Optimal Catalyst Distribution in a Dual Enzyme Sequential System

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The dual enzyme sequential reactions that decompose arginine to ammonia were investigated experimentally to determine appropriate rate equations and to test predictions of optimal distribution of the two enzymes (arginase and urease) immobilized in a packed-bed reactor.

The kinetics of this system were experimentally found to be of the kind that calls for a bang-bang control with a well-defined switching point between the two immobilized enzyme catalysts. At low values of reactor residence time, the optimum switching point is shown to approach a limiting position which depends on the kinetic order of the second reaction. In the higher ranges of residence time, the switching point moves into the latter half of the reactor, but exceptions to this generalization are found when Michaelis-Menten kinetics are applicable to both reactions. For the special circumstance where the two reactions are of zero and first order, respectively, the optimal distribution of the two catalysts is independent of the first rate constant. The experimental results are, in general, consistent with these expectations, and secondary deviations are discussed. A suboptimal policy alternative is also treated analytically and tested by experiment.

SCOPE

Multiple catalyst systems have been applied to chemical, biochemical, hydrocarbon processing, and polymer engineering systems, and the optimal distribution of these catalysts in a fixed-bed tubular reactor has been examined in a variety of studies. Although a decision on control policy should depend on the particulars of reaction system kinetics, only one of the prior studies included any experimental verification of theoretical results.

This paper describes analytic results and their experimental verification for a two-step hydrolysis system catalyzed by arginase and urease immobilized on separate inorganic supports. General control policies are deduced for the particular kinetics of interest, and optimal predictions are tested with regard to the effects of major parameters including residence time, solution pH values, feed concentration, and catalyst activity. Parallel experiments were run on a simple suboptimal arrangement to evaluate the losses to be expected from less than optimal decisions.

CONCLUSIONS AND SIGNIFICANCE

Analytic solutions show that a bang-bang policy is optimal for the distribution of catalysts for an irreversible two-step consecutive reaction system in a plug flow tubular reactor. When the kinetics for each of the reactions can be represented in Michaelis-Menten form, the optimal switching point location depends on the system parameter values, moving toward the end of the reactor as the second reaction rate increases relative to the first. In particular, the optimal switching point moves as residence time varies, but the effect is not monotonic except for the range of concentrations where zero- and first-order kinetics apply. For this simplified combination, the optimal switching point always lies in the second half of the reactor, monotonically increases with increasing values of either the residence time or the second reaction rate constant, and is independent of the first reaction rate constant. For very small residence times, the optimal switching point becomes independent of the kinetics of the first reaction and approaches the finite limit of $n/(n+1)$ for n^{th} order reaction kinetics. This finding can be used to estimate reaction order from experiments.

Experiments confirm the expectation that yield losses of at least 41% result from the choice of a suboptimal fixed composition policy for this dual enzyme system, in contrast to earlier reports on a reforming system. Consistent with the results obtained by Messing (1974), the activity of the immobilized urease more than doubled during the storage period of about two weeks, possibly due to the reducing environment generated by the hydrated transition metal oxide used as support. No such activation was observed for the arginase, but a pH activity profile was obtained for this immobilized material that is similar to that found for the homogeneous enzyme.

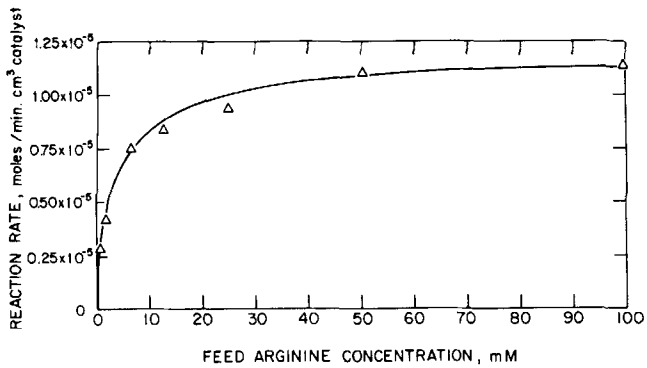

Fig. 1. Arginase activity; catalyst batch I; catalyst volume: 3 cm³; feed flow rate: 100 cm³/min; pH = 8.5

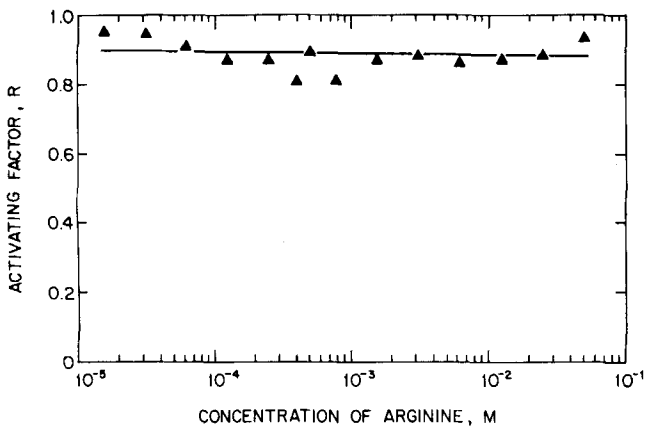

Fig. 2. Effect of arginine on urease activity; pH = 7: urea concentration: 2 mM; catalyst volume: 2 cm³.

