The Effect of Fluid Mixing on the Maximum Yield and the Optimum Temperature Profile in a Tubular Reactor (I-Autocatalytic Reaction)

By

Takeichiro TAKAMATSU*, Iori HASHIMOTO*, and Yaichiro SAWANOI*

The chemical reaction system to be taken up here is an autocatalytic reaction which converts an initial reactant A to a reaction product R according to $A+R \rightleftarrows R+R$ or $A \rightleftarrows R$.

Based on the one-dimensional diffusion model of fluid mixing which takes place only in the direction of axial flow, the effects of the axial diffusion on the maximum conversion and the optimum temperature distribution are investigated.

The numerical results are obtained for a system in which the activation energy of the reverse reaction is twice that of the forward reaction, and it is recognized that the optimum mixing condition to the conversion exists for some operating conditions.

Introduction

Examples of autocatalytic reactions in which one or more of the products act catalytically are found generally in the acidcatalyzed hydrolysis of various esters and similar compounds and in various biochemical processes such as waste treatment. The rate of reaction is influenced by the concentration of some of the products as well as that of some of the reactants. Therefore, the rate of an autocatalytic reaction in a tubular flow reactor is influenced by two important factors, i.e. the initial concentration of the autocatalytic agent and the temperature at which the reaction is carried out.

In this paper, how the optimum temperature distribution to maximize the conversion of an autocatalytic reaction is affected by Pe which expresses the degree of fluid mixing has been analyzed by means of a one-dimensional model.

L.T. Fan et al.[1] have investigated the same autocatalytic reaction i.e. how the conversion and the optimum temperature distribution are affected by the interaction of product recycle, supposing that the flow in a tubular reactor is piston flow.

---

* Department of Sanitary Engineering

Formulation of Problem

We shall consider an autocatalytic reaction of the following type which proceeds in a tubular reactor;

$$A+R \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R+R \quad \text{or} \quad A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R \tag{1}$$
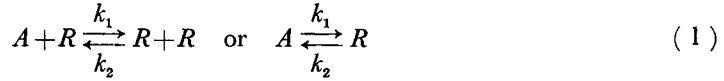
The equation of the steady-state differential material balance for reactant A in a differential section dz of the reactor is

$$E\frac{d^2C_A}{dz^2}-u\frac{dC_A}{dz}-R_A=0, \qquad 0\leqslant z \leqslant L \tag{2}$$

where C_A is molar concentration of reactant A, E is disperison or axial dispersion coefficient, L denotes the length of the tubular reactor, u is fluid velocity, and R_A is the reaction rate of reactant A.

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

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

where a, r, and s are the orders of reaction with respect to individual reactants and products, and k_1 and k_2 are the temperature dependent reaction rate constants given by the Arrhenius law of

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

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

In the above equations k_{10} and k_{20} are frequency factors, and E_1 and E_2 are activation energies. At any section of reactor we have

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

Substituting this equation into Equation (3), it becomes,

$$R_A=k_1\left(\frac{C_A}{C_0}\right)^a\left(1-\frac{C_A}{C_0}\right)^r(C_0)^{a+r}-k_2\left(1-\frac{C_A}{C_0}\right)^s(C_0)^s \tag{7}$$

Substituting equation (4) and (5) into equation (7), and inserting the resulting equation in turn, into equation (2), the following equation can be obtained,

$$E\frac{d^2C_A}{dz^2}-u\frac{dC_A}{dz}=k_1\left(\frac{C_A}{C_0}\right)^a\left(1-\frac{C_A}{C_0}\right)^r(C_0)^{a+r}-k_2\left(1-\frac{C_A}{C_0}\right)^s(C_0)^s \tag{8}$$

Suitable boundary conditions for the type of continuous flow reactor considered above have been given by Dankwerts as follows,

$$E\left(\frac{dC_A}{dz}\right)_{z=0^+} = u(C_A|_{z=0^+} - C_{A0}) \tag{9}$$

$$E\left(\frac{dC_A}{dz}\right)_{z=L^-} = 0 \tag{10}$$

In terms of the fractional molar concentration of

$$X_A = C_A/C_0, \quad X_{A0} = C_{A0}/C_0$$

we can rewrite equations (8), (9) and (10), and if we assume

$$C_0 = C_A + C_R = 1$$

Equations (8), (9) and (10) can be replaced by

$$E\frac{d^2 X_A}{dz^2} - u\frac{dX_A}{dz} = k_1(X_A)^a(1-X_A)^r - k_2(1-X_A)^s \tag{11}$$

$$E\left(\frac{dX_A}{dz}\right)_{z=0^+} = u(X_A|_{z=0^+} - X_{A0}) \tag{12}$$

$$E\left(\frac{dX_A}{dz}\right)_{z=L^-} = 0 \tag{13}$$

The following dimensionless quantities have been introduced so as to rewrite equations (11), (12) and (13) in dimensionless forms:

