Steady-State Mass Transfer with Homogeneous and Heterogeneous Reactions

A solution is obtained for convective diffusion with axial diffusion and homogeneous and heterogeous reactions in a tube. The results have been used successfully to examine the validity of a model with simplified inlet boundary condition and to establish the conditions for a one-dimensional dispersion model.

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SCOPE

The study of mass transfer of a laminar fluid flowing in a tube with chemical reactions taking place inside the fluid and at the tube wall has been investigated quite extensively in the past with simplified assumptions. Theoretical and experimental investigations previously neglected one or more of the following effects: axial diffusion, homogeneous chemical reaction, and heterogeneous chemical reaction at the wall in order to get the concentration field of the diffusing species.

These assumptions can generally lead to incomplete description of the process or erroneous conclusion of the phenomena (particularly in the entrance region of the tube). Relaxing these assumptions, only one asymptotic solution has been reported for this problem. Another method of analyzing this problem is by the dispersion model approximation. The objective of the present paper is to present a thorough, exact analysis of the problem of laminar-flow, convective diffusion with axial diffusion and homogeneous and heterogeneous reactions in a tube.

CONCLUSIONS AND SIGNIFICANCE

Concentration profiles and Sherwood numbers have been obtained analytically for convective diffusion and chemical reactions in a tube. The results indicate the significant effect of axial diffusion, homogeneous chemical reactions, and heterogeneous chemical reactions from the studies of a wide range of the parameters; i.e., Peclet number Pe, homogeneous reaction parameter K and wall reaction parameter α. When the homogeneous reaction rate parameter is large ($K \geqslant 100$), the effect of the catalytic wall reaction (in the range of $1 \leqslant \alpha \leqslant 100$) on the average concentration of the reactant is negligible.

Both the homogeneous reaction and the heterogeneous reaction tend to decrease the dimensionless inlet average concentration of the reactant from unity. When the chemical reaction parameters become larger, the dimensionless inlet average concentration of the reactant decreases more from unity. The homogeneous reaction has a more significant effect on the reduction of the dimensionless inlet average concentration than that of the heterogeneous reactions. In addition, the mass transfer rate is found to decrease with the axial coordinate of the reactor. The present analysis has been used to test the validity of a simplified dispersion model which is found to be valid for $K \lesssim 1$ and $\alpha \lesssim 1$.

INTRODUCTION

Convective diffusion of a chemical reactant flowing in a tube with homogeneous reaction in the fluid and heterogeneous reaction at the tube wall has been an important area of study in chemical engineering. Early researchers generally neglected the effect of axial diffusion in the investigation of this system.

Among many other works published, Cleland and Wilhelm (1956), Katz (1959), Solomon and Hudson (1967) examined the system analytically and/or experimentally. Another approach of studying this system is by means of one dimensional dispersion model. Wehner and Wilhelm (1956) applied Danckwerts' inlet boundary condition (1953) in their one dimensional dispersion model and found some interesting effects of backmixing in the inlet and outlet region of the tubular reactor. Bischoff (1968) and subsequently Wissler (1969) proposed a zero concentration gradient and zero concentration boundary conditions for the dispersion model with homogeneous chemical reaction, respectively, and Wissler (1969) found that results based on the zero concentration condition at the outlet of the reactor agreed well with the exact calculation. Wan and Ziegler (1970) extended the validity criteria of the dispersion model to first- and second-order chemical reactions.

A more complicated dispersion approximation was investigated by Sankarasubramanian and Gill (1973), DeGance and Jones (1980), and Aris (1980). Emphasis in the dispersion approximation was on the average concentration profile and the dispersion coefficients. Therefore, complete concentration field of the reactant was generally not presented. This provides a need to seek a solution for the complete concentration field.

In some practical situation such as oxygen atom recombination, Dickens et al. (1960) reported that the effect of axial diffusion could become very significant. Walker (1961) presented only an asymptotic solution for the problem of convective laminar flow with axial diffusion and homogeneous and heterogeneous chemical reactions in tubular reactor. In addition to the asymptotic nature of the solutions, Walker (1961) did not consider the effect of axial diffusion at the inlet of the tube. Dang and Steinberg (1980) presented an exact analysis for the same problem of Walker (1961). Their results were only accurate in the downstream region of the reactor due to the uniform inlet reactant concentration.

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It appears from the previous discussions that there does not seem to exist an exact solution for the laminar flow convective diffusion equation with axial diffusion and homogeneous and catalytic wall reactions. The objectives of the present paper are to

(1) Present the concentration distribution and Sherwood number of the chemical reactant flowing inside a tubular reactor with homogeneous and catalytic wall reactions

(2) Investigate the same reactor phenomena as (1) with the application of the inlet boundary condition of Danckwerts (1953)

(3) Propose and examine the validity conditions of a simplified dispersion model of the reactor

