ω, ω' = frequency and modified frequency of oscillation, radians/sec.

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Effects of Product Recycle and Temperature on Autocatalytic Reactions

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The effect of product recycle and temperature on the maximum yield of product for several different autocatalytic reactions taking place in a tubular reactor is studied.

A generalized version of the maximum principle is used to determine the maximum conversion and optimal temperature profile for each of the reactions considered. The fraction of product recycled, which affects the concentration of autocatalytic agent entering the reactor, is investigated to determine its effect on the maximum conversion.

An autocatalytic reaction in which one or more of the products acts catalytically gives rise to a rather unusual problem in the design of a flow reactor, for its rate of reaction is influenced by the concentration of some of the products as well as that of some of the reactants (*1*). Examples of such reactions are found in the acid-catalyzed hydrolysis of various esters and similar compounds (*2, 3*) and in various biochemical processes such as the conversion of trypsiogen into trypsin with the trypsin catalyzing the reaction (*4*).

A kinetic model of the autocatalytic type is often used to represent the rate of growth of microorganisms in various biochemical processes in which several reactions are actually taking place in the system. In these systems the kinetic equation, which is used to represent the rate of growth, is often only an approximate model that one uses to mathematically represent the system. Such a model is usually valid over only a limited range of temperature and concentration. The biochemical oxidation of process waste water is a common example of such an autocatalytic system.

The rate of an autocatalytic reaction in a steady state tubular flow reactor with product recycle is often influenced by two important factors: the initial concentration of the autocatalytic agent and the temperature at which the reaction is carried out. The initial concentration of the autocatalytic agent may be controlled by varying the rate of product recycle from the exit to the entrance of the reactor, and the temperature may be controlled artificially. This paper deals with the interaction of product recycle and temperature in a flow reactor. The interaction is studied from the standpoint of how it affects the maximum yield of the product for several different reactions taking place in a tubular flow reactor of given size with a given volumetric flow rate of fresh feed fed to the system.

FORMULATION OF EQUATIONS

We shall consider an autocatalytic reaction of the type

$$A + R \underset{k_2}{\overset{k_1}{\rightleftarrows}} R + R \quad \text{or} \quad A \underset{k_2}{\overset{k_1}{\rightleftarrows}} R \qquad (1)$$

taking place in a tubular reactor where a portion of the product is recycled to the inlet of the reactor and mixed continuously with the stream of fresh feed as shown in Figure 1. In this figure v represents the volumetric flow rate of the reacting mixture and L denotes the length of the tubular reactor.

The steady state differential material balance for reactant A in a differential section $d\xi$ of the reacting section of the system is (a unit cross-sectional area is assumed):

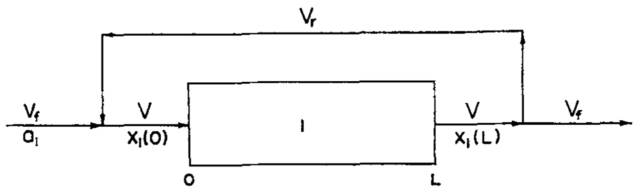

Fig. 1. Schematic diagram of continuous flow tubular reactor with product recycle.

$$\frac{dC_A}{d\xi} = \frac{1}{v}\{R_A\}, \quad 0 \leqq \xi \leqq L \tag{2}$$

The kinetic equation of the autocatalytic reaction given by Equation (1) can often be written, with respect to the production of reactant A, as

$$R_A = -k_1(C_A)^a(C_R)^r + k_2(C_R)^s \tag{3*}$$

where k_1 and k_2 are the temperature dependent reaction rate constants given by the Arrhenius law as

$$k_1 = k_{10}\exp\left(-\frac{E_1}{RT}\right) \tag{4}$$

$$k_2 = k_{20}\exp\left(-\frac{E_2}{RT}\right) \tag{5}$$

In the equations above k_{10} and k_{20} are frequency factors and E_1 and E_2 are activation energies. If at every point along the reacting section, we have

$$C_0 = C_{A0} + C_{R0} = C_A + C_R \tag{6}$$

Equation (3) may be written in terms of C_0 and C_A as

$$R_A = -k_1(C_A)^a(C_0 - C_A)^r + k_2(C_0 - C_A)^s \tag{7}$$

Substitution of Equations (4) and (5) into Equation (7) and insertion of the resulting equation in turn into Equation (2) give

$$\frac{dC_A}{d\xi} = -\frac{1}{v}\left\{k_{10}\exp\left(-\frac{E_1}{RT}\right)\left(\frac{C_A}{C_0}\right)^a \left(1 - \frac{C_A}{C_0}\right)^r (C_0)^{a+r} - k_{20}\exp\left(-\frac{E_2}{RT}\right) \left(1 - \frac{C_A}{C_0}\right)^s (C_0)^s\right\} \tag{8}$$