Dimensionless distance $\quad \eta = z/L$ $\hspace{4cm}$ (14)

Peclet number $\hspace{2cm} Pe = uL/E$ $\hspace{4cm}$ (15)

Damköhler number $\hspace{1.3cm} D_A = (Lk_{10}/u)C_0$ $\hspace{3cm}$ (16)

Dimensionless constants $K_1 = (D_A/Pe)\exp(-E_1/RT)$ $\hspace{2cm}$ (17)

$$K_2 = (D_A/Pe)(k_{20}/k_{10})\exp(-E_2/RT) \tag{18}$$

where an axial diffusion is characterized by the Peclet number Pe, and chemical reaction processes by a dimensionless Damkohler number *Da*, to be defined by equations (15), (16) respectively.

If we use dimensionless quantities defined above, equations (11), (12) and (13) can be written as follows.

Process equation;

$$\frac{1}{Pe^2}\frac{d^2X_A}{d\eta} - \frac{1}{Pe}\frac{dX_A}{d\eta} = K_1(X_A)^a (1-X_A)^r - K_2(1-X_A)^s \tag{19}$$

Boundary conditions;

$$\eta = 0; \ X_A = (X_A)_0, \quad \frac{1}{Pe}\frac{dX_A}{d\eta} = (X_A)_0 - X_{A0} \tag{20}$$

$$\eta = 1; \ X_A = (X_A)_1, \quad \frac{1}{Pe}\frac{dX_A}{d\eta} = 0 \tag{21}$$

Since it is desirable to maximize the yield of product R or equivalently to minimize the exit concentration of the reactant A, $(X_A)_1$, the performance index can be defined as follows:

$$(X_A)_1 \rightarrow \text{Minimum} \tag{22}$$

Solution by Clasical Variational Method[2],[3],[4]

Defining the following variable,

$$\xi = \exp (Pe\eta) \tag{23}$$

Process equation (19) becomes,

$$\frac{d^2X_A}{d\xi^2} = \frac{1}{\xi^2}\left\{ K_1(X_A)^a (1-X_A)^r - K_2(1-X_A)^s \right\} \tag{24}$$

and the boundary conditions are,

$$\xi = 1; \ X_A = (X_A)_0, \quad \frac{dX_A}{d\xi} = (X_A)_0 - X_{A0} \tag{25}$$

$$\xi = \xi_1 = \exp (Pe); \ X_A = (X_A)_1, \quad \frac{dX_A}{d\xi} = 0 \tag{26}$$

In principle, the control variable is the fluid temperature in a tubular reactor, however, it is easy to solve the problem in which K_1 and K_2, themselves containing the variable of T, are regarded as the control variables.

The following relations are held between K_1 and K_2,

$$K_2 = \alpha K_1^n \tag{27}$$

$$n = E_2/E_1 \tag{28}$$

$$\alpha = (k_{20}/k_{10})(Pe/D_A)^{n-1} \tag{29}$$

The optimum temperature can be uniquely determined from the optimum value of K_1 and K_2.

In order to use the variational method, the performance index $(X_A)_1$ should be rewritten as the explicit function of K_1 and K_2.

Integrating equation (24) with ξ from ξ to ξ_1, it becomes,

$$\int_\xi^{\xi_1} d\left(\frac{dX_A}{d\xi}\right) = \int_\xi^{\xi_1} \left\{K_1(X_A)^a (1-X_A)^r - K_2(1-X_A)^s\right\} \frac{1}{t^2} dt \qquad (30)$$

Taking account of the boundary condition of equation (26), the above relation becomes as follows,

$$\frac{dX_A}{d\xi} = -\int_\xi^{\xi_1} \frac{1}{t^2} \left\{K_1(X_A)^a (1-X_A)^r - K_2(1-X_A)^s\right\} dt \qquad (31)$$

and moreover, from the boundary condition of equation (25), equation (31) becomes

$$(X_A)_0 - X_{A0} = -\int_1^{\xi_1} \frac{1}{t^2} \left\{K_1(X_A)^a (1-X_A)^r - K_2(1-X_A)^s\right\} dt \qquad (32)$$

Integrating equation (31) with ξ again, it becomes

$$X_A = -\int_\xi^{\xi_1} \frac{(\xi-t)}{t^2} \left\{K_1(X_A)^a (1-X_A)^r - K_2(1-X_A)^s\right\} dt + (X_A)_1 \qquad (33)$$

then, being $\xi = 1$, the above equation is

$$(X_A)_1 = X_A \mid_{\xi=1} + \int_1^{\xi_1} \frac{(1-t)}{t^2} \left\{K_1(X_A)^2 (1-X_A)^r - K_2(1-X_A)^s\right\} dt \qquad (34)$$

