On Singular Policies in the Optimal Distribution of a Bifunctional Catalyst:

Part I. Effect of Reaction Kinetics

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Results are presented on the affects of kinetic changes on optimal, bifunctional, catalyst distribution policies for a consecutive two-reaction sequence in a plug flow tubular reactor. Earlier results on singular control arising from reversible reactions are extended to include inhibition or activation. These may arise from the affects of any reactant or product on the rate or from a subsequent or preceding reaction in a sequence. The system equations are written in dimensionless form to provide efficient computations and to allow analytic interpretation of numerical results from previous studies.

SCOPE

The catalyst mixes that are called for when bifunctional catalysts are optimally distributed along the length of a plug flow tubular reactor were studied analytically. Reaction sequences, kinetic forms, and system parameters were varied to look for significant generalizations. A computationally efficient numerical method was devised and found to include a method from previous studies as a special case. The changes in the proportions of the two catalysts along the length of the reactor were examined in terms of the postulated kinetics. For each case, physical interpretations were sought for the singular policies obtained from the application of the optimal control theory. The variables studied include reaction reversibility, reaction stoichiometry and sequence, two different objective functions, and several cases of reaction nonlinearity.

CONCLUSIONS AND SIGNIFICANCE

By writing system differential equations in dimensionless form and parametrizing the residence time, a computationally efficient numerical method was obtained that included one used by previous studies as a special case. The independence of the first switching location from the dimensionless residence time observed by Chang and Reilly (1976) was shown to be one particular case of a more general situation. Various catalyst composition profiles are explained on the basis of the slope of the switching curve and the functional forms of the two rate expressions. A specific example showed that a nonmonotonic policy profile can arise along the singular segment. The width of the singular segment does not necessarily increase monotonically with increasing residence time. Singular policies were shown to arise from either reaction reversibility, specific stoichiometry, or reaction sequence as well as from the activating or inhibitory effects of the chemical species on either or both of two consecutive reactions.

Multifunctional catalyst systems have been studied extensively for a wide range of applications that include hydrocarbon processing (Thomas and Wood, 1967; Thomas, 1971; Jenkins and Thomas, 1970; Gunn and Thomas, 1965; Al-Samadi et al., 1974), biochemical uses (Langer, 1974; Langer et al., 1976, 1977; Wingard and Pye, 1974; Wykes et al., 1975; Coughlin et al., 1975; Hervagault et al., 1976; Messing, 1974; Martensson, 1974; Bouin et al., 1976), and catalytic muffler design (Hulburt, 1975; McEvoy, 1975; Klimisch, 1975). Such catalysts present unique problems in several aspects of reactor engineering, where complications can arise from deactivation (Gould, 1972, 1974), catalyst support interaction (Forster and Roth, 1974; Messmer and Knudson, 1976), axial dispersion (Ajinkya and Ray, 1973), and macropore concentration gradients (Shadman-Yazdi and Petersen,

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1972) in a pelletized mixed catalyst and/or a compound catalyst (Clark, 1970).

For design purposes, a decision must be made in each case on the best distribution of the respective catalysts. This optimization problem has been studied by Chang and Reilly (1976), Hofer (1973), King et al. (1972), and Glasser and King (1973) for selected reaction kinetics and objective functions; by Gunn (1967) and Jackson (1968) for first-order kinetics; and by Ogunye and Ray (1971) and Dalcorso and Bankoff (1972) in terms of catalyst deactivation. In each of these studies, where optimal catalyst distribution is sought, a policy is needed for mixing catalysts over some segment of the reactor of interest.

In a packed bed, steady state, plug flow tubular reactor (PFTR), attachment of different catalysts on separate supports may be desirable if one of the catalysts is more vulnerable to deactivation than the others, or needs separate treatment for another reason. When this is the case, the distribution policy in the reactor bed may be either of the bang-bang type, moving only between its possible extremes, or the policy may demand singular control over some range defined by switching point locations. A policy is called singular when it uses intermediate values of the control effort, in this case the choice of catalyst mix. Whether a specific optimization is to be singular or bang-bang depends in general on the initial concentrations, the objective function, the functional form of the reaction kinetics, and the magnitudes of system parameter values.

For the sequential reaction scheme

$$\Sigma a_i A_i \rightleftarrows \Sigma b_{i,1} B_i \tag{1}$$

$$\Sigma b_{i,2} B_i \rightleftarrows \Sigma c_i C_i \tag{2}$$

calculational experience of the reference works indicates that bang-bang policies are optimal in the range of low residence time, and the singular policies become optimal at higher values. Since higher conversion calls for extended reaction time, optimal policies for practical problems might typically be expected to be singular, except perhaps for certain reaction schemes and kinetics. This paper examines several practical kinetic considerations which bear in an important way on optimal catalyst distribution policies in a PFTR, especially to highlight the kinds of circumstances that might be expected to produce singular policies. This question is addressed analytically to identify both conditions for occurrence of a singular policy and to locate its position between particular switching locations.

