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MIXING EFFECT ON CHEMICAL REACTION IN LIQUID PHASE

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MIXING EFFECT ON CHEMICAL REACTION IN LIQUID PHASE

by

Ming-Teh Hsu

A Dissertation submitted to the faculty of the Graduate School
of the New Jersey Institute of Technology in partial fulfillment of the
requirements for the degree of Docotoral of Engineering Science

1984

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IN LIQUID PHASE

Name of Candidate:

MING-TEH HSU

Doctor of Engineering Science, 1984

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City University of New York	1977	M.S.	1979
Chung Yuan University	1972	B.S.	1976

Major: Chemical Engineering

ABSTRACT

Title of Dissertation

Mixing Effect on Chemical Reaction in Liquid Phase

Ming-Teh Hsu

Doctor of Engineering Science, 1984

Dissertation directed by:

Dr. Ching-Rong Huang

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Mathematical models for the mixing phenomenon are proposed in this study. First model deals Newtonian and non-Newtonian fluid without chemical reaction. The new terminology " degree of mixing " is define in this model for the time-dependency of mixing toward its completeness. The velocity profile and boundary conditions are given, then the degree of mixing can be calculated by the mathematical model. The degree of mixing is influenced by fluid motion and it is function of time.

Second model deals with first-order reaction effected by mixing. A mean fractional conversion is defined to investigate the rate of chemical reaction. Results from numerical method indicate the rate of chemical reaction is greatly influenced by mixing , especially when the reaction rate is fast.

Finally, a mathematical model based on microscopic collision theory is developed for the estimation of chemical reaction rate constant in this study.

DEDICATION

To my parents,

Mo-Sung Hsu and Tasi-Chu Lee Hsu

ACKNOWLEDGEMENT

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CHAPTER I

INTRODUCTION

The mixing phenomenon is one important factor in considering the characterestics of chemical process equipment, and it covers a variety of coupled physical phenomena described by Ottino(1): fluid motion, diffusion, and chemical reaction. Mixing without reaction is important in the process of blending. Mixing with reaction is an essential part of reaction engineering analysis.

However, the mixing of fluids has lacked a sound theoretical description, due in large measure to the coupling of processes and the complex geometry and time dependency of the mixing in moving fluids. Understanding and modeling of the physical aspect of mixing has lagged far behind practical applications. Theories, models and experiments are needed to tie together to supply a quntitative understanding.

There are three different analytical approaches in investigating the mixing phenomenon: statistical model, residence time distribution theory, surface-extension model. However, only few have attempted to apply the concept with theoretical background, fluid mechanics and mass transfer, in the mixing phenomenon.

General limitations of the statistical model, well exemplified in Murthy's book(2), consist of 1. simplified flow fields in order to have solvable numerical problems. 2. dimensionality to reduce complexity. The residence time distribution, well exemplified in Levenspiel's book(3), uses simplified physical models and schemes of combinations of these models. This theory did not even include fluid mechanics in their models. The surface-extension model developed by Batchelor(4) only can be used in a simple geometry of the mixing equipment, due to complexity of the flow field.

The mixing is caused by the phenomenon of flow and diffusion When the mixing phenomenon is studied, three difficulties occur immediately. The first problem which needs to be solved is to develop a quantitative and applicable definition for the state of mixing. The definition will have practical uses, and will relate to the concentration distribution of the mixing tank. The second problem is to determine the velocity profile for different types of impellers in different shapes of mixing tanks. Finally, the concentration distribution in the mixing tank needs to be determined.

The transient response method, for its simplicity, has been used as a convenient technique to find the degree of mixing in a vessel by Danckwerts(5). However, the manner of representing the degree of mixing becomes a serious problem of utmost importance in this type of investigation. Bourne(6) has made a general review of the existing models of the degree of mixing. He comments that"the topic of degree of mixing began to be divorced from reality due to lack of a physical (e.g. fluid mechanical) basis." Many studies have been made of this problem. However, up to now, no clear definition of the degree of mixing has been established.

Mixing operations are influenced by the flow rates, velocity, and flow patterns of the fluid within an agitated vessel. There are three general types of impellers used in the mixing operations: The disk turbine, the pitched blade turbine, and the propeller. Different types of flow patterns were created by different types of impellers used in agitation. Nagata's book(7) discussed the experimental measurement of the liquid velocity in mixing.

Desouza and Pike(8) developed a two-dimensional model to calculate the velocity profile in a baffled tank with turbine impeller. However, this model described the flow in this region only qualitatively. Many researchers have made the same effort, but no satisfactory model has been found for the calculation of the velocity profile in a mixing vessel.

The basic relationship among the variables affecting uniformity of composition and rates of interfacial mass transfer are transient, partial-differential, material balance equations. When chemical changes are involved, reaction rate terms are included in the mass conservation equations for each molecular species involved. Similar energy balance equations provide the basic relationships among variables which influence heat transfer. Variables affecting fluid stress and fluid velocities are related by analogous equations for the conservation of momentum of fluids.

Detailed presentations of these basic equations in cyclindrical coordinates by Bird et al.(9) are as follows:

$$\rho\left(\frac{\partial v_r}{\partial t} + v_r\frac{\partial v_r}{\partial t} + \frac{v_\theta}{r}\frac{\partial v_r}{\partial \theta} - \frac{v_\theta^2}{r} + v_z\frac{\partial v_r}{\partial z}\right) = -\frac{\partial p_s}{\partial r} + \mu\left\{\frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}(rv_r)\right] + \frac{1}{r^2}\frac{\partial^2 v_r}{\partial \theta^2} - \frac{2}{r^2}\frac{\partial v_\theta}{\partial \theta} + \frac{\partial^2 v_r}{\partial z^2}\right\} + \rho g_r \tag{1-1}$$

$$\rho\left(\frac{\partial v_\theta}{\partial t} + v_r\frac{\partial v_\theta}{\partial r} + \frac{v}{r}\frac{\partial v_\theta}{\partial \theta} + \frac{v_r v_\theta}{r} + v_z\frac{\partial v_\theta}{\partial z}\right) = -\frac{1}{r}\frac{\partial p_s}{\partial \theta} + \mu\left\{\frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}(rv_\theta)\right] + \frac{1}{r^2}\frac{\partial^2 v_\theta}{\partial \theta^2} + \frac{2}{r^2}\frac{\partial v_r}{\partial \theta} + \frac{\partial^2 v_\theta}{\partial z^2}\right\} + \rho g_\theta \tag{1-2}$$

$$\rho\left(\frac{\partial v_z}{\partial t} + v_r\frac{\partial v_r}{\partial r} + \frac{v_\theta}{r}\frac{\partial v_z}{\partial \theta} + v_z\frac{\partial v_z}{\partial z}\right) = -\frac{\partial p_s}{\partial z} + \mu\left[\frac{1}{r}\left(r\frac{\partial v_z}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 v_z}{\partial \theta^2} + \frac{\partial^2 v_z}{\partial z^2}\right] + \rho g_z \tag{1-3}$$

$$\rho c_p\left(\frac{\partial T}{\partial t} + v_r\frac{\partial T}{\partial r} + \frac{v_\theta}{r}\frac{\partial T}{\partial \theta} + v_\theta\frac{\partial T}{\partial \theta} + v_z\frac{\partial T}{\partial z}\right) = K\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2}\right] \tag{1-4}$$

$$\frac{\partial C_A}{\partial t} + \left(v_r\frac{\partial C_A}{\partial r} + \frac{v_\theta}{r}\frac{\partial C_A}{\partial \theta} + v_z\frac{\partial C_A}{\partial z}\right) = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 C_A}{\partial \theta^2} + \frac{\partial^2 C_A}{\partial z^2}\right] + R_A \tag{1-5}$$

where V_r, V_θ, V_z are velocities in r, θ, z direction, T is temperature, C_A is concentration, and R_A is chemical reaction rate.

Because these partial differential equations are difficult to solve, the simple and practical approach will be developed in this study to explain the mixing phenomenon. The simple geometry of mixing equipment,mixing rolls, is presented for studying this subject.

There are three objectives of this study. First, to investigate the degree of mixing by solving the partial differential equation of concentration coordinate involving space and time, then define a more generally applicable degree of mixing which is related to the concentration profile in the mixing process. It is assumed that the chemical reaction does not occur in this part of study in order to simplify the mixing operation.

The second objective of this study is to investigate the rate of chemical reaction at different rotating speeds in the mixer, then define a new equation for mean fractional conversion which is related to the local concentration in the mixer. A first order reaction is assumed in this study for simplicity.

The last objective is to improve a microscopic model to predict the chemical reaction rate constant in the liquid phase without mixing. Kapral(10) states that for short distance and time, the Smoluchowski(11,12) type equations cannot be applied with confidence. A model involving collision rate, steric factor, and the activitation energy of chemical reaction will be developed to solve this problem.

CHAPTER II

DEGREE OF MIXING

The basic concept for the representation of the state of mixing is most important for studying the mixing phenomenon. However, there is no easy way to define the quantity of the state of mixing, which is called the degree of mixing. Most of scholars did not use a realistic definition in their research. A realistic model for the degree of mixing is developed in this study.

In most existing definitions of the degree of mixing, methods have been used to compare the variation of concentration distribution of the discernible solute in the sample with that of the extreme state, that is the final mixing state, or the complete separate state of the two(13). But these traditional methods start to show their inadequacy when they are applied to practical problems, so a new definition of the degree of mixing is required from a practical point of view.

Considering that most factors relating to the mixing mechanism can be understood in term of concentration variance, it would be advisable to take up the mixing phenomenon from the standpoint of concentration variance. It is the purpose of this chapter to define a more generally applicable degree of mixing by making use of the idea of concentration variance.

A. Basic Concepts

When the concentration C at an arbitrary point in a liquid is equal to the average concentration $\bar{C}$, the state of mixing is called homogenous. In order to represent the degree of mixing in a non-uniform state, a mathematical expression could be used to show the state of mixing.

Considering that a liquid in a cylindrical tank is stirred, at an arbitrary time t the concentration C is a function of r,θ,z, t as follows:

$$C = f(r,\theta,z,t) \qquad (2\text{-}1)$$

where r, θ and z, are radial distance, angle, and axial distance in cylindrical coordinates.

According to the definition of homogencity, as time approaches infinity, the concentration C can be expressed:

$$C(r,\theta,z,t) = C(t\to\infty) \qquad (2\text{-}2)$$

The general definition of the average concentration is the total moles of solute in the liquid phase divided by the total volume of the system. The average concentration can be represented as

$$C_A = \frac{\iiint C_A dV}{\iiint dV} \qquad (2\text{-}3)$$

where C_A is local concentration of solute A. If the system of mixing is a cylindrical tank, the volume change dV is equal to rdrdθdz, the Equations 2-3 can be changed to

$$\overline{C}_A = \frac{\iiint C_A \, r dr d\theta dz}{\iiint r dr d\theta dz} \tag{2-4}$$

The average concentration in a batch system is independent of time. There is no input and output concentration in a batch system. The conservation of mass will be used to prove that no matter what the progression of the time the average concentration for the system is constant. The mathematical equation is expressed as

$$\overline{C}_A\ (t=0) = \overline{C}_A(t) = \text{constant} \tag{2-5}$$

When the homogeneous state is attained in the system, the state of mixing is called perfect mixing. The state of perfect mixing is always assumed in solving chemical engineering problems. But the practical problem in chemical engineering is that the state of mixing is always between no mixing and perfect mixing. Therefore, it is very important to define a quantitative equation to express the state of mixing.

B. Definition for Degree of Mixing

To use a mathematical expression to display the state of mixing between no mixing and perfect mixing is a kind of art. The equation should not only express quantitatively the state of mixing, but also should be applicable to practical problems of mixing. A novel defintion of the degree of mixing is in the following section based on a simple and practical point of view.

When a concentration C_A at an arbitray point and time is in a cyclindrical vessel shown in Figure 1, the concentration variance σ_t^2 is defined by Equation 2-6.

$$\sigma_t^2 = \frac{\iiint [C_A(r,\theta z,t)-C_A]^2 \, rdrd\theta dz}{\iiint rdrd\theta dz} \qquad (2\text{-}6)$$

where r,θand z are coordinates of the cyclindrical vessel, and C_A is the average concentration. In this equation the average concentration is calculated only when time is approaching infinity.

At the initial time, t=0, the concentration C_O is injected into the system, and the concentration variance is

$$\sigma_o^2 = \frac{\iiint [C_O - C_A]^2 \, rdrd\theta dz}{\iiint rdrd\theta dz} \qquad (2\text{-}7)$$

As a degree of mixing, Equations 2-6 and 2-7 which consist of a concentration variance of an arbitrary unmixed state σ_t^2 and that of an initial time unmixed state σ_O^2 can be used to form the following definition:

$$H(t) = \frac{\sigma_o^2 - \sigma_t^2}{\sigma_O^2} \qquad (2\text{-}8)$$

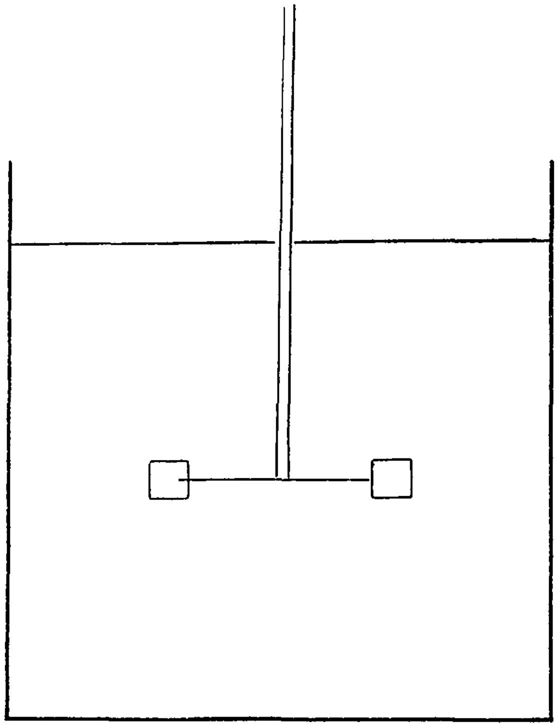

Figure 1. General Type of Mixing Configuration.

or

$$H(t) = 1 - \frac{\int\int\int(C_A - \overline{C}_A)^2 \; rdrd\theta dz}{\int\int\int(C_{A_o} - \overline{C}_A)^2 \; rdrd\theta dz} \qquad (2\text{-}8a)$$

where H is called the degree of mixing which represents the quantification of a mixing state.

In accordance with the above definition, the degree of mixing varies from zero for the initial state to values approaching unity for the final mixed state.

$$0 \leq H \leq 1 \qquad (2\text{-}9)$$

When the time is zero, the initial state is called complete segregation or no mixing. At this state the degree of mixing is

$$H(0) = \frac{\sigma_o^2 - \sigma_o^2}{\sigma_o^2} = 0 \qquad (2\text{-}10)$$

The final state of mixing is called perfect mixing. This state is not easy to attain in the actual mixing phenomenon, but it can be achieved as time approach infinity. In this state, the variance of concentration is

$$\begin{aligned}\sigma_\infty^2 &= \int\int\int(C_A - C_A)^2 \; rdrd\theta d \qquad (2\text{-}11)\\ &= 0,\end{aligned}$$

and the degree of mixing is

$$H(\infty) = \frac{\sigma_o^2 - \sigma_\infty^2}{\sigma_o^2} = 1 \qquad (2\text{-}12)$$

If the local concentrations at arbitrary point in the vessel are known, the degree of mixing can be determined by the Equation 2-8a at a specific time. The local concentration can be measured either by theoretical or by experimental methods. An experimental method is shown in the work of Ogawa and Ito(14). The theoretical approach will be presented in this study. The degree of mixing is a function of the local concentration of an arbitrary point at a specific time. The procedure of determining the degree of mixing will be illustrated by the following two sections.

C. Simple Case for Determining the Degree of Mixing

For this case, consider that plate is put into the center of the cyclindrical tank to separate the two components A and B as shown in Figure 2; one half of the tank is full of liquid A, and liquid B is in the other half of the tank. The plate is pulled suddenly out of the tank. Then the two liquids start to mix due to the molecular diffusion.

When components A and B start to mix, the different concentrations in the system begin to achieve the homogeneous state. There are no concentration differences in this state. Therefore, attaining the homogenous state due to molecular diffusion is a spontaneous phenomenon in mixing.

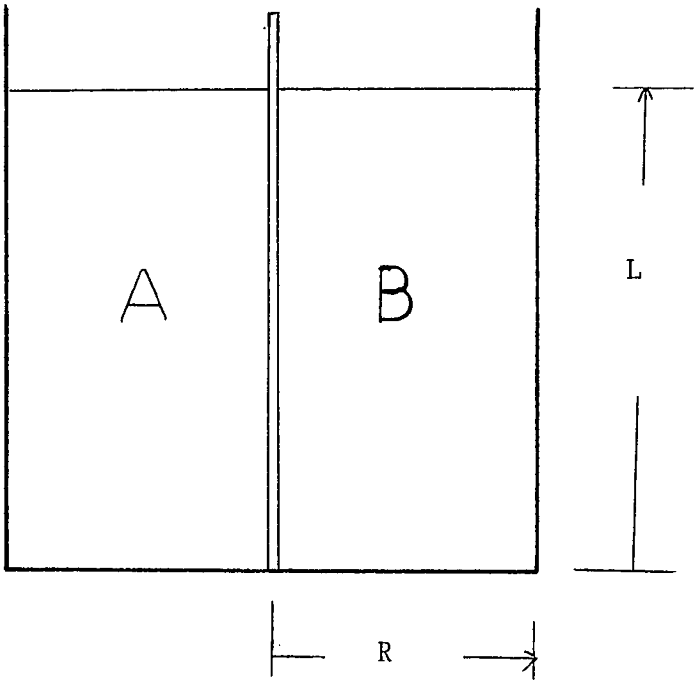

Figure 2. Mixing Due to Molecular Diffusion.

If the degree of mixing can be determined by the Equation 2-8a, the average concentration and concentration variance shall be calculated first. Therefore, the average concentration defined in Equaiton 2-4 for liquid A in this system is

$$\bar{C}_A = \frac{\int_o^L \int_o^{2\pi} \int_o^R C_A rdrd\theta dz}{\int_o^L \int_o^{2\pi} \int_o^R rdrd\theta dz} \qquad (2\text{-}13)$$

where L is the height of the tank, and R is the radius of the tank. Equation 2-13 can be divided into two terms according to the concentration distribution as follows:

$$\bar{C}_A = \frac{\int_o^L \int_o^{2\pi} \int_o^R C_{Ao} \, rdrd\theta dz}{\pi R^2 L} + 0 \qquad (2\text{-}14)$$

where C_{Ao} is the initial concentration of component A.

The second term of the right hand side of Equation (2-14) is zero, because half of tank is full of liquid B. The final result of Equation 2-14 is

$$\bar{C}_A = \frac{C_{Ao}}{2} \qquad (2\text{-}15)$$

And the concentration variance at the initial time is

$$\sigma_o^2 = \iiint (C_{Ao} - \bar{C}_A)^2 \, dV \qquad (2\text{-}16)$$

Equation 2-16 has to be separated into

$$\sigma_o^2 = \iiint (C_{Ao} - \bar{C}_A)^2 \, dV_A + \iiint (C_{Ao} - \bar{C}_A)^2 \, dV_B \qquad (2\text{-}17)$$

where V_A and V_B is the volume occupied by liquid A and B. C_{Ao} is equal to zero at the second term of rigth hard side of Equation 2-17. Then the final result of the Equation 2-17 is

$$\sigma_o^2 = \frac{C_{Ao}^2}{4} \; V \tag{2-18}$$

Therefore the degree of mixing at the initial time based on the average concentration and concentration variance is calculated as follows:

$$H(0) = \frac{\sigma_o^2 - \sigma_o^2}{\sigma_o^2} = 0 \tag{2-19}$$

At any specific time, the average concentration is the same as Equation 2-15, and the concentration variance is

$$\sigma_t^2 = \int\int\int (C_A - \bar{C}_A)^2 \, dV \tag{2-20}$$

Then the Equation 2-15 is substituted into Equation 2-20. The Equation 2-20 is changed to

$$\sigma_t^2 = \int\int\int(C_A - \frac{C_{Ao}}{2})^2 \; r \; dr \; d\theta \; dz \tag{2-21}$$

The degree of mixing is determined by Equation 2-8, 2-18 and 2-21 as

$$H(t) = 1 - \frac{\int_o^L\int_o^{2\pi}\int_o^R(C_A - \frac{C_{Ao}}{2})^2 \; rdrd\theta dz}{\frac{C_{Ao}^2}{4} \; V} \tag{2-22}$$

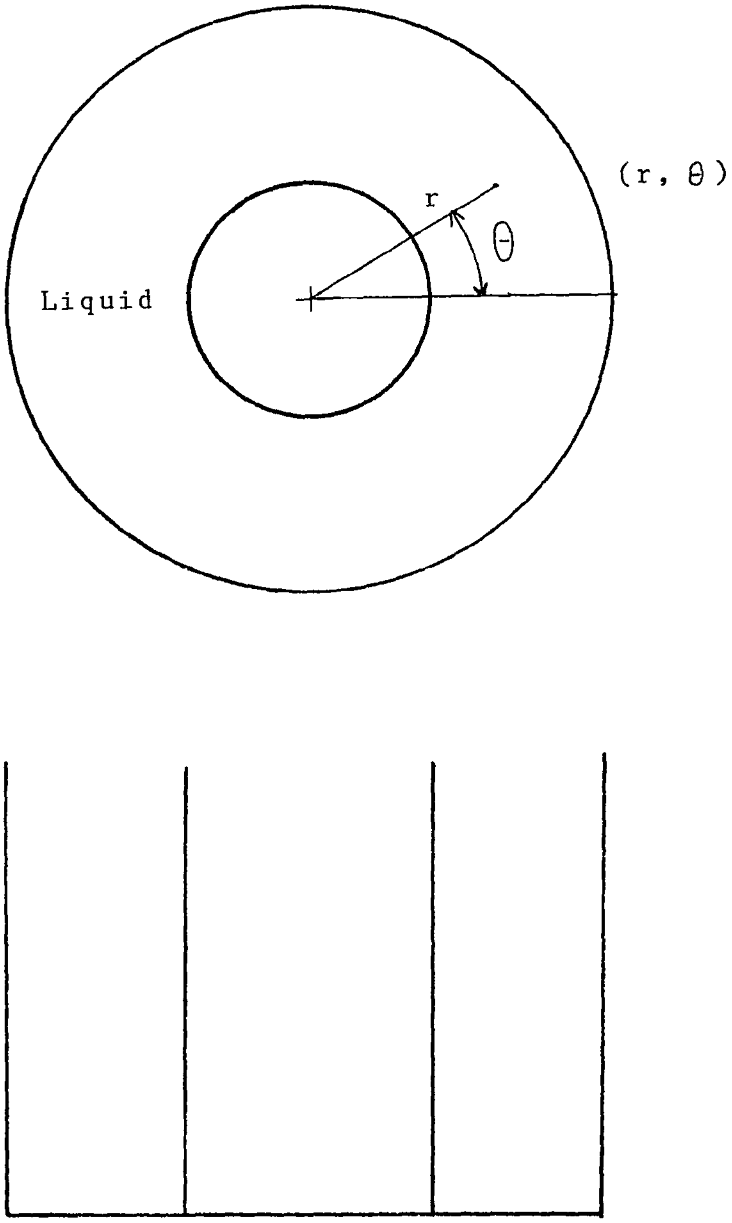

Figure 3. Annular Cylinder for Evaluating the Degree of Mixing

Modifying Equation 2-22 with $V = \pi R^2 L$, and Equation 2-22 becomes

$$H(t) = 1 - \frac{4 \int_o^{2\pi} \int_o^{R} (C_A - \frac{C_{Ao}}{2})^2 \, rdrd\theta}{\pi R^2 C_{A_o}^2} \tag{2-23}$$

The homogeneous state is obtained for the mixing of two different liquids at the time is approaching infinity. The average concentration is the same as Equation 2-15, and the concentration at this state of liquid A is

$$C_{A\infty} = \frac{C_{Ao}}{2} \tag{2-24}$$

where C_A is concentration of liquid A at infinite time. Then the concentration variance is determined by the Equation 2-6, 2-15, and 2-24 as follows:

$$\sigma_\infty^2 = 0 \tag{2-25}$$

and the degree of mixing in this state is equal to one.

