probably in the form of hydrogen bonds.

Turning now to Figure 2 for Versicol S25, we see that this is very similar to Figure 1 for Separan AP273, although the actual percentage drag reduction obtained is not as great. Here again, the high *p*H solution shows maximum drag reduction at low N_{Re}, while as the Reynolds number increases, the data for the salt, deionized water, and high *p*H solutions all merge together. The low *p*H solution gives significantly poorer drag reduction, especially as N_{Re} is increased.

These findings may be explained in exactly the same fashion as for the case of Separan AP273. In deionized water at low N_{Re}, the chain is overextended, the increase in solution viscosity offsetting the increased contact time (or time between turbulent bursts). The partially extended coil in the high *p*H solution, offering a compromise between extension and viscosity, yields optimal drag reduction. The salt and low *p*H solutions both show poor drag reduction initially, but as N_{Re} increases, the coil in the salt solution expands to a greater extent than in the low *p*H solution, giving greater friction reduction. At high Reynolds numbers, the polymer coil is maximally extended in the salt, high *p*H, and deionized water solutions, which yield identical drag reduction. The smaller extension of the polyacrylic acid molecule in the low *p*H solution is consistent with the postulate that the molecule assumes a partially helical structure in an acidic medium.

CONCLUSIONS

The experimental results in this study support the concept that increased polymer extension in solution leads to better drag reduction. The elevated solution viscosities of highly extended conformations may, however, offset any drag reduction enhancement at low Reynolds numbers and must be carefully accounted for.

The friction factor data for polyacrylamide or polyacrylic acid in deionized water, in high *p*H solution, and in 0.1M sodium chloride solution tend to merge together at high values of N_{Re}, suggesting that in each solution the polymer coils approach the same degree of extension. The much higher value of the friction factor in low *p*H solution implies that the polymer coils have become stiffened, suggesting the presence of strong intramolecular bonding, most probably in the form of hydrogen bonds.

ACKNOWLEDGMENT

Acknowledgment is made to the National Science Foundation for partial support under grant No. GK 31590. Helpful comments were provided by Professor J. L. Zakin.

LITERATURE CITED

Balakrishnan, C., and R. J. Gordon, "Influence of Molecular Conformation and Intermolecular Interactions on Turbulent Drag Reduction," *J. Appl. Polymer Sci.*, **19**, 909 (1975).

Banijamili, S. H., E. W. Merrill, K. A. Smith, and L. H. Peebles, Jr., "Turbulent Drag Reduction by Polyacrylic Acid," *AIChE J.*, **20**, 824 (1974).

Einstein, H. A., and H. Li, "The Viscous Sublayer along a Smooth Boundary," *Trans. Am. Soc. Civil Engrs.*, **82**, 293 (1956).

Frommer, M. A., A. Feder-Lavy, and M. A. Kraus, "Dependence of the Drag Reduction Efficiency of Polyelectrolytes on their Conformation in Aqueous Solutions," *J. Colloid Interfac. Sci.*, **48**, 165 (1974).

Hand, J. H., and M. C. Williams, "Effect of Scondary Polymer Structure on the Drag-Reducing Phenomenon," *J. Appl. Polymer Sci.*, **13**, 2499 (1969).

————, "DNA and Structural Effects in Turbulent Drag Reduction," *Nature*, **227**, 369 (1970).

Katsibas, P., and R. J. Gordon, "Momentum and Energy Transfer in Turbulent Pipe Flow: The Penetration Model Revisited," *AIChE J.*, **20**, 191 (1974).

Kim, O. K., R. C. Little, and R. Y. Ting, "Polymer Structural Effects in Turbulent Drag Reduction," *AIChE Symposium Ser. No. 130*, **69**, 39 (1973).

Liaw, G., J. L. Zakin, and G. K. Patterson, "Effects of Molecular Characteristics of Polymers on Drag Reduction," *AIChE J.*, **17**, 391 (1971).