From equations (25) and (32), the fractional molar concentration at the outlet of reactor, $(X_A)_1$ can be expressed by the following relation,

$$(X_A)_1 = X_{A0} - \int_1^{\xi_1} \frac{1}{t} \left\{K_1(X_A)^a (1-X_A)^r - K_2(1-X_A)^s\right\} dt \qquad (35)$$

The problem is to obtain K_1 and K_2 to minimize the value of $(X_A)_1$ represented by equation (35), and that is,

$$J = \int_1^{\xi_1} F(t, X_A, K_1) dt \to \text{Maximum} \qquad (36)$$

where,

$$F(t, X_A, K_1) = \frac{1}{\xi}\left(1 + \frac{\lambda}{\xi}\right)\left\{K_1(X_A)^a (1-X_A)^r - K_2(1-X_A)^s\right\} + \lambda \frac{d^2 X_A}{d\xi^2} \qquad (37)$$

and λ is Lagrange multiplier.

Euler's equation to equations (36) and (37) is obtained as follows,

$$\frac{\partial F}{\partial K_1} = 0 \tag{38}$$

$$\frac{\partial F}{\partial X_A} + \frac{d^2}{d\xi^2}\left(\frac{\partial F}{\partial\left(\frac{d^2 X_A}{d\xi^2}\right)}\right) = 0 \tag{39}$$

From equations (37) and (38), it is obvious to be

$$\frac{\partial}{\partial K_1}\left\{K_1(X_A)^a (1-X_A)^r - K_2(1-X_A)^s\right\} = 0 \tag{40}$$

By solving the above Euler's equation the optimum K_1 and K_2 can be obtained as follows.
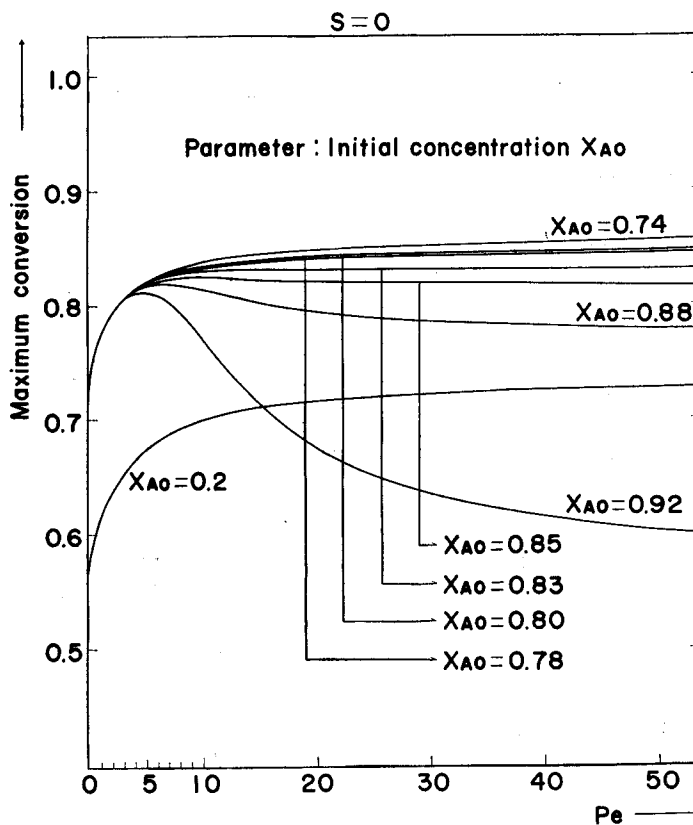
Fig. 1.   Maximum conversion vs. Pe; zeroth-order i.e. $s=0$, $a=r=1$.

$$K_1 = \left\{ \frac{1}{n\alpha} (X_A)^a (1-X_A)^{r-s} \right\}^{1/n-1} \tag{41}$$

$$K_2 = \left\{ \frac{1}{n\alpha} (X_A)^a (1-X_A)^{r-s} \right\}^{n/n-1} \tag{42}$$

Substituting equations (41) and (42) into equation (19), the following equation is obtained,

$$\frac{1}{Pe^2} \frac{d^2 X_A}{d\eta^2} - \frac{1}{Pe} \frac{dX_A}{d\eta} = \left(1-\frac{1}{n}\right)\left(\frac{1}{n\alpha}\right)^{1/n-1} (X_A)^{an/n-1} (1-X_A)^{(nr-s)/n-1} \tag{43}$$