ANALYSIS

Consider a chemical reactant with laminar flow inside a reactor. It is convenient to separate the reactor into two regions with region one as $-\infty < x \leqslant 0$ and region two as $0 \leqslant x < \infty$. Assuming the physical properties to be constant and homogeneous and catalytic wall reactions at the tube wall in region two ($0 \leqslant x < \infty$), one can write the convective diffusion equations for the two regions as

$$(1-\eta^2)\frac{\partial\theta_1}{\partial\xi} = \frac{1}{\eta}\frac{\partial}{\partial\eta}\left(\eta\frac{\partial\theta_1}{\partial\eta}\right) + \frac{1}{\mathrm{Pe}^2}\frac{\partial^2\theta_1}{\partial\xi^2} \tag{1}$$

$$(1-\eta^2)\frac{\partial\theta_2}{\partial\xi} = \frac{1}{\eta}\frac{\partial}{\partial\eta}\left(\eta\frac{\partial\theta_2}{\partial\eta}\right) + \frac{1}{\mathrm{Pe}^2}\frac{\partial^2\theta_2}{\partial\xi^2} - K\theta_2 \tag{2}$$

$$\theta_1(-\infty,\eta) = 0 \tag{3}$$

$$\frac{\partial\theta_1{}^{(\xi,0)}}{\partial\theta} = \frac{\partial\theta_1{}^{(\xi,1)}}{\partial\eta} = 0 \tag{4}$$

$$\frac{\partial\theta_2{}^{(\xi,0)}}{\partial\eta} = 0 \tag{5}$$

$$\frac{\partial\theta_2{}^{(\xi,1)}}{\partial\eta} + \alpha\theta_2(\xi,1) = 0 \tag{6}$$

$$\theta_1(0,\eta) = \theta_2(0,\eta) - 1 \tag{7}$$

$$\frac{\partial\theta_1{}^{(0,\eta)}}{\partial\xi} = \frac{\partial\theta_2{}^{(0,\eta)}}{\partial\xi} \tag{8}$$

Solutions of Eqs. 1–8 can be obtained by proposing the following forms

$$\theta_1(\xi,\eta) = \sum_{n=1}^{\infty} A_n Y_n(\eta)\exp[\alpha_n^2\xi] \tag{9}$$

$$\theta_2(\xi,\eta) = \sum_{n=1}^{\infty} B_n R_n(\eta)\exp\left[-\left(K+\frac{1}{\mathrm{Pe}}\right)\beta_n^2\xi\right] \tag{10}$$

Substituting Eq. 9 into Eqs. 1, 4, and Eq. 10 into Eqs. 2, 5 and 6, one can get the governing equations for $Y_n(\eta)$ and $R_n(\eta)$ as

$$\frac{d^2Y_n}{d\eta^2} + \frac{1}{\eta}\frac{dY_n}{d\eta} + \alpha_n^2\left[\frac{\alpha_n^2}{\mathrm{Pe}^2} - (1-\eta^2)\right]Y_n = 0 \tag{11}$$

$$\frac{dY_n{}^{(0)}}{d\eta} = \frac{dY_n{}^{(1)}}{d\eta} = 0 \tag{12}$$

$$\frac{d^2R_n}{d\eta^2} + \frac{1}{\eta}\frac{dR_n}{d\eta} + \left[(1-\eta^2)\left(K+\frac{1}{\mathrm{Pe}}\right)\beta_n^2 - K + \frac{\beta_n^4}{\mathrm{Pe}^2}\left(K+\frac{1}{\mathrm{Pe}}\right)^2\right]R_n = 0 \tag{13}$$

$$\frac{dR_n{}^{(0)}}{d\eta} = 0 \tag{14}$$

$$\frac{dR_n{}^{(1)}}{d\eta} + \alpha R_n(1) = 0 \tag{15}$$

The continuity Eqs. 7 and 8 at the connecting plane $x = 0$ are then

$$-\sum_{n=1}^{\infty} A_n Y_n(\eta) + \sum_{n=1}^{\infty} B_n R_n(\eta) = 1 \tag{16}$$

$$\sum_{n=1}^{\infty} A_n\alpha_n^2 Y_n(\eta) + \left(K+\frac{1}{\mathrm{Pe}}\right)\sum_{n=1}^{\infty} B_n\beta_n^2 R_n(\eta) = 0 \tag{17}$$

Solutions of Eqs. 11–17 will enable us to determine the concentration field of the reactor. However these equations are not Sturm-Liouville type so orthogonal eigenfunction series expansions can not be applied here. To overcome this difficulty, one can first construct an orthornomal set of functions in terms of the nonorthogonal functions $R_n(\eta)$ and $Y_n(\eta)$ in the following manner

$$\psi_j(\eta) = \sum_{n=1}^{j} a_{jn}R_n(\eta) \qquad j = 1,2\cdots\cdots\cdots \tag{18}$$

$$\phi_j(\eta) = \sum_{n=1}^{j} b_{jn}Y_n(\eta) \qquad j=1,2\cdots\cdots\cdots \tag{19}$$

where ψ_j and ϕ_j satisfy the following orthornormal properties

$$\int_0^1 \psi_i\psi_j d\eta = \begin{cases}0 \text{ if } i \neq j\\ 1 \text{ if } i = j\end{cases}; \quad \int_0^1 \phi_i\phi_j d\eta = \begin{cases}0 \text{ if } i \neq j\\ 1 \text{ if } i = j\end{cases} \tag{20}$$

One can then carry out this step by step to obtain

$$\psi_1 = \frac{R_1(\eta)}{\sqrt{\Delta_1}} \tag{21}$$

$$\psi_2 = \frac{\begin{vmatrix} \int_0^1 R_1^2 d\eta & R_1 \\ \int_0^1 R_1R_2 d\eta & R_2 \end{vmatrix}}{\sqrt{\Delta_1\Delta_2}} \tag{22}$$

and in general form

$$\psi_n = \frac{\begin{vmatrix} \int_0^1 R_1^2 d\eta & \int_0^1 R_1R_2 d\eta & \cdots\cdots & \int_0^1 R_1R_{n-1} d\eta & R_1 \\ \int_0^1 R_2R_1 d\eta & \int_0^1 R_2^2 d\eta & \cdots\cdots & \int_0^1 R_2R_{n-1} d\eta & R_2 \\ \vdots & \vdots & & \vdots & \vdots \\ \int_0^1 R_nR_1 d\eta & \int_0^1 R_nR_2 d\eta & \cdots\cdots & \int_0^1 R_nR_{n-1} d\eta & R_n \end{vmatrix}}{\sqrt{\Delta_n\Delta_{n-1}}} \tag{23}$$