Mathieson, A. R., and J. V. McLaren, "Potentiometric Study of the Conformational Transition in Poly(acrylic acid)," *J. Polymer Sci.*, **A, 3**, 2555 (1965).

Metzner, A. B., and J. C. Reed, "Flow of Non-Newtonian Fluids—Correlation of the Laminar, Transition, and Turbulent-flow Regions," *AIChE J.*, **1**, 434 (1955).

Parker, C. A., and A. H. Hedley, "Drag Reduction and Molecular Structure," *Nature Phys. Sci.*, **236**, 61 (March 27, 1972).

Virk, P. S., "An Elastic Sublayer Model for Drag Reduction by Dilute Solutions of Linear Macromolecules," *J. Fluid Mech.*, **45**, 417 (1971).

White, D., Jr., "The Effect of Molecular Conformation on Turbulent Drag Reduction," M.S. thesis, Univ. Fla. Gainesville (1975).

Manuscript received February 3, 1975; revision received June 10, and accepted June 11, 1975.

Optimal Batch Reactor Temperature Policy for Reactions with Concentration Dependent Catalyst Decay

JAMES M. POMMERSHEIM and KRISHNA CHANDRA

Department of Chemical Engineering
Bucknell University
Lewisburg, Pennsylvania 17837

Catalyst deactivation is an important practical problem that has generated considerable interest in recent years. Early work in catalyst deactivation usually involved empirical methods specific for a particular reaction. However, more recently, fundamental approaches, involving direct gradient search techniques or indirect variational methods, have been used to model catalyst deactivation

---

Krishna Chandra is with Fluor Engineers, Los Angeles, California. Correspondence concerning this note should be addressed to James M. Pommersheim.

TABLE 1. MATHEMATICAL STATEMENT OF THE PROBLEM OF FINDING AN OPTIMAL POLICY FOR A SINGLE REACTION WITH CONCENTRATION DEPENDENT DEACTIVATION

Functions*	$C_A\ (t), a\ (t), y\ (t)$
Constraints†	$\phi_1 = \mathring{C}_A + r_A\ (C_A, a, y) = 0$
	$\phi_2 = \mathring{a} + \delta\ (C_A, a, y) = 0$
End conditions	$t_o\ = 0$, a_o and C_{Ao} given, t_f and a_f given
Objective Function	$\psi \equiv [C_A]_o^f$

* The problem is defined in terms of reciprocal temperature $y = 1/T$.

† Newtonian notation (a ° above the variable) is used to represent time derivatives.

phenomena and to obtain optimal policies. For single irreversible reactions, optimal temperature policies have previously been formulated and solved for catalyst decay rates which were concentration independent. For ideal batch reactors, this problem was solved analytically by using the method of calculus of variations by Szepe and Levenspiel (1968), who showed that the optimal policy is one where the effective rate constant is held constant at its initial value. This will result in the temperature rising with time in the prescribed fashion.

By using the same analytical method, the present study extends this work to the general case for batch reactors where catalyst decay can depend not only on the catalyst activity level, but also upon reactant concentration. In catalysts where fouling or poisoning occurs, such concentration dependent decay can be of major importance. Here the rapid decay characteristic of fouling or the slow decay characteristic of poisoning are driven by concentration levels.

OPTIMAL POLICIES FOR THE DEACTIVATING IDEAL BATCH REACTOR

For a single reaction $A \rightarrow R$ over a deactivating catalyst in an ideal batch reactor, one criterion (i) of optimal operation is to maximize the final conversion (X_f) at a given reaction time (t_f) and final activity of the catalyst (a_f). Since temperature is the most important control variable for most industrial reactions, the optimal operational policy will be essentially an optimal temperature one. The problem of finding an optimal temperature policy can be attacked by the method of the calculus of variations. Table 1 is a mathematical representation of the optimization problem. The optimal temperature path that extremalizes the objective function must satisfy the Euler-Lagrange equations as well as the constraints and end conditions.

