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Manuscript received May 4, 1979; revision received June 15, and accepted July 11, 1979.

Restrictions and Equivalence of Optimal Temperature Policies for Reactors with Decaying Catalysts

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Pommersheim and Chandra (1975) present analytical solutions for the general problem of the optimal policy of batch reactor operation (and tubular reactor operation when catalyst with no slip moves with the reaction fluid) for catalyst decay rates which depend on temperature, activity and concentration. The optimal temperature and corresponding concentration and activity formulas which they present are valid whenever the Legendre-Clebsch (L-C) condition is obeyed. They list three other criteria which they claim are *equivalent* to the criterion employed by Szepe and Levenspiel (1968) for the case of concentration independent decay. This is criterion (i) of Table 1, which requires minimizing the final concentration (C_{Af}), or maximizing the final conversion, for fixed run times (t_f) and desired final activities (a_f).

The entire problem is shown in Table 1 with all four criteria stated. Solutions for the optimal policy can be shown to be identical for all four criteria. But for the optimal policy equations to be valid, the appropriate L-C conditions must be shown not to be violated. The L-C conditions may be different for these criteria, as they are derived employing the transversality conditions. The purpose of this note is to elucidate these restrictions on optimal temperature policies for the problem discussed by Pommersheim and Chandra and by example to further define the ranges of applicability of their solution.

NTH ORDER SINGLE IRREVERSIBLE REACTION

The reaction and activity rate functions considered are

$$r_A = K_A a^m C_A{}^n \tag{1}$$

and

$$\delta = K_D a^l C_A{}^k$$

with Arrhenius temperature dependency of K_A and K_D. The derivations of the optimal policy equations for concentration, activity and temperature

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

$$= \left[1 - \left(\frac{r}{C_A}\right)_0 \left(\frac{k\,E_R}{E_D} + 1 - n\right)t\right]^{\frac{1}{\frac{k\,E_R}{E_D} + 1 - n}} \tag{2}$$

$$\frac{a}{a_0} = \left[1 - \left(\frac{\delta}{a}\right)_0 \left(\frac{m\,E_D}{E_R} + 1 - l\right) t\right]^{\frac{1}{\frac{m\,E_D}{E_R} + 1 - l}} \tag{3}$$

and

$$\exp\left[\frac{E_R}{mR}(y - y_0)\right] \left[1 - \left(\frac{\delta}{a}\right)_0 \left(\frac{m\,E_D}{E_R}\right.\right.$$

$$\left.\left. + 1 - l\right)t\right]^{\frac{-1}{\frac{m\,E_D}{E_R} + 1 - l}} = \left[1 - \left(\frac{r}{C_A}\right)_0 \left(\frac{k\,E_R}{E_D}\right.\right.$$

$$\left.\left. + 1 - n\right)\, t\right]^{\frac{E_R\,k/E_D\,m}{\frac{k\,E_R}{E_D} + 1 - n}} \tag{4}$$

respectively, can be shown to the independent of the nature of the criteria which specifies the Legendre-Clebsch condition. In order that Equation (2)-(4) specify optimal profiles, the L-C condition

$$\lambda_1\, r_{yy} + \lambda_2\, \delta_{yy} \geq 0 \tag{5}$$

must be satisfied during the calculation procedure. The final form of Eq. (5) is obtained by use of the Euler-Lagrange equations and the transversality condition

TABLE 1. MATHEMATICAL STATEMENTS 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	$\phi_1 = \dot{C}_A + r_A\,(C_A,\ a,\ y) = 0$
	$\phi_2 = \dot{a} + \delta\,(C_A,\ a,\ y) = 0$
End Conditions and *Objective Functions*	
Criterion (i)	$t_0 = 0,\ a_0,\ C_{A0}$ given; $t_f,\ a_f$ given
	$\psi \equiv [C_A]^f_0$ for appropriate values of y_0 and y_f.
Criterion (ii)	$t_0 = 0,\ a_0,\ C_{A0}$ given; $t_f,\ C_{Af}$ given
	$\psi \equiv [-a]^f_0$ for appropriate values of y_0 and y_f
Criterion (iii)	$t_0 = 0,\ a_0,\ C_{A0}$ given; $a_f,\ C_{Af}$ given
	$\psi \equiv [t]^f_0$ for appropriate values of y_0 and y_f
Criterion (iv)	$t_0,\ a_0,\ C_{A0},\ y_0$ given; t_f given
	$\psi \equiv [C_A]^f_0$ for appropriate values of y_f and a_f

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

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0001-1541-80-3098-0327-$00.75.

$$\left[d\psi - C\,dt + \sum_{k=1}^{n} \frac{\partial F}{\partial \dot{y}_k}\, dg_k\right]_0^f = 0 \qquad (6)$$

Since ψ is extremalized, $\partial\psi \equiv 0$.