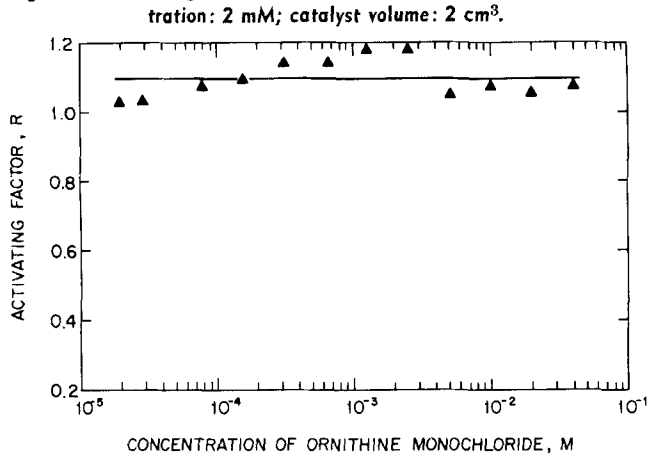

Fig. 3. Effect of ornithine monochloride on urease activity; pH = 7; urea concentration: 2 mM.

The range of sequential chemical reactions that can benefit from proper application of dual catalysts is remarkably broad. They include, for example, such diverse systems as coal hydrocracking followed by dehydrogenation of low molecular weight hydrocarbons (Stanulonis et al., 1976), benzene synthesis from aliphatics by sequential hydrocracking and aromatization (Thomas, 1971), hydrogen peroxide production by hydrogenation of quinone followed by oxidation of the intermediate hydroquinone (Satterfield, 1975), construction of interpenetrating networks of multiple polymer species (Kim et al., 1976), and a variety of enzyme catalyzed biochemical reactions (Mosbach, 1972; Messing, 1974). Many of these combinations have been the subjects of optimization studies, but among these contributions on the optimal distribution of dual function catalysts in a tubular reactor, only the work of Thomas (1971) on a hydrocarbon system included experimental work carried out to verify theoretical results.

This study examines the dual enzyme sequential reaction set that is catalyzed by arginase (X) and urease (Y), respectively:

$$R\text{—}NH\text{—}C(=NH)NH_2 + H_2O \xrightarrow{X} RNH_2 + (NH_2)_2CO \qquad (I)$$

and

$$(NH_2)_2CO + 2H_2O \xrightarrow{Y} H_2CO_3 + 2NH_3 \qquad (II)$$

Such a hydrolysis system provides an excellent opportunity for experimental tests of both theory and practice, since the expected kinetics are of the form that lend themselves to predictions of relatively simple optimal and suboptimal control policies. The specific objective to be considered is the maximization of the product ammonia. This corresponds to a minimization in the effluent of the unreacted substrates, especially desirable under circumstances where the reactants are harmful toxins (Salomme et al., 1971).

PRELIMINARY KINETICS

The apparatus, chemicals, and assay techniques used in this study are the same as previously reported (Ramachandran and Perlmutter, 1976). The immobilized enzyme catalysts were prepared by the glutaraldehyde coupling method. Arginase was assayed by using an ammonia electrode to detect the urea decomposition effected by homogeneous urease and by back calculating to the urea formed in reaction I. The immobilized arginase was stored at neutral *p*H in tris-maleic acid buffer containing 50 mM $MnSO_4 \cdot H_2O$ for Mn^{++} activation. No additional manganese was added otherwise, but arginase activity remained constant during each experimental series. Results of typical catalyst activity determinations are shown in Figure 1 for arginase at *p*H = 8.5. Similar data for urease were reported by Ramachandran and Perlmutter (1976). The same study also showed that mass transfer resistance is negligible under the conditions used for all experiments reported here.

The prior work of Hoare and Laidler (1950) established that the concentrations of ammonia and carbon dioxide generated in these experiments ($<4 \times 10^{-4}$M) do not have a significant effect on urease activity. The possible effects of arginine and ornithine were tested for separately in this investigation. The results in Figures 2 and 3 show that only small effects of about 10% exist over a range of greater than five orders of magnitude in amino acid concentrations. The experimental findings of this investigation show a similar lack of effect of urea and ornithine on the arginase reaction. In view of these findings, simple rate expressions of the Michaelis-Menten form are applicable to the reactions I and II, respectively:

$$r_1 = \frac{k_1 C_A}{K_{M1} + C_A} = \frac{k_1 C_{AO}}{K_{M1}} \frac{x_1}{1 + \mu_1 x_1} = \frac{k_1 C_{AO}}{K_{M1}} f_1(x_1) \qquad (1)$$

$$r_2 = \frac{k_2 C_B}{K_{M2} + C_B} = \frac{k_2 C_{AO}}{K_{M2}} \frac{x_2}{1 + \mu_2 x_2} = \frac{k_2 C_{AO}}{K_{M2}} f_2(x_2) \qquad (2)$$

The sensitivity of arginase activity to *p*H level was also investigated. The results presented as Figure 4 indicate, in agreement with Greenberg's work (1960) on soluble enzyme, that the arginase activity falls appreciably only when *p*H = 10.5 is exceeded.

OPTIMAL POLICY

The system under consideration is a consecutive irreversible reaction sequence

$$A \rightarrow B \rightarrow C$$

being carried out in a plug flow tubular reactor modeled by

$$v\frac{dC_A}{dz} = -ur_1 \tag{3}$$

and

$$v\frac{dC_B}{dz} = ur_1 - (1-u)r_2 \tag{4}$$

Substitution of Equations (1) and (2) and rearrangement to dimensionless form yields

$$\frac{dx_1}{d\tau} = -Puf_1 \tag{5}$$

and

$$\frac{dx_2}{d\tau} = P[uf_1 - \alpha(1-u)f_2] \tag{6}$$

For algebraic simplicity, it is convenient to let the initial $x_3 = 0$, noting, however, that the general features of the results that follow are not dependent on this assumption. With initial conditions $x_1 = 1$ and $x_2 = x_3 = 0$, the objective function is the yield of product C at $\tau = 1$