As pointed out by Szepe (1966), other criteria which are equivalent are (ii) to maximize the final activity to accomplish a desired conversion in a given time, or (iii) to minimize the time needed to reach fixed conversion-activity levels. In all of these criteria, the value of the initial temperature (T_o) is unspecified and must be found by calculation from the solution to the problem presented in Table 1, usually by iteration.

It is also possible to have as the criterion (iv) one in which both the initial temperature and reaction time are fixed by process requirements with the objective of maximizing the conversion. Such a situation might obtain for a thermally sensitive catalyst or one with both rapid deactivation and reaction rates. Here there might not be time enough to go from some base storage temperature to a preferred initial temperature.

A large number of such criteria can be formulated depending on the number of end conditions, the number of equations, and the nature of the desired objective function. With the two constraints ϕ_1 and ϕ_2 and the objective function ψ, there will be three equations with eight possible end conditions. If we exclude $t_o = 0$ and $a_o = 1$, of the remaining six end conditions, specifying three will make the problem critically determined. The objective function can be concentration (or conversion), catalyst activity, or time.

The optimization problem stated in Table 1 was formulated by Szepe and Levenspiel (1968) for the ideal batch reactor with catalyst deactivation rates of the form $K_D a^m$ and reaction rates of the form $K_A\ a\ C_A{}^n$. In this case, deactivation rates are independent of concentration and $\delta(a, y)$ alone. Under the condition that deactivation rate activation energies were greater than those for reaction, they found that the optimal temperature path rose with time such that the effective rate constant $K_A a$ is held constant. They obtained a complete analytical solution only for the special case of $m = n = 1$ for rate constants which were presumed to follow an Arrhenius temperature law.

APPLICATION TO DEPENDENT DECAY

The more general case of concentration dependent deactivation was solved in order to determine the optimal temperature policy. The treatment is more complex, since the activity is now also a function of conversion, but the calculus of variation approach is still applicable.

The rate laws for reaction and decay can be written, respectively, in power law form as

$$r_A = \frac{-dC_A}{dt} = K_A\, a^m\, C_A{}^n \tag{1}$$

$$\delta = -\frac{da}{dt} = K_D\, a^l\, C_A{}^k \tag{2}$$

The rate constants are also presumed to follow an Arrhenius temperature law.

Empirical equations of this form are capable of fitting a large number of situations (Szepe, 1966; Weller, 1956). In addition, dependent decay (with $k \neq 0$) is a more realistic condition, encompassing a wide variety of fouling and poisoning deactivations. For example, in parallel deactivation the catalyst decays as a result of the reactant serving as the fouling agent. Such deactivations can be of the form $A \rightarrow R$, $A \rightarrow P$, or of the form $A \rightarrow R + P$ (Levenspiel, 1972).

By using the formulation in Table 1, the optimal temperature policy equation was derived. The problem was addressed as a Bolza-Mayer problem in the calculus of variations (Szepe and Levenspiel, 1968). After the Lagrangian multipliers $\lambda_1(t)$ and $\lambda_2(t)$ are introduced, an augmented function can be written as

$$F = \lambda_1\{\mathring{C}_A + r\ (C_A, a, y)\} + \lambda_2\{\mathring{a} + \delta\ (a, C_A, y)\} \tag{3}$$

The resultant Euler-Lagrange equations

$$\frac{d}{dt}\left(\frac{\partial F}{\partial y_j}\right) - \frac{\partial F}{\partial y_j} = 0 \tag{4}$$

for concentration dependent decay take the form

$$\mathring{\lambda}_1 - \lambda_1 \frac{\partial r}{\partial C_A} - \lambda_2 \frac{\partial \delta}{\partial C_A} = 0 \tag{5}$$

$$\mathring{\lambda}_2 - \lambda_1 \frac{\partial r}{\partial a} - \lambda_2 \frac{\partial \delta}{\partial a} = 0 \qquad (6)$$

$$-\lambda_1 \frac{\partial r}{\partial y} - \lambda_2 \frac{\partial \delta}{\partial y} = 0 \qquad (7)$$