In terms of the fractional molar concentration

$$x_A = (C_A)/(C_0)$$

we can rewrite Equation (8) as

$$C_0\frac{dx_A}{d\xi} = -\frac{1}{v}\left\{k_{10}\exp\left(-\frac{E_1}{RT}\right)(x_A)^a(1-x_A)^r (C_0)^{a+r} - k_{20}\exp\left(-\frac{E_2}{RT}\right)(1-x_A)^s(C_0)^s\right\} \tag{9}$$

If we assume

$$C_0 = C_A + C_R = 1$$

Equation (9) can be replaced by

$$\frac{dx_A}{d\xi} = -\frac{1}{v}\left\{k_{10}(e)^{-\frac{E_1}{RT}}(x_A)^a(1-x_A)^r - k_{20}(e)^{-\frac{E_2}{RT}}(1-x_A)^s\right\} \tag{10}$$

which may be called the unit equation of the reactor.[†] The concentration of the reactant A in the fresh feed is designated as a_1.

COMPUTATIONAL PROCEDURE

A generalized version of the maximum principle is employed in this work (*5*, *6*). According to Equation (10) and the maximum principle, the unit equation of the reacting section can be written as

$$\frac{dx_1}{d\xi} = f_1(x_1(\xi),\ \theta(\xi)) = -\frac{1}{v}\left[k_{10}\exp\left(-\frac{E_1}{R\theta}\right)(x_1)^a(1-x_1)^r - k_{20}\exp\left(-\frac{E_2}{R\theta}\right)(1-x_1)^s\right] \tag{11}$$

where the subscript 1 refers to component A. The decision or control variable, temperature in this case, is denoted by θ. The boundary condition for Equation (11), which is obtained by making a material balance at the inlet of the reactor, is

$$x_1(0) = (1-\beta)a_1 + \beta x_1(L) \tag{12}$$

Since it is desired to maximize the yield of product R or equivalently to minimize the exit concentration of the reactant A, $x_1(L)$, the objective function to be minimized is

$$S = x_1(L) \tag{13}$$

The Hamiltonian function for this problem then becomes (*5*)

$$H = \left\{-\frac{k_{10}\exp\left(-\frac{E_1}{R\theta}\right)}{v}[(x_1)^a(1-x_1)^r] + \frac{k_{20}\exp\left(-\frac{E_2}{R\theta}\right)}{v}(1-x_1)^s\right\}z_1 \tag{14}$$

When the minimum of H occurs at a stationary point, we obtain the optimal value of the decision function $\theta(\xi)$ from the condition given by

$$(\partial H)/(\partial\theta) = 0 \tag{15}$$

By partially differentiating Equation (14) with respect to θ and by setting it equal to zero to solve for $\bar{\theta}$ (the optimal value of θ), we obtain

$$\bar{\theta}(\xi) = \left(\frac{E_1 - E_2}{R}\right)\frac{1}{\ln[\eta(x_1)^a(1-x_1)^{r-s}]} \tag{16}$$

where

$$\eta = \frac{k_{10}E_1}{k_{20}E_2}$$

Substitution of Equation (16) into Equation (11) yields

$$\frac{dx_1}{d\xi} = -\frac{1}{v}\{k_{10}\eta^{\lambda_1}(x_1)^{a(\lambda_1+1)}(1-x_1)^{r(\lambda_1+1)-\lambda_1 s} - k_{20}\eta^{\lambda_2}(x_1)^{a\lambda_2}(1-x_1)^{r\lambda_2 - s(\lambda_2 - 1)}\} \tag{17}$$

where $\lambda_1 = \dfrac{E_1}{E_2 - E_1}$ and $\lambda_2 = \dfrac{E_2}{E_2 - E_1}$

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[*] The exponents are written with parenthesis or brackets such as $(C_A)^2$ or $[f(C_A;\ \theta)]^2$ in order to distinguish them from superscripts.

[†] Equation (10) may also be used for the case where C_0 is not equal to one if the constants k_{10} and k_{20} are redefined to include the other constants.

Table 1. The Values of k_{20} Used for Numerical Calculations

	k_{20}	$\eta = \frac{k_{10}E_1}{k_{20}E_2}$	a_1
	Variable	Dimensionless	Dimensionless
Case 1 ($s = 1$)	1.995×10^7 hr.$^{-1}$	6.29×10^{-3}	0.99
Case 2 ($s = 0$)	1.15×10^7 moles/(cu. ft.)(hr.)	1.09×10^{-2}	0.85; 0.91; 0.95; 0.97; 0.99
Case 3 ($s = 2$)	3.46×10^7 cu. ft./(moles)(hr.)	3.63×10^{-3}	0.99

or, in integral form

$$\int d\xi = \frac{v}{k_{20}(\eta)^2 - k_{10}\eta} \int \frac{dx_1}{(x_1)^{2a}(1-x_1)^{2r-s}} \qquad (18)$$

In integrating Equation (17), it has been assumed that the activation energies of the forward and reversible reactions are such that

$$(E_2)/(E_1) = 2 \quad \text{or} \quad \lambda_1 = 1 \quad \text{and} \quad \lambda_2 = 2$$

The specific values employed are purely for the purpose of simplifying computation. It should, however, be noted that Equation (17) can be integrated for any value of the activation energies as long as $E_2 > E_1$ (when $E_1 > E_2$, the optimal policy is to use the highest permissible temperature). Equations (16) and (18) form the optimal solution of the system.