where Δ_n is the Gram determinant with its general form as

$$\Delta_n = \begin{vmatrix} \int_0^1 R_1^2 d\eta & \int_0^1 R_1 R_2 d\eta & \cdots & \int_0^1 R_1 R_{n-1} d\eta & \int_0^1 R_1 R_n d\eta \\ \int_0^1 R_2 R_1 d\eta & \int_0^1 R_2^2 d\eta & \cdots & \int_0^1 R_2 R_{n-1} d\eta & \int_0^1 R_2 R_n d\eta \\ \vdots & \vdots & & \vdots & \vdots \\ \int_0^1 R_n R_1 d\eta & \int_0^1 R_n R_2 d\eta & \cdots & \int_0^1 R_n R_{n-1} d\eta & \int_0^1 R_n^2 d\eta \end{vmatrix} \tag{24}$$

Once the functions ψ_n, ϕ_n and their associated coefficients a_n, b_n are determined, one can then express R_n and Y_n in terms of the orthonormal set of functions

$$R_j = \sum_{n=1}^{j} C_{jn}\psi_n \tag{25}$$

$$Y_j = \sum_{n=1}^{j} d_{jn}\phi_n \tag{26}$$

where the elements of the matrix C_{jn} are obtained from

$$[C_{jn}] = \begin{vmatrix} a_{11} & 0 & \cdots & \cdots & 0 \\ a_{21} & a_{22} & \cdots & \cdots & 0 \\ a_{31} & a_{32} & a_{33} & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ a_{n1} & a_{n2} & a_{n3} & \cdots & a_{nn} \end{vmatrix}^{-1} \tag{27}$$

The matrix of d_{jn} can be expressed in terms of the coefficients b_{jn} in a similar form of Eq. 27. Once $R_n(\eta)$ and $Y_n(\eta)$ are in terms of the orthonormal functions ψ_n and ϕ_n, one can then substitute them in Eqs. 16 and 17 to obtain

$$-\sum_{n=1}^{\infty}\sum_{j=n}^{\infty} A_j d_{jn}\phi_n + \sum_{n=1}^{\infty}\sum_{j=n}^{\infty} B_j C_{jn}\psi_n = 1 \tag{28}$$

$$\sum_{n=1}^{\infty}\sum_{n=j}^{\infty} A_j\alpha_j^2 d_{jn}\phi_n + \left(K + \frac{1}{\mathrm{Pe}}\right)\sum_{n=1}^{\infty}\sum_{j=n}^{\infty} B_j\beta_j^2 C_{jn}\psi_n = 0 \tag{29}$$

Since ϕ_n and ψ_n are orthonormal functions, one can multiply Eq. 28 by ψ_m and Eq. 29 by ϕ_m and then integrate with respect to η from 0 to 1, we then get

$$\sum_{n=m}^{\infty} B_n C_{nm} - \sum_{n=1}^{\infty} A_n\left(\sum_{j=1}^{n} d_{nj}\int_0^1 \phi_j\psi_m d\eta\right) = \int_0^1 \psi_m d\eta \tag{30}$$

$$\left(K + \frac{1}{\mathrm{Pe}}\right)\sum_{n=1}^{\infty} B_n\beta_n^2\left(\sum_{j=1}^{n} C_{nj}\int_0^1 \psi_j\phi_m d\eta\right) + \sum_{n=m}^{\infty} A_n\alpha_n^2 d_{nm} = 0 \tag{31}$$

In practice, the series summation in Eqs. 30 and 31 can be truncated with finite terms. In this paper, most of the calculation is based on twenty terms although fifty terms are used sometimes. By considering n terms in the series in Eqs. 30 and 31, we can solve these two equations in matrix form as

$$[A][X] = [E]$$

or

$$[X] = [A]^{-1}[E] \tag{32}$$

where

$$[X] = \begin{bmatrix} B_1 \\ B_2 \\ \vdots \\ B_n \\ A_1 \\ A_2 \\ \vdots \\ A_n \end{bmatrix}, \quad [E] = \begin{bmatrix} \int_0^1 \psi_1 d\eta \\ \int_0^1 \psi_2 d\eta \\ \vdots \\ \int_0^1 \psi_n d\eta \\ 0 \\ \vdots \\ 0 \end{bmatrix}$$

$$[A] = \begin{bmatrix} C_{11} & C_{21} & \cdots & C_{n1} & -d_{11}\int_0^1 \phi_1\psi_1 d\eta & \cdots & \cdots & -\sum_{j=1}^{n} d_{nj}\int_0^1 \phi_j\psi_1 d\eta \\ 0 & C_{22} & \cdots & C_{n2} & \vdots & & & \vdots \\ \vdots & \vdots & & \vdots & \vdots & & & \vdots \\ 0 & 0 & \cdots & C_{nn} & -d_{11}\int_0^1 \phi_1\psi_n d\eta & \cdots & \cdots & -\sum d_{nj}\int_0^1 \phi_j\psi_n d\eta \\ \left(K+\frac{1}{\mathrm{Pe}}\right)\beta_1^2 C_{11}\int_0^1 \psi_1\phi_1 d\eta & \cdots & \cdots & \left(K+\frac{1}{\mathrm{Pe}}\right)\beta_n^2\sum_{j=1}^{n} C_{nj}\int_0^1 \psi_j\phi_1 d\eta & \alpha_1^2 d_{11} & \alpha_2^2 d_{21} & \cdots & \alpha_n^2 d_{n1} \\ \vdots & & & \vdots & 0 & \alpha_2^2 d_{22} & \cdots & \alpha_n^2 d_{n2} \\ \vdots & & & \vdots & \vdots & \vdots & & \vdots \\ \left(K+\frac{1}{\mathrm{Pe}}\right)\beta_1^2 C_{11}\int_0^1 \psi_1\phi_n d\eta & \cdots & \cdots & \left(K+\frac{1}{\mathrm{Pe}}\right)\beta_n^2\sum_{j=1}^{n} C_{nj}\int_0^1 \psi_j\phi_n d\eta & 0 & 0 & \cdots & \alpha_n^2 d_{nn} \end{bmatrix}$$