Since the augmented function F is formally independent of time, it follows for a batch reactor that

$$\lambda_1 \mathring{C}_A + \lambda_2 \mathring{a} = C \qquad (8)$$

For fixed end conditions (f), the transversality condition (Szepe and Levenspiel, 1968) reduces to

$$\lambda_{1f} = -1 \qquad (9)$$

Equations (5), (6), (7), (8), and (9) can be solved simultaneously to eliminate the unknowns C, λ_1, λ_2, $\mathring{\lambda}_1$, and $\mathring{\lambda}_2$. After lengthy manipulation

$$\delta_y \, \delta r_y - \delta_y \delta \, r_y - \delta_y \delta \mathring{r}_y + \delta_y{}^2 \, \mathring{r} - \delta \delta_y \, r_c \, r_y + \delta_y{}^2 r \, r_c + \delta \, \delta_c r_y{}^2 - \delta_c \delta_y \, r r_y = 0 \qquad (10)$$

If an Arrhenius type of temperature dependence for both rate constants is presumed, considerable simplification occurs

$$\mathring{a} \frac{\partial r}{\partial a} - \frac{E_R}{R} \frac{\partial r}{\partial y} = \frac{E_R}{E_D} \frac{r^2}{\delta} \frac{\partial \delta}{\partial C_A} \qquad (11)$$

Differentiating Equations (1) and (2) and substituting into Equation (10), we get the optimal temperature policy rate expression

$$\frac{E_R}{mR} \frac{dy}{dt} = \frac{1}{a} \frac{da}{dt} - K_A \left(\frac{k}{m} \right) a^m \left(\frac{E_R}{E_D} \right) C_A{}^{n-1} \qquad (12)$$

Equations (1), (2), and (12) are a set of coupled nonlinear ordinary differential equations which can be solved to give, respectively, the conversion, activity, and temperature histories for optimal reactor operation. The objective was chosen of maximizing conversion in a given reaction time, with the initial temperature fixed (criterion iv). This criterion was useful, since it permitted a parameter study with the same initial temperature.

By applying the Lengendre-Clebsch condition, it was found that Equation (12) is valid only for cases where $E_D > E_R$. This result is the same as that reported by Szepe and Levenspiel (1968) for independent type of deactivation. For $E_D > E_R$, the policy is to use the highest possible temperature consistent with process requirements. In such a case, Equations (1) and (2) would be solved simultaneously at this maximum operating temperature until the desired reaction time were reached. This procedure is also used when $E_D > E_R$, and the temperature predicted by Equation (12) exceeds the maximum.

By combining dependent variables, Equations (1), (2), and (12) can be solved analytically to give

$$\frac{C_A}{C_{A0}} = 1 - X_A$$

$$= \left[1 - \left(\frac{r_o}{C_A} \right)_o \left(\frac{k E_R}{E_D} + 1 - n \right) t \right]^{\frac{1}{\frac{k E_R}{E_D} + 1 - n}} \qquad (13)$$

$$\frac{a}{a_o} = \left[1 - \left(\frac{\delta}{a} \right)_o \left(\frac{m E_D}{E_R} + 1 - l \right) t \right]^{\frac{1}{\frac{m E_D}{E_R} + 1 - l}} \qquad (14)$$

$$\exp \left[\frac{E_R}{mR} (y - y_o) \right]$$

$$\left[1 - \left(\frac{\delta}{a} \right)_o \left(\frac{m E_D}{E_R} + 1 - l \right) t \right]^{\frac{-1}{\frac{m E_D}{E_R} + 1 - l}}$$

$$= \left[1 - \left(\frac{r}{C_A} \right)_o \left(\frac{k E_R}{E_D} + 1 - n \right) t \right]^{\frac{E_R k / E_D m}{\frac{k E_R}{E_D} + 1 - n}} \qquad (15)$$

Equation (15) gives the temperature ($1/y$) policy to follow when $E_D > E_R$ and operating temperatures are less than the maximum. An important characteristic of Equation (15) is that it indicates a rising temperature policy with time for all cases where the constants are positive. This can also be seen by doing a sign analysis on Equation (12).