Three different cases are considered in this work:

1. The reaction is first order with respect to each component, that is, $a = r = s = 1$.
2. The forward reaction is first order with respect to each component and the backward reaction is zero order, that is, $a = r = 1$ and $s = 0$.
3. The forward reaction is first order with respect to each component and the backward reaction is second order, that is, $a = r = 1$ and $s = 2$.

The integration of Equation (18) for these cases, respectively, yields

$$\xi = \frac{v}{k_{20}(\eta)^2 - k_{10}\eta} \left[-\frac{1}{x_1(\xi)} - \ln\left(\frac{1}{x_1(\xi)} - 1\right) \right] + C_1 \qquad (19)$$

$$\xi = \frac{v}{k_{20}(\eta)^2 - k_{10}\eta} \left[-\frac{1 - 2x_1(\xi)}{x_1(\xi)(1 - x_1(\xi))} - 2\ln\left(\frac{1}{x_1(\xi)} - 1\right) \right] + C_2 \qquad (20)$$

$$\xi = \frac{v}{k_{20}(\eta)^2 - k_{10}\eta} \left[-\frac{1}{x_1(\xi)} \right] + C_3 \qquad (21)$$

The integration constants C_1, C_2, and C_3 are obtained by using the boundary condition given by Equation (12) as

$$C_1 = \frac{v}{k_{20}(\eta)^2 - k_{10}\eta} \left[\frac{1}{(1-\beta)a_1 + \beta x_1(L)} + \ln\left(\frac{1}{(1-\beta)a_1 + \beta x_1(L)} - 1\right) \right] \qquad (22)$$

$$C_2 = \frac{v}{k_{20}(\eta)^2 - k_{10}\eta} \left\{ \frac{1 - 2[(1-\beta)a_1 + \beta x_1(L)]}{[(1-\beta)a_1 + \beta x_1(L)]\,[1 - (1-\beta)a_1 - \beta x_1(L)]} + 2\ln\left[\frac{1}{(1-\beta)a_1 + \beta x_1(L)} - 1\right] \right\} \qquad (23)$$

$$C_3 = \frac{v}{k_{20}(\eta)^2 - k_{10}\eta} \left[\frac{1}{(1-\beta)a_1 + \beta x_1(L)} \right] \qquad (24)$$

Thus Equations (19), (20), and (21) become, respectively

$$\xi = \frac{v}{k_{10}\eta - k_{20}(\eta)^2} \left\{ \frac{1}{x_1(\xi)} + \ln\left[\frac{1}{x_1(\xi)} - 1\right] - \left[\frac{1}{(1-\beta)a_1 + \beta x_1(L)}\right] - \ln\left[\frac{1}{(1-\beta)a_1 + \beta x_1(L)} - 1\right] \right\} \qquad (25)$$

$$\xi = \frac{v}{k_{10}\eta - k_{20}(\eta)^2} \left\{ \frac{1 - 2x_1(\xi)}{x_1(\xi)\,[1 - x_1(\xi)]} + 2\ln\left[\frac{1}{x_1(\xi)} - 1\right] - 2\ln\left[\frac{1}{(1-\beta)a_1 + \beta x_1(L)} - 1\right] - \left[\frac{1 - 2[(1-\beta)a_1 + \beta x_1(L)]}{[(1-\beta)a_1 + \beta x_1(L)][1 - (1-\beta)a_1 - \beta x_1(L)]}\right] \right\} \qquad (26)$$

$$\xi = \frac{v}{k_{10}\eta - k_{20}(\eta)^2} \left[\frac{1}{x_1(\xi)} - \frac{1}{(1-\beta)a_1 + \beta x_1(L)} \right] \qquad (27)$$

The optimal decision $\overline{\theta}(\xi)$ is recovered from Equations (25), (26), and (27) together with Equation (16).