The average concentration for the two regions can be determined as

$$C_b(x) = \frac{\int_0^a U_m\left[1 - \left(\frac{r}{a}\right)^2\right] Crdr}{\int_0^a U_m\left[1 - \left(\frac{r}{a}\right)^2\right] rdr}$$

In terms of dimensionless quantities from Eqs. 9 and 10, one has

$$\theta_{1b}(\xi) = 1 + 4 \sum_{n=1}^{\infty} A_n \exp(\alpha_n^2 \xi) \frac{\alpha_n^2}{\mathrm{Pe}^2} \int_0^1 \eta Y_n d\eta \quad (33)$$

$$\theta_{2b}(\xi) = 4 \sum_{n=1}^{\infty} B_n \exp\left[-\left(K + \frac{1}{\mathrm{Pe}}\right)\beta_n^2 \xi\right] \times \int_0^1 (1 - \eta^2) R_n(\eta) \eta d\eta \quad (34)$$

From Eqs. 13–15, one can rewrite Eq. 34 in the following form

$$\theta_{2b}(\xi) = 4 \sum_{n=1}^{\infty} \frac{B_n \exp\left[-\left(K + \frac{1}{\mathrm{Pe}}\right)\beta_n^2 \xi\right]}{\beta_n^2 \left(K + \frac{1}{\mathrm{Pe}}\right)} \times \left\{\alpha R_n(1) + \left[K - \frac{\beta_n^4}{\mathrm{Pe}^2}\left(K + \frac{1}{\mathrm{Pe}}\right)^2\right] \int_0^1 \eta R_n d\eta\right\} \quad (35)$$

One can define the mass transfer coefficient k_L as

$$k_L = \frac{\int_0^x - D \left.\frac{\partial C_2}{\partial r}\right|_{r=a} dx}{x[C_{2b}(0) - C_{2b}(x)]}$$

Then the Sherwood number can be determined as

$$Sh = \frac{K_L 2a}{D} = \frac{\frac{2\alpha}{(K + 1/\mathrm{Pe})} \sum_{n=1}^{\infty} B_n R_n(1) \left[\frac{1 - e^{-(K + 1/\mathrm{Pe})\beta_n^2 \xi}}{\beta_n^2}\right]}{\xi[\theta_{2b}(0) - \theta_{2b}(\xi)]} \quad (36)$$

RESULTS AND DISCUSSIONS

Equations 11–15 are solved by the Runge-Kutta method and Eq. 32 is solved by the Gauss-Seidel method. Generally accuracy with tolerance of 10^{-10} is used in solving Eqs. 11–15 and 32. The range of parameters investigated in this work is $1 \leq \mathrm{Pe} \leq 20$, $1 \leq K \leq 100$, and $1 \leq \alpha \leq 100$. Due to the catalytic wall boundary condition in the present problem, the number of terms required in the series expansion solution of Eqs. 9 and 10 varies. When the wall reaction parameter α is large (i.e., $\alpha = 100$), more terms are generally required in the series expansion. A comparison has been made for the dimensionless average concentration and the Sherwood number when twenty and fifty terms are used in the series expansions. When Pe = 5, $K = 1$ and $\alpha = 100$; the deviation of the dimensionless average concentration by using twenty and fifty terms in the series expansion is less than 0.8% for all axial coordinate. However, the deviation of the Sherwood number by using twenty and fifty terms varies with the axial coordinate of the reactor. The error is 24%, 19%, 7%, 4%, 1%, 0.1% for $x/a = 0.001$, 0.009, 0.049, 0.099, 1.009, 3.109 respectively. Therefore, the error of the Sherwood number using twenty terms decreases in the downstream of the reactor.

Two limiting cases, i.e. $K = 0$ or $\alpha = 0$, can be obtained from the present analysis. When there is no catalytic wall reaction, $\alpha = 0$, Dang (1978) showed the interaction effect of homogeneous chemical reaction and axial diffusion on the concentration field. Results were also obtained for the limiting case where there is no homogeneous chemical reaction, i.e., $K = 0$. Comparing to the case without chemical reactions, one finds that the dimensionless average inlet concentration is deviated further from unity and the length of the reactor for the dispersion model to be valid increases when either homogeneous or heterogeneous chemical reaction occurs. When both homogeneous and heterogeneous reactions take place, the effect of chemical reactions on the concentration field is more significant. This can be expected from the superposition of different mechanisms such as reaction, diffusion and fluid flow on the concentration field because of a linear system considered here.