This result agrees qualitatively with that of Szepe and Levenspiel (1968) for conversion independent deactivation. Quantitatively, however, the results are not equivalent. Combining Equations (7) and (8) gives an expression for the effective rate constant $K_A \, a$:

$$\frac{K_A \, a}{(K_A \, a)_o} = \left(\frac{C_{A0}}{C_A} \right)^{\frac{E_R k}{E_D m}} \exp \left[\frac{E_R (m - 1)}{mR} (y_o - y) \right] \qquad (16)$$

Note that the effective rate constant ($K_A \, a$) will not be constant when the deactivation rate is conversion dependent. This was first shown by Lee and Crowe (1970). A policy with a constant effective rate constant will be suboptimal except for independent decay.

With $k = 0$, corresponding to independent decay, Equation (16) reduces to

$$K_A a^m = K_{A0} a_o{}^m \qquad (17)$$

This form is an extension of the result of Szepe and Levenspiel (1968) to the case of arbitrary m. Their result attends when $m = 1$. Figures 1 and 2 show the effect of k, the power of C_A in Equation (2), on conversion, activity, and operating temperature policy. Other powers were set equal to unity. Representative values of the kinetic and activation constants K_{Ao}, K_{Do}, E_R/R, and E_D/R of 5×10^{16}, 2×10^{17}, 1.9×10^4 and 2×10^4, respectively, were chosen. Initial activities, concentrations, and final reaction times were taken as unity. A maximum allowable temperature level of 521 °K was used. The independent decay case when $k = 0$ was also investigated. Note from Figure 2 that the temperature policy becomes steeper and steeper as k is raised. In cases of very steep rise, inherent thermal lags in the reactor may prevent, in practice, the implementation of the theoretical policy. Higher k values also produce higher final activities and final conversions. The activity level is independent of k until the maximum

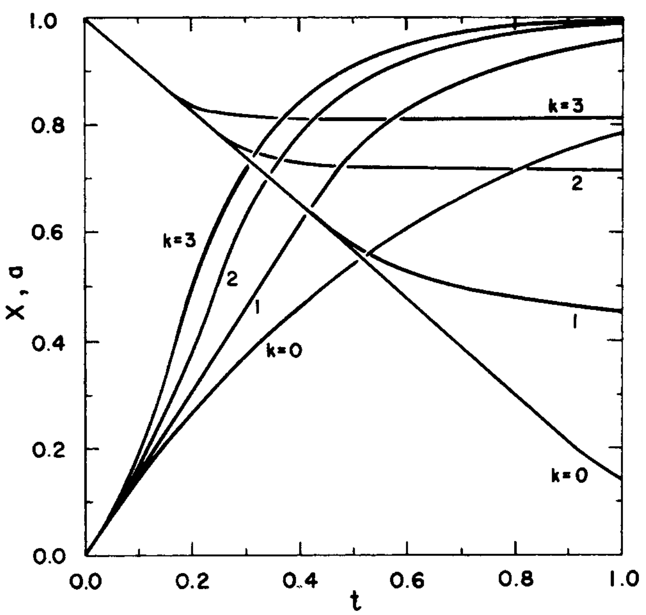

Fig. 1. Effect of parameter k on conversion and activity levels.