$$F = x_{3E} = 1 - x_{1E} - x_{2E} \tag{7}$$

to be maximized by choice of catalyst distribution between the constraints

$$0 \leq u \leq 1 \tag{8}$$

This objective is equivalent to

$$\underset{0 \leq u \leq 1}{\text{Max}} \; H = P\{-\lambda_1 uf_1 + \lambda_2[uf_1 - \alpha(1-u)f_2]\} = P(uJ + N) \tag{9}$$

with the adjoint equations

$$\frac{d\lambda_1}{d\tau} = -\frac{\partial H}{\partial x_1} \tag{10}$$

$$\frac{d\lambda_2}{d\tau} = -\frac{\partial H}{\partial x_2} \tag{11}$$

and

$$\lambda_1 = \frac{\partial F}{\partial x_1} = -1, \quad \tau = 1 \tag{12}$$

$$\lambda_2 = \frac{\partial F}{\partial x_2} = -1, \quad \tau = 1 \tag{13}$$

Although not stated explicitly, there are indications in the works of King and his co-workers (1972, 1973) that optimal policy often demands singular control (mixed catalyst composition over some segment) for reactors operating with relatively large residence time and calls for bang-bang response (the extremes of the available range) as residence time is reduced. A somewhat stronger conclusion may be drawn when the chemical kinetics are of the form

$$f_1 = f_1(x_1) \tag{14a}$$

$$f_2 = f_2(x_2) \tag{14b}$$

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. The first of these conditions calls for

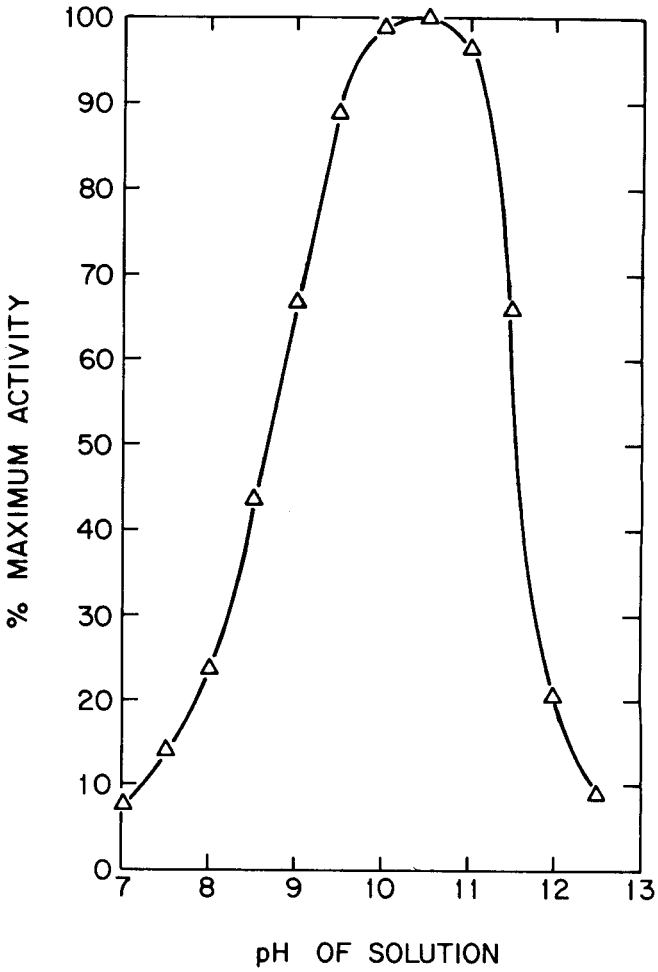

Fig. 4. Effect of pH level on arginase activity.

$$\frac{\lambda_2}{\lambda_1} = \frac{f_1}{f_1 + \alpha f_2} \tag{15}$$

and the two together require that

$$P\alpha\lambda_2\left[f_1\left(\frac{\partial f_2}{\partial x_2} - \frac{\partial f_2}{\partial x_1}\right) + \alpha\frac{f_2^2}{f_1}\left(\frac{\partial f_1}{\partial x_2}\right)\right] = 0 \tag{16}$$

With partial derivatives evaluated from Equations (14), this reduces to

$$P\alpha\lambda_2 f_1\frac{\partial f_2}{\partial x_2} = 0 \tag{17}$$

Integration of Equation (11) provides

$$\lambda_2(\tau) = -\exp\left[-\alpha P\int_\tau^1 (1-u)\frac{\partial f_2}{\partial x_2}\,d\tau\right] \tag{18}$$

which assures that $\lambda_2 \neq 0$ over a finite range of τ. Since the functions f_1 and $(\partial f_2/\partial x_2)$ are also nonzero over such a range, the relation (17) cannot be satisfied over any reactor segment when the kinetics follow the form of Equations (14). Equations (1) and (2) are of the required form; as a result, the possibility of a reactor segment of singular control can be excluded in this case, and the bang-bang policy is optimal for all values of the system parameters.

Since bang-bang control is called for, the first segment policy is simply to use all arginase and no urease ($u = 1$), and integration of Equation (5) between the feed and the switching point location gives

$$\ln x_{1s} + \mu_1(x_{1s} - 1) = -P\tau_s \tag{19}$$

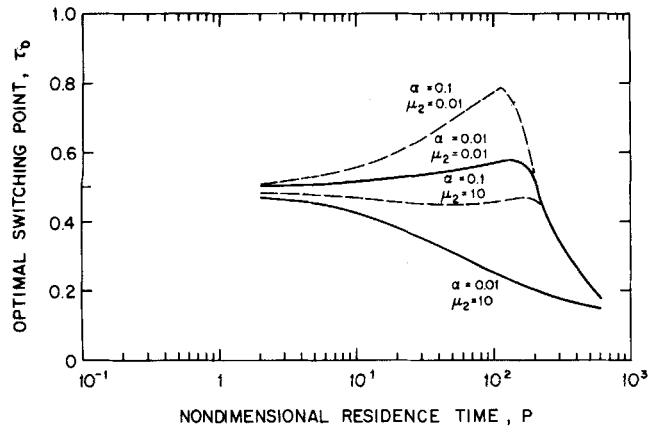

Fig. 5. Effect of reactor residence time on optimal switching point location; irreversible consecutive reactions; Michaelis-Menten kinetics with $\mu_1 = 100$.