In this case, the degree of mixing is in the range of zero to one. It is shown that the definition of degree of mixing can be applied in this simple and practical situation.

D. Complex Case for Determing the Degree of Mixing

Consider a fluid B contained in the annular region between a pair of long co-axial cylinders with radii KR and R as shown in Figure 3.

A concentration of liquid A is injected by an impulse into the annular region at the $\theta = 0$.

The calculation of the degree of mixing is very similar to the section C. The only difference is the configuration of the mixing tank. Therefore, following the same procedure discussed in the section C, the degree of mixing is

$$H(t) = 1 - \frac{\iiint (C_A - \overline{C}_A)^2 \, dV}{\iiint (C_{Ao} - \overline{C}_A)^2 \, dv} \qquad (2\text{-}26)$$

and the average concentration is

$$C_A = \frac{\iint C_A \, r dr d\theta}{\iint r dr d\theta} \qquad (2\text{-}27)$$

If the concentration distribution of the tank is known, the degree of mixing can be evaluated by Equations 2-26 and 2-27. The degree of mixing is a function of time. When time is increased to infinity, the distribution of concentration approaches uniformity. At this mixing state, the degree of mixing is equal to one. Therefore, determination of the concentration distribution is the most important factor in evaluating the degree of mixing. The next two chapters will focus on calculation of concentration distribution.

CHAPTER III

MIXING PHENOMENAN FOR NEWTONIAN FLUID

There are two mechanismS in the the batch tank to promote mixing of a solute, one is the mass transfer caused by a convection flow and the other is that caused by molecular diffusion.

The blotches of solute are deformed, and divided into pieces, and the aggregation becomes smaller by the convection flow. The contact surface area between zones of high and low concentration of solute is increased or renewed, and the mixing and transport is promoted by molecular diffusion. The aggregation may not be changed by the convection only, but is influenced by the molecular diffusion.

Figure 4 shows the process of mass transfer of solute for a lump into the surrounding liquid by the action of convection and molecular diffusion.

Mixing is carried out in a laminar state and the molecular diffusion is very small in high viscosity liquids. In this case, we must make an effort to decrease the diffusion length which must be overpowered by molecular diffusion, by stretching and subdividing the lump into small pieces.

The mass balance equations are obtained by taking the diffusion in convection flow into consideration, and the well-known partial differential equation was derived based on the assumption of constant

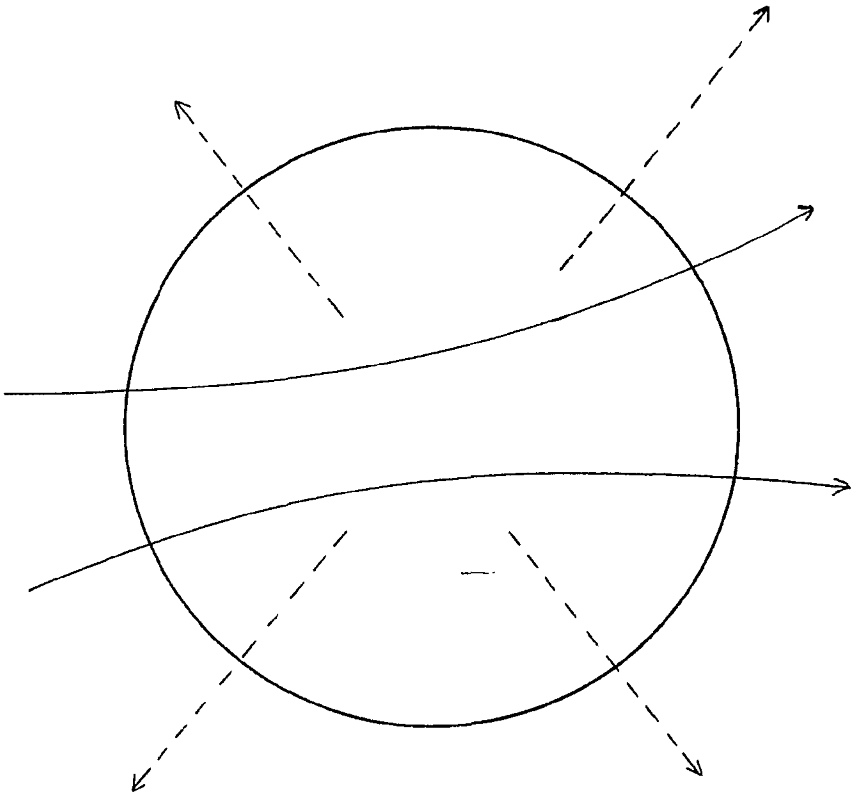

Figure 4. Process of Mass Transfer of Solute in a Lump

⟶ Mass Flux by Convection

----> Mass Flux by Diffusion

density and diffusivity by Bird et al.;$^{(9)}$

$$\frac{\partial C}{\partial t} + V_x \frac{\partial C}{\partial x} + V_y \frac{\partial C}{\partial y} + V_z \frac{\partial C}{\partial z} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial Z^2} + \frac{\partial^2 C}{\partial Z^2}\right) \qquad (3\text{-}1)$$

Also the equation of continuity must be considered

$$\frac{\partial Vx}{\partial x} + \frac{\partial Vy}{\partial y} + \frac{\partial Vz}{\partial z} = 0 \qquad (3\text{-}2)$$

Solving equation 3-1 is essential to overcome the problem of mixing. The velocity profile must be solved first before the concentration distribution can be solved. After the concentration profile is solved, the degree of mixing can be calculated by the new definition, Equation 2-8.

A. Velocity Profile

The equation of continuity and motion for the flow of a compressible, isothermal fluid are$^{(9)}$

$$\frac{\partial \rho}{\partial t} + (\nabla \cdot \rho V) = 0 \qquad (3\text{-}3)$$

$$\rho \left[\frac{\partial V}{\partial t} + (V \cdot \nabla) V\right] = - \nabla p_s + (\nabla \cdot \tau) + \rho g \qquad (3\text{-}4)$$

in which ρ is the fluid density, V is the local velocity, p_s is the static pressure, g is the external body force per unit mass, t is the time and τ is the stress tensor. The stress tensor is related to the velocity gradients for Newtonian flow thus(9):

$$\tau = - \mu[\nabla V + (\nabla V)^T] + \frac{2}{3} \mu (\nabla V)\delta \tag{3-5}$$

in which μ is the coefficient of shear viscosity, δ is the unit tensor, and $(\nabla V)^T$ in the transpose of (∇V). The special case of the above equation in cylindrical coordinates is used as the starting point in the following developments.

The assumption above of isothermal flow implies not only that there is no impressed temperature field, but that in addition the viscous dissipation term $(\tau:\nabla V)$ in the energy balance equation is negligible.

A fluid is contained in an annular region between a pair of co-axial cylinders with radii KR and R (as shown in Figure 5). At time $t < 0$, the fluid within the annulus is at rest. At $t > 0$, inner cylinder is rotated with constant angular velocitiy Ω_i, and the outer cylinder is stationary.

For an incompressible fluid this situation $v_r = v_z = 0$ and $V_\theta$is a function of r alone, so that Equations 3-4 and 3-5 become:

$$\rho \frac{\partial V\theta}{\partial t} = \mu \frac{\partial}{\partial r} \left[\frac{1}{r} \frac{\partial}{\partial r} (r V_\theta)\right] \tag{3-6}$$

This is to be solved with boundary and initial conditions: at $r = KR$, $v_\theta = KR\Omega_i$; at $r = R$, $v_\theta = 0$; at $t < 0$, $v_\theta = 0$. This problem has

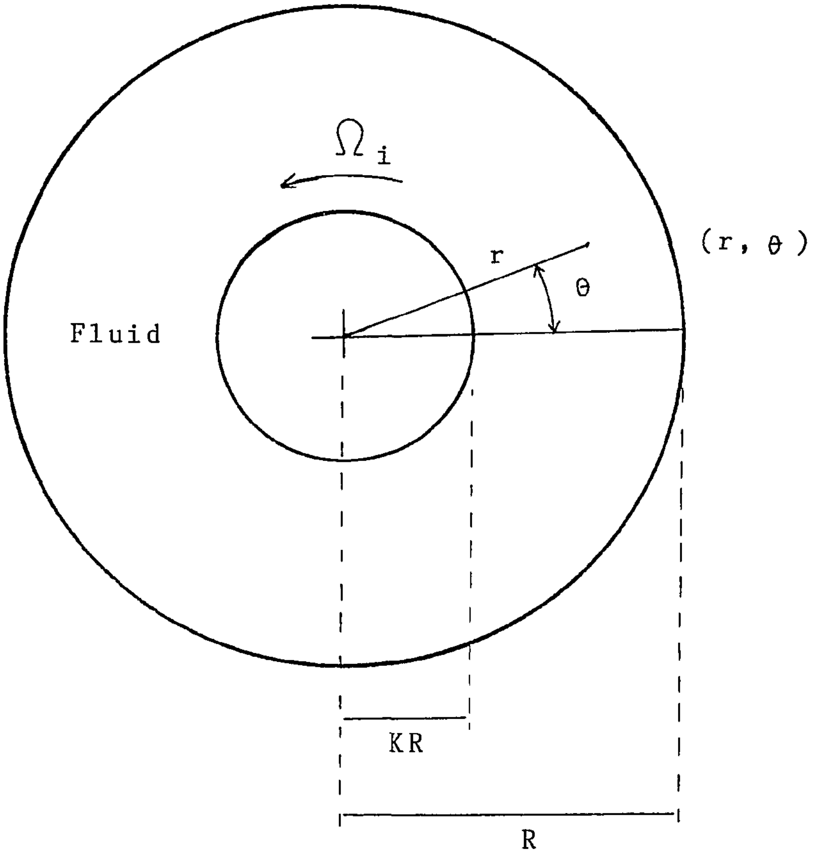

Figure 5. Annular Region in which Tangential Laminar Flow is Occurring

been solved by Bird et al.(15)

In our case, the steady state condition is assumed, and Equation 3-6 becomes:

$$\mu \frac{\partial}{\partial r} \left[\frac{1}{r} \frac{\partial}{\partial r} (r\, V_\theta) \right] = 0 \qquad (3\text{-}7)$$

Equation 3-7 may be integrated with respect to r with the boundary conditions: at $r = KR$, $v_\theta = KR\,\Omega_i$; at $r = R$, $v_\theta = 0$. The result is

$$V_\theta = \Omega_i \; K^2 r \; \frac{(R^2/r^{2}-1)}{1 - K^2} \qquad (3\text{-}8)$$

Once the velocity distribution is calculated, then the concentration distribution can be calculated from Equation 3-1. Therefore, the velocity distribution is the first step to calculate the concentration distribution in the mixing phenomenon.

B. Transition Reynolds Number

Laminar flow in this system is strongly stabilized by centrifugal forces. Thus a fluid particle from an outer layer opposed being moved inwards because the centrifuged force on it is greater than on particles nearer the axis of rotation. At the same time, its outward movement is resisted by the higher centrifugal force on particles it would have to replace. As a result, the transition to turbulent flow takes place at a much higher Reynolds number here than in the corresponding system in which the inner cyclinder is rotating and in which the centrifugal force tends to introduce instability. Both systems have been investigated,(9) and their transition Reynolds numbers are found to be strongly dependent upon the ratio of annulus thickness to the radius of the outer cylinder (1-K). When the outer cycliner is rotating, the transition Reynold number, defined as $(\Omega o R^2 \rho / \mu)_{trans}$, reaches a minimum of about 50,000 when (1-k) is about 0.05 as shown in Fig. 6. When the inner cylinder is rotating at an angular velocity Ωi (and the outer one is stationary), the transition Reynolds number may be expressed approximately as

$$\left(\frac{\Omega i \; K \; R^2}{\mu} \right)_{trans} = \frac{41.3}{(1-K)^{3/2}} \qquad (3\text{-}9)$$

C. Mathematical Modeling

After applying the law of conservation of mass of species i to a differential volume element fixed in space in a diffusion-reaction system, one obtains

$$\frac{\partial Ci}{\partial t} = - (\nabla N_i) + R_i \qquad (3\text{-}10)$$

In order to obtain the equation which is generally used to describe diffusion molar flux, N_i is replaced by the appreciate expression which includes the concentration gradient. Thus leads to the following Equation (3-11) which describes the concentration profile of the species in a diffusing system. If there are no chemical changes occurring, then r_i are all zero. Isothermal condition are assumed.

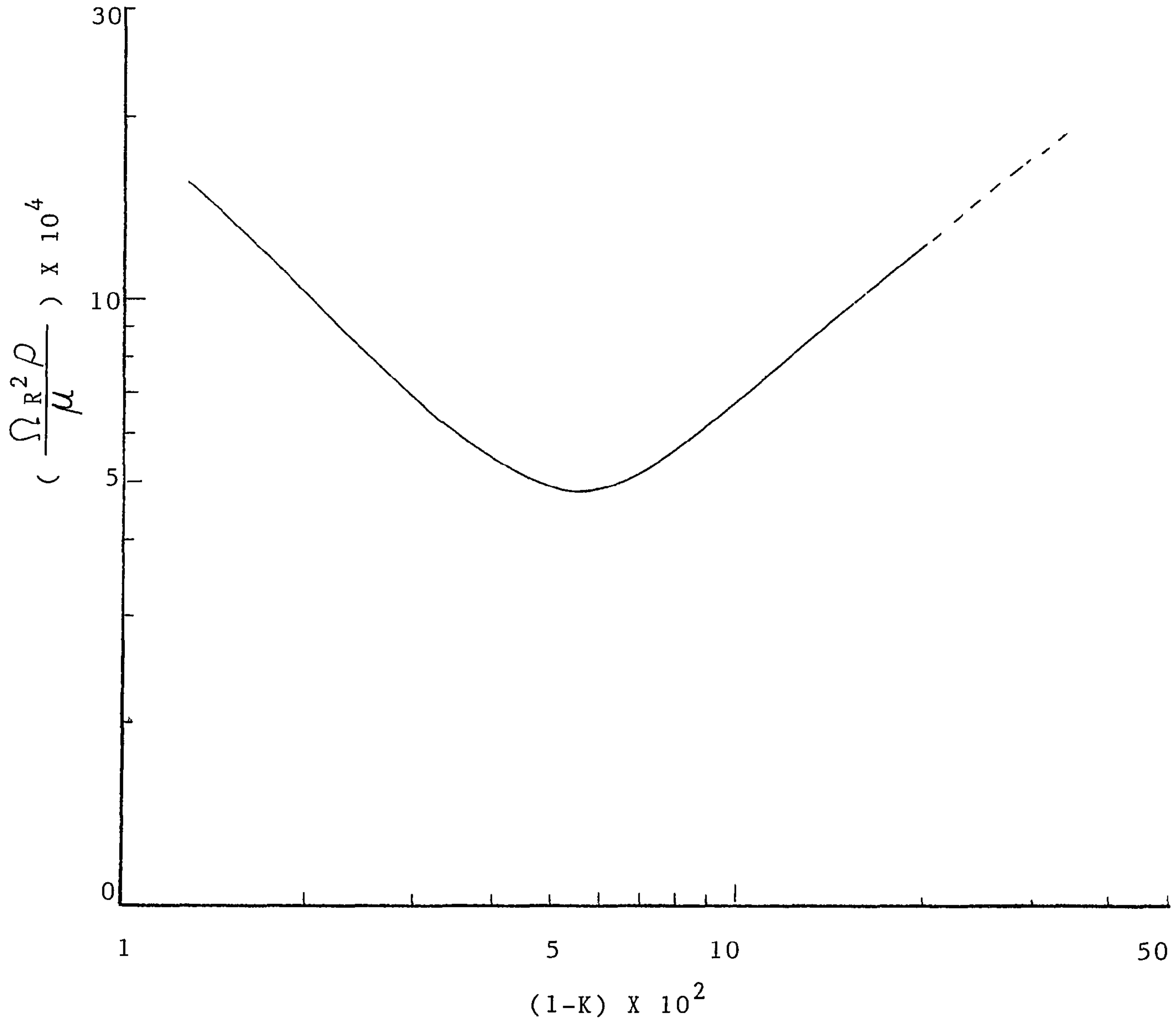

Figure 6. Critical Reynolds Number for Tangential Flow in Annulus

$$\frac{\partial Ci}{\partial t} = -(\nabla \cdot C_i \overline{V}) + (\nabla \cdot D_i DC_i) \qquad (3\text{-}11)$$

If D_i is assumed to be constant, Equation 3-11 becomes

$$\frac{\partial Ci}{\partial t} = - C_i (\nabla \cdot \overline{V}) - (\overline{V}\nabla \cdot C_i) + D_i \nabla^2 C_i \qquad (3\text{-}12)$$

For a constant density ρ, equation of continuity is

$$\nabla \cdot \overline{V} = 0 \qquad (3\text{-}13)$$

Applying Equation 3-13 into equation 3-12, then the Equation 3-12 becomes

$$\frac{\partial Ci}{\partial t} + (\overline{V} \cdot \nabla C_i) = D_i \nabla^2 C_i \qquad (3\text{-}14)$$

In Equation 3-14 the second term of the left hand side equation is due to the power of the stirrer and type of the impeller. This term in called mass transfer caused by convection flow. Different velocity profiles are caused by different types of impellers in the tank. Therefore, to choose a right impeller is a very important factor in designing a mixing tank. The right hand side term of Equation 3-14 is the mass transfer caused by molecular diffusion. Molecular diffusion is caused by the concentration gradient in the system.

Considering a binary liquid solution in an annular region between a pair of infinitey long co-axial cylinders with radii KR and R is shown in Figure 5. The component B is within the annulus at time $t<0$. At $t<0$, the inner cylinder is rotated with constant angular velocity Ω_i, and the outer cylinder is stationary. When the steady state velocity V_θ is reached as shown in Equation 3-8, the component A is injected by impulse into the annulus region at $\theta = 0$.

The steady-state flow, without chemical reaction and density change, of component A through an annulus which contains component B is assumed. In this physical situation, V_r and $V_r = 0$, V_θ is the function of r-direction only, and molecular diffusion in the z-direction is negligible. Therefore, the concentration of component A is a function of r, θ, t. Then the Equation 3-14 is modified to

$$\frac{\partial C_A}{\partial t} + \frac{V_\theta}{r}\frac{\partial C_A}{\partial \theta} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right)\right] \qquad (3\text{-}15)$$

If the v_θ in Equation 3-15 is replaced by Equation 3-8. Equation 3-15 becomes

$$\frac{\partial C_A}{\partial t} + \left[A\left(\frac{1}{r}\right)^2 - B\right]\frac{\partial C_A}{\partial \theta} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right)\right] \qquad (3\text{-}16)$$

where

$$A = \frac{\Omega_i K^2 R^2}{1 - K^2}$$

$$B = \frac{\Omega_i K^2}{1 - K^2}$$

In this case, K is always less than 1, and Ω_i and R are always greater then zero. Therefore, A and B are always positive and real number.