Solving the above equation with the boundary conditions of equations (20) and (21), the fractional molar concentration at any point in the reactor under the optimum condition can be obtained.
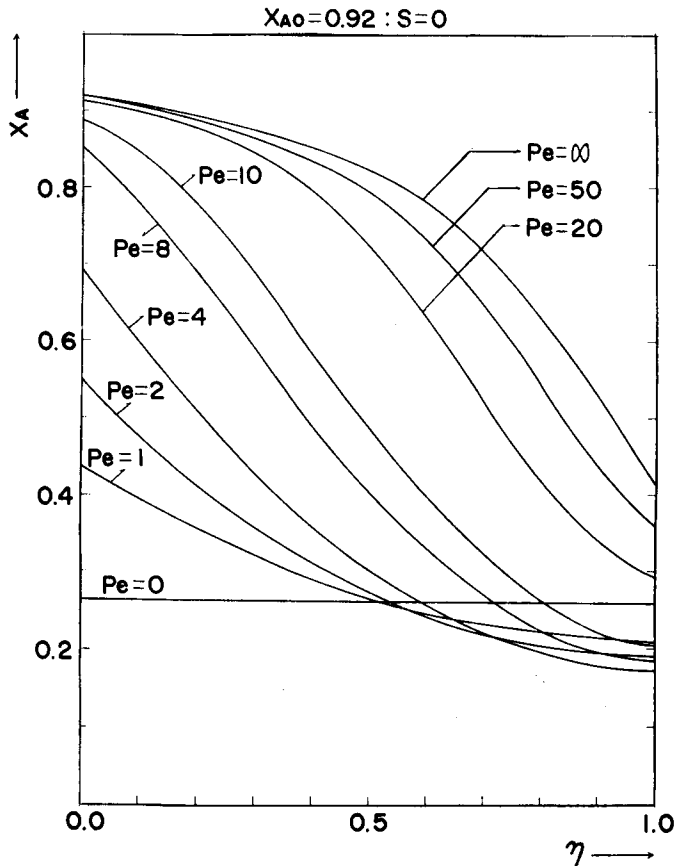

Fig. 2. Optimal concentration profile $s=0$, $a=r=1$; $X_{A0}=0.92$.

In this paper, only the case of $n=2$ is considered.

Defining the following new parameter μ,

$$D_A = \mu(k_{20}/k_{10}) \tag{44}$$

Equation (41) becomes

$$K_1 = \frac{\mu}{2Pe}(X_A)^a(1-X_A)^{r-s} \tag{45}$$

and equation (43) can be shown by

$$\frac{1}{Pe^2}\frac{d^2X_A}{d\eta^2} - \frac{1}{Pe}\frac{dX_A}{d\eta} = \frac{1}{4\alpha}(X_A)^{2a}(1-X_A)^{(2r-s)} \tag{46}$$

Solving the above equation under the boundary condition of equations (20)
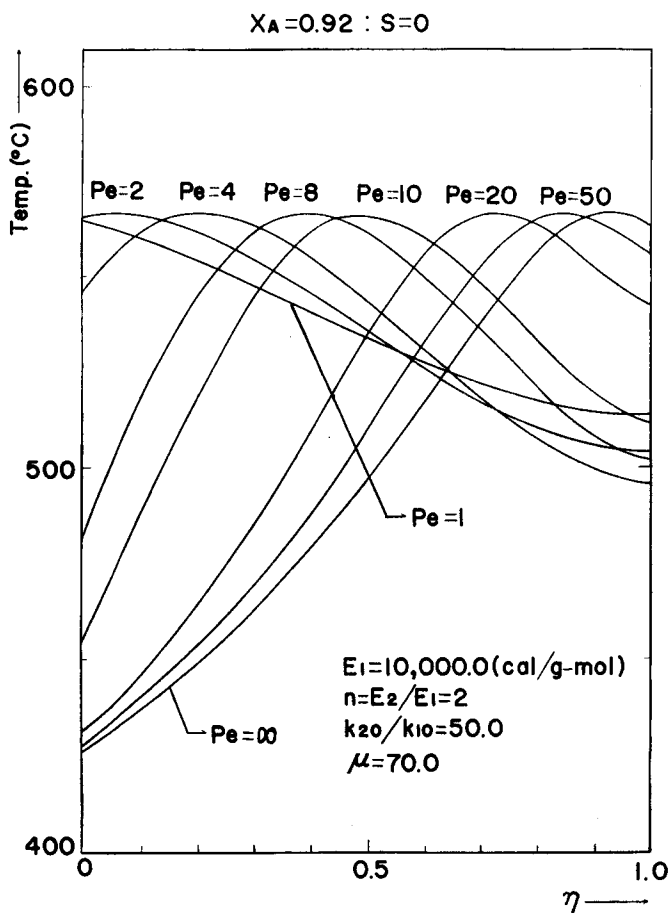
$X_A = 0.92 : S = 0$