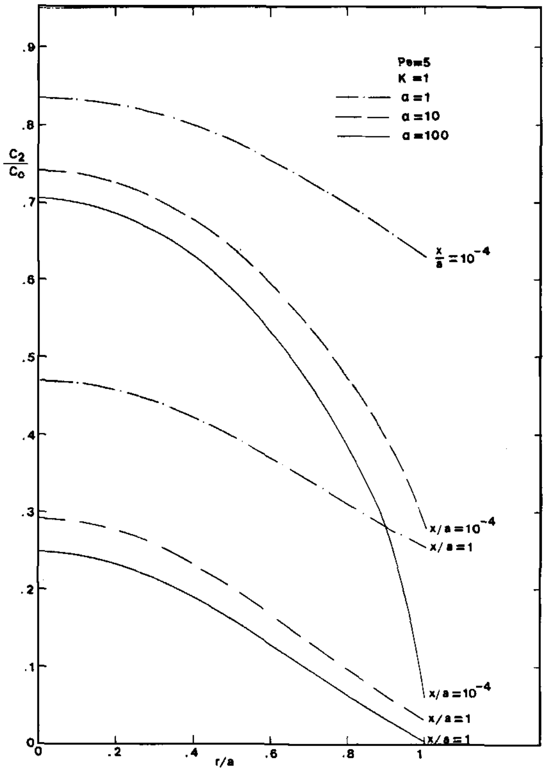

Figure 1. Dimensionless radial concentration distribution at two different axial position ($0 \leq x/a < \infty$) for various values of wall reaction parameter (α = 1, 10, 100) and Pe = 5, K = 1.

Presented in Figure 1 is the dimensionless radial concentration for Pe = 5, $K = 1$ and $\alpha = 1$, 10, 100 at two axial distances in the second region of the reactor. When the Peclet number decreases, the effect of back mixing increases so the concentration profile becomes flatter for the same values of K and α. When the wall reaction parameter α increases, the radial concentration profile becomes steeper. Because of convective diffusion and homogeneous chemical reaction, the radial concentration profile becomes flatter in an axial distance further away from the inlet planes $x = 0$.

The dimensionless average concentrations for both regions one and two along the axial coordinate of the reactor for Pe = 1, 5, 10, $K = 10$ and $\alpha = 1$, 10, 100 is shown in Figure 2. It is seen that the effect of axial diffusion causes the penetration of the reactant to the upstream section of the reactor (region one) so that the dimensionless average concentration at $x = 0$ is less than unity. When the Peclet number decreases, the dimensionless average concentration at $x = 0$ deviates more from unity. At $K = \alpha = 1$, the dimensionless average concentration at $x = 0$ is 0.2710, 0.7625, 0.9039 and 0.9470 for Pe = 1, 5, 10 and 20 respectively. Because both the homogeneous and the heterogeneous chemical reactions act like a sink to the reactant, the effect of these reactions can superimpose to the effect of the axial diffusion on the dimensionless average concentration. The larger the values of the reaction parameter; the larger the deviation of the dimensionless average concentration from unity. The effect of axial diffusion can also be observed throughout the whole reactor. When the Peclet number is small, the dimensionless average concentration penetrates further distance upstream (region one) to reach the inlet constant concentration but it takes a shorter distance in the downstream (region two) to deplete the reactant. This indicates the effect of strong back mixing. As one

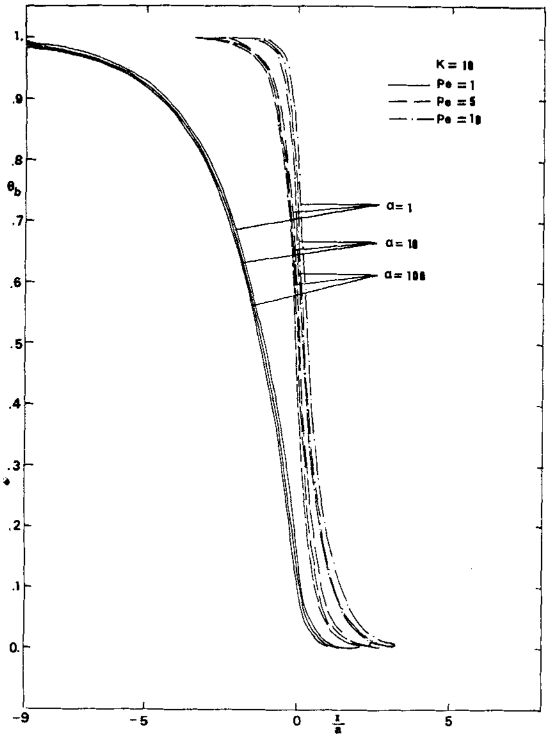

Figure 2. Dimensionless average concentration vs. dimensionless axial distance. K = 10; Pe = 1, 5, 10; α = 1, 10, 100.

would expect, the effect of the wall reaction is more significant in the radial concentration profile than the axial concentration profile. But the effect of homogeneous chemical reaction is very significant in the axial concentration profile, particularly at large values of K. At $K = 100$, the dimensionless average concentration is the same for $\alpha = 1, 10, 100$ and Pe = 1, 5, 10. At this large value of K, homogeneous chemical reaction has a more dominating effect than the wall reaction on the dimensionless average concentration. Therefore, indistinguishable values of the dimensionless average concentrations are observed for different values of $\alpha = 1, 10, 100$. Furthermore the dimensionless average reactant concentration decreases to practically zero at $x/a \simeq 1$ when $K = 100$.