The biochemical literature offers numerous examples of reaction sequences that can be viewed in the framework of Equations (1) and (2). Of these, many can be reduced to special subcases. Consider, for example, the fumurate hydratase-aspartate ammonia lyase system:

$$\text{L-Malate} \xrightleftharpoons{\text{Fumarate Hydratase}} \text{Fumarate} + H_2O$$

and

$$\text{Fumarate} + NH_4^+ \xrightleftharpoons{\text{Aspartate Ammonia Lyase}} \tag{3}$$

$$\text{L-Aspartate} \tag{4}$$

which may be approximated at pH in the range of 6.5 to 6.8 and high concentrations of water and NH_4^+ by *a simplified single-substrate reaction sequence:*

$$\text{L-Malate} \rightleftarrows \text{Fumarate} \rightarrow \text{L-Aspartate} \tag{5}$$

As a second illustration, one may examine the combination of

$$R + O_2 + H_2O \xrightarrow{\text{Oxidase}} RO + H_2O_2 \tag{6}$$

and

$$H_2O_2 \xrightarrow{\text{Catalase}} \frac{1}{2} O_2 + H_2O \tag{7}$$

which may at relatively dilute levels of oxygen and peroxide be modeled by

$$A_1 + A_2 \rightarrow B_1 + B_2 \tag{8}$$

and

$$B_2 \rightarrow cC \tag{9}$$

Other examples may be drawn from an ATP regeneration system (Langer, 1974; Langer et al., 1976) and the blood clotting phenomena (Burton, 1965; Lorand, 1976), where each of the five major consecutive steps triggers the next in sequence. Among these five steps are included the two enzymatic steps in which the thromboplastins released from platelets and injured tissues catalyze the conversion of prothrombin to thrombin which in turn participates in the conversion of fibrinogen to fibrin.

With these combinations in mind, two reaction sequences were chosen for detailed study, both special subcases of reactions (1) and (2). The first sequence is

$$\begin{array}{c} A \rightleftarrows B \\ B \rightarrow C \end{array} \tag{I}$$

and the second is

$$\begin{array}{c} S + A \rightarrow R + B \\ B \rightarrow cA \end{array} \tag{II}$$

The objective for the first sequence is to maximize the concentration of C at the reactor exit, and that for the second is to maximize the effluent concentration of R. It should be noted that the end product of sequence II is also a reactant in the first reaction of the set, as was the case, for example, in the oxidase-catalase system.

SYSTEM EQUATIONS

A reaction sequence of the form of Equations (1) and (2) is to be carried out in a PFTR under isothermal conditions. With the assumption that each of the two reactions of interest occurs at a rate proportional to the relative amount of specific catalyst introduced, component mass conservation in terms of reaction extent variables gives

$$\frac{d\xi_1}{d\tau} = Puf_1 \tag{10}$$

$$\frac{d\xi_2}{d\tau} = P(1-u)\alpha f_2 \tag{11}$$

subject to the initial conditions applicable at the reactor feed location. The relationships between the extent variables and concentration variables conform to general convention and are the same as those given by King et al. (1972). A specific objective function is to be maximized subject to the constraint on the fraction of total catalyst volume allocated to the first catalyst:

$$0 \leq u \leq 1 \tag{12}$$

Following the suggestion of Hlavacek and Hofmann (1971), Equations (10) and (11) may be rearranged to obtain

$$\frac{d\xi_1}{d(P\tau)} = uf_1 \tag{13}$$

$$\frac{d\xi_2}{d(P\tau)} = (1-u)\alpha f_2 \tag{14}$$

which is essentially a parametrization on the dimensionless residence time. This modified time scale is useful in setting up the customary adjoint equations and their boundary conditions that correspond to the Hamiltonian to be maximized at every reactor position in the well-known manner (Choi and Perlmutter, 1977):

$$\max_{0 \leq u \leq 1} \quad H = P[\lambda_1 u f_1 + \lambda_2(1-u)\alpha f_2] = P(uJ + N) \tag{15}$$

If a region of singular control is to exist, it is necessary that $J = 0$ and $(dJ/d\tau) = 0$ over the same finite region (Jackson, 1968). The first of these conditions calls for

$$\frac{\lambda_1}{\lambda_2} = \frac{\alpha f_2}{f_1} \tag{16}$$

and the two together require that

$$\alpha = \frac{f_1^2 \dfrac{\partial f_2}{\partial \xi_1}}{f_2^2 \dfrac{\partial f_1}{\partial \xi_2}} \tag{17}$$