NUMERICAL RESULTS AND DISCUSSION

The numerical data used are: $L = 10$ ft., $v_f = 1{,}000$ cu.ft./hr., $E_1 = 10{,}000$ cal./g.-mole, $E_2 = 20{,}000$ cal./

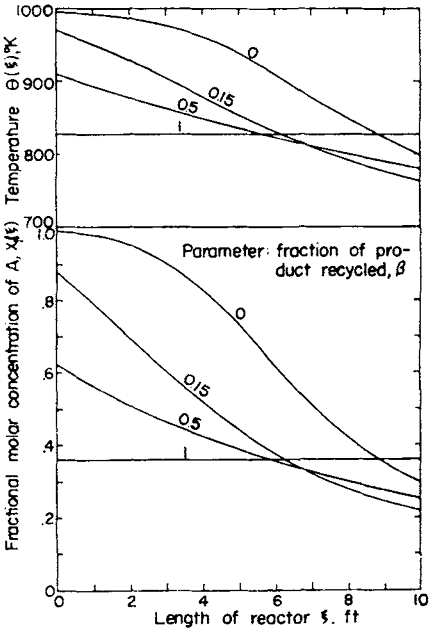

Fig. 2. Optimal concentration and temperature profiles for the autocatalytic reaction $A + R \rightleftarrows R + R$ with the initial concentration of $a_1 = 0.99$; first order with respect to the reversible reaction, that is, $s = 1$.

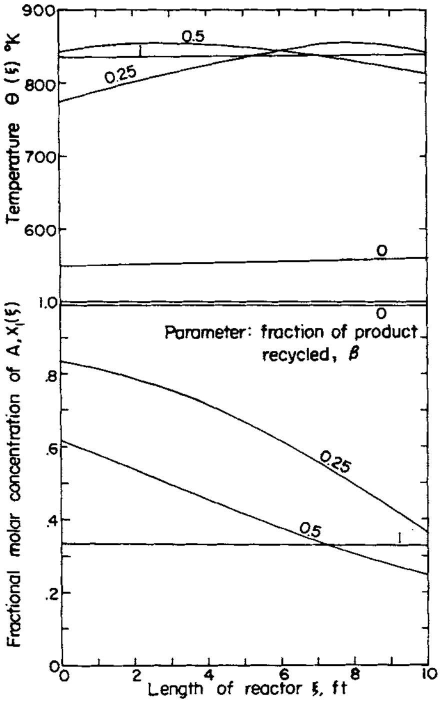

Fig. 3. Optimal concentration and temperature profiles for the autocatalytic reaction $A+R \rightleftarrows R+R$ with the initial concentration of $a_1 = 0.99$; zero order with respect to the reversible reaction, that is, $s = 0$.

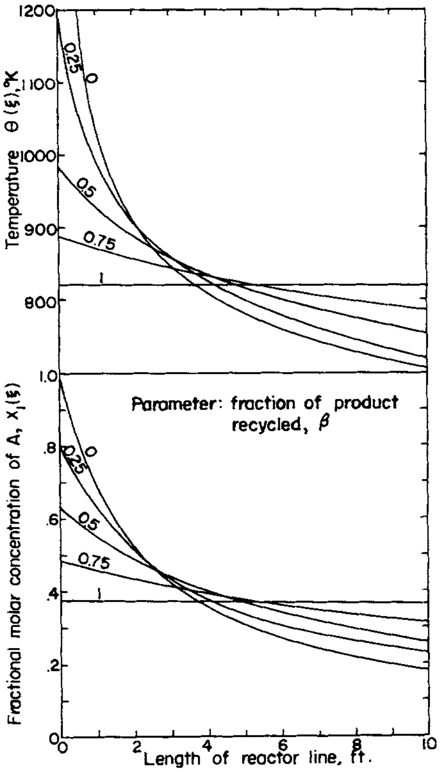

Fig. 4. Optimal concentration and temperature profiles for the autocatalytic reaction $A+R \rightleftarrows R+R$ with the initial concentration of $a_1 = 0.99$; second order with respect to the reversible reaction, that is, $s = 2$.

g.-mole, $k_{10} = 2.51 \times 10^5$ cu.ft./(hr.)(mole), k_{20} = variable (see Table 1).

The optimal concentration and temperature profiles for all three cases considered are plotted for an initial concentration of $a_1 = 0.99$ in Figures 2 through 4 with the fraction of product recycled, β, as a parameter. A better picture of the conditions required for the optimal performance of the autocatalytic reactor is perhaps obtained through a plot of the maximum conversion of the reactant against β, as shown in Figures 5 through 7. In this paper percent conversion is defined as

$$\frac{a_1 - x_1(L)}{a_1} \times 100$$

For a given initial concentration, these figures show that the maximum conversion reaches its highest value for a specific value of β. For instance, Figure 5 indicates that, when $a_1 = 0.99$, the maximum conversion is highest at $\beta = 0.15$ for the first case, that is, $s = 1$.

Occurrence of peaks in the curves of the maximum conversion vs. β is due to two counteracting effects of the recycle; while the product in the recycle stream accelerates the reaction, it also lowers the concentration of the reactant and thus tends to reduce the rate of reaction.