The Sherwood number as a function of axial coordinate for Pe = 1, $K = 1, 10, 100$ and $\alpha = 1, 10, 100$ is shown in Figure 3. Along the axial distance of the reactor, the radial concentration gradient decreases because the concentration of the reactant depletes in the downstream of the reactor as can be seen in Fig. 1. Therefore the Sherwood number decreases rapidly along the axial coordinate of the reactor. It is found that there exists a complicated interaction effect of the flow field and the chemical reaction. When the homogeneous reaction parameter K is small, the Sherwood number will increase when the Peclet number increases for all values of the wall reaction parameter α. For example, at $x/a = 1$, $K = 1$ and $\alpha = 100$; Sherwood number is 3.24, 4.39 and 6.62 for Pe = 1, 5 and 10 respectively. However, when the homogeneous reaction parameter K becomes large, the Sherwood number decreases when the Peclet number increases for all values of the wall reaction parameter α. For example, at $x/a = 1$, $K = 100$, the Sherwood number is 1.79, 1.45 and 1.32 for Pe = 1, 5 and 10, respectively. When K is small, the rate controlling step on the radial concentration gradient and hence the Sherwood number is the homogeneous chemical reaction and the effect of axial diffusion is less important. Therefore the Sherwood number is larger as Peclet number increases. When K becomes large, the rate controlling step on the radial concentration gradient is the axial diffusion so the Sherwood number decreases as Peclet number increases.

It is possible to obtain the asymptotic inlet concentration of the reactant by using the first term of the series expansion from Eq. 35 as

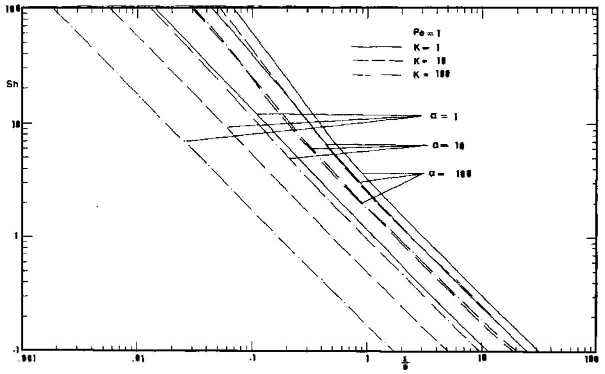

Figure 3. Sherwood number vs. axial distance for Pe = 1; K = 1, 10, 100 and α = 1, 10, 100.

$$\theta_{2b}(0) = \frac{4B_1}{\beta_1^2\left(K+\frac{1}{\mathrm{Pe}}\right)}\left\{\alpha R_1(1) + \left[K - \frac{\beta_1^4}{\mathrm{Pe}^2}\left(K+\frac{1}{\mathrm{Pe}}\right)^2\right]\int_0^1 \eta R_1 d\eta\right\} \tag{37}$$

Comparison of this asymptotic expression with the exact analysis of Eq. 35 shows an error of 0.19%–6.5% depending on the values of Pe, K and α. The error is larger when the values of K and α become larger.

By truncating the series in Eq. 36 for large ξ, one can obtain an asymptotic Sherwood number for the downstream of the reactor as

$$\mathrm{Sh} = \frac{\alpha R_1(1)}{2\xi\left\{\alpha R_1(1) + \left[K - \frac{\beta_1^4}{\mathrm{Pe}^2}\left(K+\frac{1}{\mathrm{Pe}}\right)^2\right]\int_0^1 \eta R_1 d\eta\right\}} \tag{38}$$

This asymptotic expression is good for small values of K and α ($K \lesssim 1$, $\alpha \lesssim 1$) for all the values of the Peclet number considered in the present analysis. For $K = \alpha = 1$ and Pe = 1, 10, the error of application of Eq. 38 is about 10% and 1% at $\xi = 1$ and 10 respectively. Therefore, Eq. 38 can be used well for the downstream of the reactor.

SIMPLIFIED ANALYSIS

One can analyze the present problem by means of a convective diffusion boundary condition as used by Danckwerts (1953), Wehner and Wilhelm (1956). In this manner, only a semi-infinite region needs to be considered and the analysis becomes simpler. In this manner, only Eqs. 2, 5 and 6 together with the following inlet boundary condition will be considered

$$\frac{1}{\mathrm{Pe}^2}\frac{\partial \theta_2}{\partial \xi} = (1-\eta^2)(\theta_2 - 1) \qquad \text{at } \xi = 0 \tag{39}$$

The solution of this set of Eqs. is still the same form as Eq. 10. To determine the coefficients B_n in Eq. 10, one has to substitute Eq. 10 in Eq. 39 and then makes use of Eqs. 13–15 to obtain the following set of linear algebraic equations. This procedure is similar to the one proposed by Dang (1980).

$$B_n J_n + \sum_{\substack{m=1 \\ m \neq n}}^{\infty} \Gamma_{n,m} B_m = I_n \qquad n = 1,2,3\ldots \tag{40}$$

where

$$J_n = \int_0^1 \left[(1-\eta^2) + \frac{1}{\mathrm{Pe}^2}\left(K+\frac{1}{\mathrm{Pe}}\right)\beta_n^2\right] R_n^2 \eta d\eta \tag{41}$$

$$\Gamma_{n,m} = \frac{\left(K+\frac{1}{\mathrm{Pe}}\right)\beta_n^2}{\mathrm{Pe}^2}\int_0^1 R_n R_m \eta d\eta \tag{42}$$

$$I_n = \int_0^1 (1 - \eta^2) R_n \eta d\eta \qquad (43)$$

B_n are determined by solving a set of algebraic Eqs. 40 by Gauss-Seidel method after Eqs. 41–43 are evaluated. The dimensionless average concentration and Sherwood number have the same form as Eqs. 35 and 36 respectively.