Fig. 3.   Optimal temperature profile $s=0$, $a=r=1$; $X_A=0.92$.

and (21), the optimal conversion profile is obtained, but at first, let us consider the extreme cases of $Pe=0$ (i.e. Perfect mixing flow) and and $P=\infty$ (i.e. Piston flow).

i)   The case for $Pe=0$

Solving equation (46) under the boundary condition of equation (20) it is,

$$\frac{1}{Pe}\frac{dX_A}{d\eta}-(X_A-X_{A0})=\int_0^\eta \frac{\mu}{4}(X_A)^{2a}(1-X_A)^{(2r-s)}d\eta \qquad (47)$$

and by taking account of equation (21) the following relation can be obtained.

$$X_{A0}-(X_A)_1=\int_0^1 \frac{\mu}{4}(X_A)^{2a}(1-X_A)^{(2r-s)}d\eta \qquad (48)$$

$Pe=0$, that is,

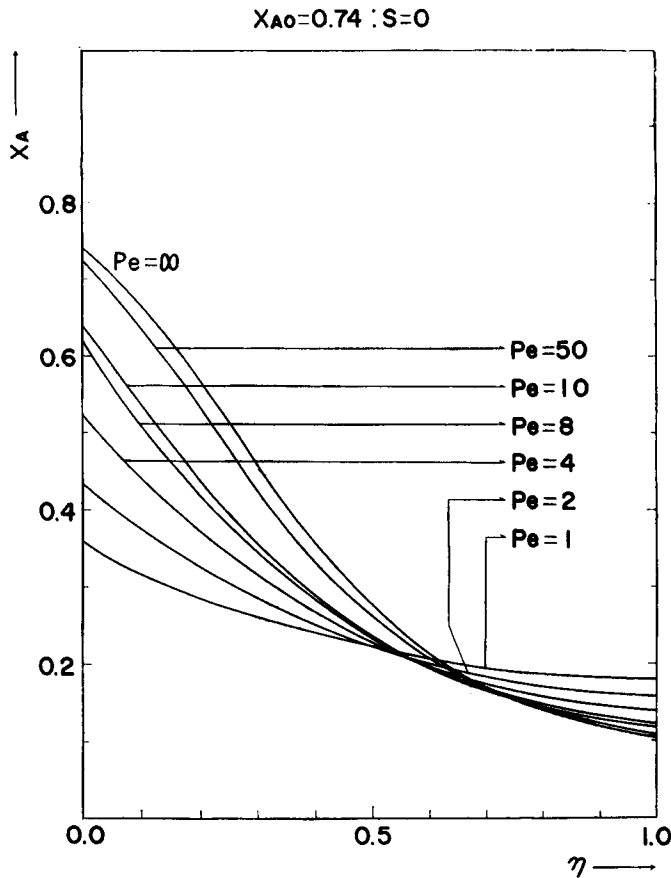**X$_{AO}$=0.74 ∶ S=0**

Fig. 4.   Optimal concentration profile $s=0$, $a=r=1$; $X_{A0}=0.74$.

