Martinelli, R. C., L. M. Boelter, E. B. Weinberg, and S. Yakal, "Heat Transfer to a Fluid Flowing Periodically at Low Frequency in a Vertical Tube," *ibid.*, 65, 789 (1943).
McMichael, W. J., "Interphase Heat and Mass Transfer in Pulsatile Flow," Ph.D. thesis, Rice Univ., Texas (1972).
Romie, F. E., "Heat Transfer to Fluids Flowing with Velocity Pulsations in a Pipe," Ph.D. dissertation, Univ. California, Los Angeles (1956).
Sexl, T., as reported by H. Schlichting, *Boundary Layer Theory*, pp. 229-230 (1960).
West, F. B., and A. T. Taylor, "The Effect of Pulsations on Heat Transfer," *Chem. Engr. Progr.*, 48, 39 (1952).

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Diffusion and Reaction in Turbulent Flow of a Power-Law Fluid in a Circular Tube

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Simultaneous diffusion and homogeneous reaction during the turbulent flow of a power-law fluid in a tubular reactor has been studied using the correlations for the velocity profile and eddy diffusivity proposed by Krantz and Wasan. The results of the theory indicate that while the cup-mixing concentration is unaffected by variations in the Reynolds number, the Schmidt number, or the flow behavior index, it is significantly influenced by the reaction parameter and the reaction order.

SCOPE

The flow of a non-Newtonian fluid in various geometries is a problem that has received considerable attention in recent years. For the turbulent flow of a power-law fluid in a pipe, Krantz and Wasan presented correlations for both velocity profile and eddy diffusivity and predicted significant influence of non-Newtonianism on the axial dispersion coefficient. However, the role of non-Newtonianism on chemical reaction in tubular reactors has not been determined so far.

In this work, simultaneous diffusion and homogeneous reaction in a tubular reactor for the turbulent flow of a power-law fluid has been investigated using the velocity profile and eddy diffusivity correlations proposed by Krantz and Wasan. The resulting differential equation has been solved for Neumann boundary conditions using the Crank-Nicholson finite difference sheme.

CONCLUSIONS AND SIGNIFICANCE

The dimensionless cup-mixing concentration is unaffected by variations in the Reynolds number or the flow behavior index since the dimensionless velocity profile for the turbulent flow of a power-law fluid changes by less than 10%, even for wide variations in these parameters. The conversion is insensitive to variations in Schmidt numbers ranging from 10 to 10^6. However, the length of a reactor for a given conversion is inversely proportional to the reaction parameter for all orders of reaction. Furthermore, the cup-mixing concentration is significantly influenced by the reaction order, the conversion being larger for reactions of lower order. It is therefore concluded that for simultaneous diffusion and reaction in turbulent tubular flow of a power law fluid the major factors influencing the conversion are the reaction parameter and reaction order.

The problem of diffusion and reaction in isothermal tubular reactors has received much attention. The laminar flow of Newtonian fluids has been widely studied starting with the work of Lauwerier (1959), Cleland and Wilhelm (1956), and Hsu (1965) for single homogeneous first-order reactions, Vignes and Trambouze (1962) for second-order reactions, Wissler and Schechter (1961) for consecutive first-order reactions and, Walker (1961) and Solomon and Hudson (1967) for simultaneous homogeneous and heterogeneous first-order reactions. The turbulent flow situation, on the other hand, has been neglected. The wall catalyzed first-order reaction was studied by Wissler and Schechter (1962) for the turbulent flow of a Newtonian fluid in a circular tube and by Randhava and Wasan (1972a) for reactions of arbitrary orders. The corresponding problem for homogeneous reactions with Dirichlet boundary conditions was analyzed by Randhava and Wasan (1971, 1972b).

From a practical standpoint, the analogous problem for the flow of non-Newtonian fluids deserves more attention

than what it has received so far. Non-Newtonian flow is encountered in a variety of situations including processing of liquid foods and biological treatment of wastes. The only work to the authors' knowledge is that of Homsy and Strohman (1971) who treated the problem of diffusion and first-order irreversible reaction during the laminar flow of power law and Prandtl-Eyring fluids in a tubular reactor. The corresponding turbulent flow problem for the power-law fluid has not been studied so far.

It is the objective of this work to study the simultaneous diffusion and homogeneous reaction in a tubular reactor for the turbulent flow of a power-law fluid using the velocity profile and eddy diffusivity correlations proposed by Krantz and Wasan (1971, 1974) and to evaluate the role of non-Newtonianism and the reaction parameters.