The system adjoint equations may be combined to give

$$\frac{d(\lambda_1/\lambda_2)}{d(P\tau)} = u\left[-\frac{\lambda_1}{\lambda_2}\frac{\partial f_1}{\partial \xi_1} + \frac{\lambda_1^2}{\lambda_2^2}\frac{\partial f_1}{\partial \xi_2}\right] + (1-u)\alpha\left[-\frac{\partial f_2}{\partial \xi_1} + \frac{\lambda_1}{\lambda_2}\frac{\partial f_2}{\partial \xi_2}\right] \tag{18}$$

valid throughout the reactor. The control decision in the first segment of the reactor is selected by comparing the initial feed concentration with the switching curve defined by Equation (17) and selecting one of the two extreme values of u such that the system trajectory approaches the switching curve.

The Equations (13) to (18) lend themselves to a relatively straightforward algorithm that makes it possible to easily generate P and α from preassigned values of other system parameters and the extent variables at the first switching point. The set of values for P and α generated from such computations can, in turn, be used as a data reservoir to recover by interpolation values of the extent variables from given values of P and α. This is computationally more efficient than working from the beginning with Equations (10), (11), (17), and (18).

It is worth noting that the algorithm used by King et al. (1972) is a special case of the one developed here in that they generated only P from a grid of α values, each point requiring a numerical solution for the extent variable at the first switching point. Further, the numerical observation made by Chang and Reilly (1976) to the effect that the first switching position does not vary with total residence time is explainable in analytic terms, since P enters the equations only as a linear multiplicative factor and the value of the extent variable at the first switching point is independent of P.

REACTION SEQUENCE I

Consider the reaction scheme I and the initial conditions $X_{A_0} = 1$, $X_{B_0} = X_{C_0} = 0$. Assume that the reaction kinetics are of the form

$$f_1 = \frac{X_A}{1 + \mu X_A} - \beta X_B \tag{19}$$

$$f_2 = X_B \tag{20}$$

As an objective, it is desired to maximize the yield of C at reactor exit. By matching the switching Equation (17) with the state variables obtained by simultaneous integration of the state and adjoint equations, the switching locations are determined as

$$\tau_1 = \frac{1}{P\delta}\left[(1+\mu-\rho_1\mu)\ln\frac{\rho_1 - X^*}{\rho_1} - (1+\mu-\rho_2\mu)\ln\frac{\rho_2 - X^*}{\rho_2}\right] \tag{21}$$

$$\tau_2 = 1 - \frac{1}{P\alpha}\ln\left(1 + \sqrt{\frac{\alpha}{\beta}}\right) \tag{22}$$

and the width of the singular segment is

$$\Delta\tau = \tau_2 - \tau_1 = 1 - \frac{1}{P}\ln\left[(1+\sqrt{\alpha/\beta})^{1/\alpha}\left(\frac{\rho_1 - X^*}{\rho_1}\right)^{\frac{(1+\mu-\rho_1\mu)}{\delta}}\left(\frac{\rho_2 - X^*}{\rho_2}\right)^{-\frac{(1+\mu-\rho_2\mu)}{\delta}}\right] \tag{23}$$

When $\mu = 0$, the Michaelis-Menten kinetics are replaced by first-order kinetics, and Equations (21) to (23) reduce to

$$\tau_1 = \frac{1}{P}\ln\left[1 + \frac{1+\beta}{\sqrt{\alpha\beta}}\right]^{(1+\beta)} \tag{24}$$

$$\tau_2 = 1 - \frac{1}{P}\ln\,[1 + \sqrt{\alpha/\beta}]^{1/\alpha} \tag{25}$$

$$\Delta\tau = 1 - \frac{1}{P}\ln[1 + \sqrt{\alpha/\beta}]^{1/\alpha}\left[1 + \frac{1+\beta}{\sqrt{\alpha\beta}}\right]^{(1+\beta)} \tag{26}$$

The corresponding expressions for zero-order kinetics are

$$\tau_1 = \frac{1}{P\beta}\ln(1 + \sqrt{\beta/\alpha}) \tag{27}$$

$$\Delta\tau = 1 - \frac{1}{P}\ln(1 + \sqrt{\alpha/\beta})^{1/\alpha}(1 + \sqrt{\beta/\alpha})^{1/\beta} \tag{28}$$

whereas the expression for the second switching point remains the same as Equation (25). In either case, the width of the singular region increases with residence time until it occupies the total reactor length, suggesting that any bang-bang segment might be of negligible importance for high conversion reactors.