Equation 3-16 shall be solved with the following boundary conditions and initial conditions:

$$\begin{aligned}
&\text{I.C.} && \text{at } t = 0,\ C_A = 0,\ KR \leq r \leq R,\ 0 \leq \theta \leq 2\pi \\
&\text{B.C.1} && \text{at } r = KR,\ \frac{\partial CA}{\partial r} = 0,\ \text{all } t,\ 0 \leq \theta \leq 2\pi \\
&\text{B.C.2} && \text{at } r=R \quad \frac{\partial CA}{\partial r} = 0,\ \text{all } t,\ 0 \leq \theta \leq 2\pi \qquad (3\text{-}17) \\
&\text{B.C.3} && \text{at } \theta=0 \quad C_A = N\delta(t),\ KR< r< R
\end{aligned}$$

$\delta(t)$ is a unit impulse function, and N is in units of mole• seconds/ cm^3 .

D. Computer Simulation

The partial differential equation, Equation 3-16, with boundary conditions and initial conditions of Equation 3-17 has not been solved either analytically or numerically. The analytic method is too complex to apply in this case. Therefore, the numerical approach is applied to solve the partial differential equation. But this equation is still not so easy to solve even with special boundary conditions and three coordinates r, θ, t. The implicit alternating direction method (IAD),(16) discussed by Peaceman and Rachford, will be used to solve the partial differential equation with particular boundary conditions.

The IAD method avoids the disadvantages of a considerable amount of computation by other computer methods, and still manages to use a system of equations with a tridiagonal coefficent matrix for which the algorithm of Equation 3-20 affords a straightforward solution. This method will be discussed in the following section.

The solution of a system of equation resulting from the IAD method is discussed first. If the system of equation is

$$\begin{aligned}
b_1v_1 + c_1v_2 &= d_1\\
a_2v_1 + b_2v_2 + c_2v_3 &= d_2\\
a_3v_2 + b_3 + c_3\ v_4 &= d_3\\
a_iv_{i-1} + b_iv_i + c_iv_{i+1} &= d_i \qquad (3\text{-}18)\\
a_{n-1}v_{n-2} + b_{n-1}v_{n-1} + c_{n-1}\ v_n &= d_{N-1}\\
a_nv_{n-1} + b_nv_n &= d_N
\end{aligned}$$

where a_i, b_i, c_i are coefficients of the equations, and v_i are the unknown of the equations. The matrix of coefficients a, b, c alone is called a tridiagonal matrix.

The solution of Equation 3-18 can be solved by a Gaussian elimination method(17) by Carnahan et al.; with a maximum of three variables per equation. The complete algorithm for the solution of the Equation 3-18 is

$$V_n = V_N$$

$$V_i = V_i - \frac{C_i \; V_i}{i} \qquad i = N\text{-}1,\ N\text{-}2,\ \ldots.,\ 1 \tag{3-19}$$

where the 's and 's are determined from the following recursion formulas

$$\begin{aligned} \beta_{i1} &= b_1, & V_1 &= d_1/\beta_1 \\ \beta_1 &= b_i - \frac{a_i \; C_{i-1}}{\beta_{i-1}} & i &= 2,3,\ldots,N \\ V_i &= \frac{d_i - a_i \; V_i}{\beta_i} \end{aligned} \tag{3-20}$$

The principle of the IAD method essentially is to employ two different equations which are used in turn over successive time-steps each of duration $\Delta t/2$. The first equation is implicit only in the r-direction (i) and the second equation is implicit in the θ-direction (j). Thus, if $C^*_{i,j}$ is an intermediate value at the end of the first time-step, the partial differential equation, Equation 3-16, is transformed to

$$\begin{aligned} \frac{C^*_{i,j} - C_{i,j,n}}{\Delta t/2} + \left[A\left(\frac{1}{(\Delta r)i}\right)^2 + B\right] \delta_\theta C_{i,j} &= D\delta^2_r \, C^*_{i,j} \\ &+ \frac{D}{(\Delta r)i} \; \delta_r \, C^*_{i,j} \end{aligned} \tag{3-21}$$

and

$$\begin{aligned} \frac{C_{i,j,n+1} - C^*_{i,j}}{\Delta t/2} + \left[A\left(\frac{1}{(\Delta r)i}\right)^2 + B\right] \delta_\theta C^*_{i,j,n+1} &= \\ D \, \delta^2_r \; C^*_{i,j} + \frac{D}{(\Delta r)i} \; \delta_r \, C^*_{i,j} \end{aligned} \tag{3-22}$$

Written out in full and rearranged, Equations 3-21 and 3-22 become

$$\left(\frac{\lambda_1}{2} - \frac{\lambda_1}{4i}\right) C^*_{i-1,j} - (\lambda_1+1)\, C^*_{i,j} + \left(\frac{\lambda_1}{2} + \frac{\lambda_1}{4i}\right) C^*_{i+1,j} \qquad (3\text{-}23)$$

$$= -\,(X-Y)\, C_{i,j-1,n} + C_{i,j,n+1} + (X-Y)\, C_{i,j+1,n}$$

and

$$-(X-Y)\, C_{i,j-1,n} + C_{i,j,n+1} + (X-Y)\, C_{i,j+1,n} \qquad (3\text{-}24)$$

$$= \left(\frac{\lambda_1}{2} - \frac{\lambda_1}{4i}\right) C^*_{i-1,j} + (1-\lambda_1)\, C^*_{i,j} + \left(\frac{\lambda_1}{2} + \frac{\lambda_1}{4i}\right) C^*_{i+1,j}$$

where

$$X = \frac{A}{4} \left(\frac{1}{i\Delta r}\right)^2 \frac{\Delta t}{\Delta\theta}$$

$$Y = \frac{B}{4} \frac{\Delta t}{\Delta\theta}$$

$$\lambda_1 = \frac{\Delta t}{(\Delta r)^2} D$$

$$\lambda_2 = \frac{\Delta t}{\Delta\theta}$$

The first equation is solved for the intermediate values C^*, which are then used in the second equation, thus leading to the solution $C_{i,j,n+1}$ at the end of the whole time interval Δt.

Equations 3-23 and 3-24 can apply only to the inside points of the system. Other equations are needed to solve the boundary points of the system. The system of equations is divided into six different subsystems of equations due to the particular boundary and initial conditions.

The translation of boundary and initial conditions into finite difference equations depends on the particular boundary points which are applied. As an example, we deal with a typical boundary point such as (0,j), and the boundary condition is

$$\frac{dC}{dx} = 0$$

and partial differential equation is

$$\frac{d^2C}{dX^2} + \frac{d^2C}{dy^2} = \frac{dC}{dt} \tag{3-25}$$

$\frac{dc}{dt}$ and $\frac{d^2c}{dy^2}$ present no difficulty; $\frac{d^2c}{dX^2}$ is obtained from Taylor's expression:

$$C_{1,j} = C_{o,j} + \frac{dc}{dX}\Delta x + \frac{d^2C}{dX^2}\frac{(\Delta x)^2}{2!} + 0\ [(\Delta x)^3]$$

that is

$$\frac{d^2C}{d^2X} = \frac{2}{(\Delta X)^2}(C_{1,j} - C_{o,j} - \frac{dc}{dX}\Delta x) + 0\ [(\Delta x)^3].$$

When the boundary condition is applied into the above equations, it yields

$$\frac{d^2C}{dX^2} = \frac{2}{(\Delta X)^2}(C_{1,j} - C_{o,j}) + O[(\Delta x)] \tag{3-26}$$

When the above principle is applied to these boundary and initial conditions, then the system of finite difference equation is summarized into two time intervals. The first interval which calculated the intermediate value C^* at the end of the half time step is divided into three zones. These three zones are divided according to the boundary conditions. The second interval is to calculate the final value C at the end of the whole time step. This interval also consists of three zones.

Let C and C^* refer to concentration at the beginning and end of a half time-step $\Delta t/2$. The solution on transformation on Equation 3-16 with Equation 3-17 into finite difference equations is summarized as follows:

(1) At half time intervals

(1.a) General Zone (j = 2, ..., N-1)

$$-(1+\lambda_1)\,C^*_{1,j} + \lambda_1\,C^*_{2,j} = d_1$$

$$\left(\frac{\lambda_1}{2} - \frac{\lambda_1}{4i}\right) C^*_{1,j} - (1+\lambda_1)\,C^*_{2,j} + \left(\frac{\lambda_1}{2} + \frac{\lambda_1}{4i}\right) C^*_{3,j} = d_2$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\left(\frac{\lambda_1}{2} - \frac{\lambda_1}{4i}\right) C_{i-1,j} - (1+\lambda_1)\,C^*_{i,j} + \left(\frac{\lambda_1}{2} - \frac{\lambda_1}{4i}\right) C^*_{i+1,j} = d_i \qquad (3\text{-}27)$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\left(\frac{\lambda_1}{2} - \frac{\lambda_1}{4i}\right) C^*_{M-2,j} - (1+\lambda_1)\,C^*_{M-1,j} + \left(\frac{\lambda_1}{2} + \frac{\lambda_1}{4i}\right) C^*_{M,j} = d_{M-1}$$

$$\lambda_1\,C^*_{M-1,j} + (1-\lambda_1)\,C^*_{M,j} = d_M$$

with

$$d_i = -(X-Y)\,C_{i,j-1,n} - C_{i,j,n} + (X-Y)\,C_{i,j+1,n}$$

for i = 1,2, ..., M-1

$$d_M = -C_{M,j,n} \qquad (3.27a)$$

where

$$X = \frac{A}{B} \left(\frac{1}{i\Delta r}\right)^2 \frac{\Delta t}{\Delta\theta}$$

$$Y = \frac{B}{4} \frac{\Delta t}{\Delta\theta}$$

$$1 = \frac{\Delta t}{(\Delta r)^2} D$$

$$2 = \frac{\Delta t}{\Delta\theta}$$

$$A = \frac{\Omega_i K^2}{1-K^2} R^2$$

$$B = \frac{\Omega_i K^2}{1-K^2}$$

(1.b) Boundary zone (at j=1)

This case is discussed at $\theta=0$. The finite difference equation is the same as Equation 3-27 except Equation 3-27a. Therefore Equation 3-27a is changed to

$$d_i = - C_{i,j,n} + (X-Y)\, C_{i,j+1,n} \text{ for } i = 1,2,\ldots, M-1 \qquad (3\text{-}28)$$

$$d_M = - C_{M,j,n}$$

(1.c)Boundary Zone (at j=N)

This case is discussed at $\theta=2\pi$. The finite difference equation is the same as Equation 3-27, and the Equation 3-27a becomes

$$di = (X-Y)\, C_{i,j-1,n}\, C_{i,j,n} \text{ for } i=1, 2, \ldots, M-1 \qquad (3\text{-}29)$$

$$d_M = - C_{M,j,N}$$

Applying these Equations 3-27 to 3-29, $C^*_{i,j}$ can be calculated at every point of the annulus.

(2) At whole time intervals

(2.a) General Zone (i=2, ..., M-1)

$$
\begin{array}{lr}
C_{i,1,n+1} + (X-Y)\, C_{i,2,n+1} & = d_1 \\
-(X-Y)\, C_{i,1,n+1} + C_{i,2,n=1} + (X-Y)\, C_{i,3,n+1} & = d_2 \\
\hdashline
-(X-Y)\, C_{i,j-1,\ n+1} + C_{i,j,n+1} + (X-Y)\, C_{i,j,n+1} & = d \\
\hdashline
-(X-Y)\, C_{i,N-2,n+1} + C_{i,N-1,n+1} + (X-Y)\, C_{i,N,n+1} & = d_{N-1} \\
-(X-Y)\, C_{i,N-1,n+1} + C_{i,N,n+1} & = d_N
\end{array}
\qquad (3\text{-}30)
$$

with

$$d_j = \left(\frac{\lambda_1}{2} - \frac{\lambda_1}{4i}\right) C^*_{i-1,j} + (1-\lambda_1)\, C^*_{i,j} + \left(\frac{\lambda_1}{2} + \frac{\lambda_1}{4i}\right) C^*_{i+1,j} \qquad (3\text{-}30a)$$

for $j = 1,2, \ldots, N$

(2.b) Boundary Zone (at i=1)

This case is discussed at r=kR. The finite difference equations is the same as Equations 3-30 except Equation 3-30a. Therefore Equation 3-30a

is changed to

$$d_j = (1-\lambda_1)\, C_{i,j} + \lambda_1\, C_{i+1,j} \text{ for } j=1,2,\ldots,N \qquad (3\text{-}31)$$

(2.c) Boundary Zone (at i=M)

This case is discussed at r=R. The finite difference equations are

$$
\begin{array}{lr}
C_{i,1,n+1} & = d_1 \\
C_{i,2,n+1} & = d_2 \\
\hdashline
C_{i,j,n+1} & = d_j \\
\hdashline
C_{i,N-1,n+1} & = d_{N-1} \\
C_{i,N,n+1} & = d_N
\end{array}
\qquad (3\text{-}32)
$$

with

$$d_j = \lambda_1 C^*_{i-1,j} + (1-\lambda_1) C^*_{i,j} \text{ for } j = 1,2,\ldots, N$$

The $C_{i,j,n+1}$ can be calculated by making use of the above equations at whole time step. If the concentration of the next time step is to be calculated, the values of $C_{i,j,n+1}$ substitute into the original $C_{i,j,n}$. Then the same procedure is repeated after the time limitation is reached.

After the concentration distribution is calculated, the degree of mixing can be calculated by Equations 2-26 and 2-27. The program of computer simulation for Newtonian fluid to evaluate the degree of mixing versus time is listed in Appendix B.

E. Stability of the IAD Method

The stability of this procedures is investigated by the von Neuman method.(17) Substitution of the term $\Psi(t)e^{j\alpha x} e^{j\alpha y}$ (j here denote- $\sqrt{-1}$) into the difference equations which derive from equation (3-25), and elimination of the intermediate function $\Psi(t+\Delta t/2)$, yields the following expresisons for the amplification factor across a whole time-step.:

$$\xi = \frac{\psi\ (t + \Delta t)}{\psi\ (t)} \qquad (3\text{-}33)$$

Clearly, $|\xi| \leq |$ for any value of Δt, and the procedure is unconditionally stable.

CHAPTER IV

THE MIXING PHENOMENON FOR NON-NEWTONIAN FLUID

In Chapter III, the mixing phenomenon of Newtonian fluids has been discussed. But many fluids used in the industry are non-Newtonian fluids. This chapter is devoted to the generalized Newtonian model, which can describe the shear rate dependence of the viscosity. There are several empirical models for non-Newtonian fluids(18). The use of this model is illustrated by going through the example in detail; an example deals with problems which are so complex that an analytical solution cannot be obtained. For solving these somewhat more complicated problems, a numerical approach is available, and it is described and illustrated in Chapter III. To avoid more complication we assume that the flow is isothermal.

In almost all industrial problems, the non-Newtonian fluid can be presented as a power-law model. The model has been widely accepted both by industry and by research. In the present study, the power law model is applied and the velocity profile is more complicated. The power law model for a rectangular coordinate expressed mathematically is

$$\tau_{yx} = - m \left| \frac{dVx}{dy} \right|^{n-1} \frac{dVx}{dy} \qquad (4\text{-}1)$$

For n=1, it reduces to Newton's law of viscosity with m=u; thus the deviation of n from unity indicates the degree of deviation from Newtonian behavior. For values of n less than unity, the behavior is pseudoplastic, whereas for n greater than unity the behavior is dilatant. Approximate values of m and n for various fluids are given in Tablel 1. Most macromolecular fluids are pseudoplastic and the value of n in the range of 0.15 to 0.6 are common.

A. Velocity Profile

The Newtonian law of viscosity has been discussed in somewhat more general form(9); the expressions in the Cartesian coordinate is also an analogous expression for cylindrical and spherical coordinates. In this study the similar generalization of non-Newtonian models will be discussed. We restrict this discussion, however, to incompressible flow.

First the Newton's law of viscosity for an incompressible fluid is

$$\tau = - \mu \Delta \tag{4-2}$$

in which Δ is the symmetrical rate of deformation tensor with cartesian components

$$\Delta_{ij} = \frac{\partial V_i}{\partial X_j} + \frac{\partial V_j}{\partial X_i} \tag{4-3}$$

The coefficient of viscosity depends on the local pressure and temperature.

For non-Newtonian materials, the relation between τ and Δ is not the simple proportional given in Equation 4-2. We can, however, write an equation for certain simple types of non-Newtonian fluids

$$\tau = - \eta \Delta \qquad (4\text{-}4)$$

in which the non-Newtonian viscosity η, a scaler, is a function of (or a function of τ) as well as of temperature and pressure. The assumption of various empirical functions to describe the dependence of η on Δ (or on τ) corresponds to the assumption of various models in Bird el at.(9).

The power-law model for non-Newtonian fluild is described in the following:

$$\tau = - \left\{ m \left| \sqrt{\frac{1}{2} (\Delta : \Delta)} \right|^{n-1} \right\} \Delta \qquad (4\text{-}5)$$

in which

$$\Delta : \Delta = \Sigma_i \Sigma_j \Delta_{ij} \Delta_{ji} \qquad (4\text{-}6)$$

Δ is the rate of deformation tensor, and m and n are parameters of a power-law model (See Table 1). The Equation 4-5 is readily available in rectangular, cylindrical, and spherical coordinates. Equation 4-5 is an empirical expression designed to approximate the actual behavior of various materials; the only thing we have done here is to write the expression in such a way that they transform properly in going from one coordinate system to another. Otherwise we could not be assured that parameter - m and n, for example - would be the same when determined in various geometrical arrangements.

TABLE 1

POWER MODEL PARAMETERS FOR VARIOUS FLUIDS

Fluid Composition (weight %)	m (lb_f sec^n ft^{-2})	n (dimensionless)
1.5 % CMC[a] in water	0.0653	0.554
3.0 % CMC in water	0.194	0.566
33 % lime in water	0.150	0.171
10 % napalm in kerosene	0.0893	0.520
4 % paper pulp in water	0.418	0.575

[a] Carboxymethylcellulose

A polymeric liquid is being sheared in the annular region between two cylindrical surface of length L of radu KR and R (with $K < 1$). The inner cylinder is rotating with an angular velocity Ω_i, and the outer cylinder is fixed (Figure 5).

In steady-state laminar flow the non-Newtonian fluids move in a circular pattern, and the velocity components V_r and V_z are zero. There is no pressure gradient in the θ-direction. In cylindrical coordinates, then, the only non-zero component of velocity will be V_θ. We further postualate the V_θ as well as the components Δ_{ij} of the defomation tensor will depend only on the radial position r. Therefore all except $\Delta_{r\theta}$ are zero. With these assumptions, the equation of continuity(9) as written in cylindrical coordinates is zero, and the equation of motion(9) reduces to

$$\frac{1}{r^2}\frac{d}{dr}(r^2\,\tau_{r\theta}) = 0 \qquad (4\text{-}7)$$

The Equation 4-5 is rewritten for the system at $\tau_{r\theta}$;

$$\tau_{r\theta} = -\;\left\{M\left|\sqrt{\tfrac{1}{2}(\Delta:\Delta)}\right|^{n-1}\right\}\Delta_{r\theta} \qquad (4\text{-}8)$$

For the power-law model, the analytical expression of Equation 4-8 to be used depends on the value of

$$\frac{1}{2}(\Delta:\Delta) = \Sigma_i\Sigma_j\,\Delta_{ij}\Delta_{ji} = (\Delta_{r\theta})^2 \qquad (4\text{-}9)$$

From Table 2 and the velocity V_r is zero at θ-direction, we know

$$\Delta_{r\theta} = r\frac{d}{dr}\left(\frac{V_\theta}{r}\right) \qquad (4\text{-}10)$$

TABLE 2

COMPONENTS OF THE STRESS TENSOR FOR NEWTONIAN FLUIDS IN CYLINDRICAL COORDINATES

(A) $$\tau_{rr} = - \mu[2 \frac{\partial Vr}{\partial r} - \frac{2}{3} (\nabla \cdot V)]$$

(B) $$\tau_{\theta\theta} = - \mu[2 (\frac{1}{r} \frac{\partial V}{\partial\theta} + \frac{Vr}{r}) - \frac{2}{3} (\nabla \cdot V)]$$

(C) $$\tau_{zz} = - \mu[2 \frac{\partial Vz}{\partial z} - \frac{2}{3} (\nabla \cdot V)]$$

(D) $$\tau_{r\theta} = \tau_{\theta r} = - \mu[r \frac{\partial}{\partial r} (\frac{V\theta}{r}) + \frac{1}{r} \frac{\partial Vr}{\partial\theta}]$$

(E) $$\tau_{\theta z} = \tau_{z\theta} = - \mu[\frac{\partial V}{\partial z} + \frac{1}{r} \frac{\partial Vz}{\partial\theta}]$$

(F) $$\tau_{zr} = \tau_{rz} = - \mu[\frac{\partial Vz}{\partial r} + \frac{\partial Vr}{\partial z}]$$

The Equations 4-8, 4-9 and 4-10 were substituted into Equation 4-7, and the equation was integrated with the boundary condition as follows:

$$\begin{aligned} &\text{B.C.1} \qquad V_\theta = o \text{ at } r=R \\ &\text{B.C.2} \qquad V_\theta = \Omega_i KR \text{ at } r=KR \end{aligned} \qquad (4\text{-}11)$$

Then the result of velocity profile is

$$V_\theta = \Omega_i\, r\, \frac{\left(\frac{R}{r}\right)^{2/n} - 1}{\left(\frac{1}{K}\right)^{2/n} - 1} \qquad (4\text{-}12)$$

After the velocity profile is found, the concentration distribution can be derived by equation of continuity and Ficks law of diffusion.