By adding Equations (5) and (6) and integrating the sum, we get

$$x_{1s} = 1 - x_{2s} \tag{20}$$

Further integration between the switching point location and the reactor exit requires combinations among the system equations with $u = 0$, the adjoint equations, and the $J = 0$ condition that characterizes the switching point. The results of such manipulations have been developed by Jackson (1968) and by King and his coworkers (1972) to yield the implicit relations

$$\frac{f_{2s}}{f_{2E}} = 1 + \alpha f_{2s}\left(\mu_1 + \frac{1}{1 - x_{2s}}\right) \tag{21}$$

and

$$\ln \frac{x_{2E}}{x_{2s}} + \mu_2(x_{2E} - x_{2s}) + \alpha \ln x_{1s} + \alpha\mu_1(x_{1s} - 1) = -P\alpha \tag{22}$$

as well as the calculational procedures for such equation sets.

The results of a series of solutions of Equations (19) to (22) are shown in Figures 5 to 8 in terms of the optimal switching point location for different residence times and kinetic constants. The trends show that one should allocate a larger fraction of the reactor volume to the first catalyst to compensate for a relatively greater

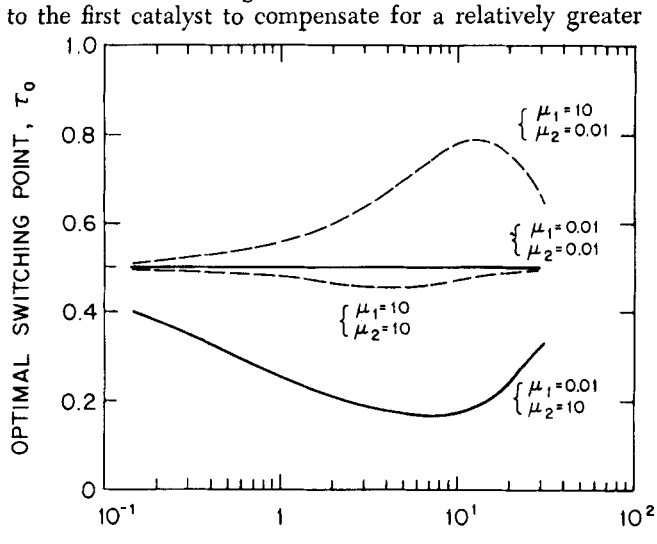

Fig. 7. Effect of reactor residence time on optimal switching point location; irreversible consecutive reactions; Michaelis-Menten kinetics with $\alpha = 1$.

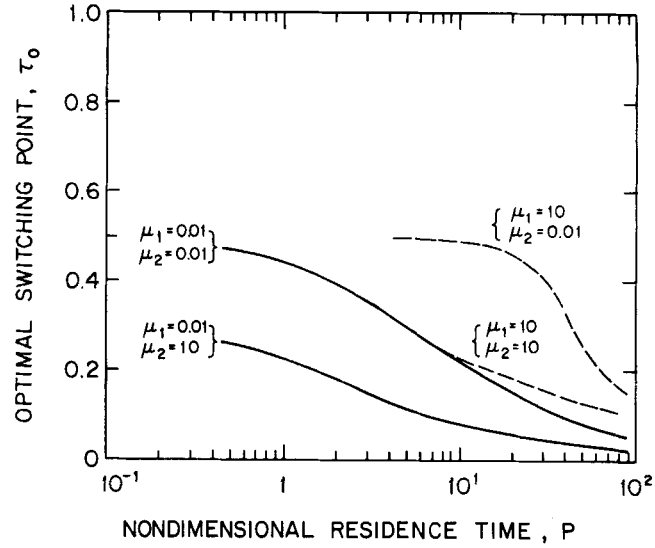

Fig. 6. Effect of reactor residence time on optimal switching point location; irreversible consecutive reactions; Michaelis-Menten kinetics with $\alpha = 0.01$.

second reaction rate. It is interesting to note that the variation of switching location with residence time is not always monotonic, and that the switching location approaches the midpoint for small P. This limit can also be derived analytically for conversion levels that are so small that the reaction rate functions f_1 and f_2 are effectively constant. With this restriction, Equation (5) can be integrated over the first segment where $u = 1$ to give

$$x_1 - x_{1s} = Pf_1\tau_s \tag{23}$$

and Equation (6) can be integrated over the final segment where $u = 0$ to give

$$x_{2E} - x_{2s} = -P\alpha f_{2s}(1 - \tau_s) \tag{24}$$

By using Equation (7) together with the limiting relationship $f_{2s} = x_{2s}$, substitution in Equation (24) yields

$$x_{3E} = P\alpha f_{2s}(1 - \tau_s) = P\alpha x_{2s}(1 - \tau_s) \tag{25}$$

Combining Equations (23) and (25) with the stoichiometric relation $x_{2s} = (x_{1o} - x_{1s})$, we get