If both steps of the reaction scheme I are assumed to be irreversible ($\beta = 0$), Equations (19) and (20) reduce to the form

$$f_1 = f_1(X_A) \tag{29}$$

$$f_2 = f_2(X_B) \tag{30}$$

Elsewhere (Choi and Perlmutter, 1976), the authors have shown that singular control cannot arise if the reaction kinetics are of this form. Evidently there occurs a transition as β is reduced that eliminates the region of singular policy. The critical value of β may be identified from Equations (26) and (28) as the locus of points in α-β-P space for which $\Delta\tau = 0$. Numerical results are given in Figure 1, showing the critical values of β for the transition to bang-bang control for the given values of

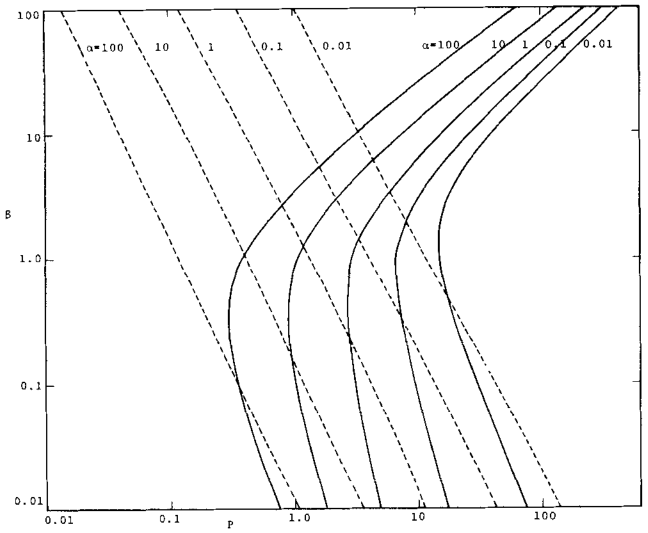

Fig. 1. Critical values of β for which $\Delta_T = 0$ for given α and P; the solid lines are for first-order and the dashed lines are for zero-order kinetics for the first forward step.

α and P. Decreasing values of α monotonically reduced the reactor domain of singular policy; changes in β produced similar uniformity for zero-order kinetics but nonmonotonic behavior for first-order kinetics.

Further results that may be obtained from this treatment include the singular trajectory derived from the switching curve and the control policy of the singular segment. These are given in Table 1 for the case at hand and for the two special kinetics where the Michaelis-Menten forms reduce to their zero- and first-order limits. Using these intermediate results, one can go on to obtain optimal product yields such as those shown in Figures 2 and 3. The first of these was derived from case A using the Michaelis constant as a parameter, and also includes case B when $\mu = 0$. Figure 3 compares case C results with case A for the same value of $\mu = 10$. Although the results shown on Figure 2 for relatively high values of P are those from the optimal singular policy, the calculational experience indicates that the results from the bang-bang policy are within 10% for values of P up to 30. This observation justifies the use of bang-bang policy as a suboptimal substitute for the optimal singular policy but is in sharp contrast to the use of the suboptimal fixed composition policy for still higher values of residence time. Equations (23) or (26) show the widening of the singular segment with increasing P under conditions of high conversion. By comparing the various results with the one for $\mu = 0$, Figure 2 also gives information on the errors that can arise by approximating correct Michaelis-Menten kinetics by first-order forms. The errors increase with μ. Figure 3 shows that similar errors can arise when one substitutes zero-order forms for the Michaelis-Menten kinetics. In this case, the error increases as μ decreases. For this order kinetics, the effluent concentration of the species B is

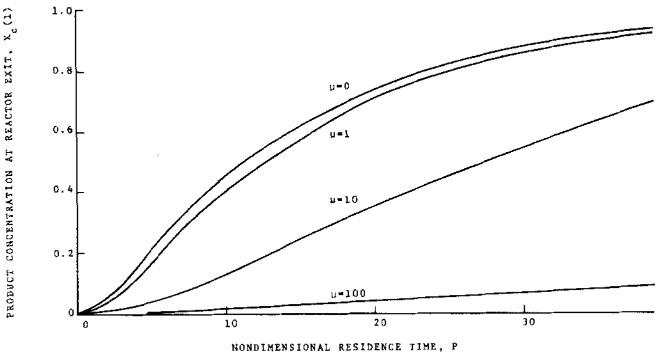

Fig. 2. Effect of reactor residence time on optimal product yield for kinetics of case A in Table 1; $\alpha = 0.1$, $\beta = 0.1$, $X_{Ao} = 1$, $X_{Bo} = X_{Co} = 0$.