For criteria (i) and (iv) of Table 1, which have concentration as the objective function, the transversality condition becomes

$$[(1 + \lambda_1)\, dC_A + \lambda_2\, da - C dt]_0^f = 0 \qquad (7)$$

For criterion (i), Equation (7) reduces to $\lambda_{1f} = -1$. Then, indeed, it can be shown that the optimal policy equations are valid, if $E_D > E_R$ for either concentration dependent or independent catalyst decay rates.

For other criteria, however, $E_D > E_R$ does not necessarily result in an optimal policy. Consider the criterion (iv), presented by Pommersheim and Chandra, which requires the initial temperature T_0 and reaction time t_f to be specified with the object of maximizing conversion. For this scheme, the final activity is not fixed and the transversality condition must be

$$(1 + \lambda_{1f})\, dC_{Af} + \lambda_{2f}\, da_f = 0 \qquad (8)$$

Substitution of (8) into (5) and use of the Euler-Lagrange equations gives

$$\frac{E_D - E_R}{\left[\frac{E_D}{E_R}(m + n - 1) - (l + k - 1)\right] t_f - \left[\left(\frac{a}{\delta}\right)_0 - \frac{E_D}{E_R}\left(\frac{C_A}{r}\right)_0\right]} > 0 \qquad (9)$$

In deriving Equation (9) for criterion (iv), we used Equations (2), (3) and (4).

When $E_D > E_R$, a positive denominator in Equation (9) is required. This may or may not occur depending on the desired value of t_f and the specific values of the kinetic and thermal parameters. It is even possible for some parameter sets to have optimal policies, where $E_D > E_R$, as is illustrated later.

In general, the time given by the root of Equation (9), that is

$$t_f^* = \frac{\left(\frac{a}{\delta}\right)_0 - \frac{E_D}{E_R}\left(\frac{C_A}{r}\right)_0}{\frac{E_D}{E_R}(m + n - 1) - (l + k - 1)} = \frac{\alpha}{\beta} \qquad (10)$$

will be critical in determining whether or not the optimal policy Equations (2), (3) and (4) are valid. Here α and β represent, respectively, the numerator and denominator of Equation (10). Table 2 summarizes the possibilities. Valid, invalid and conditionally valid policies are possible, depending on the signs of α and β as well as their numerical values.

For the specific parameter set given by Pommersheim and Chandra (K_{A0}, K_{D0}, E_R/R and E_D/R: 5×10^{16}, 2×10^{17}, 1.9×10^4 and 2×10^4, respectively) application of this procedure shows that the optimal policy equations are not valid, except for $k=0$ and $t_f \geq 0.48$. For $k=1$, the policy would be valid if $t_f \geq 9.6$ were possible, but a temperature limit is reached first. In addition, times greater than $t_f = 0.67$ cannot occur since the concentration is driven to zero at that time, while the temperature becomes unbounded.

In general, Equations (3) and (2) predict limits on reaction times, given, respectively, by