B. Mathematical Modeling

The basic geometrical system used in this study is shown in Figure 5. The component A is injected by an impluse into the annulus at $\theta = 0$, and the annulus filled with non-Newtonian fluid, component B. The flow is set at a steady state condition. The concentration of A, C_A, is function of r-direction, θ-direction, and time. Though these assumptions the equation of continuity is reduced to

$$\frac{\partial C_A}{\partial t} + \frac{V_\theta}{r}\frac{\partial C_A}{\partial \theta} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right)\right] \qquad (4\text{-}13)$$

The velocity profile Equation 4-12 is substitued into Equation 4-13, and modifying the Equation 4-13 to

$$\frac{\partial C_A}{\partial t} + \left[A^* \left(\frac{1}{r}\right)^n - B^* \right] \frac{\partial C_A}{\partial \theta} = D\left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_A}{\partial r}\right)\right] \tag{4-14}$$

where

$$A^* = \frac{\Omega_i \; K^{2/n}}{1-K^{2/n}} R^{2/n}$$

$$B^* = \frac{\Omega_i \; K^{2/n}}{1-K^{2/n}} \tag{4-14a}$$

n is parameter of the power-law model, shown on Table 1. When n=1, the liquid is Newtonian fluid, and the Equation 4-14 is similar to Equation 3-16. Most of the polymeric liquids are $n < 1$ and values of n are in the range of 0.15 to 0.6.

The Equation 4-14 is solved with the following boundary and initial conditions:

I.C. at $t = 0$, $C_A = 0$, $KR \leq r \leq R$, $0 \leq \theta \leq \pi$

B.C.1 at $r=KR$, $\frac{\partial C_A}{\partial r} = 0$, all t, $0 \leq \theta \leq \pi$

B.C.2 at $r=R$, $\frac{\partial C_A}{\partial r} = 0$, all t, $0 \leq \theta \leq \pi$

B.C.3 at $=0$, $C_A = N\delta(t)$, $KR < r < R$

$\delta(t)$ is the unit impulse function, and this function is

$$\delta(t) = \begin{cases} \infty & \text{, at } t = 0 \\ o & \text{, at } t < 0 \text{ or } t > 0 \end{cases} \tag{4-16}$$

The numerical solution of the Equation 4-15 with the Equation 4-16 will be discussed in the next section.

C. Computer Simulation

The velocity profile of non-Newtonian fluid is more complicated than that of Newtonian fluid. But the transformation of the partial differential equation to the finite difference equations is similar to that described in Chapter III. The system of equations is divided to two time intervals according to the IAD method$^{(16)}$.

Let C and C^* refer to concentration at the beginning and end of a half time step $\Delta t/2$. And n, parameter of the power-law model, is assumed to be equal to 0.5. To summarize, the complete algorithm for the solution of the Equation 4-14 with Equation 4-15 is as follows:

(1) At half time intervals

The system of difference equations is divided into three zones as follows:

(1.a) General Zone ($j = 2, \ldots N-1$)

$$\begin{array}{ll}
-(1+\lambda)\, C_{1,J} + \lambda_1\, C_{2,J} & = d_1 \\
\left(\frac{\lambda_1}{2} - \frac{\lambda_1}{4i}\right) C_{1,J} - (1+\lambda_1)\, C_{2,J} + \left(\frac{\lambda_1}{2} + \frac{\lambda_1}{4i}\right) C_{3,j} & = d_2 \\
\hdashline
\left(\frac{\lambda_1}{2} - \frac{\lambda_1}{4i}\right) C_{M-1,J} - (1+\lambda_1)\, C_{M-1,J} + \left(\frac{\lambda_1}{2} + \frac{\lambda_1}{4i}\right) C_{M,J} & = d_i \\
\hdashline
\left(\frac{\lambda_1}{2} - \frac{\lambda_1}{4i}\right) C_{M-1,j} - (1+\lambda_1)\, C_{M-1,j} + \left(\frac{\lambda_1}{2} + \frac{\lambda_1}{4i}\right) C_{M,j} & = d_{M-1} \\
\lambda_1\, C_{M-1,j} - (1+\lambda_1)\, C_{M,j} & = d_M
\end{array} \qquad (4\text{-}17)$$

with

$$d_i = -(X-Y)\, C_{i,J-1,} - C_{i,j,n} + (X-Y)\, C_{i,j+1,n} \qquad (4\text{-}17a)$$

for $i = 1,2,\ldots, n-1$

$d_M = C_{M,j,n}$

where

$$\lambda_1 = \frac{\Delta t}{(\Delta r)^2} D$$

$$\lambda_2 = \frac{\Delta t}{\Delta \theta}$$

$$A' = \frac{\Omega_i K^4}{1-K^4} R^4$$

$$B' = \frac{\Omega_i K^4}{1-K^4}$$

$$X' = \frac{A'}{4} \left(\frac{1}{i\Delta r}\right)^4 \frac{\Delta t}{\Delta \theta}$$

$$Y' = \frac{B'}{4} \quad \frac{\Delta t}{\Delta \theta}$$

(1.b) Boundary Zone (at $j = 1$)

Equation 4-17

with

$$d_i = - C_{i,j,n} + (X'-Y')\, C_{i,j+1,n} \text{ for } i = 1,2, \ldots M-1$$

$$d_M = - C_{M,j,n} \tag{4-18}$$

(1.c) Boundary zone (at $j=N$)

Equation 4-17 with

with

$$d_i = (X'-Y')\, C_{i,j,1,n} - C_{i,j,n} \text{ for } i = 1,2, \ldots, M-1 \tag{4-19}$$

$$d_M = - C_{M,j,n}$$

(2) At whole time intervals

Three zones are divided as follows:

(2.a) General zone (i = 2,3,..., M-1)

$$
\begin{array}{rl}
C_{i,1,n+1} + (X'-Y')\,C_{i,2,n+1} & = d_1 \\
-(X-Y)\,C_{i,1,n+1} + C_{i,2,n+1} + (X-Y)\,C_{i,3,n+1} & = d_2 \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots & \\
-(X-Y)\,C_{i,n-1,n+1} + C_{i,j,n+1} + (X-Y)\,C_{i,j+1,n+1} & = d_j \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots & \\
-(X-Y)\,C_{i,j-1,n+1} + C_{i,N-1,n+1} + (X-Y)\,C_{i,N,n+1} & \\
-(X-Y)\,C_{i,N-1,n+1} + C_{i,N,n+1} & = d_N
\end{array}
\qquad (4\text{-}20)
$$

with

$$d_j = \left(\frac{\lambda_1}{2}-\frac{\lambda_1}{4i}\right) C^*_{i-1,j} + (1-\lambda_1)\ C^*_{i,j} + \left(\frac{\lambda_1}{2}+\frac{\lambda_1}{4i}\right) C^*_{i+1,j}$$

for j = 1,2,-..., N

(2.b) Boundary Zone (at I = 1)

Equation 4-20

with

$$d_j = (1-\lambda_1)\ \overset{*}{C}_{i,j} + \lambda_1\ \overset{*}{C}_{i+1,j} \qquad (4\text{-}21)$$

for j = 1,2, ..., N

(2.c) Boundary Zone (at =M)

$$
\begin{array}{rl}
C_{i,1,n+1} & = d_1 \\
C_{i,2,n+1} & = d_2 \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots & \\
C_{i,j,n+1} & = d_j \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots & \\
C_{i,n-1,n+1} & = d_{N-1} \\
C_{i,N,\ n+1} & = d_N
\end{array}
\qquad (4\text{-}22)
$$

with

$$d_j = \lambda_1\ C^*_{i-1,j} + (1-\lambda_1)\ C^*_{i.j}$$

The concentration distribution can be determined by Equations 4-17 to 4-22. Then the degree of mixing can be calculated by substituting the concentration into Equations 2-26 and 2-27. The computer program of this calculation is listed in Appendix C.

CHAPTER V

FLUID MOTION AND CHEMICAL REACTION

It is useful at the outset to indicate why mixing is important in chemical reactions. In general two or more substances need to be mixed to make products, and this mixing must be sufficiently fine-grained that molecular transport becomes effective. Mixing is used also to provides uniformity of temperature and concentration in the chemical reactor; this uniformity is particularly important when selecting of the reaction is to be maximized. It is therefore important to know the positive or negative contributions which the mixing may contribute to reaction performance.

The general requirements for calculatinig the conversion in a chemical reactor are knowledge of the temperature and concentration fields in the reactor and kinetics and transport parameters of the reaction. A new fractional conversion is defined to study the reaction performance with mixing. Also in this study, the batch mixing process accompanied by a first-order reaction is investigated through solving a mathematical model relating to fractional conversion versus time by numerical method.

A. Fractional Conversion

A second-order reaction of two components is assumed and it is of the type:

$$A + B \quad \text{products.} \tag{5-1}$$

and the chemical reaction rate is

$$R_A = K\, C_A\, C_B. \tag{5-2}$$

When a large excess of reactant B is used, then its concentration does not change appreciably ($C_B = C_{Bo}$) and the reaction approaches first-order behavior with respect to the limiting component A, or

$$- R_A = K\, C_A\, C_B = (K\, C_{Bo})\, C_A = K'\, C_A \tag{5-3}$$

Considering the tangential laminar fluid flow in a co-axial cylinders with radii KR and R (Figure 5). The component A is injected into the annulus by the following function:

$$C_A = N\ \delta(t) \tag{5-4}$$

where $\delta(t)$ is an unit impulse function.

The fractional conversion X_A of a given reactant A is defined as the fraction of reactant converted into product,

$$\text{or} \qquad X_A = \frac{N\Delta t\ \Delta V - \int CA\ dV}{N\ \Delta\ t\ \ \Delta V} \tag{5-5}$$

$$= \frac{\text{moles of A reacted at any time t}}{\text{total moles of A at t = 0}}$$

Fractional conversion is a convenient variable to represent the percentage of reactant which was consumed in the chemical reactor at a specific time.

B. Mathematical Modeling

As shown in Figure 5, the fluid B is in the annulus. When the inner rotating cylinder reaches the steady state velocity, the component A is injected by a function, Equation 5-4, into the annulus.

The simplification we adopt is to treat only simple reactions. The simple reactions means essentially a one-step, first-order, irreversible reactions. These reactions have received most of the research attention in this subject. Also the laminar flow is assumed in this system to simplify the model.

A typical mass balance equation of species A in the reactive system described by Equation 5-1 can be written

$$\frac{\partial C_A}{\partial t} + V \cdot \nabla C_A = D \nabla^2 \, C_A - R_A \qquad (5\text{-}6)$$

where C_A is concentration of species A, V is the velocity field taken as incompressible, D is diffusivity, and R_A is the reaction rate of species A.

The Equation (5-6) applied to this system with those simplifications can be modified to

$$\frac{\partial C_A}{\partial t} + \frac{V_\theta}{r}\frac{\partial C_A}{\partial \theta} = D\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) - K\,C_A \qquad (5\text{-}7)$$

The Equation 5-7 is substituted by Equation 3-8 and is modified to

$$\frac{\partial C_A}{\partial t} + \left[A\left(\frac{1}{r}\right)^2 - B\right]\frac{\partial C_A}{\partial \theta} = D\,\frac{1}{r}\,\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right) - K\,C_A \qquad (5\text{-}8)$$

where

$$A = \frac{\Omega_i\,K^2\,R^2}{1-K^2}$$

$$B = \frac{\Omega_i\,K^2}{1-K^2}$$

The Equation 5-7 is solved with the following initial condition and boundary conditions:

I.C. at $t = 0$, $C_A = 0$, $KR \leq r \leq R$, $0 \leq \theta \leq 2\pi$

B.C.1 at $r = KR$, $\frac{\partial C_A}{\partial r} = 0$, all t, $0 \leq \theta \leq 2\pi$ (5-9)

B.C.2 at $r=R$, $\frac{\partial C_A}{\partial r} = 0$, all t, $0 \leq \theta \leq 2\pi$

B.C.3 at $\theta = 0$, $C_A = N\delta(t)$, $KR < r < R$

C. Computer Simulation

The transformation of the Equation 5-8 with Equation 5-9 to a finite difference equations is by making use of the implicit alternating - direction method described in the Chapter III. Let C and C^* refer to concentration at the beginning and end of a half time-step t/2.

Then an appropriate set of finite-difference equation corresponding to Equations 5-8 and 5-9 can be summarized as follows:

(1) At half time intervals

(1.a)General Zone ($j=2, \ldots, N-1$)

$$\begin{array}{lll}
-(1+\lambda_1)\overset{*}{C}_{i,j}+\lambda_1\overset{*}{C}_{2,j} & & \\
\left(\frac{\lambda_1}{2}-\frac{\lambda_1}{4i}\right)\overset{*}{C}_{i,j}-(1+\lambda_1)\overset{*}{C}_{2,j}+\left(\frac{\lambda_1}{2}+\frac{\lambda_1}{4i}\right)\overset{*}{C}_{3j} & = d_2 & \\
\hdashline
\left(\frac{\lambda_1}{2}-\frac{\lambda_1}{4i}\right)\overset{*}{C}_{i-1j}-(1+\lambda_1)\overset{*}{C}_{1,j}+\left(\frac{\lambda_1}{2}+\frac{\lambda_1}{4i}\right)\overset{*}{C}_{i+1,j} & = d_i & \\
\hdashline
\left(\frac{\lambda_1}{2}-\frac{\lambda_i}{4i}\right)\overset{*}{C}_{M-2,j}-(1+\lambda_1)\overset{*}{C}_{M-1,j}+\left(\frac{\lambda_1}{2}+\frac{\lambda_1}{4i}\right)\overset{*}{C}_{M,j} & = d_{M-i} & (5\text{-}10) \\
\lambda_1\overset{*}{C}_{M-1,\, j}+(1+\lambda_1)\overset{*}{C}_{M,j} & = d_M &
\end{array}$$

with

$$d_i = -(X-Y)\,C_{i,j,n}-(1-K)\,C_{i,j,n}+(X-Y)\,C_{i,j+1,n} \qquad (5\text{-}10a)$$

for $i = 1,2,\ldots, M-1$

$$d_M = -(1-K)\,C_{M,j,n}$$

where

$$\lambda_1 = \frac{\Delta t}{(\Delta r)^2}\,D$$

$$\lambda_2 = \frac{\Delta t}{\Delta\theta}$$

$$A = \frac{\Omega_i\,K^2R^2}{1-K^2}$$

$$B = \frac{\Omega_i\,K^2}{1-K^2}$$

$$X = \frac{A}{B}\left(\frac{1}{i\Delta r}\right)^2\frac{\Delta t}{\Delta\theta}$$

$$Y = \frac{B}{4}\,\frac{\Delta t}{\Delta\theta}$$

(1.b) Boundary Zone (at j = 1)

Equation 5-10

with

$$d_i = (1-K)\ C_{i,j,n} + (X-Y)\ C_{i,j+1,n} \qquad (5\text{-}11)$$

for $i = 1,2,\ldots, M-1$

$$d_M = -\ (1-K)\ C_{M,j,n}$$

(1.c) Boundary Zone (at J=N)

Equation 5-10

with

$$d_i = (X-Y)\ C_{i,j-1,n} - (1-K)\ C_{i,j,n} \qquad (5\text{-}12)$$

for $i = 1,2,\ldots, M-1$

$$d_M = -\ (1-K)\ C_{M,j,n}$$

(2) At whole time intervals

(2.a)General Zone ($i = 2,3, \ldots, M-1$)

$$(1+K)\ C_{i,1,n+1}\ (X-Y)\ C_{i,2,n+1} = d_1$$

$$-(X-Y)\ C_{i,1,n+1} + (1+K)\ C_{i,2,n+1} + (X-Y)\ C_{i,3,n+1} = d_2$$

$$- -$$

$$-(X-Y)\ C_{i,j,n+1} + (1+K)\ C_{i,j,n+1} + (X-Y)\ C_{i,j+1,n+1} = d_j \qquad (5\text{-}13)$$

$$- -$$

$$-(X-Y)\ C_{i,N-2,n+1} + (1+K)\ C_{i,N-1,n+1} + (X-Y)\ C_{i,N,n+1} = d_{N-1}$$

$$-(X-Y)\ C_{i,N-1,n+1},\ (1+K)\ C_{i,N,n+1} = d_N$$

with

$$d_j = \left(\frac{\lambda_1}{2} - \frac{\lambda_1}{4i}\right) C^*_{i-1,j} + (1-\lambda_1)\ C^*_{i,j} + \left(\frac{\lambda_1}{2} + \frac{\lambda_1}{4i}\right) C^*_{i+1,j} \qquad (5\text{-}13a)$$

(2.b) Boundary Zone (at i = 1)

Equation 5-13

with

$$d_j = (1-\lambda_1)\, C^*_{i,j} + {}_1\, C^*_{i+1,j}) \qquad (5\text{-}14)$$

(2.c) Boundary Zone (at i=M)

$$\begin{array}{lr}
(1+K)\, C_{i,1,n+1} & = d_i \\
(1+KL)\, C_{i,2,n+1} & = d_2 \\
\hdashline
(1+K)\, C_{i,j,n+1} & = d_j \\
\hdashline
(1+K)\, C_{i,N-1,n+1} & = d_N \\
(1+K)\, C_{i,N,n+1} & = d_N
\end{array} \qquad (5\text{-}15)$$

with

$$d_j = {}_1\, C^*_{i-1,j} + (1-{}_1)\, C^*_{i,j}$$

The concentration distribution can be determined by Equations 5-10 to 5-15 with substituting into Equation 5-5 to obtain the relations between fractional conversion and time. This computer program is listed in Appendix D.

CHAPTER VI

MODELING ON CHEMICAL REACTION RATE CONSTANT WITHOUT MIXING IN LIQUID PHASE

This chapter studies the chemical reaction rate constant in a liquid phase without mixing. The kinetics of reactions in the liquid phase cannot be interpreted in terms of kinetic theory and statistical mechanism of gases. The interpretation of rates in the liquid phase is necessarily more complicated from a molecular viewpoint because of the much greater interaction between molecules. However, bimolecular reactions in solution cannot occur more rapidly than the reactant molecules can diffuse together, and this rate may be calculated from measured diffusion coefficients. A number of reactions in the liquid phase occur at diffusion-controlled rates, and special methods(19,20,21) have been developed for studying the rates of these reactions.

The chemical reaction rate constant in the liquid phase derived in this study is based on collision theory in term of collision rate, steric factor and energy factor. The collision rate of the molecules which reactants can diffuse together in liquid phase may be calculated using the macroscopic theory of diffusion. This new model can resolve the disadvantage of Smoluchowski's theory(22) which has been widely accepted in chemical reaction engineering.

The basic assumptions of this model will be discussed first. Then the molar flux of molecules in the collision rate is calculated by making use of the diffusion equation(9). The new model of chemical reaction rate constant will be developed by the diffusion equation with specific boundary conditions.

A. Diffusion Equation

If a solution contains a non-uniform distribution of solute molecules, there is a flux from the more concentrated to the less concentrated region. If n is the net excess of molecules passing in the negative direction through a plane surface of area A because of a concentration gradient along coordinate perpendicular to A,

$$\frac{dC}{dt} = D\nabla C \qquad (6\text{-}1)$$

where c is the concentration of solute in mole/cm^3 and c=nA, and D is the dfiffusivity; usually reported in unit of cm^2/sec. The equation 6-1 is known as Fick's first law of diffusion.

Assumed diffusivity, D, is regarded as constant, and Equation 6-1 has been simplified by Bird et al.(9) to

$$\frac{\partial C}{\partial t} = D\nabla^2 C \qquad (6\text{-}2)$$

This equation is generally known as Fick's second law of diffusion or the diffusion equation. This equation is used for diffusion in solids or stationary liquids.

B. Collision Rate

Let us begin by considering that the molecules are rigid and non-attracting spherical particles of the radius of r_A and r_B, and the radius of molecules A is much smaller than the radius of molecules B. Molecules B compared to modecules A are stationary. All molecules A are free to move all directions, and travel at same speed. The arrangement of all molecules is shown in Figure 7.

Assume that velocity $\overline{v}_A$ for molecule A is same at all directions. A molecule A in a direction may collide with a distance of its center, $r_A + r_B$. And in a time interval Δt, a molecule A in a direction sweeps out a volume $\pi(r_A + r_B)^2$ in cross section and u_A Δt long. The volume which a molecule A swept out is

$$V_A = \pi(r_A + r_B)^2 \overline{V}_A \Delta t \tag{6-3}$$

The number of collisions by the molecule A with molecules B is equal to the number of molecules B in the volume which molecule A sweeps out. Therefore the number of collisions of a molecule A and molecules B per molecule A in the time interval Δt is

$$C_{Bo} N_o \pi (r_A + r_B)^2 \overline{V}_A \Delta t \tag{6-4}$$

which N_0 is Avogardo's number, and C_{Bo} is the concentration of molecules B, units is $\mathrm{mole/cm^3}$.