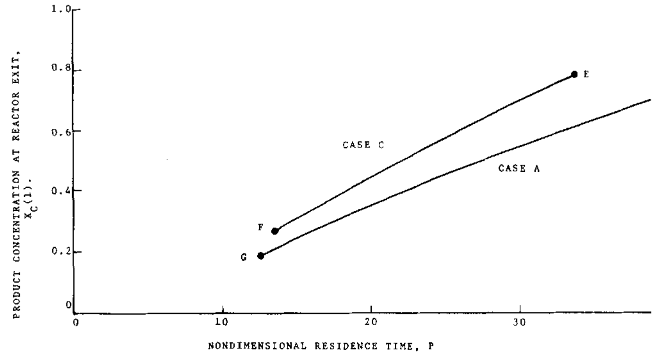

Fig. 3. Effect of reactor residence time on optimal product yield for kinetics of cases A and C in Table 1; $\mu = 10$, $\alpha = 0.1$, $\beta = 0.1$.

$$X_2 = \frac{1}{\alpha\beta\mu^2(1+\sqrt{\alpha\beta})^2} \tag{31}$$

regardless of the residence time. The effluent concentration of species A is given by

$$X_1 = 1 - \frac{1}{\beta\mu(1+\sqrt{\alpha/\beta})} - \frac{\alpha}{\beta\mu(1+\sqrt{\alpha/\beta})^2}\Big[P$$

TABLE 1. SINGULAR SEGMENT CONTROL POLICIES FOR SEVERAL KINETIC ALTERNATIVES IN REACTION SEQUENCE I

	Order of first reaction		Order of second reaction		
Case	Forward	Reverse	Forward	Switching line*	Control policy in the singular segment
A	Michaelis-Menten	1	1	$X_B = \frac{\gamma X_A}{1+\mu X_A}$	$u_m = \frac{\gamma\beta(1+\mu X_A)^2}{\gamma^2\beta + (1+\mu X_A)^2(1+\sqrt{\alpha\beta})}$
B	1	1	1	$X_B = \gamma X_A$	$u_m = \frac{\gamma\sqrt{\alpha\beta}}{\gamma^2\beta+1}$
C	0	1	1	$X_B = \gamma/\mu$	$u_m = \gamma\sqrt{\alpha\beta}$

* Note: $\gamma = \frac{1}{\beta + \sqrt{\alpha\beta}}$

$$- \frac{1}{\alpha} \ln(1 + \sqrt{\alpha/\beta}) - \frac{1}{\beta} \ln(1 + \sqrt{\beta/\alpha}) \Big] \quad (32)$$

It may be noted that there is an upper critical value of residence time

$$P_2 = \frac{1}{\alpha} \ln(1 + \sqrt{\alpha/\beta}) + \frac{1}{\beta} \ln(1 + \sqrt{\beta/\alpha}) + \frac{[\beta\mu(1 + \sqrt{\alpha/\beta}) - 1](1 + \sqrt{\alpha/\beta})}{\alpha} \quad (33)$$

above which X_1 would be negative. This limit is shown in Figure 3 as point E. A lower limit on residence time is also attainable at the value of

$$P_1 = \frac{1}{\alpha} \ln(1 + \sqrt{\alpha/\beta}) + \frac{1}{\beta} \ln(1 + \sqrt{\beta/\alpha}) \quad (34)$$

for which $\Delta\tau = 0$ in Equation (28). This point is indicated by F on Figure 3, and the corresponding point for case A kinetics is labeled as point G.

A somewhat different kinetic form arises when liquid-phase inhibitors or gas-phase inerts are significant for the first reaction, and

$$f_1 = \frac{X_A - \beta X_B}{1 + (X_I/K_I)} \quad (35)$$

where X_I is a constant inhibitor concentration. By letting

$$\mu_I = X_I/K_I \quad (36)$$

$$\alpha' = \alpha(1 + \mu_I) \quad (37)$$

$$P' = P/(1 + \mu_I) \quad (38)$$

the system Equations (10) and (11) are reduced to the forms corresponding to the case without inhibitor. The prior control policy is therefore applicable, provided the new constants are substituted. The net result is that the policy has not changed, but the magnitudes of the control effort in the singular segment and the switching points change. The inhibition causes an increase in u_m and a shrinkage from both sides of the width of the singular segment. The increase in τ_1 is more pronounced than the decrease in τ_2. These results can be interpreted physically to imply that one needs a greater fraction of the reactor volume dedicated to the first reaction to maintain conversion to the desired final product by compensating for the effective increase in the second reaction rate.