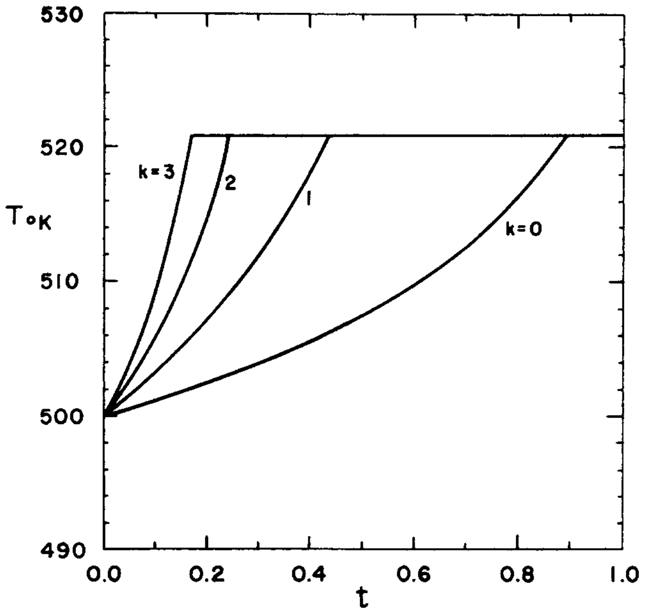

Fig. 2. Effect of parameter k on the optimal temperature policy.

temperature is reached, as predicted by Equation (14). Similarly, Equation (13) shows that optimal conversion levels are independent of the order l, the power of a in Equation (2). These facts have obvious implications. Note that Equations (13) and (14) predict that the activity and concentration can be zero, but at different times. Equation (15) also yields a time corresponding to infinite temperature ($y = 0$). In general, it can be shown that this latter time occurs first, so that the activity and concentration will remain at finite nonzero values.

LITERATURE CITED

Lee, S. I., and C. M. Crowe, "Optimal Temperature Policies for Batch Reactors with Decaying Catalyst," *Chem. Eng. Sci. Comm.*, **25**, 743-744 (1970).

Levenspiel, Octave, *Chemical Reaction Engineering*, 2nd ed., p. 538, Wiley & Sons, New York (1972).

Szepe, S., Ph.D. thesis, "The Deactivation of Catalysts and Some Related Optimization Problems," Illinois Institute of Technology, Chicago (1966).

———, and Octave Levenspiel, "Optimal Temperature Policies for Reactors Subject to Catalyst Deactivation-I Batch Reactor," *Chem. Eng. Sci.*, **23**, 881-894 (1968).

Weller, Sol, "Analysis of Kinetic Data for Heterogeneous Reactions," *AIChE J.*, **2**, 59 (1956).

NOTATION

a = catalyst activity
A = reactant
C = constant of integration
C_A = concentration of A
E_R = activation energy for reaction
E_D = activation energy for deactivation
F = augmented function
K_A = rate constant for reaction
K_{A0} = frequency factor for reaction
K_D = rate constant for deactivation
K_{D0} = frequency factor for deactivation
P = product which deactivates catalyst
r_A = rate of reaction of A
$r_y = \dfrac{d}{dt}\left(\dfrac{\partial r_A}{\partial y}\right)$
R = gas constant; product of reaction
t = reaction or batch time
t_f = total reaction time
T = absolute temperature
X = conversion of A to R
y = reciprocal absolute temperature ($1/T$)
y_j = dependent variable in Bolza problem

Greek Letters

δ = deactivation rate
$\delta_c = \dfrac{d}{dt}\,(\partial\delta/\partial C_A)$
λ_j = j^{th} Lagrange multiplier
ϕ_j = j^{th} constraint equation
ψ = objective function

Superscripts

l, k, m, n = powers, Equations (1) and (2)

Subscripts

c = partial derivative with respect to C_A
f = final or end condition
j = index
o = initial condition
y = partial derivative with respect to y

Manuscript received April 16, 1975; revision received May 15, and accepted May 16, 1975.