$$X_A = (X_A)_0 \tag{49}$$

and then $(X_A)_1$ is given by

$$(X_A)_1 = X_{A0} - \frac{\mu}{4} (X_A)_1^{2a} (1-(X_A)_1)^{2r-s)} \tag{50}$$

ii)   The case for $Pe = \infty$

At the condition of $Pe = \infty$, equation (46) becomes

$$-\frac{dX_A}{d\eta} = \frac{\mu}{4} (X_A)^{2a} (1-X_A)^{(2r-s)} \tag{51}$$

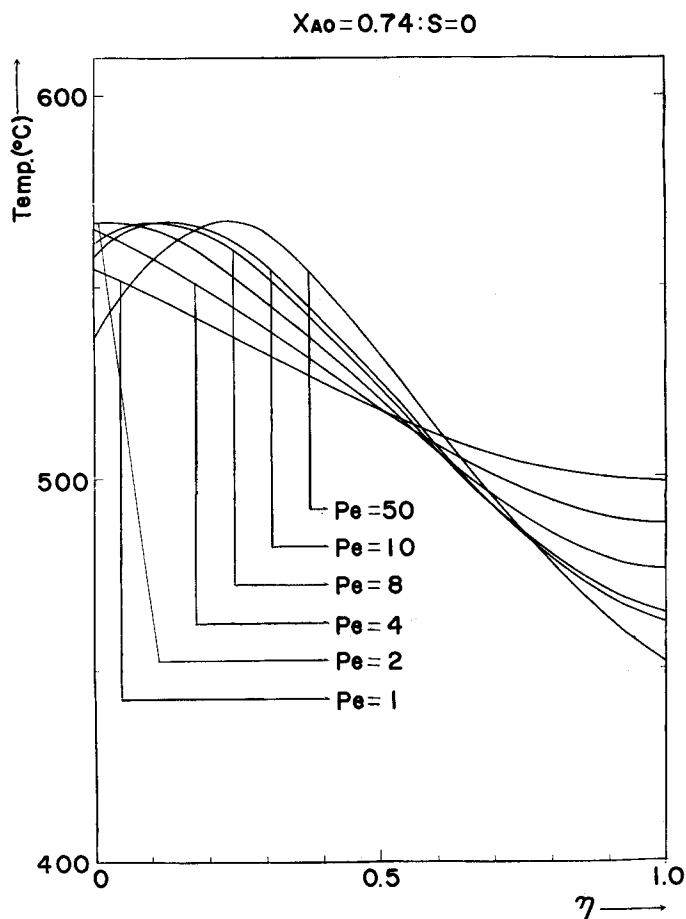(A)   The case for chemical reaction of $a=r=1$, and $s=0$ orders

Fig. 5.   Optimal temperature profile $s=0$, $a=r=1$; $X_0=0.74$.

The Effect of Fluid Mixing on the Maximum Yield and the Optimum Temperature
Profile in a Tubular Reactor I-Autocatalytic Reaction

235

$$\frac{\mu\eta}{4} = \left[2ln\left(\frac{X_A}{1-X_A}\right) + \frac{2X_A-1}{X_A(1-X_A)}\right]_{X_A}^{X_{A0}}$$

(52)

(B) $a=r=1$, $s=2$ orders

$$\frac{\mu\eta}{4} = \left[-\frac{1}{X_A}\right]_{X_A}^{X_{A0}}$$

(53)

Then, the optimal conversion at $\eta=1$ is obtained by trial and error.

Numerical Calculations

The value of parameters used to solve equation (46) are:

$$E_1 = 10000.0 \ (cal/g\text{-}mol)$$
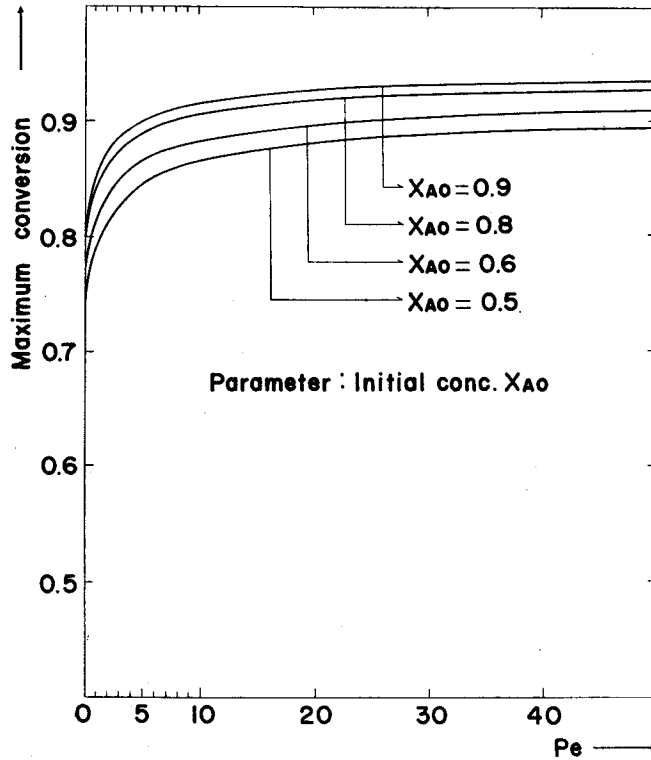$$E_2 = 20000.0 \ (cal/g\text{-}mol)$$

Fig. 6.   Maximum conv.vs. *Pe*, $s=2$, $a=r=1$.

$$k_{10} = 10.0 \ (cm^3/sec \cdot g\text{-}mol)$$
$$k_{20} = 500.0 \ (g\text{-}mol/cm^3 \cdot sec)$$
$$L = 350.0 \ (cm); \quad u = 1.0 \ (cm/sec)$$
$$\mu = 70.0$$

Solving equation (46) with equations (20) and (21) by using the above values, the optimum value of X_A can be calculated, and the optimum value of K_1 can be obtained from this X_A by using equation (45). Substituting the values of K_1 and K_2 into equations (17) and (18), respectively, the optimum temperature in a reactor is easily obtained.