The curve in Figure 7 does not contain a peak. It is, however, not unreasonable to assume that a peak might occur when the initial concentration of the reactant is extremely high and/or the values of various data are different from those used in this work.

The results obtained for the case where the reverse reaction is zero order, that is, $s = 0$, appear to be of particular interest. For this case the reverse reaction proceeds at a constant rate which is independent of the concentration of R. When the concentration of R is very low, the reverse reaction proceeds faster than the forward reaction and the concentration of R decreases as the materials move through the reactor. If the concentration of R in

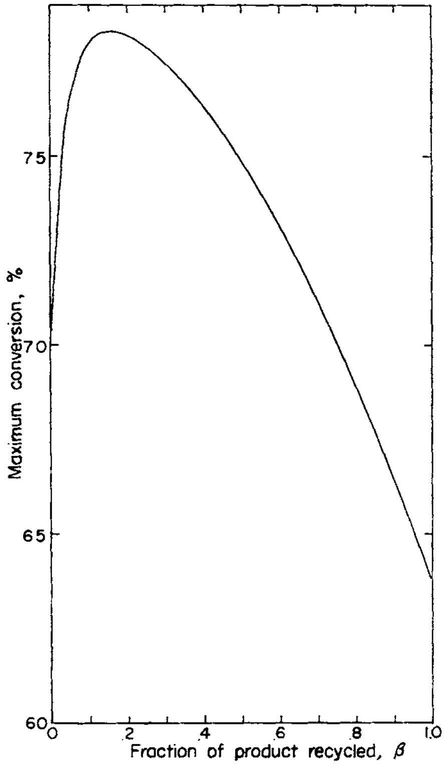

Fig. 5. Maximum conversion vs. fraction of product recycled; initial concentration, $a_1 = 0.99$; first order with respect to the reversible reaction, that is, $s = 1$.

the product stream is lower than the concentration of R in the feed stream, recycle has an undesirable effect in that it lowers the concentration of R in the feed to the reactor. For $a_1 = 0.99$ and $0 < \beta < 0.23$ the maximum conversion was found to be less than or equal to zero, indicating that the reverse reaction does proceed faster than the forward reaction for these particular conditions.

When the reverse reaction is zero order, the maximum conversion is strongly affected by the fraction of product recycled, β. This is illustrated in Figure 6 for several values of a_1. The sharpness of these curves illustrates the important effect of the concentration of the autocatalytic agent R on the maximum conversion. The concentration of R to the reactor is influenced by both the fraction of product recycled and the concentration of R in the recycle stream, as well as the concentration of R in the feed stream.

Comparison With Other Models

When the recycle flow rate is much larger than the fresh feed flow rate, the condition of a tubular reactor approaches that of a completely mixed stirred-tank reactor. Therefore, the condition $\beta = 0.99$ should approximately correspond to that of a stirred-tank reactor. The performance equations of a stirred-tank reactor for the three types of reactions considered are:

Case 1: $a = r = 1$ and $s = 1$

$$x_1{}^1 = \frac{\left(1+\frac{k_2}{k_1}+\frac{1}{tk_1}\right)-\sqrt{\left(1+\frac{k_2}{k_1}+\frac{1}{tk_1}\right)^2-4\left(\frac{x_1{}^0}{tk_1}+\frac{k_2}{k_1}\right)}}{2} \tag{28}$$

Case 2: $a = r = 1$ and $s = 0$

$$x_1{}^1 = \frac{\left(1+\frac{1}{tk_1}\right)-\sqrt{\left(1+\frac{1}{tk_1}\right)^2-4\left(\frac{x_1{}^0}{tk_1}+\frac{k_2}{k_1}\right)}}{2} \tag{29}$$

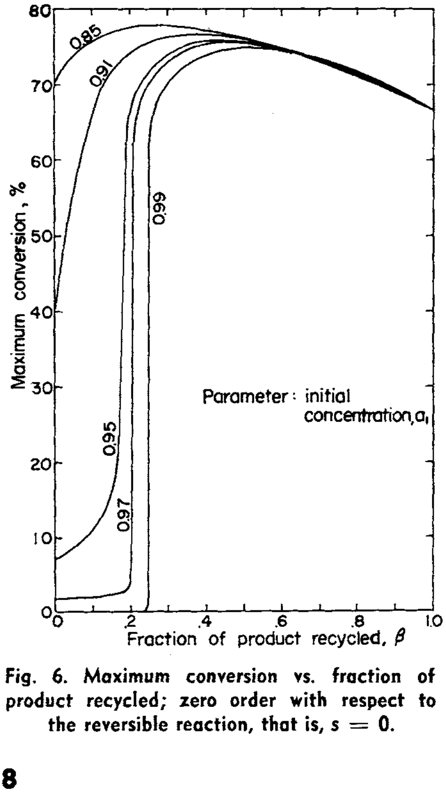

Fig. 6. Maximum conversion vs. fraction of product recycled; zero order with respect to the reversible reaction, that is, $s = 0$.