$$x_{3E} = P^2\alpha f_1\tau_s(1 - \tau_s) \tag{26}$$

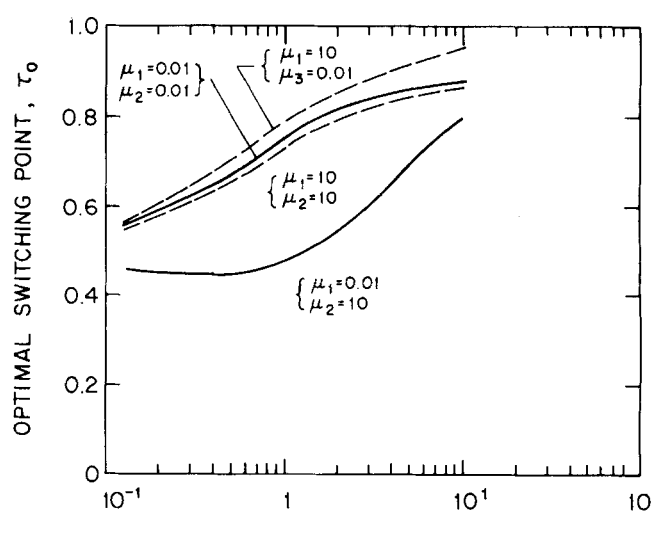

Fig. 8. Effect of reactor residence time on optimal switching point location; irreversible consecutive reactions; Michaelis-Menten kinetics with $\alpha = 10$.

To maximize the product at exit, the derivative of x_{3E} with respect to τ_s is set equal to zero, resulting in $\tau_o = 0.5$. If in the foregoing derivation the reaction function f_2 had been of the form

$$f_2 = x_2^n \tag{27}$$

then the exit concentration would have been

$$x_{3E} = P\alpha f_{2s}(1 - \tau_s) = P\alpha x_{2s}^n(1 - \tau_s)$$
$$= P^{n+1}\alpha f_1^n \tau_s^n(1 - \tau_s) \tag{28}$$

and the optimal choice of τ for $P \to 0$ would be

$$\tau_o = \frac{n}{n+1} \tag{29}$$

Equation (29) may be used to estimate the reaction order in the low concentration range from measurement of τ_o.

APPROXIMATION WITH ZERO- AND FIRST-ORDER KINETICS

As a particular case, one can consider a reactor operating at low conversion with feed containing arginine at relatively high concentration such that the first reaction is approximated by zero-order kinetics and the second reaction by first-order kinetics. For this case, Equations (14) and (15) become

$$f_1 = 1 \tag{30}$$

and

$$f_2 = x_2 \tag{31}$$

Integrating Equations (5) and (6) with these rate equations and the bang-bang policy, we get the ammonia concentration at the reactor exit as

$$x_{3E} = 2P\tau_s[1 - e^{-P\alpha(1-\tau_s)}] \tag{32}$$

Either simple differentiation or the application of optimal control theory gives an implicit expression for the optimal switching point:

$$\ln(1 + P\alpha\tau_o) = P\alpha(1 - \tau_o) \tag{33}$$

This relationship is shown in Figure 9 from which it is seen that $0.5 < \tau_o < 1.0$ over the full range of the product $(P\alpha)$.

This behavior is quite different from that shown in Figures 5 to 8 for the general Michaelis-Menten kinetics, except for the higher values of α. It should be noted also that since

$$P\alpha = \frac{k_1 L}{K_{M1} v} \frac{k_2 K_{M1}}{k_1 K_{M2}} = \frac{k_2 L}{K_{M2} v} = \frac{kL}{v} \tag{34}$$

this product function does not depend on the rate constant for the first reaction; as a consequence the optimal switching point for this particular case should be independent of the first reaction rate constant as well as the arginine feed concentration.

RESULTS AND DISCUSSION

A series of experiments were run to test the models and optimization expectations derived above. Because they supplied straightforward tests of the foregoing relatively simple predictive and correlating equations, the tests were run over ranges of arginine and urea concentrations, where the reactions I and II could be considered to be effectively zero and first order, respectively. This required that the feed to the arginase segment

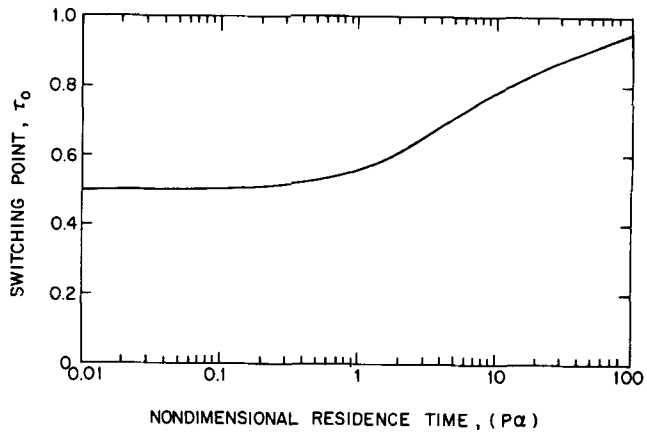

Fig. 9. Effect of reactor residence time on optimal switching point location; irreversible consecutive reactions; zero- and first-order kinetics.

TABLE 1. EXPERIMENTAL CONDITIONS

Series and profile number	Enzyme catalyst batches	Feed arginine concentration, mM	pH of process stream Over arginase	Over urease
1	I	50	8.5	7
2(a)	I	50	7	7
2(b)	I	50	10	7
3	II	50	9	7
4	II	50	9	9
5	III	50	8.8	7
6	III	50	8.9	7
7	III	3	8.5	7
8	III	3	8.5	7

of the overall reactor be free of urea and relatively concentrated in arginine ($C_A >> K_{M1}$), and that the feed to the urease segment be dilute in urea ($C_B << K_{M2}$).