$$t_f < \frac{(a/\delta)_0}{\left(\frac{mE_D}{E_r} + 1 - l\right)} \qquad (11)$$

and

$$t_f < \frac{(C_A/r)_0}{\left(\frac{kE_R}{E_D} + 1 - n\right)} \qquad (12)$$

The limits given by Equations (11) and (12) occur when (and if) the activity and concentration, respectively, go to zero. The limiting time will be whichever limit occurs first. Thus for some conditions, we can have t_f bounded between t_f^* and one of these limits. This can occur for both $E_D > E_R$ and $E_D < E_R$ situations. This point is further illustrated by the selection of appropriate parameter sets. Consider the case where no upper temperature limit exists, and take $m = n = l = k = 1$, with $E_D/R = 20{,}000$, $E_R/R = 19{,}000$, $K_{A0} = 2.0 \times 10^{19}$, and $K_{D0} = 2.9 \times 10^{16}$. Application of the procedure presented here shows that the optimal policy equations will be valid in the range $0.4 < t_f < 1.8$. Similarly one finds the same validity range for the parameter set $E_D/R = 19{,}000$, $E_R/R = 20{,}000$, $K_{A0} = 2.0 \times 10^{17}$, and $K_{D0} = 2.9 \times 10^{16}$. For any desired run time in this range the Equation (2), (3) and (4) for concentration, activity and temperature will be valid. For $t_f \leq 0.4$, these equations will be invalid.

The equations of Pommersheim and Chandra apply if criterion (i) of maximizing conversion at fixed t_f and a_f is used, with trial and error on the initial temperature T_0, such that the condition $\lambda_{1f} = -1$ is met at the desired final time t_f. In this case the L-C condition $E_D > E_R$ suffices. The figures given by these authors represent the corresponding traces of activity and concentration for all (t_f, a_f) pairs having the same initial temperature. Due to the split end conditions peculiar to this problem, a trial and error procedure must always be followed, to make sure that the transversality condition (Equation 6) is obeyed.

SOME MULTIPLE REACTIONS

The transversality condition prescribes the necessary conditions needed to provide the general solution to the optimal path of reactor operation. Consider the single reaction $A \rightarrow R$, for the case where t_f is not fixed, with fixed a_f, C_{A0} and a_0. The transversality condition becomes $\lambda_{1f} = -1$ with $C = 0$ (where $C = -\lambda_1 r - \lambda_2 \delta$ is the constant in first integral). This leads to obvious simplifications in the equations for the optimal temperature policy. When we have only a single reaction $A \rightarrow R$, the criterion of minimizing C_A will be the equivalent to one of maximizing C_R. This is identical, mathematically, to the case $A \rightarrow R + S$ where the side reactions are slow enough not to effect the material balance relations.

But, whenever we have series, or parallel, or both series and parallel reaction schemes, such as

$$A \rightarrow R \rightarrow S$$

or

$$A \rightarrow R$$
$$A \rightarrow S$$

or

$$A \rightarrow R \rightarrow S$$
$$A \rightarrow S$$

respectively, the two criteria are no longer equivalent.

Consider the irreversible series and parallel reaction scheme.

TABLE 2. REGIONS OF VALIDITY OF OPTIMAL POLICY EQUATIONS (CRITERION iv).

α	β	$E_D > E_R$	$E_D < E_R$
$+^*$	$+^\dagger$	$t_f > t_f^* = \beta/\alpha$	$t_f < t_f^*$
$-$	$-$	$t_f < t_f^*$	$t_f > t_f^*$
$+$	$-$	all t_f	invalid
$-$	$+$	invalid	all t_f

---

*positive α occurs for $E_R(\alpha/\delta)_0 > E_D\,(C_A/r)_0$

†positive β occurs for $E_D\,(m+n-1) > E_R(l+k+1)$

$$A \rightarrow R \rightarrow S$$
$$A \rightarrow S$$

with concentration dependent catalyst decay, and reaction rates which depend on reactant concentrations.

Let r_{12}, r_{23} and r_{13} be the rates of reaction of A to R, R to S and A to S, respectively. For this case the constraints become

$$(i)\ \phi_1 = \dot{C}_A + r_{12}(C_A, a, y) + r_{13}(C_A, a, y) = 0 \qquad (13)$$
$$(ii)\ \phi_2 = \dot{C}_R + r_{23}(C_R, a, y) - r_{12}(C_A, a, y) = 0 \qquad (14)$$
$$(iii)\ \phi_3 = \dot{a} + \delta(C_A, a, y) = 0 \qquad (15)$$