TABLE 2. COMPARISON OF PLUG FLOW REACTOR OF $\beta = 0.99$ WITH A COMPLETELY STIRRED-TANK REACTOR

	Case 1 ($s = 1$)		Case 2 ($s = 0$)		Case 3 ($s = 2$)	
	θ, °K.	Conv., %	θ, °K.	Conv., %	θ, °K.	Conv., %
Plug flow reactor with $\beta = 0.99$	827	63.6	838.6	66.6	817	63.0
Completely stirred-tank reactor	827	64.343	838.6	66.969	817	62.696

Case 3: $a = r = 1$ and $s = 2$

$$x_1{}^1 = \frac{1}{2}\left\{\frac{t(k_1+2k_2)+1}{t(k_1+k_2)} - \sqrt{\left[\frac{t(k_1+2k_2)+1}{t(k_1+k_2)}\right]^2-\frac{4(tk_2+x_1{}^0)}{t(k_1+k_2)}}\right\} \tag{30}$$

where t is the holding time defined as V/v, $x_1{}^0$ is the mole fraction of A in the fresh feed, and $x_1{}^1$ is the mole fraction of A in the product stream.

The optimal temperature and the maximum conversion for all three cases can be obtained by ordinary differentiation. The results are shown in Table 2 together with the optimal temperature and maximum conversion for a tubular reactor for which $\beta = 0.99$. As shown in this table, the two sets of results are in good agreement.

It is also interesting to compare conversions from a reactor operated isothermally with those from a reactor operated optimally. For an isothermal tubular reactor Equation (10) can be integrated to give the following expressions for the three cases considered.

Case 1: $a = r = 1,\quad s = 1$

$$\xi = \frac{v}{k_1-k_2}\ln\left[\frac{x_1(L)-1}{x_1(0)-1}\cdot\frac{k_1x_1(0)-k_2}{k_1x_1(L)-k_2}\right] \tag{31}$$

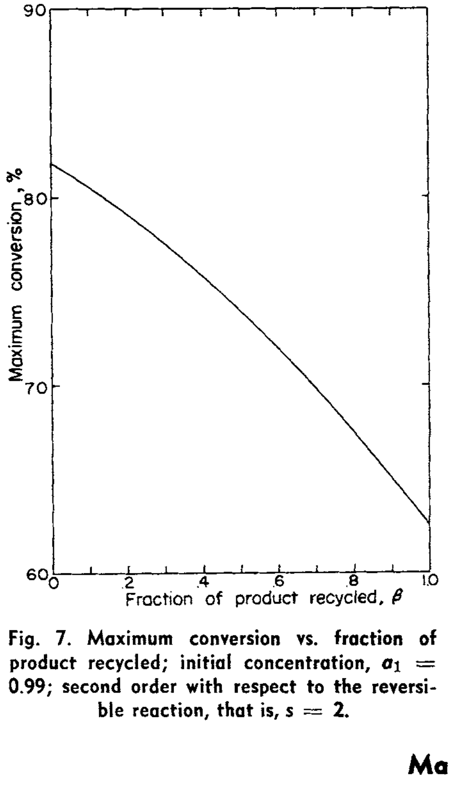

Fig. 7. Maximum conversion vs. fraction of product recycled; initial concentration, $a_1 = 0.99$; second order with respect to the reversible reaction, that is, $s = 2$.

TABLE 3. COMPARISON OF CONVERSION OBTAINED BY OPTIMAL OPERATION WITH THAT OBTAINED BY ISOTHERMAL OPERATION FOR $a_1 = 0.99$

	Case 1 $a = r = s = 1$	Case 2 $a = r = 1$ $s = 0$	Case 3 $a = r = 1$ $s = 2$
	$\beta = 0.15$	$\beta = 0.5$	$\beta = 0.5$
Optimal (non-isothermal)	78.1%	74.7%	74%
Isothermal	71.8% $\theta_{\text{ave.}} = 879°\text{K}.$	74.7% $\theta_{\text{ave.}} = 840°\text{K}.$	68.3% $\theta_{\text{ave.}} = 869°\text{K}.$

Case 2: $a = r = 1, \quad s = 0$

$$\xi = \frac{v}{(k_1)^2 - 4k_1k_2} \ln\left[\frac{2k_1x_1(L) - k_1 - \sqrt{(k_1)^2 - 4k_1k_2}}{2k_1x_1(0) - k_1 - \sqrt{(k_1)^2 - 4k_1k_2}} \cdot \frac{2k_1x_1(0) - k_1 + \sqrt{(k_1)^2 - 4k_1k_2}}{2k_1x_1(L) - k_1 + \sqrt{(k_1)^2 - 4k_1k_2}}\right] \tag{32}$$