THEORETICAL DEVELOPMENT

Consider the turbulent flow of a power-law fluid in a tubular reactor in which an irreversible mth-order reaction occurs in the bulk. The diffusion in the axial direction is neglected compared to the convective terms. The governing differential equation is

$$u\frac{\partial c}{\partial x} = \frac{1}{r}\frac{\partial}{\partial r}\left(\alpha r \frac{\partial c}{\partial r}\right) - kc^m \tag{1}$$

where $\alpha = D + \epsilon_D$ is the total diffusivity in the radial direction, D is the molecular diffusion coefficient and ϵ_D, the radial diffusivity for mass transfer.

The boundary conditions are

$$\frac{\partial c}{\partial r} = 0 \quad \text{at} \quad r = 0 \quad \text{and} \quad r = R \tag{2}$$

$$c = c_0 \quad \text{at} \quad x = 0$$

Equation (1) is made dimensionless by defining the groups

$$z = r/R; \quad u^+ = u/u_*; \quad \alpha^+ = \alpha/Ru_*; \quad W = c/c_0; \tag{3}$$

$$\beta = kRc_0^{m-1}/\langle u\rangle; \quad \text{and} \quad \xi = xkc_0^{m-1}/\langle u\rangle.$$

Thus, Equation (1) becomes

$$u^+\frac{\partial W}{\partial \xi} = \frac{1}{\beta z}\frac{\partial}{\partial z}\left(\alpha^+ z \frac{\partial W}{\partial z}\right) - \frac{\langle u\rangle}{u_*} W^m \tag{4}$$

The boundary conditions become

$$\frac{\partial W}{\partial z} = 0 \quad \text{at} \quad z = 0 \text{ and } 1 \tag{5}$$

$$W = 1 \quad \text{at} \quad \xi = 0$$

The velocity profile in the turbulent core region was given by Bogue and Metzner (1963)

$$u^+ = 2.42 \ln\left(\frac{1-z}{n\psi}\right) + C(z,f) + I(n, Re) \qquad (0 \le z \le z_c) \tag{6}$$

where

$$\psi = \frac{2(f/2)^{(n-2)/2n}}{\left(\frac{3n+1}{4}\right)8^{(n-1)/n}Re^{1/n}} \tag{7}$$

and f is the Fanning friction factor and Re, the generalized Reynolds number for the non-Newtonian fluid defined as (Dodge and Metzner, 1959)

$$Re = 2R\langle u\rangle/\nu$$

with ν, the generalized non-Newtonian viscosity given by

$$\nu = \left(\frac{3n+1}{4n}\right)^n \left(\frac{4\langle u\rangle}{R}\right)^{n-1} K/\rho$$

The functions $C(z, f)$ and $I(n, Re)$ are defined by

$$C(z,f) = 0.05\sqrt{2/f}\exp\left[-(0.2-z)^2/0.15\right] \tag{8}$$

$$I(n, Re) = -2.42 \ln\left\{\left(\frac{3n+1}{8n}\right)\left[Re(f/2)^{(2-n)/2}8^{n-1}\right]^{1/n}\right\} + 3.63 + 0.984\sqrt{2/f} \tag{9}$$

The friction factor appearing in Equations (6) to (9) is obtained from the correlation of Dodge and Metzner (1959)

$$\frac{1}{\sqrt{f}} = \frac{4}{n^{0.75}}\log\left\{Re\, f^{(2-n)/2}\right\} - \frac{0.4}{n^{1.2}} \tag{10}$$

The dimensionless radial coordinate z is related to the dimensionless distance from the wall by

$$z = 1 - n\psi y^+ \tag{11}$$

where

$$y^+ = y\, u_*^{(2-n)/n}(\rho/K)^{1/n}$$

The edge of the turbulent core $z = z_c$ is obtained using Equation (11) and the expression for y_c^+ given by Krantz and Wasan (1971)

$$0.6\, y_c^+ - \frac{3}{20}\psi (y_c^+)^2 - \frac{1}{60}(n-1)\psi^2 (y_c^+)^3 + 1.09 = 2.42 \ln y_c^+ + I(n, Re) \tag{12}$$

For the wall region, the velocity distribution developed by Krantz and Wasan (1971) is used.

$$u^+ = \left[1 - \frac{\psi}{2}y^+ - \frac{(n-1)}{6}\psi^2 (y^+)^2\right] y^+ + U_4^+ (y^+)^4 + U_5^+ (y^+)^5 \quad (z_c \le z \le 1) \tag{13}$$

where the functions U_4^+ and U_5^+ are defined by

$$U_4^+ = \frac{3}{4}\frac{\psi}{(y_c^+)^2} + \frac{(n-1)\psi^2}{4\, Y_c^+} - \frac{1}{(y_c^+)^3} + \frac{3.03}{(y_c^+)^4} \tag{14}$$

and

$$U_5^+ = \frac{1}{5(y_c^+)^5}\left[3y_c^+ - 2\psi (y_c^+)^2 - 0.5(n-1)\psi^2 (y_c^+)^3 - 9.68\right] \tag{15}$$

Equations (14) and (15) satisfy the equations of motion and boundary conditions in the wall region and provide a smooth and continuous transition to the universal mean velocity profile in the turbulent core.