If the molar flux of molecules A, N_A, and the concentration of molecules, C_A are known in liquid phase, the average velocity of molecules A can be presented as the ratio of the molar flux of molecules A to concentration of molecules A, or

$$\overline{v}_A = \frac{N_A}{C_A} \tag{6-5}$$

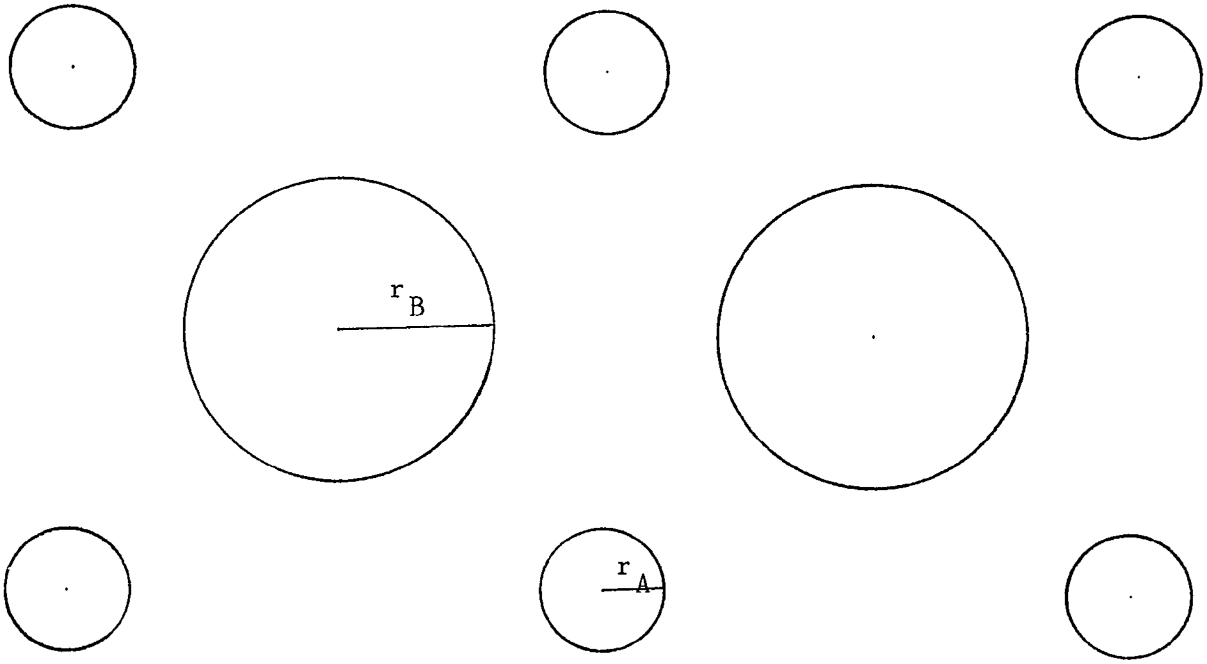

Figure 7. Molecular Structure in Liquid Phase.

Also, if we know the concentration of molecules A in the system, the total number of molecules of A in a volume V is

$$N_A = V\ C_A\ N_0 \qquad (6\text{-}6)$$

The collision rate of molecules A and B in a volume V can be represented by combining the Equations 6-4, 6-5, and 6-6 as follows:

$$C_{B0}N_0{}^2\ \pi(r_A + r_B)^2\ N_AV \qquad (6\text{-}7)$$

Therefore, the collision rate of molecules A and B in a unit volume is

$$Z = C_{B0}N_0{}^2\pi(r_A + r_B)^2\ N_A \qquad (6\text{-}8)$$

Where Z is the collision rate in number of collisions per cm^3 per second.

C. Molar Flux

In order to find the molar flux let us consider the distribution of molecules A diffusing toward molecules B as shown in Figure 7. Asumme diffusivity D is constant. The concentration C_A for molecules A satisfies the diffusion equation, Equation 6-2, in sperical coordinates

$$D\ (\frac{\partial^2 C_A}{\partial^2 r^2} + \frac{2}{r}\ \frac{\partial C_A}{\partial r}) = \frac{\partial C_A}{\partial t} \qquad (6\text{-}9)$$

The Equation 6-9 is solved with the following initial and boundary conditions:

I.C. $C_A = C_{Ao}$, at $t = 0$

B.C.1. $C_A = 0$, at $r=r_A + r_B$ (6-10)

B.C.2 $\frac{\partial C_A}{\partial r} = o$, at $r=d$, $t > o$

To solve the Equation 6-9 with 6-10, a new dimensionless qunatity is introduced as followings:

$$\frac{f}{r} = \frac{C_A}{C_{Ao}} \tag{6-11}$$

The Equation 6-9 and 6-10 become

$$\frac{\partial^2 f}{\partial r^2} = \frac{1}{D} \frac{\partial f}{\partial t} \tag{6-12}$$

I.C. at $t = o$, $f = r$

B.C.1 at $r = r_A + r_B$, $f = o$ (6-13)

B.C.2 at $r=d$

$r\frac{\partial f}{\partial r}\Big|_{r=d} - f\Big|_{r=d} = o$

In addition we introduce a new independent variable,

$$s = r - (r_A + r_B) \tag{6-14}$$

the Equation 6-12 and 6-13 is modified to

$$\frac{\partial^2 f}{\partial s^2} = \frac{1}{D} \frac{\partial f}{\partial t} \tag{6-15}$$

I.C. at $t = o$, $f = s + r_A + r_B$

B.C.1 at $s = o$, $f = o$ (6-16)

B.C.2 at $s = d - (r_A + r_B)$

$$d \frac{\partial f}{\partial s} \Big|_{s=d-(r_A+r_B)} = f \Big|_{s=d-(r_A+r_B)}$$

We present here the classical solution to the partial differential equation, Equation 6-15, for conditions, Equation 6-16, by the method of separation of variables. The solution for Equation 6-15 with 6-16 is

$$r \frac{C_A}{C_{Ao}} = f = \sum_{n=1}^{\infty} C_n e^{-D\beta^2{}_n t} \sin \{\beta_n [\, r-(r_A + r_B)] \} \tag{6-17}$$

where

$$C_n = \frac{4 \sin \theta_n - 4\, d\, \beta_n \cos \theta_n + 4\, \beta_n (r_A + r_B)}{2\, \beta_n^2\, \theta_n - \beta_n \sin (2\, \theta_n)}$$

$$\theta_n = \beta_n [d - (r_A + r_B)\,]$$

There are an infinite number of eigenvalues β_n, and β_n is solved by the following equation:

$$\tan \beta_n [d - (r_A + r_B)\,] = d\, \beta_n \tag{6-18}$$

The molar flux of A can be computed from Equation 6-17:

$$N_A = - D \frac{dC_A}{dr} \tag{6-19}$$

$$= - D\, C_{Ao} \sum_{n=1}^{\infty} C_n \{ \frac{\beta_n}{d} \cos \beta_n [d- (r_A + r_B)] - \frac{1}{d^2} \sin \beta_n [\, d- (r_A + r_B)] \}$$

By introducing a new function,

$$f(d) = \sum_{n=1}^{\infty} C_n \left\{ \frac{\beta_n}{d} \cos \theta_n - \frac{1}{d^2} \sin \theta_n \right\} \qquad (6\text{-}20)$$

the Equation 6-19 can be simplified as follows:

$$N_A = - D\, C_{Ao}\, f(d) \qquad (6\text{-}21)$$

After the equation of molar flux is determined, the collision rate for this system can be computed by combining the Equations 6-8 and 6-21:

$$Z = - N_o\, \pi r^2_{AB}\, D\, f(d)\, C_{Ao}\, C_{Bo} \qquad (6\text{-}22)$$

D. Reaction Rate Constant

If every collision between reactant molecules results in the transformation of reactants into products, then the collision rate gives the rate of bimolecular reaction. The actual rate is usually much lower than predicted, and the indicates that only a small fraction of all collisions result in reaction. This suggests that only the more energetic and violent collisions, or more specially, only those collisions that involve energies in excess of a given minimum energy E and right effective collisions lead to reaction. Therefore, there are three factors affecting the reaction rate, Z collision rate; energy factor, the energy equation is $e^{-E/RT}$; steric factor, p.

The equation of the reaction rate is represented as

$$-R_A = -\frac{1}{V}\frac{dNA}{dt} = K\ C_A\ C_B$$

$$= \left(\frac{\text{collision rate}}{\text{mole/cm}^3\ \text{sec}}\right)(\text{ energy factor})\quad(\text{steric factor}) \qquad (6\text{-}24)$$

$$= Z\ .\ e^{-E/RT}\ .\ p\ \frac{1}{N_o}$$

where p is the steric factor, E is activation energy, and N_O is Avogardo's number.

Equation 6-22 substitutes into Equation 6-24, and modifiying the Equation gives

$$k = -\pi r^2{}_{AB}\ N_O\ D\ \ f(d)\ \exp\ (^{-E/RT}).\ p \qquad (6\text{-}25)$$

where D is diffusivity, $r_{AB} = r_A + r_B$, R is ideal gas law constant,

$$f(d) = \sum_{n=1}^{\infty} C_n\{\frac{\beta_n}{d}\ \cos\ \theta_n - \frac{1}{d^2}\ \sin\theta_n\ \}$$

$$C_n = \frac{4\ \sin\ \theta_n - 4\ d\ \beta_n\ \cos\ \theta_n + 4\ \beta_n\ (r_A + r_B)}{2\ \beta_n^2\ \theta_n - \beta_n\ \ \sin\ 2\ \theta_n}$$

$$\theta_n = \beta_n\ [d - (r_A + r_B)\ ],$$

and β_n is calculated from Equation 6-18.

The chemical reaction rate constant is proporational to the diffusivity from Equation 6-25. f(d) is a negative value because the chemical reaction rate constant is positive.

CHAPTER VII

RESULTS AND DISCUSSIONS

The output data generated by the programs, which are written in Fortran IV, are divided into three computer runs. Both runs were made on the UNIVAC system. A complete list of the programs is presented in the Appendix.

The input data for the computer programs are listed in Table 3. For the mixing phenomenon, the computer runs were made at different angular velocity Ω_i from 5 to 20 radians per second, and the reaction rate constant is zero. The computer runs used to estimate the rate of chemical reaction were made at different angular velocity and different reaction rate constant in the range of 0.1 to 0.4. The chemical reaction is assumed to be first order.

A. Mixing

The numerical results of the mixing phenomenon for Newtonian and non-Newtonian fluids are shown in Figure 8 to 12. Figure 8 shows the most effective rate for the mixing occurs at time zero. After reaching almost perfect mixing, the mixing phenomenon will take approximately ten times to reach the perfect state. This means that the perfect mixing is the ideal state of mixing.

The degree of mixing for Newtonian fluid is influenced by the different rotating speed is shown in Figure 9. The degree of mixing

TABLE 3

INPUT DATA FOR PROGRAMS OF MIXING PHENOMENON

$D = 1.0 \times 10^{-7} - 1.0 \times 10^{-7}\ \mathrm{cm^2/sec}$

$\Omega_i = 5 - 20$ radians/sec

$k = 0.1 - 0.4$ 1/sec

$K = 0.8$

$R = 10$ cm

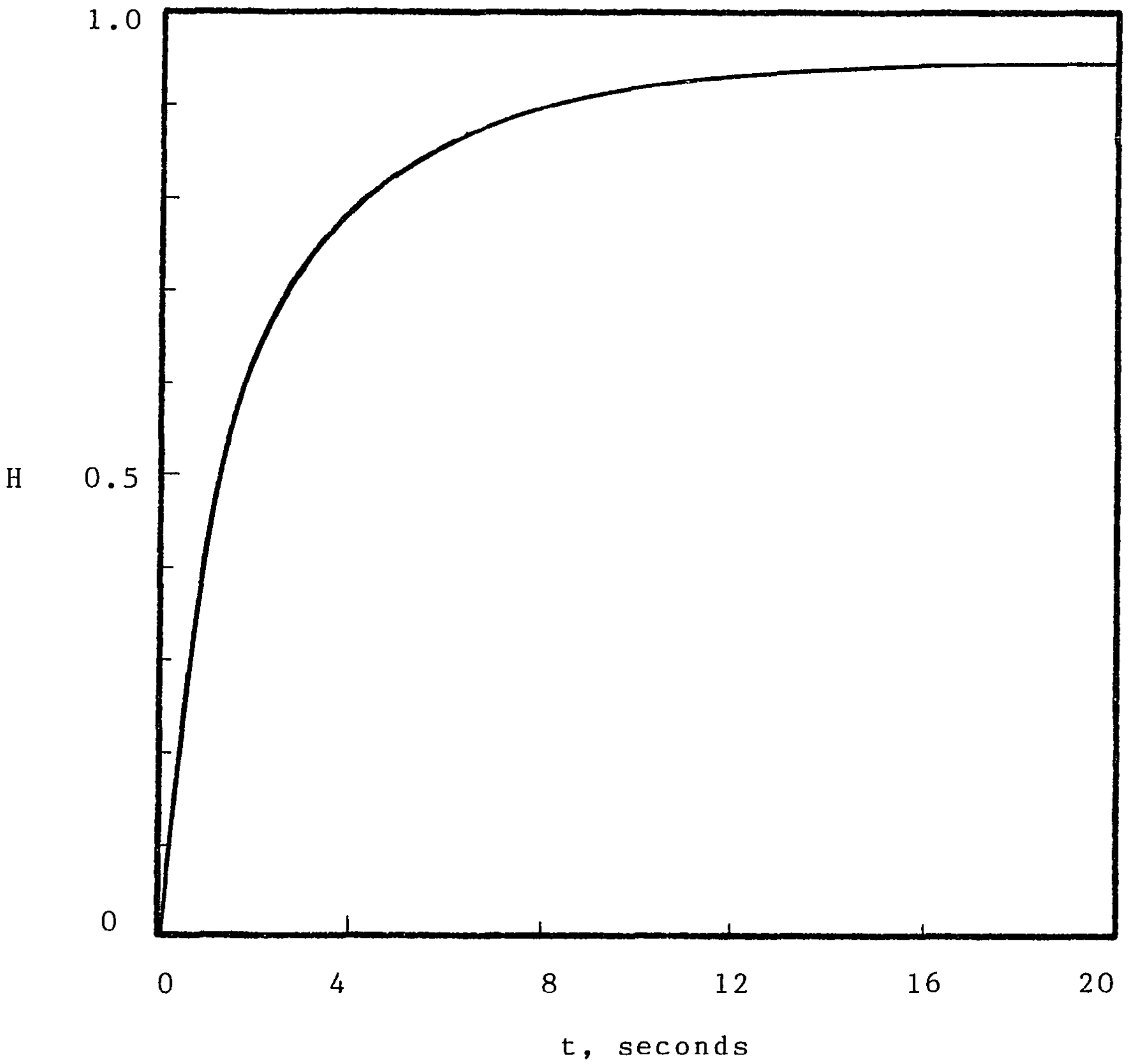

Figure 8. Degree of MIxing verse Time for Newtonian Fluid.

increased as the rotating speed accelerated at a specific time. It should be noted that it takes a long time to reach the perfect mixing at a low rotating speed. Therefore, the rate of the degree of mixing is greatly increased at a high rotating speed.

It is assumed that the flow pattern is similar regardless of rotating speed when the mixing is done in the laminar range. Then, there is some possibility that all of these data for different rotating speeds are related to dimenionless time, n^*t. the relationship expected above is confirmed clearly in Figure 10. In this study, n^* is the rotating speed in revolution per second.

The degree of mixing for non-Newtonian fluid was influenced by the different rotating speeds as shown in Figure 11. These curves are similar to Figure 9. The only difference is that different fluids have different velocity profiles. Therefore, the different rates of the degree of mixing are created by a different velocity profile in the mixing vessel.

Similar to the Figure 10, Figure 12, shows a relationship between the degree of mixing versus dimensionless time n^*t, for non-Newtonian fluid compared to Figure 10. It also shows that the degree of mixing is decreased as viscosity of fluid increases.

It should be pointed out that a plot similar to Figure 9 was also obtained by Ogawa et al.(23). Their experiments showed the same result as this study about the effect on the mixing is dependent on the velocity profile.

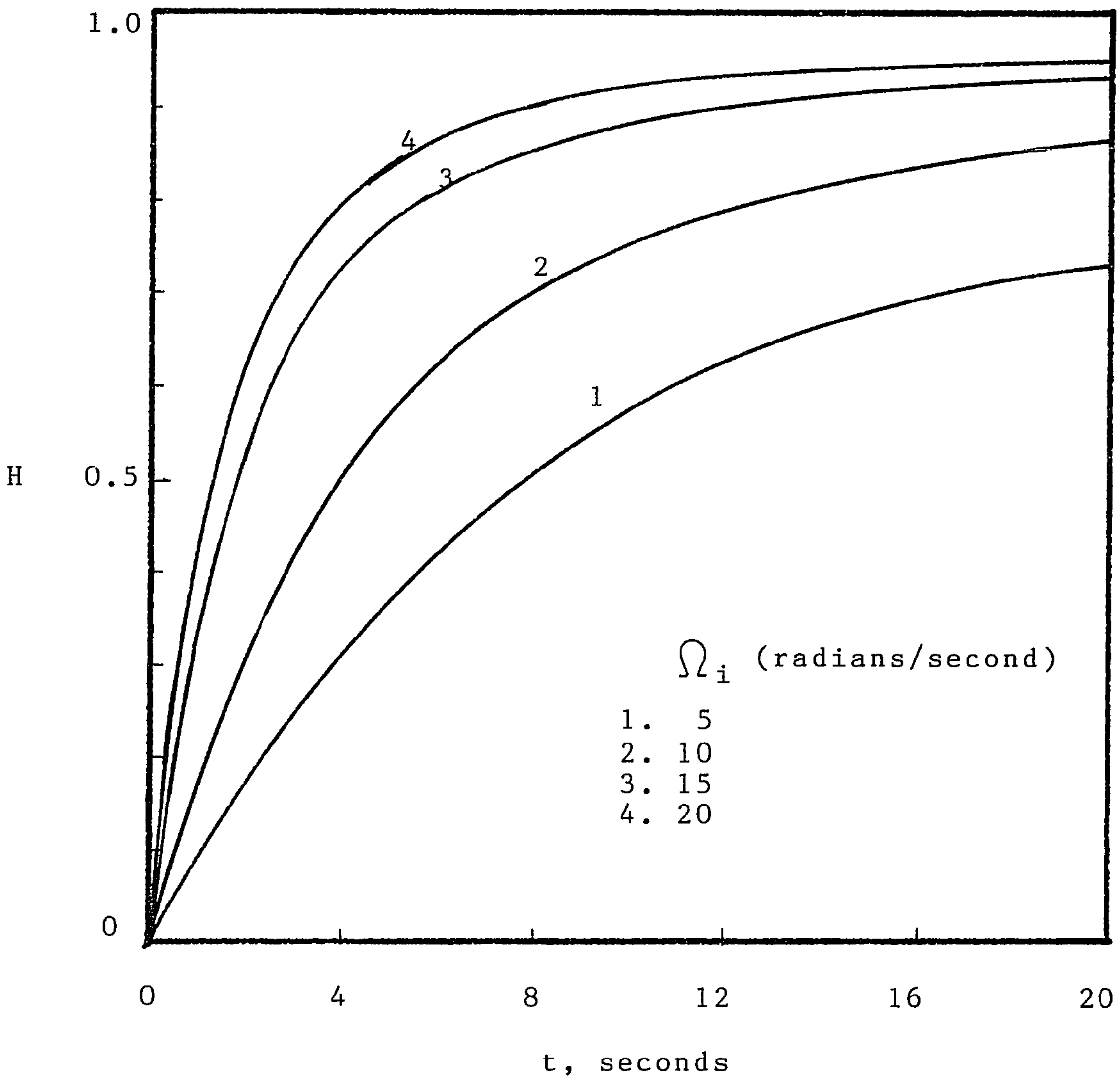

Figure 9. Degree of Mixing vs. Time for Newtonian Fluid at Different Rotating Speeds.