Case 3: $a = r = 1, \quad s = 2$

$$\xi = \frac{v}{k_1} \ln\left\{\left[\frac{x_1(L) - 1}{x_1(0) - 1}\right]\left[\frac{x_1(0) - \dfrac{k_2}{k_1 + k_2}}{x_1(L) - \dfrac{k_2}{k_1 + k_2}}\right]\right\} \tag{33}$$

It should be remembered that $x_1(0) = (1 - \beta)a_1 + \beta x_1(L)$ according to Equation (12). The temperature for the isothermal operation has been taken as the arithmetic average of the inlet and outlet temperatures under the optimal operation. In Table 3 the conversions obtained by the use of Equations (31) through (33) are compared with the optimal conversions for $a_1 = 0.99$. The results indicate a considerable decrease in conversion for cases 1 and 3 when the reactor is operated isothermally. For case 2 the optimal temperature profile as shown in Figure 3 is nearly isothermal and the effect of isothermal operation on conversion is very small. This comparison allows one to make a quick estimate of the size of the incentive for nonisothermal operation.

A variation in the plug flow with recycle (PFWR) model is a combination of two plug flow reactors connected in series with intermediate product withdrawal, as shown in Figure 8. This is similar to the PFWR model, except that a portion of the product stream leaving the first reactor undergoes further reaction in the second reactor before it is mixed with fresh feed. For such a reactor arrangement and for the same autocatalytic reaction considered previously, we can again derive the optimal solution as

$$\bar{\theta}_1{}^n = \left(\frac{E_1 - E_2}{R}\right)\frac{1}{\ln\{\eta(x_1{}^n)^a(1 - x_1{}^n)^{r-s}\}} \tag{34}$$

where the superscript $n = 1, 2$ denotes the first and second reactors, respectively, and

$$\int d\xi^1 = \frac{v^1}{k_{20}(\eta)^2 - k_{10}\eta}\int\frac{dx_1{}^1}{(x_1{}^1)^{2a}(1 - x_1{}^1)^{2r-s}}$$
$$0 \leq \xi^1 \leq L^1 \tag{35}$$

$$\int d\xi^2 = \frac{v^2}{k_{20}(\eta)^2 - k_{10}\eta}\,\frac{dx_1{}^2}{(x_1{}^2)^{2a}(1 - x_1{}^2)^{2r-s}} \tag{36}$$
$$0 \leq \xi^2 \leq L^2$$

The boundary conditions for these two equations are

$$x_1{}^2(0) = x_1{}^1(L^1)$$

and the material balance at the inlet of the first reactor is given by

$$x_1{}^1(0) = (1 - \beta)a_1 + \beta x_1{}^2(L^2)$$

When the reaction is first order with respect to each component, that is, $a = r = s = 1$, Equations (35) and (36) can be integrated to give

$$\xi^1 = \frac{v^1}{k_{20}(\eta)^2 - k_{10}\eta}\left[\left(\frac{1}{(1 - \beta)a_1 + \beta x_1{}^2(L^2)}\right) + \ln\left(\frac{1}{(1 - \beta)a_1 + \beta x_1{}^2(L^2)} - 1\right) - \frac{1}{x_1{}^1(\xi^1)} - \ln\left(\frac{1}{x_1{}^1(\xi^1)} - 1\right)\right] \tag{37}$$

$$\xi^2 = \frac{v^2}{k_{20}(\eta)^2 - k_{10}\eta}\left[\frac{1}{x_1{}^1(L^1)} + \ln\left(\frac{1}{x_1{}^1(L^1)} - 1\right) - \frac{1}{x_1{}^2(\xi^2)} - \ln\left(\frac{1}{x_1{}^2(\xi^2)} - 1\right)\right] \tag{38}$$

Equations (37) and (38) have been solved simultaneously by a trial-and-error technique for $a_1 = 0.90$ with the same data as were used previously for the same reaction and $L^2 = 10$ ft. The results of such computations are plotted in Figure 9. As before, the optimal yield is replotted against β, as shown in Figure 10. Figure 10 also shows that there is a certain value of β at which we should operate in order to obtain the maximum yield.

When the reactor arrangement shown in Figure 8 is employed, the maximum yield is obtained at a lower value of β than for the single reactor system. This can be expected, because the concentration of the product which catalyzes the reaction is increased in the second reactor in the recycle path. In the treatment of process waste waters containing a low fraction of soluble organics by the contact stabilization process (9), this geometric reactor arrangement is used. However, in contact stabilization there is an added incentive for this design in that the colloidal and suspended waste material (component A) is adsorbed by the biological floc (component R) and separated from the effluent in the product stream so that a more concentrated mixture of A and R enters the recycle reactor and thus the total reactor volume requirement is reduced.