The conditions of the various runs are summarized in Table 1 and assure the applicability of Equations (30) and (31). By combining these kinetic forms with Equations (3) and (4) and the appropriate $u = 1$ or $u = 0$ for each reactor segment, one obtains integrated results for the zero-order rate constant

$$k_1 = \frac{Q}{V}(C_{AO} - C_{As}) \tag{35}$$

and the first-order rate constant:

$$k = \frac{k_2}{K_{M2}} = \frac{Q}{(V - V_s)} \ln \frac{C_{BE}}{C_{BS}} \tag{36}$$

These forms lend themselves to tests of kinetic form on the one hand and to comparisons of activity levels among catalyst batches on the other. Both purposes are served by using experimental data to evaluate the rate constants; the results of these determinations are reported in Figures 10 and 11. The evident lack of any discernible trend within a series supports the kinetic models presented above, and the considerable variation in the rate constants from series to series reflects the very significant differences among catalyst batches, preparation histories, and pH of the process stream.

Comparing series 1 and 2 as reported in Table 1, the only difference in conditions would appear to be in the pH level of the arginase segment. The pH dependence shown in Figure 4 would thus suggest that k_1 should about double between these series. In fact, the series 2 result

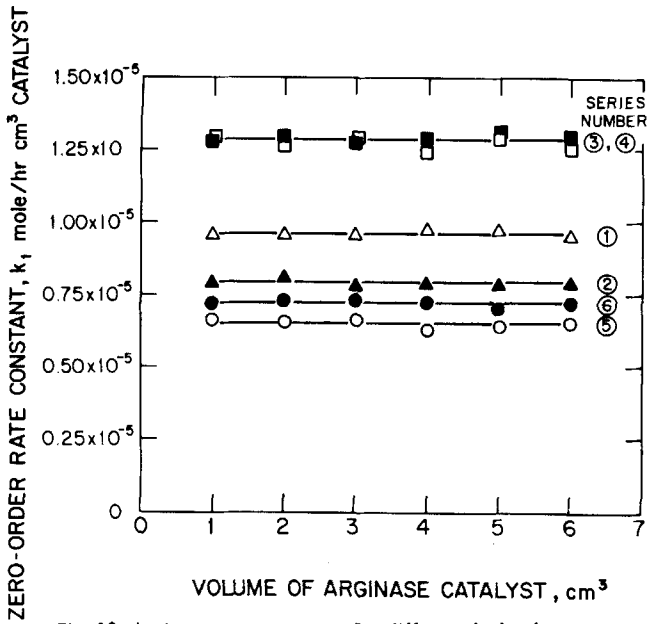

Fig. 10. Arginase rate constants for different bed volumes.

is smaller by some 20%, a consequence of an intermediate test of the catalyst when it was subjected to harsh treatment at elevated pH. Such permanent loss of arginase activity was not experienced as long as the alkalinity did not exceed $p\mathrm{H} = 10$. That the activity did not otherwise change significantly during the course of these experiments is shown by the close agreement obtained for the duplicate series 3 and 4. The series 5 and 6 were run with yet another catalyst batch of slightly lower intrinsic activity. The very small increase from series 5 to 6 may be attributed to the small pH increment.

Activities for several batches of urease may be seen in Figure 11. Series 1 and 2 results differ by about 25% in activity, a response to urease catalyst storage for two weeks. Similarly, a notable increase in activity on storage is clear in comparing the trends between series 5 to 8,

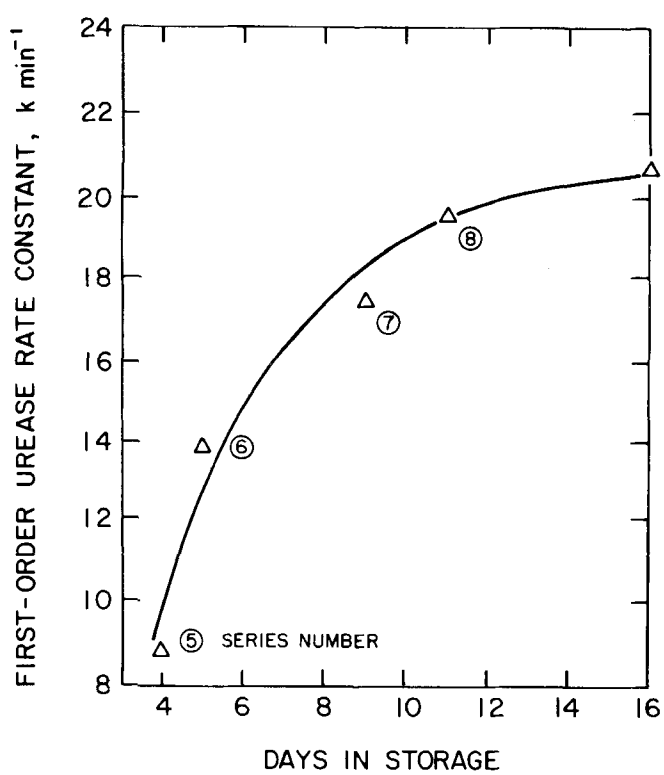

Fig. 12. Effect of storage on urease activity.