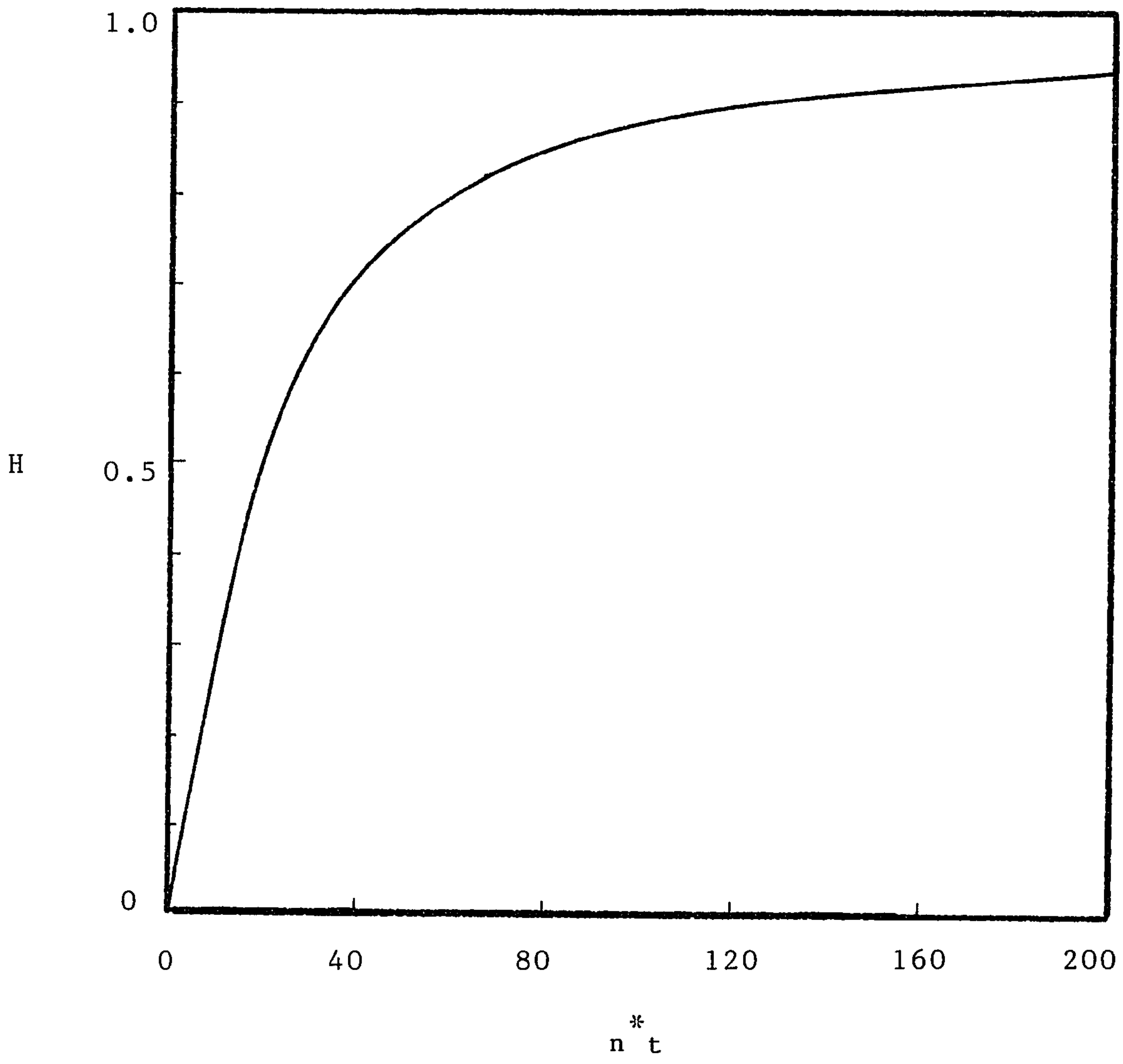

Figure 10. H vs. n^*t for Newtonian Fluid

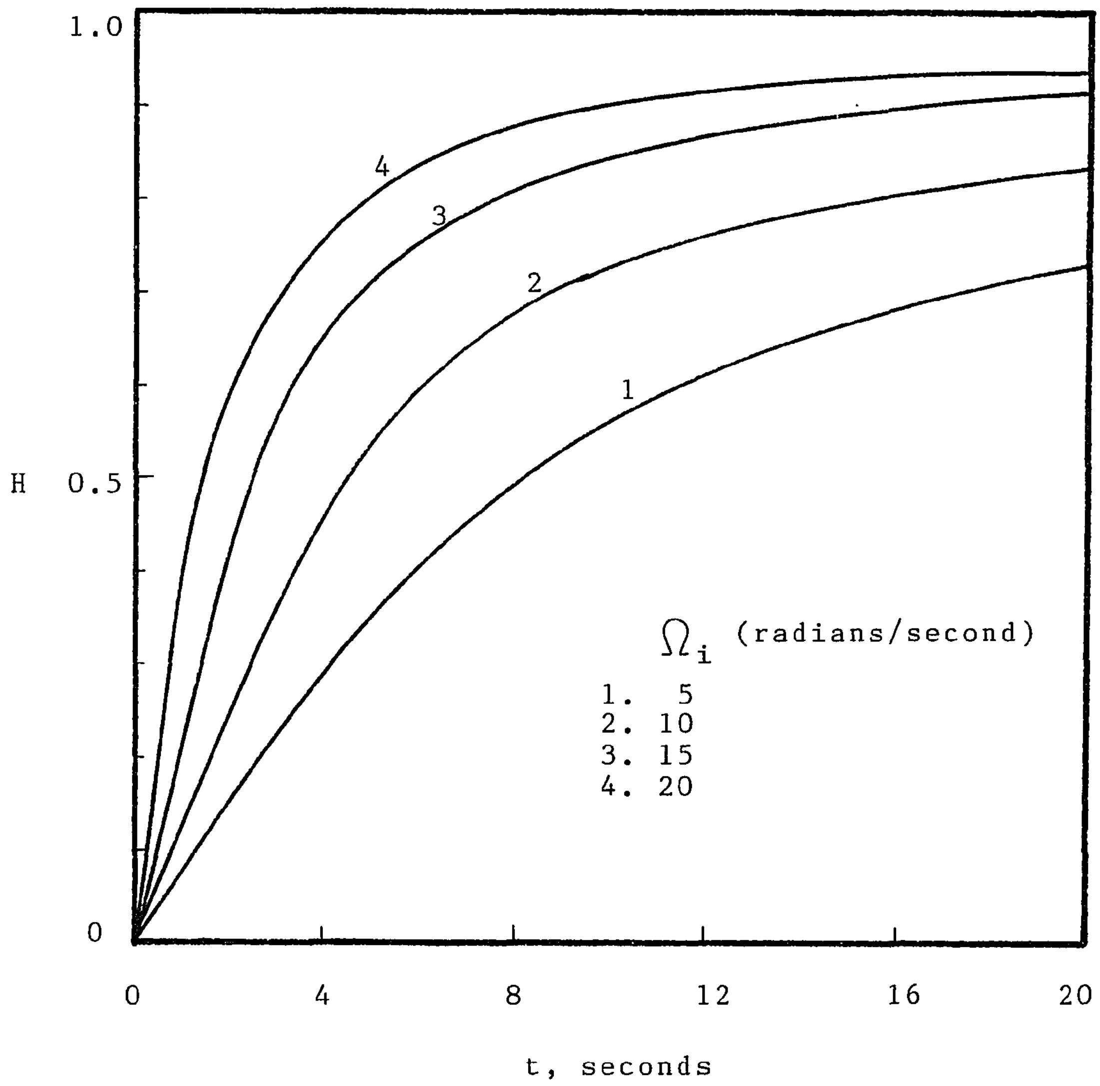

Figure 11. Degree of Mixing vs. Time for Non-Newtonian Fluid at Different Rotaing Speeds.

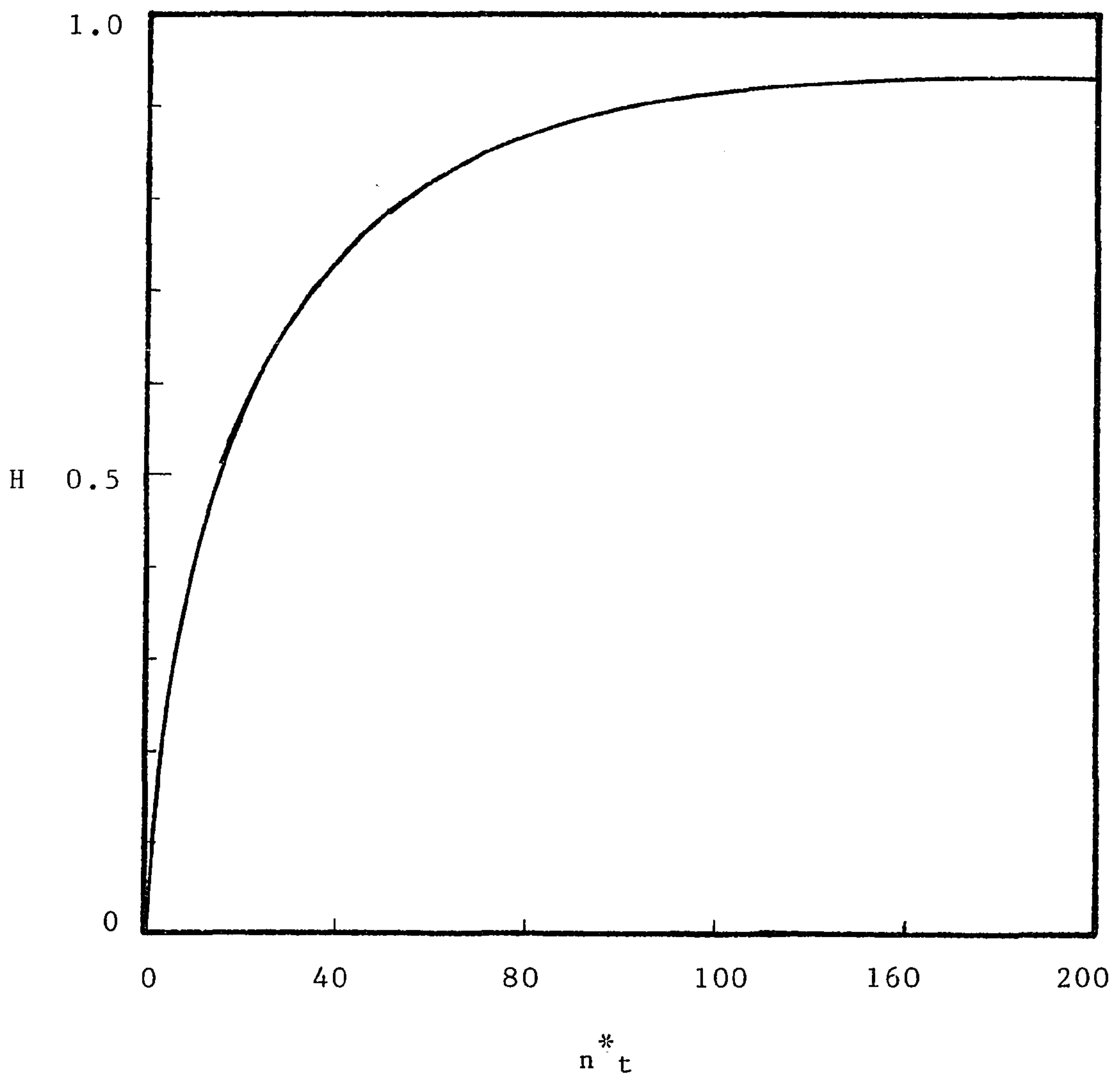

Figure 12. H vs. n^*t for Non-Newtonain Fluid

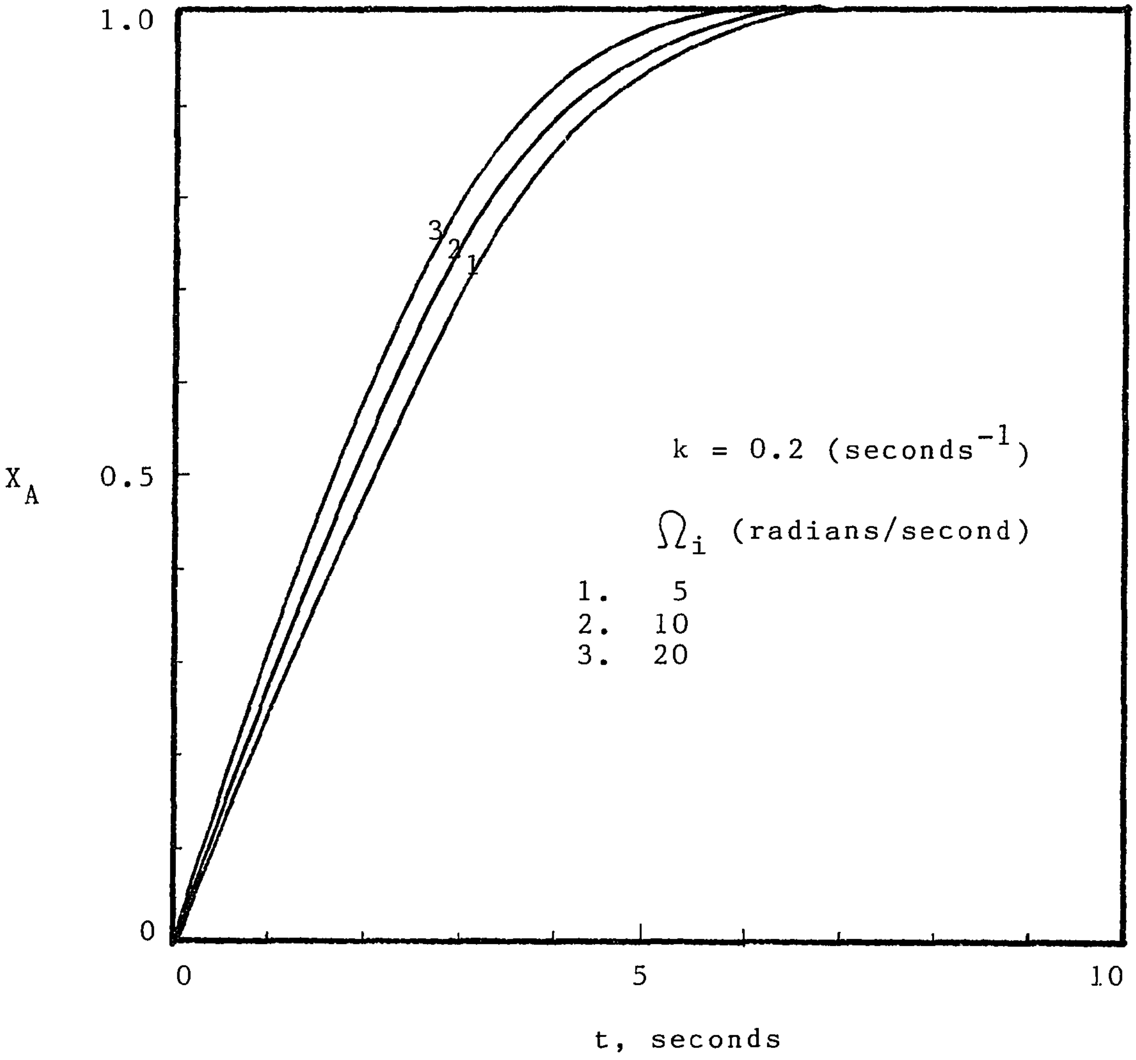

Figure 13. Fractional Conversion vs. Time at Different Rotating Speeds.

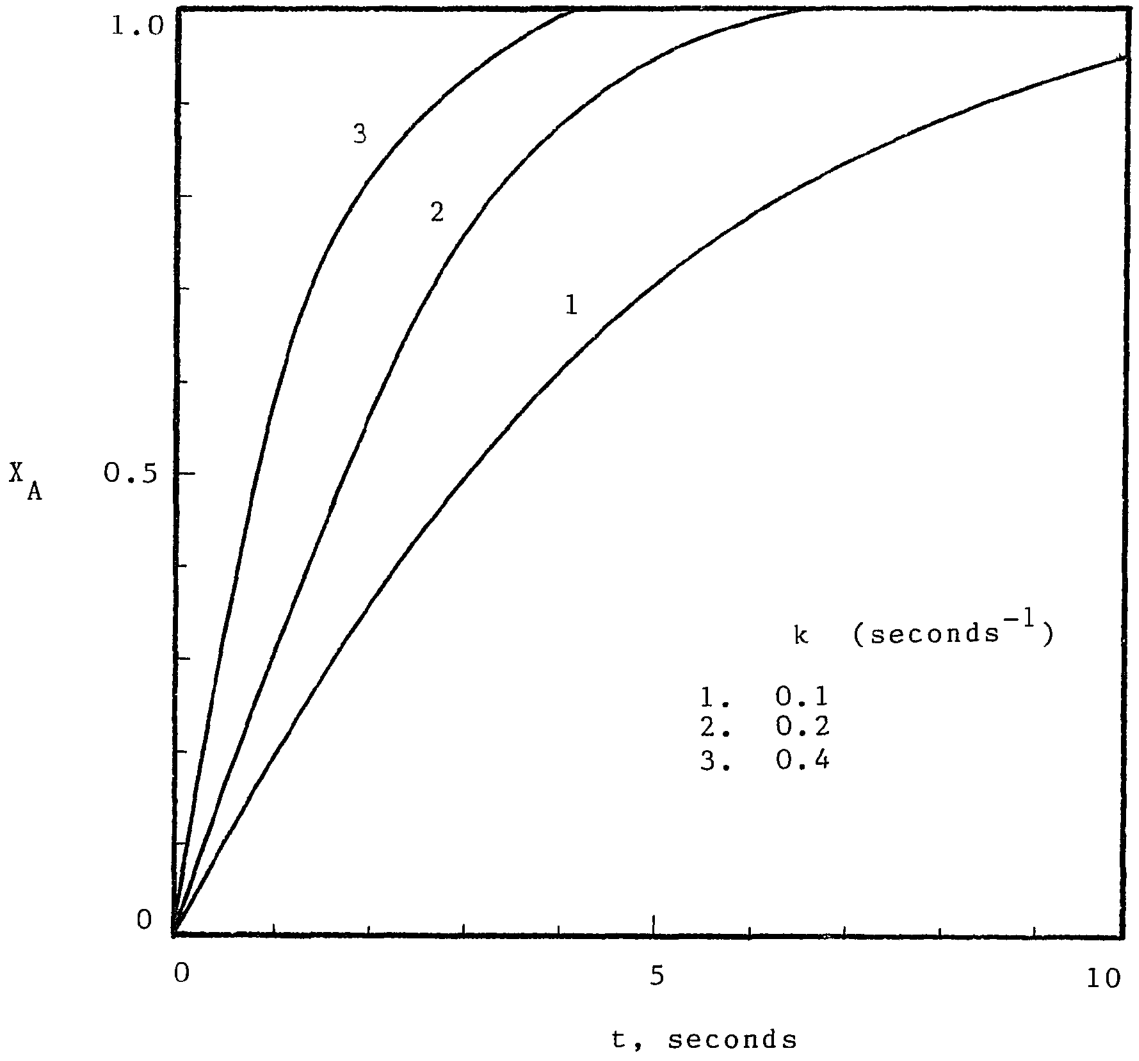

Figure 14. Fractional Conversion vs. Time at Different Chemical Reaction Rate Constant.

B. Reaction

Fractional conversion affected by different mixing speeds is shown in Figure 13. At a fixed diffusivity and reaction rate constant, the reactant consumed was increased as the rotating speed of the mixing rolls accelerated. Therefore, the mixing speed is one of the most important factors in control of extent of reaction conversion in designing a chemical reactor for a specific application.

The reaction rate constant affected the fractional conversion as shown in Figure 14. At the same rotating speed, the high reaction rate constant means that more reactants were consumed in the reactor. Also a small change of reaction rate constant caused the fractional conversion to shift greatly. Therefore, the reaction rate constant is the most effective factor to control this system.

It should be pointed out that a plot similar to Figure 13 was also obtained by Takav et al.(24) Their experiments showed the same result as this study: that mixing has a signifcant effect on chemical reaction.

CHAPTER VIII

CONCLUSIONS

(1) A new definition of the degree of mixing is presented for studying the mixing phenomenon. According to this definition, the degree of mixing varies from zero for the complete separate state to values approaching unity for the final mixing state or the complete mixing state.

(2) It is made clear that there is a definite basic relationship between the degree of mixing and dimensionless time, n^*t. Also it become possible to estimate the degree of mixing at an arbitrary time and rotating speed.

(3) The fact that mixing has a significant effect on chemical reaction in the liquid phase is confirmed in this study.

(4) This is the first attempt applying theoretical background, fluid mechanics and mass transfer, to the study of mixing phenomenon.

(5) This work presents a mathematical foundation for the mixing pheonomenon which is often claimed to be understand only in a qualitative sense. Although attaining the goal of full understanding of mixing lies in the future, this treatment should provide a rational setting for future developments.

APPENDIX A

PRECALCULATAION FOR THE COMPUTER PROGRAMS OF MIXING PHENOMENON

Laminar flow is assumed in this study to avoid the complexity of turbulent flow. The criterion of the fluid in the area of laminar flow is that the Reynolds number obeys the following equation:

$$N_{Re} = \frac{\Omega_i K R^2 \rho}{u} = \frac{4.13}{(1-K)^{3/2}} \qquad \text{(A-1)}$$

Data shown in Table 4 are substituted into the Equation A-1. Equation A-1 is simplified to:

$$\Omega_i \leq 5.79 \frac{u}{\rho} \qquad \text{(A-2)}$$

The value of $\frac{u}{\rho}$ for Newtonian fluid is in the range of 0.1 - 10 square centimeters/second. In this study, the value of $\frac{u}{\rho}$ is assumed to be 5 square centimeters/second. Therefore, the criterion of angular velocity for laminar flow is as follows:

$$\Omega_i \leq 28.85 \text{ radians/second} \qquad \text{(A-3)}$$

After the angular velocity is known, the velocity profile of the fluid inside the anulus is calcualted by the following equation:

$$\frac{V_o}{r} = A \left(\frac{1}{r}\right)^2 - B \qquad \text{(A-4)}$$

where

$$A = \frac{\Omega_i K^2 R^2}{1-K^2}$$

$$B = \frac{\Omega_i K^2}{1-K^2}$$

TABLE 4

DATA FOR THE NEWTONIAN FLUIDS IN COMPUTATION

$R = 10$ cm

$\theta = 360 = 2\pi$

$D = 1.0 \times 10^{-5}$ cm^2/sec

$K = 0.8$

$C_o = 1$ mole/cm^3

$\Delta r = 0.2$ cm

$\Delta\theta = 0.1256$

$u/p = 5$ cm^2/sec

Equation A-4 is essential in calculation of the concentration distribution and the degree of mixing. The degree of mixing is defined as

$$H(t) = 1 - \frac{\iiint (C_A - C_A)\, dv}{\iiint (C_{Ao} - C_A)\, dv / \iiint dv} \qquad \text{(A-5)}$$

The average concentration can be calculated by the following equation:

$$C_A = \frac{\iiint C_A d_V}{\iiint dV} \qquad \text{(A-6)}$$

The local concentrations are zero except O=O at initial time. Equation A-6 and 2-5 can be modified
to

$$C_A = \sum_{i=1}^{n} \frac{C_{Ao} r_i \; \Delta r \nabla \theta}{(\pi R^2 - \pi\, r^2)} \qquad \text{(A-7)}$$

The value of average concentration is calculated by substitating data in Table 4 into Equation A-7, and is as follows:

$$C_A = 0.02 \qquad \text{(A-8)}$$

Similarly, the value of the concentration variance is as follows:

$$\sigma_o^2 = 0.0196 \qquad \text{(A-9)}$$

Equation a-5 is substituted by Equations A-8 and A-9, and is simplified into:

$$H(t) = 1 - \frac{\iiint (C_A - 0.02)\, dv / \iiint dv}{0.196} \qquad \text{(A-10)}$$

Equation A-10 can save considerable amount of computation time than Equation A-5.