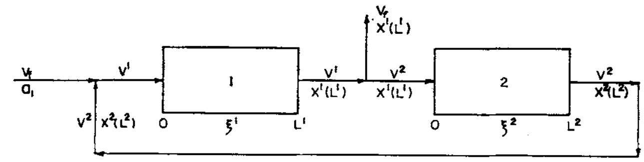

Fig. 8. Schematic diagram of a system of two continuous flow tubular reactors connected in series with recycle and intermediate product withdrawal.

SUMMARY

This work illustrates how an autocatalytic reaction system may be studied by applying the maximum principle to optimize a model of the system. For a rather general

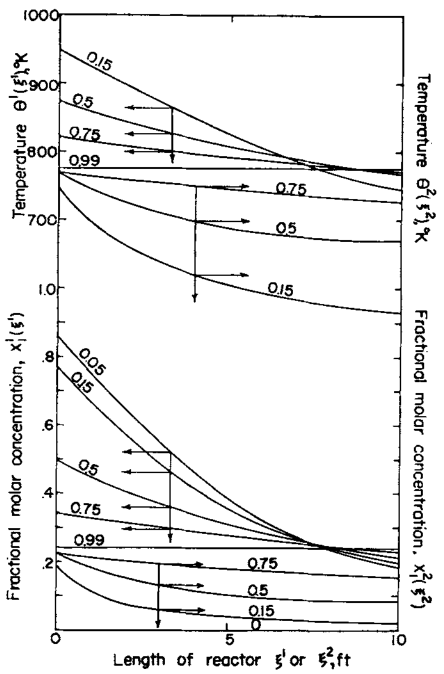

Fig. 9. Optimal concentration and temperature profiles for the autocatalytic reaction $A+R \rightleftarrows R+R$ taking place in two tubular reactors connected in series with intermediate product withdrawal; initial concentration, $a_1 = 0.9$. First-order reaction with respect to each component $a = r = s = 1$.

kinetic model, the effects of temperature and fraction of product recycled on the yield of product R are considered for a plug flow tubular reactor model. A differential equation [Equation (17)] which can be numerically integrated to give the optimal concentration as a function of position in the reactor for a given fraction of product recycled is derived. Once a kinetic equation with the form of the kinetic model has been obtained, Equation (17) can be numerically integrated and the optimal temperature and concentration profiles can be determined.

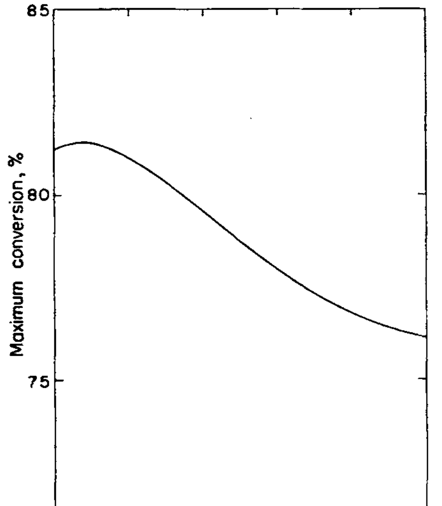

Fig. 10. Maximum conversion vs. β for two reactors connected in series; initial concentration $a_1 = 0.9$ and first-order reaction with respect to each component, $a = r = s = 1$.

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NOTATION

a = order of forward reaction with respect to reactant A
a_1 = initial fractional molar concentration of reactant 1
A = chemical specie
C_A = molar concentration of reactant A
C_i = molar concentration of reactant i
C_{i0} = molar concentration of component i in fresh feed
E_1 = activation energy for forward reaction
E_2 = activation energy for backward reaction
H = Hamilton function
k_1 = rate constant for forward reaction
k_2 = rate constant for backward reaction
k_{10} = frequency factor for forward reaction
k_{20} = frequency factor for backward reaction
L^n = length of n^{th} reactor
r = order of forward reaction with respect to reactant R
R = chemical specie
R_A = rate of production of reactant A
R_i = rate of production for reactant i
s = order of backward reaction
S = objective function
t = V/v = residence time
T = temperature
v_f = volumetric flow rate of fresh feed stream
v_r = volumetric flow rate of recycle stream
v = $v_f + v_r$ = total volumetric flow rate
V = volume of reactor
x_i = fractional molar concentration of reactant i
z_1 = adjoint variable

Greek Letters

β = v_r/v = fraction of product recycled
η = $(k_{10}E_1/k_{20}E_2)$
θ = decision variable, temperature, °K.
λ_1 = $(E_1/E_2 - E_1)$
λ_2 = $(E_2/E_2 - E_1)$
ξ = distance variable in flow direction

Subscripts

i = component number
1 = forward reaction
2 = backward reaction

Superscript

n = n^{th} reactor

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