In addition to the simplicity of the solution compared to the exact analysis, the series expansion for the dimensionless concentration converges more rapidly by the simplified method. A comparison of the dimensionless inlet concentration between the exact analysis and the simplified solution is made. Good agreement can be obtained between these two methods as Peclet number becomes larger. The dimensionless average concentration and Sherwood number also show good agreement between these two methods at the downstream of the reactor. The error of the dimensionless inlet average concentration applying this method lies between 0.5% for Pe = 20, $K = 1$, $\alpha = 1$ to 51.44% for Pe = 1, $K = 1$, $\alpha = 1$ for the parameters investigated. The error increases when K or α increases or Pe decreases.

COMPARISON WITH DISPERSION MODEL

It is possible to propose a steady-state Taylor-type dispersion model with the inlet boundary condition similar to that of Danckwerts as

$$K_2 \frac{d^2C}{dx^2} + K_1 \frac{dC}{dx} + (K_0 - K)C = 0 \qquad (44)$$

and the inlet and exit boundary conditions are

$$x = 0, \qquad K_1 C + K_2 \frac{dC}{dx} = K_1 C_0 \qquad (45)$$

$$x = \infty, \qquad C = 0 \qquad (46)$$

where K_0, K_1 and K_2 are the effective wall reaction, convection and dispersion coefficients in the dispersion of the reactant in the concentration field. K is the homogeneous first-order chemical reaction.

Solution of Eqs. 44–46 is then

$$\frac{C}{C_0} = \frac{2}{1 + \sqrt{1 - \frac{4K_2}{K_1^2}(K_0 - K)}} \exp\left\{\frac{-1 + \sqrt{1 - 4\frac{K_2}{K_1^2}(K_0 - K)}}{2K_2/K_1} x\right\} \qquad (47)$$

When there is no surface wall reaction K_0, Wan and Ziegler (1970), Wissler (1969) and Bischoff (1968) established some criterion for the validity of the dispersion model without considering the effect of axial molecular diffusion. Since axial molecular diffusion is considered in the present analysis, it is worthwhile to compare the proposed dispersion model, Eq. 47 with the present analysis. In this case, $K_1 = -U_{av}$ and $K_2 = D + a^2U_{av}^2/48D$ in Eq. 47. Comparison has been made between the present analysis with the proposed dispersion model for some values of the parameter Pe and K. Two dimensionless quantities, xU_{av}/D_L and Kx/U_{av}, have been used previously as an indication for the validity of the dispersion model.

$$\frac{xU_{av}}{D_L}\left(= \frac{x/U_{av}}{\frac{D}{U_{av}^2} + \frac{a^2}{48D}}\right)$$

can be considered as the ratio of the residence time of the reactant to the combined time of the axial convective transport and the radial diffusive transport together. When the radial diffusive transport is rapid, the radial concentration gradient is negligible and the dispersion model which assumes the lumped concentration at each cross section becomes more realistic. Kx/U_{av} can be considered as the ratio of the residence time to the reaction time in the tube. For a slow reaction or long reaction time constant compared with the residence time of the reactant, it is expected that the dispersion model to be valid according to Taylor criterion. Another important parameter is K $(= ka^2/D)$ which can be considered as the ratio of the radial diffusioin time to the chemical reaction time. When the radial diffusion time is shorter than the chemical reaction time, it is then expected that the one dimensional axial dispersion model to be valid. Similar to the non-reactive case, small radial diffusion time implies negligible radial concentration gradient and the dispersion model can be used to approximate for the realistic situations the deviation from the plug flow model. Comparison of the results of the dispersion model and the exact analysis in Table 1 follows closely with the physical interpretation above. At $K \gtrsim 1$, good comparison is obtained between the dispersion model and the exact analysis. Furthermore, at $xU_{av}/D_L \gtrsim 1$, the comparison between the dispersion model and the exact analysis is even better.

TABLE 1. COMPARISON BETWEEN THE PRESENT ANALYSIS AND THE DISPERSION MODEL WITH HOMOGENEOUS CHEMICAL REACTION

$K = 1$

x/a	Present Analysis Eq. 35	Dispersion Model Eq. 47	$\frac{xU_{av}}{D_L}\left(= \frac{x/U_{av}}{\frac{D}{U_{av}^2} + \frac{a^2}{48D}}\right)$	$\frac{Kx}{U_{av}}$
Pe = 1				
0	0.3923	0.3896	0	0
0.2	0.3359	0.3334	0.0995	0.4
0.4	0.2875	0.2853	0.1990	0.8
0.6	0.2461	0.2441	0.2984	1.2
0.8	0.2106	0.2089	0.3979	1.6
1.0	0.1802	0.1787	0.4974	2.0
1.5	0.1221	0.1211	0.7461	3.0
2.0	0.0827	0.0820	0.9948	4.0
4.0	0.0174	0.0173	1.9896	8.0
6.0	0.0037	0.0036	2.9844	12.0
Pe = 5				
0	0.8773	0.8648	0	0
0.1	0.8481	0.8354	0.2212	0.04
0.3	0.7921	0.7795	0.6636	0.12
0.5	0.7396	0.7274	1.106	0.2
1.	0.6226	0.6119	2.212	0.4
1.5	0.5238	0.5147	3.318	0.6
2.0	0.4407	0.4330	4.424	0.8
4.0	0.2207	0.2168	8.848	1.6
6.0	0.1105	0.1085	13.272	2.4
8.0	0.0553	0.0543	17.696	3.2
10.	0.0277	0.0272	22.12	4.0
Pe = 10				
0	0.9418	0.9456	0	
0.5	0.8678	0.8604	1.644	0.1
1	0.7946	0.7828	3.288	0.2
2	0.6598	0.6480	6.576	0.4
3	0.5464	0.5364	9.864	0.6
4	0.4523	0.4440	13.152	0.8
5	0.3744	0.3676	16.44	1.0
6	0.3099	0.3043	19.73	1.2
7	0.2565	0.2519	23.02	1.4
8	0.2123	0.2085	26.30	1.6
9	0.1757	0.1726	29.59	1.8