APPENDIX B

COMPUTER PROGRAM OF MIXING FOR NEWTONIAN FLUID

```
C.....THIS PROGRAM IS TO STUDY ABOUT MIXING PHENOMENA.
C.....THE NON-NEWTONIAN FLUID I ASSUMED IN THIS SYSTEM.
C.....PARTIAL DIFFERENTIAL EQUATION IS SOLVED BY IAD METHOD
C.....WHEN TIME IS ZERO,CONCENTRATION ARE ZERO EXCEPT AT CITA=0
C.....READ AND CHECK INPUT PARAMETER
      DOUBLE PRECISION A(101),B(101),E(101),D(101),CP(101)
      DOUBLE PRECISION CPS(21,101),C(21,101)
      DOUBLE PRECISION X,Y,XA,YA,Z
      DTAU=0.5
      RV=30
      M=50
      R=10
      DI=1.0E-7
      FM=M
      DR=10/FM
      DC=6.282/FM
      RAT1=(DTAU*DI)/(DR*DR)
      RAT2=DTAU/DC
      XK=0.8
C
C.....SET INTIAL AND BOUNDARY VALUES
      N=M
      M=11
      DO 2 I=1,M
      C(I,1)=1.
      DO 2 J=2,N
    2 C(I,J)=0.
C
C.....PERFORM CALCULATIONS OVER SUCCESSIVE TIME STEPS
      TAU=0.
C
C.....COMPUTE CONCENTRATION AT END OF HALF TIME INCREMENT
      Y1=XK**4
      Y=(RV*Y1)/(1-Y1)
      X=Y*(R**4)
    1 TAU=TAU+DTAU
      DO 21 J=1,N
      DO 22 I=1,M
      K=I+39
      A(I)=(RAT1/2)-(RAT1/(4*K))
      B(I)=-(1+RAT1)
      E(I)=(RAT1/2)+(RAT1/(4*K))
      A(1)=0
      A(M)=RAT1
      E(1)=RAT1
      E(M)=0.
      XA=(RAT2*X)/((DR*K)**4*4)
      YA=(RAT2*Y)/4
      Z=(XA-YA)
      ZZ=Z*2
```

```
      IF(I.EQ.M)GO TO 61
      IF(J.NE.1)GO TO 24
      D(I)=-C(I,J)+Z*C(I,J+1)
      GO TO 22
   24 IF(J.EQ.N)GO TO 25
      D(I)=-Z*C(I,J-1)-C(I,J)+Z*C(I,J+1)
      GO TO 22
   25 D(I)=-Z*C(I,J-1)-C(I,J)
   22 CONTINUE
   61 D(M)=-C(M,J)
      CALL TRIDAG(1,M,A,B,E,D,CP)
      DO 21 I=1,M
      IF(CP(I).LT.0.1E-3)GO TO 26
      CPS(I,J)=CP(I)
      GO TO 21
   26 CPS(I,J)=0.
   21 CONTINUE
C
C.....COMPUTER CONEENTRATION AT END OF WHOLE TIME INCREMENT
      L=M-1
      DO 27 I=1,L
      DO 28 J=1,N
      K=I+39
      XA=(RAT2*X)/((DR*K)**4*4)
      YA=(RAT2*Y)/4
      Z=(XA-YA)
      ZZ=Z*2
      A(J)=-Z
      B(J)=1.0
      E(J)=Z
      A(1)=0
      E(N)=0.
      IF(I.NE.1)GO TO 30
      D(J)=(1-RAT1)*CPS(I,J)+RAT1*CPS(I+1,J)
      GO TO 28
   30 XXX=1
      TA=RAT1/2-RAT1/(4*K)
      TB=RAT1/2+RAT1/(4*K)
      D(J)=TA*CPS(I-1,J)+(1-RAT1)*CPS(I,J)+TB*CPS(I+1,J)
   28 CONTINUE
      CALL TRIDAG(1,N,A,B,E,D,CP)
      DO 27 J=1,N
      IF(CP(J).LT.0.1E-3)GO TO 32
      C(I,J)=CP(J)
      GO TO 27
   32 C(I,J)=0.
   27 CONTINUE
      DO 3 J=1,N
      D(J)=RAT1*CPS(M-1,J)+(1.-RAT1)*CPS(M,J)
      IF(D(J).LT.0.1E-3)GO TO 4
```

```
      C(M,J)=D(J)
      GO TO 3
    4 C(M,J)=0
    3 CONTINUE
      PRINT 112,TAU
  112 FORMAT(2X,'TIME=',F5.2)
C
C.....CALCULATE THE DEGREE OF MIXING
      SUM=0.
      DO 11 J=1,N
      DO 12 I=1,10
      K=I+39
      AVG=(C(I,J)+C(I+1,J))/2
      VAR=(AVG-0.02)**2
      SUM=VAR*(K*DR)*DR*DC+SUM
   12 CONTINUE
   11 CONTINUE
      SUM=SUM/(3.141*36)
      DM=1.0-SUM/0.0196
      PRINT 13,DM
   13 FORMAT(2X,'DEGREE OF MIXING=',F11.6,/)
      IF(TAU.LT.20.0)GO TO 1
      STOP
      END
C.....SUBROUTINE FOR SOLVING A SYSTEM OF LINEAR SIMULTANEOUS
C.....EQUATIONS HAVING A TRIDIAGONAL COEFFICIENT MATRIX
      SUBROUTINE TRIDAG(IF,L,A,B,C,D,V)
      DOUBLE PRECISION A(101),B(101),C(101),D(101),V(101)
      DOUBLE PRECISION BETA(101),GAMMA(101)
      BETA(IF)=B(IF)
      GAMMA(IF)=D(IF)/BETA(IF)
      IFP1=IF+1
      DO 1 I=IFP1,L
      BETA(I)=B(I)-A(I)*C(I-1)/BETA(I-1)
    1 GAMMA(I)=(D(I)-A(I)*GAMMA(I-1))/BETA(I)
C.....COMPUTE FINAL SOLUTION VECTOR V
      V(L)=GAMMA(L)
      LAST=L-IF
      DO 2 K=1,LAST
      I=L-K
    2 V(I)=GAMMA(I)-C(I)*V(I+1)/BETA(I)
      RETURN
      END
```

APPENDIX C

COMPUTER PROGRAM OF MIXING FOR NON-NEWTONIAN FLUID

```
C.....THIS PROGRAM IS TO STUDY ABOUT MIXING PHENOMENA.
C.....THE NEWTONIAN FLUID I ASSUMED IN THIS SYSTEM.
C.....PARTIAL DIFFERENTIAL EQUATION IS SOLVED BY IAD METHOD
C.....WHEN TIME IS ZERO,CONCENTRATION ARE ZERO EXCEPT AT CITA=0
C.....READ AND CHECK INPUT PARAMETER
      DOUBLE PRECISION A(101),B(101),E(101),D(101),CP(101)
      DOUBLE PRECISION CPS(21,101),C(21,101)
      DOUBLE PRECISION X,Y,XA,YA,Z
C
C.....DATAS INPUT
      DTAU=0.5
      RV=20
      M=50
      R=10
      DI=1.0E-5
      FM=M
      DR=10/FM
      DC=6.282/FM
      RAT1=(DTAU*DI)/(DR*DR)
      RAT2=DTAU/DC
      XK=0.8
C
C.....SET INTIAL AND BOUNDARY VALUES
      N=M
      M=11
      DO 2 I=1,M
      C(I,1)=1.
      DO 2 J=2,N
    2 C(I,J)=0.
C
C.....PERFORM CALCULATIONS OVER SUCCESSIVE TIME STEPS
      TAU=0.
C
C.....COMPUTE CONCENTRATION AT END OF HALF TIME INCREMENT
      Y1=XK**2
      Y=(RV*Y1)/(1-Y1)
      X=Y*(R**2)
    1 TAU=TAU+DTAU
      DO 21 J=1,N
      DO 22 I=1,M
      K=I+39
      A(I)=(RAT1/2)-(RAT1/(4*K))
      B(I)=-(1+RAT1)
      E(I)=(RAT1/2)+(RAT1/(4*K))
      A(1)=0
      A(M)=RAT1
      E(1)=RAT1
      E(M)=0.
      XA=(RAT2*X)/((DR*K)**2*4)
      YA=(RAT2*Y)/4
```

```
      Z=(XA-YA)
      ZZ=Z*2
      IF(I.EQ.M)GO TO 61
      IF(J.NE.1)GO TO 24
      D(I)=-C(I,J)+Z*C(I,J+1)
      GO TO 22
   24 IF(J.EQ.N)GO TO 25
      D(I)=-Z*C(I,J-1)-C(I,J)+Z*C(I,J+1)
      GO TO 22
   25 D(I)=-Z*C(I,J-1)-C(I,J)
   22 CONTINUE
   61 D(M)=-C(M,J)
      CALL TRIDAG(1,M,A,B,E,D,CP)
      DO 21 I=1,M
      IF(CP(I).LT.0.1E-3)GO TO 26
      CPS(I,J)=CP(I)
      GO TO 21
   26 CPS(I,J)=0.
   21 CONTINUE
C
C.....COMPUTER CONEENTRATION AT END OF WHOLE TIME INCREMENT
      L=M-1
      DO 27 I=1,L
      DO 28 J=1,N
      K=I+39
      XA=(RAT2*X)/((DR*K)**2*4)
      YA=(RAT2*Y)/4
      Z=(XA-YA)
      ZZ=Z*2
      A(J)=-Z
      B(J)=1.0
      E(J)=Z
      A(1)=0
      E(N)=0.
      IF(I.NE.1)GO TO 30
      D(J)=(1-RAT1)*CPS(I,J)+RAT1*CPS(I+1,J)
      GO TO 28
   30 XXX=1
      TA=RAT1/2-RAT1/(4*K)
      TB=RAT1/2+RAT1/(4*K)
      D(J)=TA*CPS(I-1,J)+(1-RAT1)*CPS(I,J)+TB*CPS(I+1,J)
   28 CONTINUE
      CALL TRIDAG(1,N,A,B,E,D,CP)
      DO 27 J=1,N
      IF(CP(J).LT.0.1E-3)GO TO 32
      C(I,J)=CP(J)
      GO TO 27
   32 C(I,J)=0.
   27 CONTINUE
      DO 3 J=1,N
```

```
      D(J)=RAT1*CPS(M-1,J)+(1.-RAT1)*CPS(M,J)
      IF(D(J).LT.0.1E-3)GO TO 4
      C(M,J)=D(J)
      GO TO 3
    4 C(M,J)=0
    3 CONTINUE
      PRINT 112,TAU
  112 FORMAT(2X,'TIME=',F5.2)
C
C.....CALCULATE THE DEGREE OF MIXING
      SUM=0.
      DO 11 J=1,N
      DO 12 I=1,10
      K=I+39
      AVG=(C(I,J)+C(I+1,J))/2
      VAR=(AVG-0.02)**2
      SUM=VAR*(K*DR)*DR*DC+SUM
   12 CONTINUE
   11 CONTINUE
      SUM=SUM/(3.141*36)
      DM=1.0-SUM/0.0196
      PRINT 13,DM
   13 FORMAT(2X,'DEGREE OF MIXING=',F11.6,/)
      IF(TAU.LT.20.0)GO TO 1
      STOP
      END
C
C.....SUBROUTINE FOR SOLVING A SYSTEM OF LINEAR SIMULTANEOUS
C.....EQUATIONS HAVING A TRIDIAGONAL COEFFICIENT MATRIX
      SUBROUTINE TRIDAG(IF,L,A,B,C,D,V)
      DOUBLE PRECISION A(101),B(101),C(101),D(101),V(101)
      DOUBLE PRECISION BETA(101),GAMMA(101)
      BETA(IF)=B(IF)
      GAMMA(IF)=D(IF)/BETA(IF)
      IFP1=IF+1
      DO 1 I=IFP1,L
      BETA(I)=B(I)-A(I)*C(I-1)/BETA(I-1)
    1 GAMMA(I)=(D(I)-A(I)*GAMMA(I-1))/BETA(I)
C.....COMPUTE FINAL SOLUTION VECTOR V
      V(L)=GAMMA(L)
      LAST=L-IF
      DO 2 K=1,LAST
      I=L-K
    2 V(I)=GAMMA(I)-C(I)*V(I+1)/BETA(I)
      RETURN
      END
```

APPENDIX D

COMPUTER PROGRAM FOR NEWTONIAN FLUID WITH CHEMICAL REACTION

```
C.....THIS PROGRAM IS TO STUDY ABOUT MIXING PHENOMENA WITH
C.....CHEMICAL REACTION.  THE NEWTONIAN FLUID IS ASSUMED
C.....IN THIS SYSTEM.
C.....PARTIAL DIFFERENTIAL EQUATION IS SOLVED BY IAD METHOD
C.....AT TIME=0 THE CONCENTRATION IS ZERO EXCEPT AT CITA=0
C.....READ AND CHECK INPUT PARAMETER
      DOUBLE PRECISION A(101),B(101),E(101),D(101),CP(101)
      DOUBLE PRECISION CPS(21,101),C(21,101)
      DOUBLE PRECISION X,Y,XA,YA,Z
      DOUBLE PRECISION F(50)
C
C.....DATAS INPUT
      RK=0.5
      RSUM=0
      RV=5
      DTAU=0.5
      M=50
      R=10
      DI=1.0E-5
      FM=M
      DR=10/FM
      DC=6.282/FM
      RAT1=(DTAU*DI)/(DR*DR)
      RAT2=DTAU/DC
      XK=0.8
C
C.....SET INTIAL AND BOUNDARY VALUES
      N=M
      M=11
      DO 2 I=1,M
      C(I,1)=1.
      DO 2 J=2,N
    2 C(I,J)=0.
C
C....PERFORM CALCULATIONS OVER SUCCESSIVE TIME STEPS
      TAU=0.
C
C.....COMPUTE CONCENTRATION AT END OF HALF TIME INCREMENTR
      Y1=XK**2
      Y=(RV*Y1)/(1-Y1)
      X=Y*(R**2)
    1 TAU=TAU+DTAU
      DO 21 J=1,N
      DO 22 I=1,M
      K=I+39
      A(I)=(RAT1/2)-(RAT1/(4*K))
      B(I)=-(1+RAT1)
      E(I)=(RAT1/2)+(RAT1/(4*K))
      A(1)=0
```

```
      A(M)=RAT1
      E(1)=RAT1
      E(M)=0.
      XA=(RAT2*X)/((DR*K)**2*4)
      YA=(RAT2*Y)/4
      Z=(XA-YA)
      ZZ=Z*2
      IF(I.EQ.M)GO TO 61
      IF(J.NE.1)GO TO 24
      D(I)=-(1-RK)*C(I,J)+Z*C(I,J+1)
      GO TO 22
   24 IF(J.EQ.N)GO TO 25
      D(I)=-Z*C(I,J-1)-(1-RK)*C(I,J)+Z*C(I,J+1)
      GO TO 22
   25 D(I)=-Z*C(I,J-1)-(1-RK)*C(I,J)
   22 CONTINUE
   61 D(M)=-(1-RK)*C(M,J)
      CALL TRIDAG(1,M,A,B,E,D,CP)
      DO 21 I=1,M
      IF(CP(I).LT.0.1E-3)GO TO 26
      CPS(I,J)=CP(I)
      GO TO 21
   26 CPS(I,J)=0.
   21 CONTINUE
C
C.....COMPUTER CONEENTRATION AT END OF WHOLE TIME INCREMENT
      L=M-1
      DO 27 I=1,L
      DO 28 J=1,N
      K=I+39
      XA=(RAT2*X)/((DR*K)**2*4)
      YA=(RAT2*Y)/4
      Z=(XA-YA)
      ZZ=Z*2
      A(J)=-Z
      B(J)=1.0
      E(J)=Z
      A(1)=0
      E(N)=0.
      IF(I.NE.1)GO TO 30
      D(J)=(1-RAT1-RK)*CPS(I,J)+RAT1*CPS(I+1,J)
      GO TO 28
   30 XXX=1
      TA=RAT1/2-RAT1/(4*K)
      TB=RAT1/2+RAT1/(4*K)
      D(J)=TA*CPS(I-1,J)+(1-RAT1-RK)*CPS(I,J)+TB*CPS(I+1,J)
   28 CONTINUE
      CALL TRIDAG(1,N,A,B,E,D,CP)
      DO 27 J=1,N
```

```
      IF(CP(J).LT.0.1E-3)GO TO 32
      C(I,J)=CP(J)
      GO TO 27
   32 C(I,J)=0.
   27 CONTINUE
      DO 3 J=1,N
      D(J)=RAT1*CPS(M-1,J)+(1-RAT1-RK)*CPS(M,J)
      IF(D(J).LT.0.1E-3)GO TO 4
      C(M,J)=D(J)/(1+RK)
      GO TO 3
    4 C(M,J)=0
    3 CONTINUE
      WRITE(6,112)TAU
  112 FORMAT(2X,'TIME=',F5.2)
C
C.....CALCULATE THE EFFECTIVENESS FACTOR
      SUM=0.
      DO 11 J=1,N
      DO 12 I=1,10
      K=I+39
      AVG=(C(I,J)+C(I+1,J))/2
      SUM=AVG*(K*DR)*DR*DC+SUM
   12 CONTINUE
   11 CONTINUE
      SUM=SUM/(3.141*36)
      REL=1-(SUM/0.02)
      XT=EXP(-RK*TAU)
      THE=1.0-XT
      WRITE(6,500)THE,REL
  500 FORMAT(2X,2F11.5)
      IF(TAU.LT.10.0)GO TO 1
      STOP
      END
C
C.....SUBROUTINE FOR SOLVING A SYSTEM OF LINEAR SIMULTANEOUS
C.....EQUATIONS HAVING A TRIDIAGONAL COEFFICIENT MATRIX.
      SUBROUTINE TRIDAG(IF,L,A,B,C,D,V)
      DOUBLE PRECISION A(101),B(101),C(101),D(101),V(101)
      DOUBLE PRECISION BETA(101),GAMMA(101)
      BETA(IF)=B(IF)
      GAMMA(IF)=D(IF)/BETA(IF)
      IFP1=IF+1
      DO 1 I=IFP1,L
      BETA(I)=B(I)-A(I)*C(I-1)/BETA(I-1)
    1 GAMMA(I)=(D(I)-A(I)*GAMMA(I-1))/BETA(I)
C
C.....COMPUTE FINAL SOLUTION VECTOR V
      V(L)=GAMMA(L)
```

```
      LAST=L-IF
      DO 2 K=1,LAST
      I=L-K
    2 V(I)=GAMMA(I)-C(I)*V(I+1)/BETA(I)
      RETURN
      END
```