and the augmented function is given by

$$F = \lambda_1\phi_1 + \lambda_2\phi_2 + \lambda_3\phi_3 = 0 \qquad (16)$$

The corresponding Euler-Lagrange equations take the form

$$\dot{\lambda}_1 - \lambda_1(r_{12C_A} + r_{13C_A}) + \lambda_2 r_{12C_A} - \lambda_3\delta_{C_A} = 0 \qquad (17)$$
$$\dot{\lambda}_2 - \lambda_2 r_{23C_R} = 0 \qquad (18)$$
$$\dot{\lambda}_3 - \lambda_1(r_{12a} + r_{13a}) - \lambda_2(r_{23a} - r_{12a}) - \lambda_3\delta_a = 0 \qquad (19)$$
$$-\lambda_1(r_{12y} + r_{13y}) - \lambda_2(r_{23y} - r_{12y}) - \lambda_3\delta_y = 0 \qquad (20)$$

while the First Integral is given by

$$C = -\lambda_1(r_{12} + r_{13}) - \lambda_2(r_{23} - r_{12}) - \lambda_3\delta \qquad (21)$$

Taking C_{A0}, C_{R0}, a_0, t_0, a_f and t_f as fixed, with the objective of maximizing conversion of reactant A (or minimizing the concentration C_A) then

$$\psi = [C_A]_0^f \qquad (22)$$

The transversality condition yields

$$\lambda_{1f} = -1;\ \lambda_{2f} = 0 \qquad (23)$$

If r_{23C_R} is positive (typically true for irreversible nth order kinetics), equation 18 implies that λ_2 is either a monotonically increasing or decreasing function depending on the sign of λ_2. In addition $\dot{\lambda}_2$, the time derivative, will always have the same sign as λ_2.

Using these facts and Equation (23), it follows that $\lambda_2(t) = 0$. This simplifies the above formulation to that presented by Pommersheim and Chandra since $r_{12} + r_{13}$ represents the overall rate at which reactant A appears.

This result can be extended by induction to any number of irreversible parallel or series reactions. The only restriction is that none of the decay rates for the reactant A can depend on the concentration of any of the reaction products. If the decay rates are of the power law form, then equations similar to Equations (2), (3), and (4) for the optimal policy of operation can be derived by the methods given by Pommersheim and Chandra.

If the objective is to maximize the concentration of intermediate product R, then the objective function is

$$\psi = [-C_R]_0^f \qquad (24)$$

In this case, no such simplification arises since the transversality conditions are of the form

$$\lambda_{1f} = 0;\ \lambda_{2f} = 1 \qquad (25)$$

The solution to the Euler-Lagrange equations would be a second-order differential equation (or two coupled first-order differential equations) which requires two boundary conditions. These are specified by Equation (25), and must be included in the trial and error solutions for the optimal path of reactor operation.

BOUNDED CONTROL

In previous works (Pommersheim and Chandra 1975, and Szepe and Levenspiel 1968), a limit or maximum temperature of reactor operation was presumed. It was argued that since the temperature is essentially a rising one throughout, holding the temperature at this limit value, once it is attained, represents the best method of operation. Such a change in the mode of control, from a (supposedly optimal) rising temperature sub-arc to a constant temperature represents a discontinuity in the control variable, and is a problem in bounded control (Miele, A. 1962).

Applying the Weirstrass-Erdmann Corner Condition which is relevant to this problem, yields

$$\left(\frac{\partial F}{\partial \dot{y}_{k-}}\right) = \left(\frac{\partial F}{\partial \dot{y}_{k+}}\right) k = 1, \ldots, n \qquad (26)$$

and

$$\left(-F + \sum_{k=1}^{n} \frac{\partial F}{\partial \dot{y}_k}\dot{y}_k\right)_- = \left(-F + \sum_{k=1}^{n} \frac{\partial F}{\partial \dot{y}_k}\dot{y}_k\right)_+ \qquad (27)$$

in which the negative and positive signs denote conditions immediately before and after the corner point, respectively. For the particular case in which the fundamental is explicitly independent of t, these equations imply that

$$\lambda_{i+} = \lambda_{i-} \qquad (28)$$

and

$$C_+ = C_- \qquad (29)$$

which means that the Lagrangian multipliers, λ_i, and the integration constant, C, must be the same in the neighborhood of the corner and that the value of C is the same for all the sub-arcs forming the complete extremal arc.

For the case of Pommersheim and Chandra, these additional restrictions imply that,

$$\lambda_{1-} = \lambda_{1+};\ \lambda_{3-} = \lambda_{3+} \qquad (30)$$

and

$$C_- = C_+ \qquad (31)$$

have to be satisfied for their discontinuous solution to be optimal.