With irreversible kinetics but with intermediate product inhibiting the first catalyst

$$f_1 = \frac{X_A}{1 + \mu_1 X_A + \mu_2 X_B} \quad (39)$$

$$f_2 = \frac{X_B}{1 + \mu_3 X_B + \mu_4 X_C} \quad (40)$$

The conditions for a singular decision segment give the expression for the singular trajectory as

$$X_B = \frac{1 + \mu_4 a_o}{\mu_4 + \alpha\mu_2} - \frac{\mu_4}{\mu_4 + \alpha\mu_2} X_A \quad (41)$$

With reactor feed consisting of pure reactant A, the initial concentration $a_o = X_{Ao} = 1$ and Equation (41) can be rearranged to

$$X_A = 1 + \frac{1}{\mu_4} - \left(1 + \frac{\alpha\mu_2}{\mu_4}\right) X_B \quad (42)$$

With the policy $u = 1$ in the first reactor segment, the corresponding trajectory is

$$X_A + X_B = 1 \quad (43)$$

The singular trajectory given by Equation (42) only crosses the first segment trajectory if

$$\alpha\mu_2 > 1 \quad (44)$$

and this is, therefore, a necessary condition for a singular region to exist.

The foregoing argument may be turned in an opposite direction by considering kinetics where the first reactant is an activator for the second catalyst. Using, for example, the forms developed by Ramachandran and Perlmutter (1976) and Choi and Perlmutter (1976)

$$f_1 = \frac{X_A}{1 + \mu X_A} \quad (45)$$

and

$$f_2 = X_B \left[1 + \frac{X_A}{K_M + X_A} (\sigma - 1)\right] \quad (46)$$

The corresponding expression for the singular trajectory is obtained from Equation (17) as

$$(K_M + X_A)(K_M + \sigma X_A) = X_M K_B (\sigma - 1) \quad (47)$$

This equation can have positive solutions for X_A only when $\sigma \geqq 0$. Further, it can only intersect the trajectory of Equation (43) when

$$\sigma > (1 + K_M) \quad (48)$$

and this is therefore a necessary condition for a region of singular policy. This means, in effect, that early introduction of the second catalyst makes possible its activation by the first reactant while it is still in high concentration. With this same condition of product free feed, the concentration of species A at the first switching point is

$$X_{As} = K_M \left[\left(1 - \frac{1}{\sigma}\right)\left(1 + \frac{1}{K_M}\right) - 1\right] \quad (49)$$

from which the necessary condition given by Equation (48) can also be deduced, since it assumes a positive solution for Equation (49), If the reaction kinetics for the second reaction are modified to include a Michaelis-like dependence on X_B

$$f_2 = \frac{X_B}{1 + \mu_3 X_B} \left[1 + (\sigma - 1) \frac{X_A}{K_M + X_A}\right] \quad (50)$$

the switching equation becomes

$$(K_M + X_A)(K_M + \sigma X_A) = X_B(1 + \mu_3 X_B) K_M (\sigma - 1) \quad (51)$$

By applying the same reasoning as before, the lower bound on σ is obtained as

$$\sigma > 1 + \frac{K_M}{1 + \mu_3} \quad (52)$$

which shows an increase in the range of σ for which the singular policy is possible.

REACTION SEQUENCE II

Turning to the reaction sequence II with the objective of maximizing intermediate product R in the effluent, it is convenient to examine the relatively simple nonlinear kinetics where

$$f_1 = X_s X_A \quad (53)$$

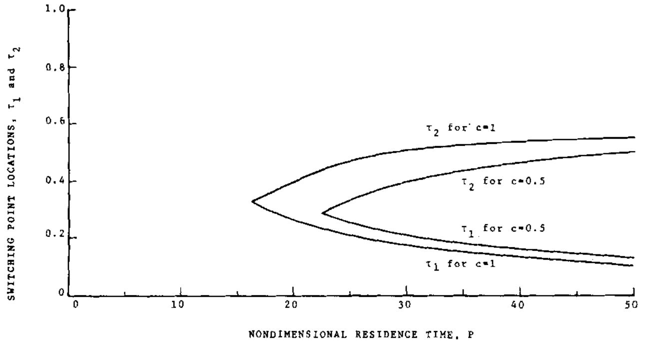

Fig. 4. Effect of stoichiometry on optimal switching point locations; $X_{So} = X_{Ao} = 1, X_B = X_R = 0, \alpha = 0.01$.