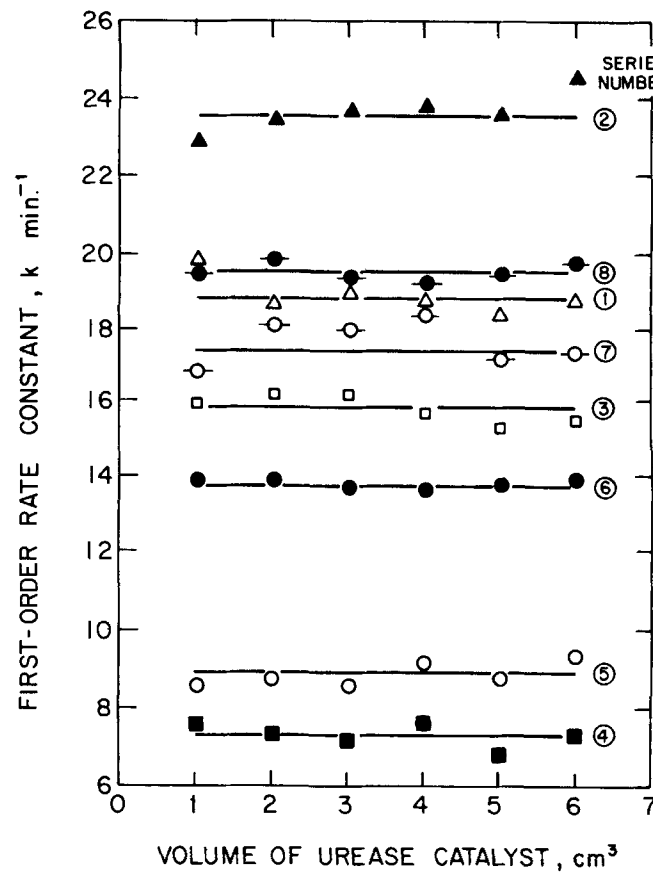

Fig. 11. Urease rate constants for diiferent bed volumes.

shown in summary by Figure 12. Observations with a scanning electron microscope showed a strong titanium peak for the urease catalyst support material (textured glass bead GCS-021, Analab, North Haven, Connecticut), and it is possible that the increase in urease activity is attributable to the reducing environment generated by titania upon hydration in storage (Messing, 1974*a* and *b*). Series 3 and 4 of Figure 11 differ only with regard to urease pH and indicate that a sharp activity reduction accompanies the pH increase from 7 to 9. The activity level at the higher pH is only 45% of the value of the neutral $p\mathrm{H} = 7$, in good agreement with the earlier result of Ramachandran and Perlmutter (1976).

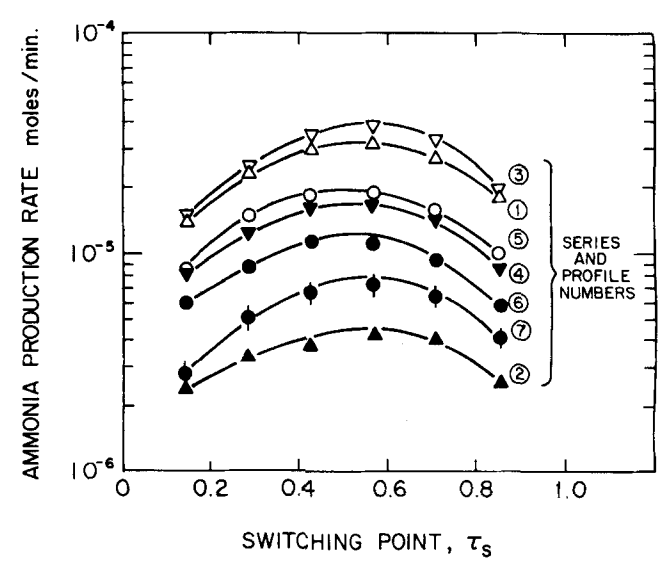

Fig. 13. The effect of switching point location on reactor performance; catalyst total volume: 7 cm^3; feed flow rate: 100 cm^3/min.

The optimization results are presented graphically as Figure 13, in which the solid lines are from calculations and the points are from experiments. Since the control policies for the kinetics of this system are all of the bang-bang type, the only remaining decision was the experimental location of the switching point, that is, the fractional bed volume to be occupied by the first of the two immobilized enzyme catalysts. The seven profiles given in Figure 13 differ with respect to arginase or urease activity (various batches, some with different pH exposure histories) or arginine substrate feed concentration. In spite of these differences, each of the profiles shown goes through a maximum at about the same value of τ_s. Since the series 1, 2, 5, 6, and 7 differ only in arginase activity or arginine feed concentration, this result is in accordance with the above derived expectation that the optimal switching point is independent of the first rate constant. For profile 1, for example, evaluation of the right side of Equation (34) gives the product $P\alpha = 1.32$, and the τ_o predicted by Equation (33) or Figure 9 is 0.57, in excellent agreement with the experimental result.

Profiles 3 and 4 differ only in the urease activity level between pH of 7 and 9. Since these activities differ by a factor of 2, Equation (34) would predict a change in $(P\alpha)$ of 0.66. The corresponding shift in τ_o can be estimated from Equation (33) to be about 0.05 units. This small shift is consistent with the findings shown in Figure 13.

SUBOPTIMAL POLICY

For ease in practical operation, it is sometimes more convenient to pack a reactor with a single mixed catalyst than to split the process at a predetermined switching point. It is therefore worth considering this suboptimal policy to determine what loss in conversion one might expect to encounter as the price of such convenience. To develop this comparison, the optimal ammonia yield for the bang-bang policy is already available as Equation (32). A corresponding result for the suboptimal fixed composition policy may be derived by letting $u = \tau_s$ over the entire length of the reactor. By incorporating also the simplified kinetics of Equations (30) and (31), the system Equations (5) and (6) may be written as

$$\frac{dx_1}{d\tau} = -P\tau_s \tag{37}$$

$$\frac{dx_2}{d\tau} = P[\tau_s - \alpha(1-\tau_s)x_2] \tag{38}$$

and integrated to give the suboptimal ammonia concentration in the reactor effluent as

$$x^*_{3E} = 2P\tau_s\left[1 - \frac{1}{\gamma}(1-e^{-\gamma})\right] \tag{39}$$

where $\gamma = P\alpha(1-\tau_s)$. The penalty for the suboptimal decision can therefore be obtained by subtracting Equation (32) from (39) to give

$$\Delta x_{3E} = x_{3E} - x^*_{3E} = \frac{2P\tau_s}{\gamma}[1-(1+\gamma)e^{-\gamma}] \tag{40}$$

and the fractional loss of the desired product written as

$$\phi = \frac{\Delta x_{3E}}{x_{3E}} = \frac{1-(\gamma+1)e^{-\gamma}}{\gamma(1-e^{-\gamma})} \tag{41}$$