The total mass diffusivity in the turbulent core is given by

$$\alpha^+ = -\frac{z}{Sc_t\frac{du^+}{dz}} \qquad (0 \le z \le z_c) \tag{16}$$

where Sc_t is the turbulent Schmidt number. The corresponding value in the wall region is

$$\alpha^+ = \frac{n\psi}{Sc_t}\frac{\overline{uv}^+}{\frac{du^+}{dy^+}} + \frac{2}{Re\, Sc\sqrt{f/2}} \tag{17}$$

where $\overline{uv}^+$, the Reynolds stress, is given by

$$\overline{uv}^+ = -\left[U_4^+ + \frac{(n-1)(2n-1)}{24}\psi^3 \right] 4n\,(y^+)^3 - \left[5U_5^+ - (4n-1)\,U_4^+\,\psi - \frac{(n-1)(n-3)(2n-1)}{24}\psi^4 \right] n(y^+)^4 \quad (18)$$

FINITE DIFFERENCE FORMULATION

Equation (4), with boundary conditions given by Equation (5) and the velocity and mass diffusivity distributions given by Equations (6) to (18), is solved by the Crank-Nicholson implicit scheme (Lapidus, 1962).

Equation (4) can be written as

$$u^+ \frac{\partial W}{\partial \xi} = \frac{\alpha^+}{\beta}\frac{\partial^2 W}{\partial z^2} + \frac{1}{\beta}\frac{\partial W}{\partial z}\left(\frac{\partial \alpha^+}{\partial z} + \frac{\alpha^+}{z}\right) - \frac{\langle u \rangle}{u_*} W^m \quad (19)$$

Denoting the radial and axial mesh points by i and j and evaluating the nonlinear term at $j + 1/2$ by the Taylor series forward projection method of Douglas (Von Rosenberg 1969), Equation (19) becomes

$$F_i W_{i-1,j+1} + B_i W_{i,j+1} + A_i W_{i+1,j+1} = D_i \qquad i = 1, 2, \ldots, N-1 \quad (20)$$

where N is the number of radial divisions and

$$A_i = \frac{\alpha_i^+}{2\beta(\Delta z)^2} + \frac{\left(\frac{\partial \alpha^+}{\partial z}\right)_i + \frac{\alpha_i^+}{z_i}}{4\beta(\Delta z)} \quad (21)$$

$$B_i = -\frac{u_i}{\Delta \xi} - \frac{\alpha_i^+}{\beta(\Delta z)^2} - \frac{\langle u \rangle}{2u_*}\left(W_{i,j+1/2}^{m-1}\right) \quad (22)$$

$$F_i = \frac{\alpha_i^+}{2\beta(\Delta z)^2} - \frac{\left(\frac{\partial \alpha^+}{\partial z}\right)_i + \frac{\alpha_i^+}{z_i}}{4\beta(\Delta z)} \quad (23)$$

$$D_i = -A_i W_{i+1,j} - F_i W_{i-1,j} + \left[\frac{\alpha_i^+}{(\Delta z)^2} - \frac{u_i^+}{\Delta \xi}\right] W_{i,j} + \frac{\langle u \rangle}{2u_*}\left(W_{i,j+1/2}\right)^{m-1} \quad (24)$$

At the wall, $i = N$, $u^+ = 0$ and $\partial W/\partial z = 0$. Writing Equation (19) in terms of the Crank-Nicholson implicit scheme gives rise to oscillations in wall concentration and hence the backward difference method is used. Equation (19) becomes

$$F_N W_{N-1,j+1} + B_N W_{N,j+1} = D_N \quad (25)$$

where

$$F_N = \alpha_N^+/\beta(\Delta z)^2 \quad (26)$$

$$B_N = -F_N - \frac{\langle u \rangle}{2u_*}\left(W_{N,j+1/2}\right)^{m-1} \quad (27)$$

and

$$D_N = \frac{\langle u \rangle}{2u_*}\left(W_{N,j+1/2}\right)^{m-1} W_{N,j} \quad (28)$$

At the center of the tube, $i = 0$, $\alpha^+ = 0$ and $\partial W/\partial z = 0$. Equation (19) in finite difference form yields

$$B_0 W_{0,j+1} = D_0 \quad (29)$$

where

$$B_0 = \frac{-u_0^+}{\Delta \xi} + \frac{\langle u \rangle}{2u_*} W_{0,j+1/2}^{m-1} \quad (30)$$

and

$$D_0 = \left[-\frac{u_0^+}{\Delta \xi} + \frac{\langle u \rangle}{2u_*}\left(W_{0,j+1/2}\right)^{m-1}\right] W_{0,j} \quad (31)$$

Equations (20), (25), and (29) form a set of $(N+1)$ linear equations whose coefficients can be written as a tridiagonal matrix.