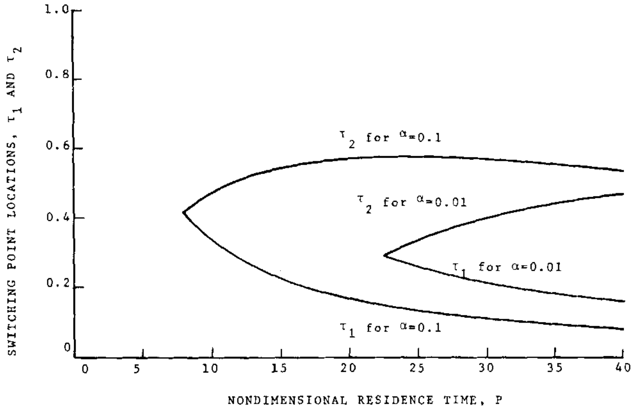

Fig. 5. Effect of second reaction rate constant on location of optimal switching points for reaction sequence II; $X_{Ao} = X_{So} = 1$, $X_{Ro} = X_{Bo} = 0$, $c = 0.5$.

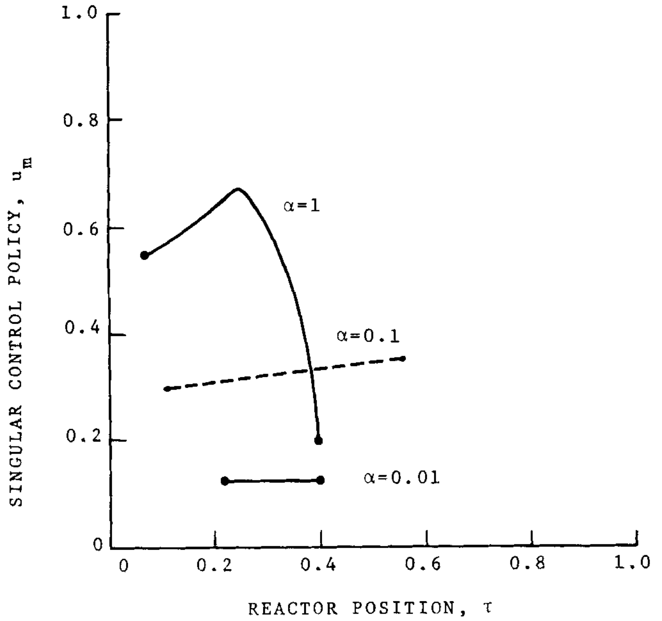

Fig. 6. Optimal singular control policies for three values of reaction rate constant at $P = 30$; the policies are $u = 1$ in both the first and final reactor segments.

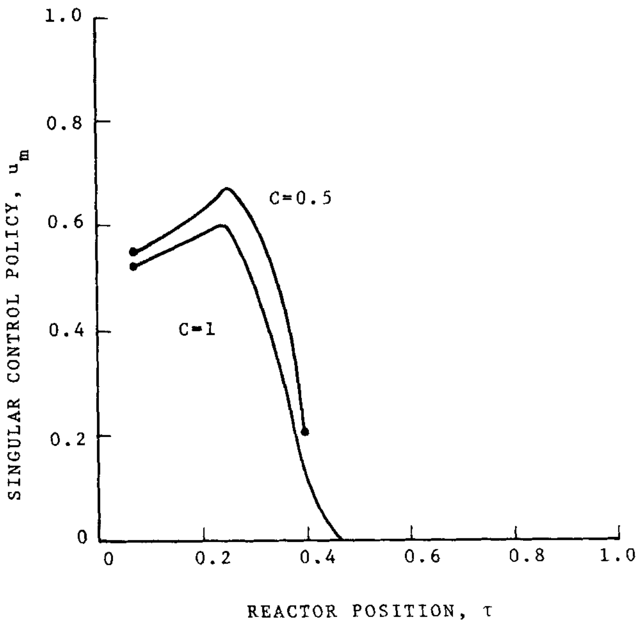

Fig. 7. Optimal singular control policies for two stoichiometries at $P = 30$, $\alpha = 1$; the policies are $u = 1$ in both the first and final reactor segments.

$$f_2 = X_B \tag{54}$$

For these kinetics, the switching Equation (17) becomes

$$X_B = \frac{\sqrt{X_S}[X_A + cX_{Bo} + (c-1)(X_{So} - X_S)]}{\sqrt{c\alpha} + c\sqrt{X_S}} \tag{55}$$

The corresponding switching point locations are dependent on the stoichiometric coefficient. Typical results for two choices of c are presented in Figure 4, showing that the width of the singular segment increases with increase of the stoichiometric coefficient. A parallel result may be found in Figure 5, where the variation is in the rate constant for the second reaction. The observation that the middle singular segment does not necessarily take up the total reactor volume as one increases the residence time makes an interesting comparison with the cases in Table 1, for which the width of the singular segment increases monotonically with increasing residence time until it takes up the total reactor volume. In contrast, the width of the singular segment for the case at hand decreased with increasing value of P for high values of α.