Results of experiments run with suboptimal fixed composition packing are compared in Figure 14 with those

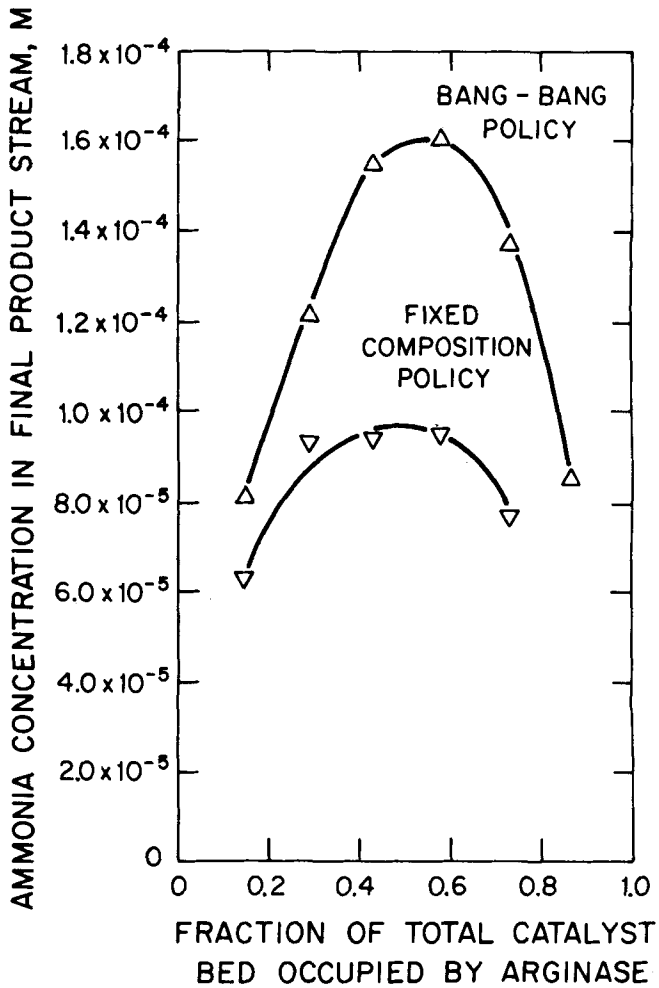

Fig. 14. Comparison between results of bang-bang optimization and suboptimal fixed composition policy; enzyme catalyst batch: II; pH = 9; arginine feed concentration: 50 mM; total catalyst volume: 7 cm³; flow rate: 100 cm³/min.

obtained by applying the corresponding optimal bang-bang decision. Again, the solid lines show the calculated results, and the points represent experimental data. The best result with the suboptimal policy is 41% lower than the corresponding result of the bang-bang policy. This relatively large difference between the results from optimal and suboptimal policies is in sharp contrast to the report of Thomas (1971) for the methylcyclopentane reforming reaction where the suboptimal policy gave a result within 5% of the optimal one, demonstrating that a considerable incentive can exist for some systems to develop truly optimal decisions.

The same data can also provide comparison with the prediction of Equation (41), which indicates that the fractional loss is reduced with increase in the parameter γ and never exceeds the limit of $\phi = 0.5$ at $\gamma = 0$. The comparable experimental findings are in the range $0.21 < \phi < 0.44$, as expected. It is worth noting that the kinetic rate constants of Figures 10 and 11 can also be used to predict the end product concentrations for the suboptimal policy. The results of such computations are within 5% of the experimental data reported in Figure 14, giving further confidence in the foregoing interpretations.

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NOTATION

C_i = concentration of species i
C_{io} = initial concentration of species i
F = objective function
f_i = normalized reaction rate for i^{th} reaction
H = Hamiltonian function
J = $f_1(\lambda_2 - \lambda_1) + f_2\lambda_2\alpha$
k_1, k_2 = reaction rate constants for arginase and urease, respectively
k = k_1/K_{M1}
K_{M1} = Michaelis constant for arginase
K_{M2} = Michaelis constant for urease
L = reactor length
n = reaction kinetic order
N = $-f_2\lambda_2\alpha$
P = $k_1L/K_{M1}v$
Q = volumetric flow rate
r_i = reaction rate for i^{th} reaction
u = fraction of bed which is arginase catalyst
v = linear superficial velocity
V = total volume of reactor bed
x_i = C_i/C_{Ao}
z = reaction length coordinate

Greek Letters

α = $\dfrac{k_2}{k_1}\dfrac{K_{M1}}{K_{M2}}$
μ_i = C_{Ao}/K_{Mi}
τ = z/L
λ_1, λ_2 = adjoint variables
ϕ = fractional loss of product

Subscripts

s = switching point value
o = optimal value
E = at exit of reactor

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Transport of Nitrate Ion in Unsteady, Unsaturated Flow in Porous Media

A simplified model of nitrate ion transport (and other nonadsorbing solutes) in unsteady, unsaturated flow in porous media has been developed. The model represents nitrate flow in infiltration and drainage in sand quite well and can be applied to unsaturated flow in other homogeneous media with only minimum extra experimental data needed to describe the medium.

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SCOPE

Nitrate contamination of soil and groundwater may originate from the application of agricultural fertilizer, waste treatment facilities, feedlot wastes, irrigation systems, and similar sources of nitrate ion. In spite of extensive work on the transport of solutes in saturated flow, very little literature exists that can predict transport in nonadsorbing media under unsteady state, unsaturated conditions.

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