Discussion of Results

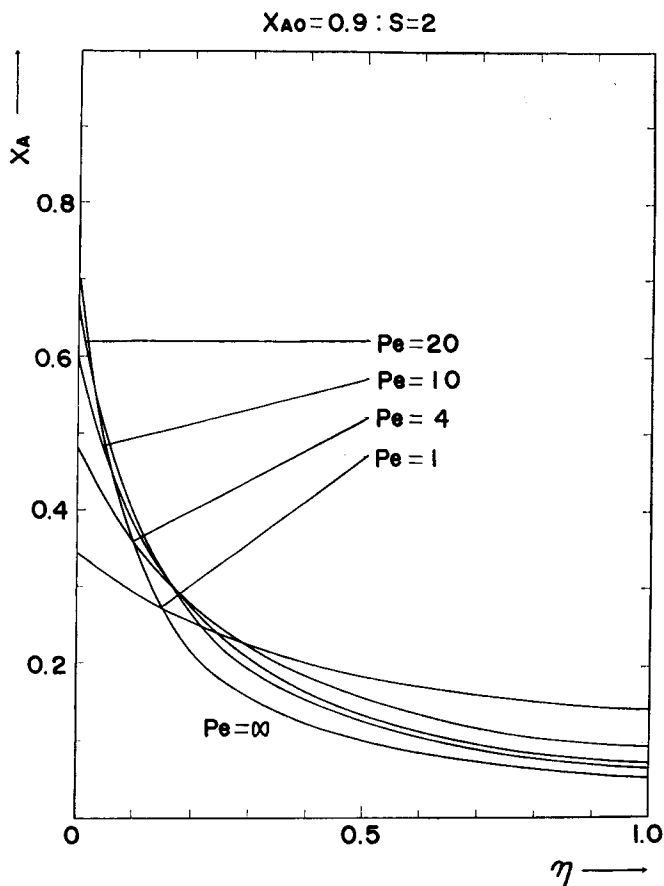The results of the numerical computation for various values of Pe in the case

Fig. 7. Optimal concentration profile, $s=2$, $a=r=1$; $X_{A0}=0.9$.

of $\mu=(k_{10}/k_{20})(L/u)k_{10}C_0=70.0$ are plotted in Figs. 1, 2, 3, 4, 5, 6, 7, and 8. Now, Figs. 1, 2, 3, 4, and 5 show the results in the case of the zeroth-order with respect to the reversible reaction, i.e. $s=0$ and the first-order to the forward reaction, i.e. $a=r=1$.

The cases of second-order to the reversible reaction, i.e. $s=2$ and $a=r=1$ to the forward are plotted in Figs. 6, 7, and 8.

Fig. 1 shows how the maximum conversion is affected by the dimensionless Pecret number. The parameter in Fig. 1 is the concentration of the reactant A in the feed X_{A0}.

The following statements can be made about Fig. 1.

(i) In the case of the large value of $X_{A0}(X_{A0}>0.83)$, there exists the optimum Pe to maximize the conversion at the outlet.
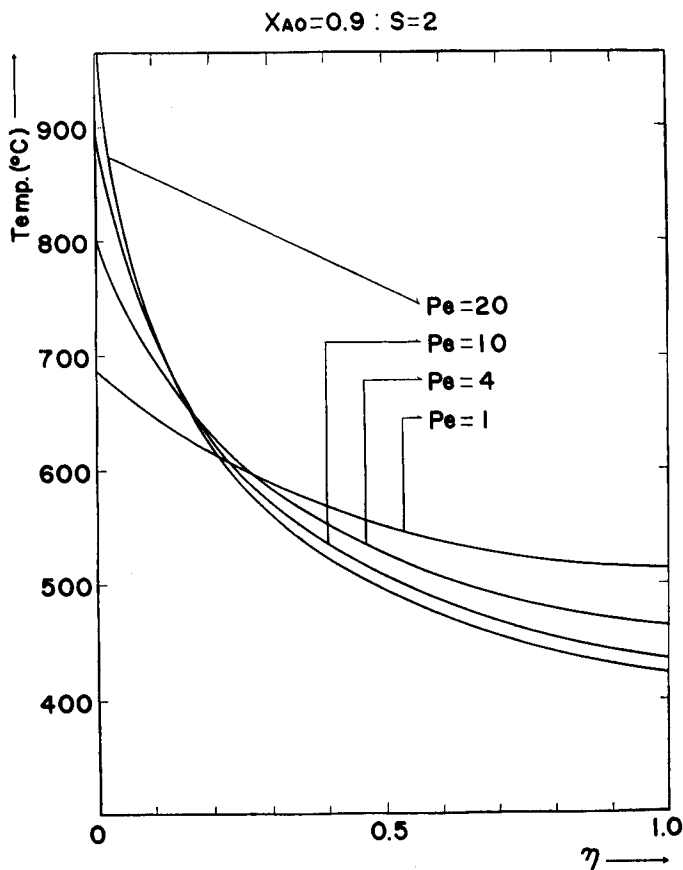

Fig. 8. Optimal temperature profile $s=2$, $a=r=1$; $X_{A0}=0.9$.