APPENDIX E

COMPUTER PROGRAM FOR NON-NEWTONIAN FLUID WITH CHEMICAL REACTION

```
C.....THIS PROGRAM IS TO STUDY ABOUT MIXING PHENOMENA WITH
C.....CHEMICAL REACTION.  THE NON-NEWTONIAN FLUID IS ASSUMED
C.....IN THIS SYSTEM.
C.....PARTIAL DIFFERENTIAL EQUATION IS SOLVED BY IAD METHOD
C.....AT TIME=0 THE CONCENTRATION IS ZERO EXCEPT AT CITA=0
C.....READ AND CHECK INPUT PARAMETER
      DOUBLE PRECISION A(101),B(101),E(101),D(101),CP(101)
      DOUBLE PRECISION CPS(21,101),C(21,101)
      DOUBLE PRECISION X,Y,XA,YA,Z
      DOUBLE PRECISION F(50)
C
C.....DATAS INPUT
      RK=0.02
      RSUM=0
      RV=30
      DTAU=0.5
      M=50
      R=10
      DI=1.0E-7
      FM=M
      DR=10/FM
      DC=6.282/FM
      RAT1=(DTAU*DI)/(DR*DR)
      RAT2=DTAU/DC
      XK=0.8
C
C.....SET INTIAL AND BOUNDARY VALUES
      N=M
      M=11
      DO 2 I=1,M
      C(I,1)=1.
      DO 2 J=2,N
    2 C(I,J)=0.
C
C....PERFORM CALCULATIONS OVER SUCCESSIVE TIME STEPS
      TAU=0.
C
C.....COMPUTE CONCENTRATION AT END OF HALF TIME INCREMENTR
      Y1=XK**4
      Y=(RV*Y1)/(1-Y1)
      X=Y*(R**4)
    1 TAU=TAU+DTAU
      DO 21 J=1,N
      DO 22 I=1,M
      K=I+39
      A(I)=(RAT1/2)-(RAT1/(4*K))
      B(I)=-(1+RAT1)
      E(I)=(RAT1/2)+(RAT1/(4*K))
      A(1)=0
```

```
      A(M)=RAT1
      E(1)=RAT1
      E(M)=0.
      XA=(RAT2*X)/((DR*K)**4*4)
      YA=(RAT2*Y)/4
      Z=(XA-YA)
      ZZ=Z*2
      IF(I.EQ.M)GO TO 61
      IF(J.NE.1)GO TO 24
      D(I)=-(1-RK)*C(I,J)+Z*C(I,J+1)
      GO TO 22
   24 IF(J.EQ.N)GO TO 25
      D(I)=-Z*C(I,J-1)-(1-RK)*C(I,J)+Z*C(I,J+1)
      GO TO 22
   25 D(I)=-Z*C(I,J-1)-(1-RK)*C(I,J)
   22 CONTINUE
   61 D(M)=-(1-RK)*C(M,J)
      CALL TRIDAG(1,M,A,B,E,D,CP)
      DO 21 I=1,M
      IF(CP(I).LT.0.1E-3)GO TO 26
      CPS(I,J)=CP(I)
      GO TO 21
   26 CPS(I,J)=0.
   21 CONTINUE
C
C.....COMPUTER CONEENTRATION AT END OF WHOLE TIME INCREMENT
      L=M-1
      DO 27 I=1,L
      DO 28 J=1,N
      K=I+39
      XA=(RAT2*X)/((DR*K)**4*4)
      YA=(RAT2*Y)/4
      Z=(XA-YA)
      ZZ=Z*2
      A(J)=-Z
      B(J)=1.0
      E(J)=Z
      A(1)=0
      E(N)=0.
      IF(I.NE.1)GO TO 30
      D(J)=(1-RAT1-RK)*CPS(I,J)+RAT1*CPS(I+1,J)
      GO TO 28
   30 XXX=1
      TA=RAT1/2-RAT1/(4*K)
      TB=RAT1/2+RAT1/(4*K)
      D(J)=TA*CPS(I-1,J)+(1-RAT1-RK)*CPS(I,J)+TB*CPS(I+1,J)
   28 CONTINUE
      CALL TRIDAG(1,N,A,B,E,D,CP)
      DO 27 J=1,N
```

```
      IF(CP(J).LT.0.1E-3)GO TO 32
      C(I,J)=CP(J)
      GO TO 27
   32 C(I,J)=0.
   27 CONTINUE
      DO 3 J=1,N
      D(J)=RAT1*CPS(M-1,J)+(1-RAT1-RK)*CPS(M,J)
      IF(D(J).LT.0.1E-3)GO TO 4
      C(M,J)=D(J)/(1+RK)
      GO TO 3
    4 C(M,J)=0
    3 CONTINUE
      WRITE(6,112)TAU
  112 FORMAT(2X,'TIME=',F5.2)
C
C.....CALCULATE THE EFFECTIVENESS FACTOR
      SUM=0.
      DO 11 J=1,N
      DO 12 I=1,10
      K=I+39
      AVG=(C(I,J)+C(I+1,J))/2
      SUM=AVG*(K*DR)*DR*DC+SUM
   12 CONTINUE
   11 CONTINUE
      SUM=SUM/(3.141*36)
      K=TAU/DTAU
      K=K+1
      F(1)=0.02
      F(K)=SUM
      RSUM=RSUM+((F(K-1)+F(K))/2)*0.5
      XT=EXP(-RK*TAU)
      XX=(0.02*(1-XT))/RK
      EFF=RSUM/XX
      WRITE(6,500)RSUM,XX,EFF
  500 FORMAT(2X,3F11.5)
      WRITE(6,13)EFF
   13 FORMAT(2X,'DEGREE OF MIXING=',F11.6,//)
      IF(TAU.LT.20.0)GO TO 1
      STOP
      END
C
C.....SUBROUTINE FOR SOLVING A SYSTEM OF LINEAR SIMULTANEOUS
C.....EQUATIONS HAVING A TRIDIAGONAL COEFFICIENT MATRIX.
      SUBROUTINE TRIDAG(IF,L,A,B,C,D,V)
      DOUBLE PRECISION A(101),B(101),C(101),D(101),V(101)
      DOUBLE PRECISION BETA(101),GAMMA(101)
      BETA(IF)=B(IF)
      GAMMA(IF)=D(IF)/BETA(IF)
```

```
      IFP1=IF+1
      DO 1 I=IFP1,L
      BETA(I)=B(I)-A(I)*C(I-1)/BETA(I-1)
    1 GAMMA(I)=(D(I)-A(I)*GAMMA(I-1))/BETA(I)
C
C.....COMPUTE FINAL SOLUTION VECTOR V
      V(L)=GAMMA(L)
      LAST=L-IF
      DO 2 K=1,LAST
      I=L-K
    2 V(I)=GAMMA(I)-C(I)*V(I+1)/BETA(I)
      RETURN
      END
```

APPRENDIX F

DERIVATION OF EQUATION 6-17 FROM EQUATION 6-15

Solving Equation 6-15 by seperation of variables.

$$\frac{{}^{2}f}{s^{2}} = \frac{1}{D}\,\frac{f}{t} \qquad \text{(F-1)}$$

the initial and boundary conditions are

I.C. at $t = 0$, $f = s + r_A + r_B$

B.C.1 at $s=0$, $f = 0$ (F-2)

B.C.2 $s = d - (r_A + r_B)$

$$d\,\frac{\delta f}{\delta r}\,\Big|s = d- (r_A + r_B) = f\Big|\; s = d - (r_A + r_B)$$

The separation of variables is introduced as the following:

Let $f(s,t) = S(s)\cdot T(t)$ (F-3)

Equation F-3 substitutes inot Equation F-1 gives

$$T\,\frac{\delta^{2} S}{\delta s} = \frac{1}{D}\,\frac{\delta T}{\delta t}\,S \qquad \text{(F-4)}$$

Equation F-4 divided by TS gives

$$\frac{S''}{S} = \frac{1}{D}\,\frac{T'}{T} = -\ \beta^{2} \qquad \text{(F-5)}$$

Equation F-5 yields the two ordinary linear differtial equations

$$\frac{dT}{dt} = - \; D \beta^2 T \qquad \text{(F-6)}$$

and

$$\frac{d^2S}{ds^2} + \beta^2 s = 0 \qquad \text{(F-7)}$$

Case (1): $\beta^2 = 0$

The solution is

$T = C'$ and $S = C_2 s + C_3$

Case (2): β^2 = negative

this case is physically impossible

Case (3): β^2 = positive

the solution is

$$T = C_4 e^{-D\beta^2 t}$$

$$S = C_5 \sin \beta s + C_6 \cos \beta s$$

so the general solution of Equation of (F-1) by combining the solutions of three cases is

$$f = C_1 + C_2 + e^{-D\beta^2 t} (C_3 \sin \beta s + C_4 \cos \beta s) \qquad \text{(F-8)}$$

By applying the B.C.1, at s = 0, f = 0, in Equation (F-8) gives

$C_1 = 0, \; C_4 = 0$

and

$$f = C_2 s + C_3 \quad e^{-D\beta^2 t} \sin \beta s \qquad \text{(F-9)}$$

By applying the B.C.2 at $s = d - (r_A + r_B)$

$$d \frac{\delta f}{\delta f} |s = f|s$$

$$d \ \{C_2 + C_3 \ \beta C^{-D^{2\beta 2}t} \ \cos\beta \ [d- (r_A + r_B)]\}$$

$$= C_2 \ [d- (r_A + r_B)] + C_3 \ e^{-D\beta^2 t} \ \sin\beta \ [d- (r_A + r_B)]$$

which gives

$$C_2 = 0$$

and

$$d \ \beta\cos \beta[d- (r_A + r_B)] = \sin \beta[d- (r_A + r_B)]$$

or

$$\tan \{\beta[d- (r_A + r_B)] \}= d\beta \qquad \text{(F-10)}$$

Engenvalues can be calculated from Equation F-10.

Then the Equation F-9 becomes

$$f = \sum_{n=1}^{\infty} C_n \ e^{-D \ \beta^2 nt} \ \sin \beta ns \qquad \text{(F-11)}$$

By applying I.C. at $t = 0$, $f = s + r_A + r_B$, the C_n can be determined as follows:

$$s + r_A + r_B = \sum_{n=1}^{\infty} C_n \sin \beta_n s \qquad \text{(F-12)}$$

Since this is a Sturm-Liouville system, multiply both side of Equation F-12 by sin (βms) ds and integrate from s=0 to s=d - (r_A + r_B).

$$(s + r_A + r_B) \sin (\beta m^s) \ ds = \sum_{n=1}^{\infty} C_n \int_{o}^{s=d-(r_A + r_B)} \sin (\beta_n s) \sin (\beta_m s) \ ds \qquad \text{(F-13)}$$

since

$$\int x \sin (ax) \ dx = \frac{1}{a^2} \sin (ax) - \cos (ax)$$

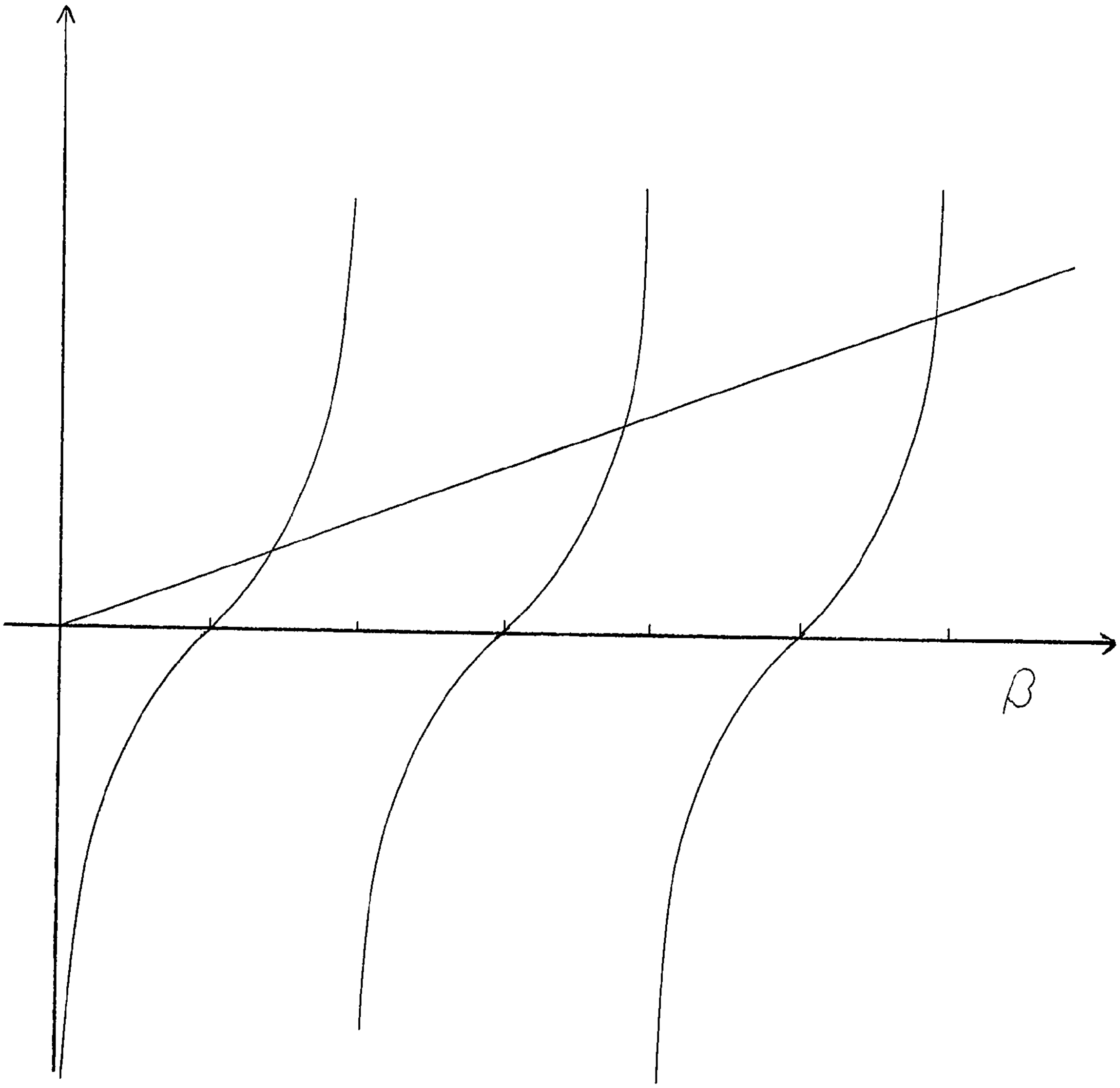

Figure 15. Location of Eigenvalues for $\tan\left\{\beta_n\left[d-(r_A + r_B)\right]\right\} = d\beta_n$.

$$\int \sin^2 (ax)\, dx = \frac{1}{2}x - \frac{1}{4a} \sin(2ax),$$

$$\int \sin ax\, dx = - \frac{\cos ax}{a}$$

The left hand side of equation F-13 is

$$\text{L.H.S.} = \int_{0}^{s=d-(r_A+r_B)} (s + r_A + r_B) \sin (ms)\, ds$$

$$= \frac{1}{\beta_m^2} \sin \beta_m [d-(r_A + r_B)] - \frac{d}{\beta_m} \cos \beta_m [d-(r_A + r_B)] + \frac{r_A + r_B}{\beta_m}$$

$$+$$

The right hand side of equation F-13 is equal to zero when n=m, and

$$\text{R.H.S} = \int_{o}^{s=d-(r_A+r_B)} \{\sin (\beta_m s) \}^2 ds \quad \text{when } n=m$$

$$= \frac{d-(r_A+r_B)}{2} - \frac{1}{4\beta_m} \sin\{ 2 \beta_m\, d-(r_A+r_B) \}$$

Therefore C_n is

$$C_n = \frac{4 \sin \{\beta_n\, d-(r_A+r_B) \} - 4\, d\, \beta_n \cos\{\beta_n\, d-(r_A+r_B) \}+ 4\, \beta_n (r_A+r_B)}{2\, \beta_n^2\, d-(r_A+r_B) - \beta_n \sin \{ 2\, \beta_n\, d- (r_A+r_B) \}}$$

Simply the equation

$$C_n =$$

$$C_n = \frac{4 \sin \theta_n - 4d\, \beta_n \cos \theta_n + 4\, \beta_n (r_A+r_B)}{2\, \beta_n \theta_n - \beta_n \sin 2\theta_n} \qquad \text{(F-14)}$$

where $\theta_n = \beta_n [d- (r_A + r_B)]$

The final solution of the Equation (F-1) is

$$r \frac{C_A}{C_{Ao}} = f \sum_{n=1}^{\infty} C_n\, e^{-D\, \beta_n^2 t} \{ \sin \beta_n [r-(r_A+r_B)] \} \qquad \text{(F-15)}$$

where C_n is in Equation F-14.

APPENDIX G

COMPUTER PROGRAM FOR CHEMICAL REACTION RATE CONSTANT WITHOUT MIXING

```
C
C.....THIS PROGRAM IS FOR CHEMICAL REACTION RATE CONSTANT
      DIMENSION B(50),RC(50),C(50)
C
C.....DATAS INPUT
      D=1.77E-5
      R=4.3E-8
      AR=4.5
      DAB=4.0E-5
      Z=D-R
C
C.....CALCULATE THE EIGENVALUES
      DO 1 I=1,10
      CALL EG(AR,Z,D,BA)
      B(I)=BA
      RC(I)=B(I)*Z
      YA=4*SIN(RC(I))-4*D*B(I)*COS(RC(I))
      YB=2*B(I)*B(I)*RC(I)-B(I)*SIN(2*RC(I))
      C(I)=(YA+4*B(I)*R)/YB
      AR=RC(I)+3.141
1     CONTINUE
      V=0
      DO 2 I=1,10
      V=V+C(I)*((B(I)/D)*COS(RC(I))-(SIN(RC(I))/(D*D)))
2     CONTINUE
C
C.....CALCULATE THE RATE CONSTANT
      RA=6.02E23*3.141*R*R*DAB*V
      PRINT 20
20    FORMAT(10X,'DIF',11X,'FD',12X,'K')
      PRINT 10,DAB,V,RA
10    FORMAT(2X,3E13.3)
      STOP
      END
C
C.....SUBROUTINE FOR DETERMINATING THE EIGENVALUES
      SUBROUTINE EG(AR,Z,D,BA)
      BA=AR/Z
3     FB=SIN(AR)/COS(AR)-BA*D
      DFB=(Z/(COS(AR)**2))-D
      XA=FB/DFB
      BB=BA-XA
      ERR=ABS((BA-BB)/BA)
      BA=BB
      AR=BA*Z
      IF(ERR.GT.1.0E-4)GO TO 3
      RETURN
      END
```

NOMENCLATAURE

Symbol	Definition
A:	$\Omega_i K^2R^2/1-K^2$, defined by Equation 3-16
A^*:	$\frac{\Omega_i k^{2/n}}{1-k^{2/n}}$ $R^{2/n}$, defined by Equation 4-15.
A'	$\frac{\Omega_i k^4}{1-k^4}$ R^4, defined by Education 4-17.
A_i	Coefficient of the equations, defined by Equation 3-18.
B	$\frac{\Omega_i k^2}{1-k^2}$, defined by Equation 3-16.
B^*	$\frac{\Omega_i k^2}{1-k^2}$, defined by Equation 4-15.
B'	$\frac{\Omega_i k^4}{1-k^4}$, defined by Equation 4-17.
b_i	Coefficient of the equation, defined by Equation 3-18. 3-18.
C	Concentration, gmole/cm^3.
$\bar{C}$	Average concentration, gmole/cm^3.
C^*	Concentration at the end of the first half time
C_A	Concentration of component A, gmole/cm^3.

C_{Ao}	Initial concentration of component A, $gmole/cm^3$.
C_A	Concentration of component A at infinite time, $gmole/cm^3$.
C_B	Concentration of component B, $gmole/cm^3$.
C_{Bo}:	Initial concentration of component B, $gmole/cm^3$.
C_o•	Initial concentration, $gmole/cm^3$.
C_i	Coefficeint of the equaitons, defined by Equation 3-18.
C_n	Defined by Equation 6-17.
C_p	Heat Capacity.
D	Diffusivity
d	Average distance between molecules A and B.
g	Gravitational acceleration.
H	Degree of mixing.
K	Ratio of radius of inner cylinder to that of outer cylinder.
k	Chemical reaction rate constant.
L	Height of annulus.
m	Parameter of power-law model.
N	Defined by Equation 3-17.
N_A	Number of molecules A.
n	Parameter of power-law model.
n^*	Rotating speed, rps.
P	Steric factor, defined by Equation 6-24.
Ps	Static pressure.
R	Radius of cylinder, cm.
R_i	Reaction rate of species i

r_A	Radius of molecules A, cm.
r_B	Radius of molecule B, cm.
T	Temperature, ^oC.
t	time, second.
V	Velocity, cm/sec.
u	Average velocity, cm/sec.
V_r, V_v V_z:	Velocity in r-direction, 0-direction and z-direction, cm/sec.
X:	Defined by Equation 3-24
X'	Defined by Equation 4-17
X_A	Defined by Equation 4-17 Fractional conversion.
Y	Defined by Equation 3-24.
Y'	Defined by Equation 4-17.
Z:	Collision rate, defined by Equation 6-8.

Greek Symbol	Definition
β_n:	Eigenvalue, defined by equation 6-18
δ	Unit tenor.
δ_r	Central-difference operator in term of r.
δ_θ	Central-difference operator in term of .
$\delta(t)$	Unit impulse function.
λ_1	Defined by Equation 3-24
λ_2	Defined by Equation 3-24
θ	Cylindrical coordinates
θ_n	Defined by Equation 6-17.
υ	Viscosity
ρ	Fluid density, cm^3/sec.
σ_t^2	Initial concentration variance.
σ_t^2	Concentration variance.
τ	Shear Stress
Δ	Rate of deformation
Ω	Angular velocity, radians/second.

REFERENCES

(1) Ottino, J.M., Chem. Eng. Sci., 35, 1377 (1980).

(2) Marthy, S.N.B., (Ed.) *Turbulent Mixing fin Non-reactive and* Reactive Flows. Plenum Press, New York, 1975.

(3) Levenspiel, O., Chemical Reaction Engineering. Wiley, New York, 1962.

(4) Batchelor, G.K., J. Fluid Mech. 5, 113 (1959).

(5) Danckwerts, P.V., Chem. Eng. Sci., 2, 1 (1953).

(6) Bourne, J.R., Chem. Eng. Sci., 38, 5 (1983).

(7) Nagata, S., 'Mixing' Wiley, New York (1975).

(8) Desouza, A. and R.W. Pike Cand. J. of Chem. Eng. 50, 15 (1972).

(9) Bird, R.B., W.E. Stewart, and E.N. Rightfoot, "Transport Phenomena", Wiley, New York (1960).

(10) Kapral, R., J. of Chem. Phy., 68, 1903 (1978).

(11) North, A.M. 'The Collision theory of Chemical Reactions in Liquids', Wiley, New York (1964).

(12) M.V. Smoluchowski, Phys. Z. 17, 557 (1916).

(13) Weidenbaum, S.S. and C.F. Bonilla: Chem. Eng. Prog., 51, 27 (1955).

(14) Ogawa, K. and S. Ito, J. of Chem. Eng. of Japan 8, 148 (1975).

(15) Bird, R.B. and C.F. Curtiss, Chem. Eng. Sci., 11, 108 (1959).

(16) Peaceman, D.W. and H.H. Rachford, Jr., J. Soc. Indust. Appl. Math, 3, 28 (1955).

(17) Carnahan, B., H.A. Luther and J.O. Wilkes 'Applied Numerical Methods' John Wiley & Sons, Inc. New York, NY (1969).

(18) Bird, R.B., R.C. Armstrong, and O. Hassager "Dynamics of Polymeric Liquids" Wiley, New York (1977).

(19) Porter, G., Progress in Reaction Kinetics, 1, 128 (1961).

(20) Wilemski, G. and M. Fixman, J. Chem. Phy., 58, 4009 (1973).

(21) North, A.M., The Kinetics of Free Radical Polymerization, Pergamon Press, (1966).

(22) Kapral, R., J. of Chem. Phys., 69, 15 (1978).

(23) Ogawa, K., S. Ito, and Y. Matsumura, J. Chem. Eng. Japan 13, 324 (1980).

(24) Takao, M., T. Yamato, Y. Murakami and Y. Sato, J. Chem. Eng. Japan, 11, 481 (1978).