Comparison has also been made between the present analysis and the dispersion model when catalytic wall reaction is considered. Some of the results are shown in Table 2. Dispersion coefficients K_0, K_1 and K_2 calculated from Sankarasubramanian and Gill (1973) are used in Eq. 47. The parameter $\alpha (= k_w a/D)$ can be considered as the ratio of the radial diffusion time to the wall reaction depletion time. When the wall reaction is slow compared to the radial diffusion, the radial concentration gradient can be

TABLE 2. COMPARISON BETWEEN THE PRESENT ANALYSIS AND THE DISPERSION MODEL WITH HOMOGENEOUS AND HETEROGENEOUS REACTIONS AT THE WALL

$K = 1, \alpha = 1$

x/a	Present Analysis Eq. 35	Dispersion Model Eq. 47	$\frac{xU_{av}}{D_L}$ $\left(= \frac{x/U_{av}}{\frac{D}{U_{av}^2} + \frac{a^2}{48D}} \right)$	$\frac{K_x}{U_{av}}$
Pe = 1				
0	0.2710	0.2979	0	0
0.509	0.1402	0.1505	0.2532	1.018
1.009	0.0720	0.0769	0.5019	2.018
2.109	0.0165	0.0176	1.049	4.218
3.109	0.0043	0.0046	1.546	6.218
4.109	0.0011	0.0012	2.044	8.218
5.109	0.0003	0.0003	2.541	10.218
Pe = 5				
0	0.7625	0.7829	0	0
0.510	0.5390	0.5467	1.126	0.204
1.010	0.3797	0.3841	2.232	0.404
2.110	0.1750	0.1768	4.665	0.844
3.110	0.0864	0.0873	6.877	1.244
4.110	0.0427	0.0431	9.089	1.644
5.110	0.0211	0.0212	11.301	2.044
7.110	0.0051	0.0052	15.725	2.844
Pe = 10				
0	0.9039	0.9038	0	0
0.51	0.7373	0.7346	1.674	0.102
1.01	0.6014	0.5993	3.318	0.202
2.11	0.3842	0.3829	6.934	0.422
3.11	0.2557	0.2549	10.222	0.622
4.11	0.1702	0.1696	13.510	0.822
5.11	0.1133	0.1129	16.798	1.022
7.11	0.0502	0.0500	23.374	1.422
9.11	0.0222	0.0222	29.950	1.822
Pe = 20				
0	0.9650	0.9473	0	0
0.509	0.8630	0.8498	1.651	0.052
1.009	0.7732	0.7638	3.273	0.102
2.109	0.6096	0.6040	6.840	0.212
3.109	0.4921	0.4880	10.083	0.312
4.109	0.3975	0.3942	13.327	0.412
5.109	0.3211	0.3184	16.570	0.512
7.109	0.2096	0.2078	23.056	0.712
9.109	0.1368	0.1356	29.543	0.912
11.109	0.0893	0.0885	36.030	1.112
21.109	0.0106	0.0105	68.462	2.112

neglected and it is reasonable to approximate the system by the dispersion model. Therefore, one can see good agreement between the dispersion model and the exact analysis for $K = 1$, $\alpha = 1$. In addition to the small values of the parameters K and α, one finds that the dispersion model can represent the realistic phenomena more closely at $xU_{av}/D > 1$ in Table 2 in the same manner as the case without surface wall reaction discussed above. When $K > 1$, $\alpha > 1$; the dispersion model deviates from the exact analysis. The deviation is larger as K and/or α becomes larger. Hence, the one dimensional dispersion model can be used for $K \lesssim 1$ and $\alpha \lesssim 1$.

NOTATION

a = radius of tube
A_n = series expansion coefficients in Eq. 9
B_n = series expansion coefficients in Eq. 10
C = concentration of reactant
C_0 = inlet concentration
C_b = average concentration
D = molecular diffusivity
D_L = dispersion coefficient, $D + a^2U^2_{av}/48D$
I_n = integral defined by Eq. 43
J_n = integral defined by Eq. 41
k = first order homogeneous reaction rate constant
k_L = mass transfer coefficient
k_w = surface wall reaction rate constant
K = ka^2/D
Pe = aU_m/D
K_0 = effective wall reaction coefficient in the dispersion model Eq. 44
K_1 = effective convection coefficient in the dispersion model, Eq. 44
K_2 = effective dispersion coefficient in the dispersion model, Eq. 44
r = radial coordinate
R_n = eigenfunction in Eq. 10
Sh = $2k_La/D$
u = point velocity
U_{av} = average velocity
U_m = maximum velocity
x = axial coordinate
Y_n = eigenfunction in Eq. 9

Greek Symbols

α = k_wa/D
α_n = eigenvalues in Eq. 9
β_n = eigenvalues in Eq. 10
$\Gamma_{n,m}$ = integral defined by Eq. 42
θ = C/C_0
θ_1 = $(C_1 - C_0)/C_0$
θ_2 = C_2/C_0
θ_b = C_b/C_0
η = r/a
ξ = x/aPe

Subscripts

1 = region one without chemical reaction
2 = region two with chemical reaction

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Manuscript received April 6, 1981; revision received September 18, and accepted January 13, 1982.