Figure 6 shows the singular control policies that are optimal over the reactor for several choices of α. Such nonmonotonic behavior was not observed in either the King et al. (1972) or Chang and Reilly (1976) studies, and it is important to understand why this departure can occur. The diverse results can be rationalized by combining switching Equation (17) with the system Equations (10) and (11), using singular optimal policies where called for. The resulting control policy is

$$u_m = \frac{\nu\alpha f_2}{f_1 + \nu\alpha f_2} \tag{56}$$

where $\nu = d\xi_1/d\xi_2$ is the slope of the switching line. The dependent variable u_m of Equation (56) will increase, for example, if f_1 decreases along a singular segment over which the magnitudes of f_2 and ν change only slightly. The same policy variable will, on the other hand, decrease over a reactor segment where the product $(\nu\alpha f_2/f_1)$ decreases. It appears that the previously cited works of King et al. (1972) and Chang and Reilly (1976) fit these two circumstances, respectively.

A change in the stoichiometric coefficient of the second reaction of scheme II produced only the relatively small effect on policy shown in Figure 7. The lower values of u_m for higher values of the stoichiometric coefficient reflect the need to increase the fraction of the first catalyst to compensate for the increased feedback from the second reaction.

ACKNOWLEDGMENT

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NOTATION

a_i, b_i, c_i = stoichiometric coefficients of species i
a_o = $X_{Ao} + X_{Bo} + X_{Co}$
A, B, C, S, R = chemical species
f_i = dimensionless reaction rate for the i^{th} reaction
H = Hamiltonian
J = the coefficient of the control variable in the Hamiltonian
k = rate constant for first forward reaction
K_M = $1/\mu_A$
L = reactor length
N = the group of terms in the Hamiltonian not containing the control variable
P = nondimensional residence time = kL/v
u = fraction of the total catalyst allocated for the first reaction
v = superficial linear velocity
X_i = dimensionless concentration of species i
X_1 = effluent concentration of species A
X_2 = effluent concentration of species B
X^* = concentration of B at first switching point

$$\frac{1 + \gamma + \mu - \sqrt{(1 + \gamma + \mu)^2 - 4\gamma\mu}}{2\mu}$$

Greek Letters

α = ratio of the second forward rate constant to the first forward rate constant
β = ratio of the first backward rate constant to the first forward rate constant
γ = $\dfrac{1}{\beta + \sqrt{\alpha\beta}}$
δ = $\sqrt{(1 + \beta + \beta\mu)^2 - 4\beta\mu}$
λ_i = adjoint variables
μ_i = ratio of the initial concentration of a reference species to the i^{th} Michaelis constant
μ_I = ratio of inhibitor concentration to the inhibition constant
ν = $d\xi_1/d\xi_2$ = the slope of the switching curve
ξ_i = extent variable for the i^{th} reaction
ρ_1 = $\dfrac{1 + \beta + \beta\mu + \delta}{2\beta\mu}$
ρ_2 = $\dfrac{1 + \beta + \beta\mu - \delta}{2\beta\mu}$
σ = activating factor
τ = normalized reactor coordinate

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Part II. Effect of Diffusional and Mass Transfer Resistances

The effects of diffusional and mass transfer resistances on the optimal distribution of a bifunctional catalyst were studied for the case where each catalyst is supported on a separate carrier in the packed bed of a plug flow, tubular reactor. The width of the segment requiring a catalyst mixture is reduced by the presence of transport resistance due to shifts of both switching points away from the ends of the reactor. The extent of the change in each of the two switching point locations depends upon the relative magnitudes of the effectiveness factors for the two reactions, as does also the change of packing policy in the singular segment. As observed in Part I, the first switching location is again independent of the dimensionless residence time; in the presence of the transport resistance, however, the first switching location increases by the multiplier of the respective inverse effectiveness factors. The results from previous numerical studies were shown to be particular cases of these general analytic results, and one specific reaction scheme with first-order kinetics was studied in detail for illustration.

SCOPE

Processes involving chemical reactions using multiple catalysts may be optimized by choosing a best catalyst distribution along a tubular reactor. This problem is most conveniently handled by the application of optimization theory. In this paper, results are reported on the effect of transport resistance on the optimal distribution of bifunctional catalysts in a plug flow, tubular reactor. Corresponding parameter comparisons are used to gain insight into the problem at hand, based upon results of a simpler standard problem. The general results are applied to a particular case with first-order reaction kinetics.

CONCLUSIONS AND SIGNIFICANCE

The absolute and relative magnitudes of effectiveness factors are both significant in determining optimal policies in systems that include mass transfer resistance. In the presence of transport resistance, the width of the singular segment decreases. This shrinkage can occur from either side, depending on the particular reaction to be favored in the bordering segments of bang-bang policy. The choice of catalyst mix in the singular policy segment

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