(ⅱ) For relatively low $X_{A0}(X_{A0}<0.8)$, the conversion at the outlet is increased, if Pe is increased.

(ⅲ) Particularly noticeable is the fact that there is an optimum X_{A0} to maximize the conversion at the outlet for the constant Pe. Figs. 2 and 3 show the relation of the fractional molar concentration X_A vs η with Pe as a parameter and the optimum temperature distribution in the case of $X_{A0}=0.92$.

Figs. 4 and 5 give the relation of X_A vs η and the optimum temperature distribution with Pe as a parameter in the case of $X_{A0}=0.74$. Noticeable facts to be drawn from the Figs. 3 and 5 are that there are extremum points of the optimum temperature distributions in the tubular reactor and that the location of the extremum point moves to the outlet of the reactor, when the flow in the reactor nears piston flow.

Figs. 6 answers the question as to how Pe affects the maximum conversion with X_{A0} as a parameter in the case of $s=2$, and $a=r=1$. The curves displayed in this figure show that for any value of X_{A0} the maximum conversion increases steadily with the increase of Pe. Furthermore, with Pe considered as a constant the maximum conversion is monotonously increased as X_{A0} becomes larger.

Figs. 7 and 8 show the relation of X_A vs η and the optimum temperature distribution with Pe as a parameter at the case of $X_{A0}=0.9$. These Figs. denote that there are not any extremum points of the optimum temperature distribution, and it decreases monotonously from the entrance to the outlet of the tubular reactor.

Conclusions

Methods and results were presented of the effect of axial diffusion on the optimum yield and the optimum temperature distribution of a tubular reactor with an autocatalytic reactions.

Nomenclatares

E :   Back mixing coefficient (cm²/sec)

C_A, C_R: molar concentrations of reactant A & product R (g-mol/cm³)

L :   length of tubular reactor (cm)

u :   fluid linear velocity (cm/sec)

a, r, s :   orders of reaction

R_A :   reaction rate of reactant A (g-mol/cm³·sec)

k_{10}, k_{20} :   frequency factors

E_1, E_2 :   activation energies (cal/g-mol)

R :   gas constant (cal/g-mol°K)

T :   reaction temperature (°K)

X_A :   fractional molar concentration defined by $X = C_A/C_{A0}$ (—)

k_1, k_2 :   reaction rate constants defined by $k_1 = k_{10} \exp(-E_1/RT)$ & $k_2 = k_{20} \exp(-E_2/RT)$

Pe :   Peclet number defined by $Pe = uL/E$ (—)

D_A :   Damköhler number defined by $D_A = (Lk_{10}/u)\,C_{A0}$ (—)

K_1 :   dimensionless constant defined by $K_1 = (D_A/Pe) \exp(-E_1/RT)$ (—)

K_2 :   dimensionless constant defined by $K_2 = (D_A/Pe)\,(k_{20}/k_{10}) \exp(-E_2/RT)$ (—)

z :   distance from tubular reactor inlet (cm)

η :   dimensionless distance defined by $\eta = z/L$ (—)

ξ :   variable defined by $\xi = \exp(Pe\eta)$ (—)

n :   parameter defined by $n = E_2/E_1$ (—)

α :   parameter defined by $\alpha = (k_{20}/k_{10})\,(Pe/D_A)^{n-1}$ (—)

λ :   Lagrange multiplier (—)

μ :   parameter defined by $\mu = (k_{10}/k_{20})\,(L/u)k_{10}C_0$

References

1) Y.K. Ahn, L.T. Fan, and L.E. Erickson: Preprints 18a. Presented by the Symposium on Selected Papers in Kinetics. Fifty-seventh National Meeting, Minneapolis, Minnesota Sep. 26–29, 1965.

2) J. Adler and D. Vortmyer: Chem. Eng. Sci. **18**, 99 (1963)

3) J. Adler and D. Vortmyer: Chem. Eng. Sci. **19**, 413 (1964)

4) I.M. Gelfand and S.V. Fomin: "Calculus of Variations" p. 22. Prentice-Hall, Inc. 1963.