Clearly any discontinuity in the temperature is reflected in the integration constant, C, since

$$C = -\lambda_1 r - \lambda_3\delta \qquad (32)$$

unless both λ_1 and λ_3 are zero in the neighborhood of the corner. But the transversality condition states that λ_1 is always less than zero, and greater than or equal to -1. Hence the Weirstrass-Erdmann corner conditions are not satisfied. This means that the policy of keeping the temperature at the maximum permissible temperature, once it is reached, is not optimal. This result is independent of the nature of the transversality condition. Thus for problems where the optimal temperature policy exceeds feasible reactor temperatures, the overall solution of Pommersheim and Chandra (1975) and Szepe and Levenspiel (1968) will be invalid. However when the problem is unbounded, their solution will still be valid provided both the transversality condition, and Legendre-Clebsch conditions are obeyed.

It is important to emphasize these restrictions on optimal temperature policies for reactors containing a decaying catalyst, for even though the optimal policy equation itself will not change, the region of validity is often affected.

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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} = rate constant for deactivation reaction
K_D = rate constant for deactivation
K_{D0} = frequency factor for deactivation
r_A = rate of reaction of A
r_{12} = rate of reaction for $A \rightarrow R$
r_{23} = rate of reaction for $R \rightarrow S$
r_{13} = rate of reaction for $A \rightarrow S$
r_y = $(\partial r_A/\partial_y)$
R = gas constant
t = reaction or batch time
t_f = total reaction time
t_f^* = limit defined by Equation (10)
T = absolute temperature
X_A = conversion of A
y = dependent variable in Bolza problem
y_j = dependent variable in Bolza problem

Greek Letters

α, β = numerator, denominator, respectively of Equation (10)
δ = deactivation rate
λ_j = jth Lagrange multiplier
ϕ_j = jth constraint equation
ψ = objective function

Superscripts

l, k, m, n = powers, Equation (1)

Subscripts

f = final or end condition
i = index
0 = initial condition
y = partial derivative with respect to y
yy = second partial

Manuscript received April 5, 1979; revision received July 3, and accepted July 12, 1979.

BOOKS

The Chemical Reactor Omnibook, Octave S. Levenspiel; Oregon State University Book Stores, 1979. 685 pages. $20.00 plus $1.75 mailing charge.

The Chemical Reactor Minibook, Octave S. Levenspiel; Oregon State University Book Stores, 1979. 226 pages. $7.00 plus $1.40 mailing charge.

These unique and imaginative companion volumes provide a concise compendium of useful results for a selected variety of chemical reactor design situations, and a large collection of problems (1382 in the Omnibook, 729 in the Minibook) which vary in difficulty and which should keep most undergraduate students very interested in learning more about the subject. The Omnibook is intended by the author to serve as "a reference book for methods in reactor design, a supplementary text for a course of study, or a basis for a self-paced or self-study course on the subject." It is divided into sections on single phase reactions, reactors with solid catalysts, catalytic reactors with two changing phases, gas/liquid and liquid/liquid reactions, reaction of solids, flow through reactors, and enzyme and microbial reactions. The emphasis is on the presentation of the important performance equations, guidelines, and relationships needed to solve practical and somewhat simplified problems in these areas, rather than on the derivation or detailed discussions found in most textbooks. While it succeeds very well in its stated goals, a reading of it alone may leave teachers of the subject feeling somewhat unfulfilled.

The Minibook is a condensed version of topics from the Omnibook, and is intended to supplement a standard text on the subject. Included are about 75% of the sections on single phase reactors, solid catalyst reactors, reactions of solids, and flow through reactors, and of course a reduced number of problems.

Professor Levenspiel's inimitable wit pervades these treatments and the associated problems, and makes for a delightful reading experience. He makes no claim to cover the wide range of topics that many texts attempt, and discussions of reaction mechanisms and the thermodynamics of chemical reactions are notably absent. An interesting production feature is that the authors handwritten copy has been directly reproduced, and consequent advantage of this has been taken to produce a concise and legible mixture of text, equations, and figures.

In summary, teachers and students of beginning and intermediate chemical reactor design should find either of these volumes extremely useful and stimulating, either as an associated teaching aid or as a valuable reference.

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