NUMERICAL RESULTS AND DISCUSSION

The parameters for the problem are the Reynolds number Re, the Schmidt number Sc, the turbulent Schmidt number Sc_t, the flow behavior index n, the reaction number β, and the reaction order m. For a given Re and n, the Fanning friction factor f and the value of y_c^+ are calculated from Equations (10) and (12) by a damped Newton-Raphson iteration. In the absence of experimental data, the turbulent Schmidt number is taken as unity.

Using the velocity profile, the average velocity $\langle u \rangle/u_*$ is computed. The tridiagonal matrix coefficients are then evaluated and Equations (20), (25), and (29) solved for each axial distance using the algorithm of Thomas (Lapidus, 1962).

The cup-mixing concentration is obtained by the equation

$$W_m = \frac{\int_0^1 W u^+ z\,dz}{\int_0^1 u^+ z\,dz} \quad (32)$$

The integrals are evaluated by a Simpson's rule quadrature.

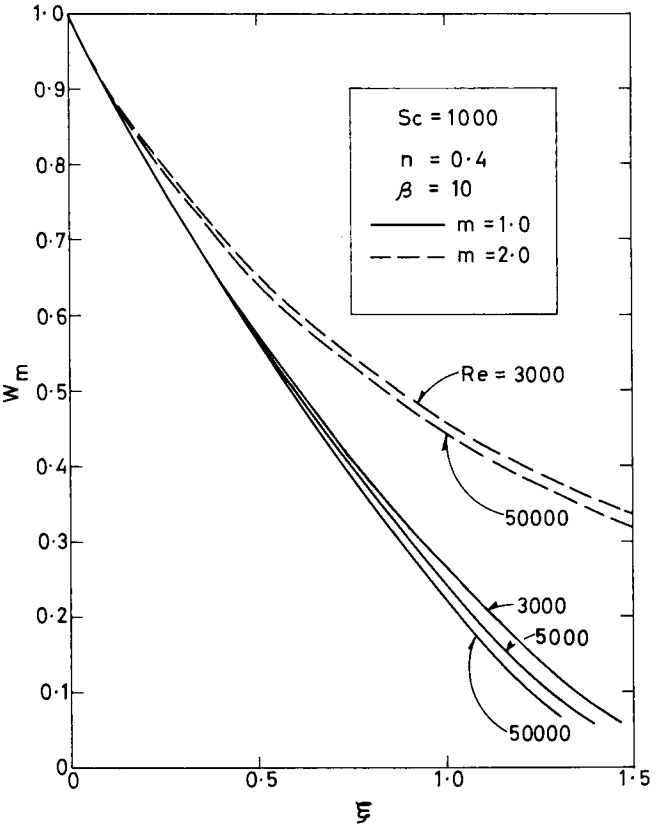

Fig. 1. Effect of Reynolds number on the cup-mixing concentration.

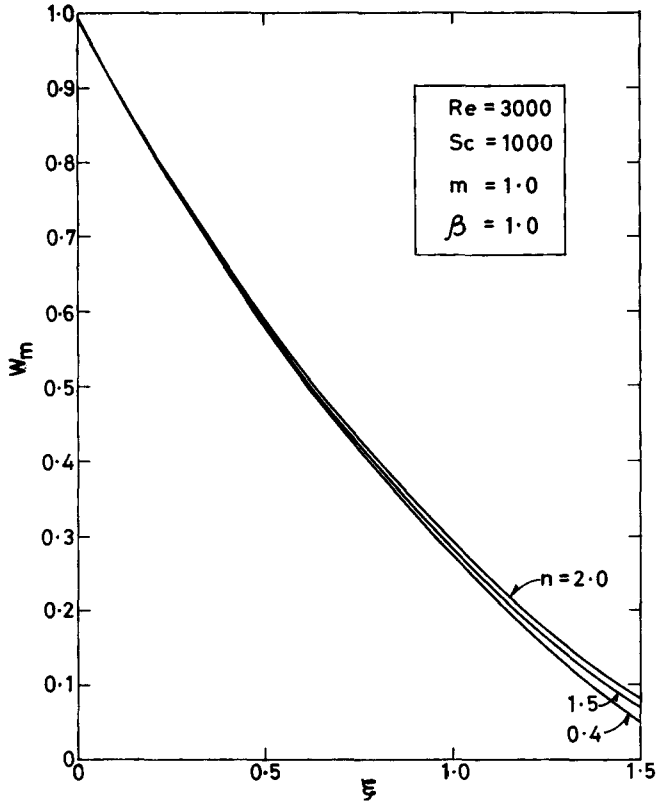

Fig. 2. Effect of the flow behavior index, n on the cup-mixing concentration.

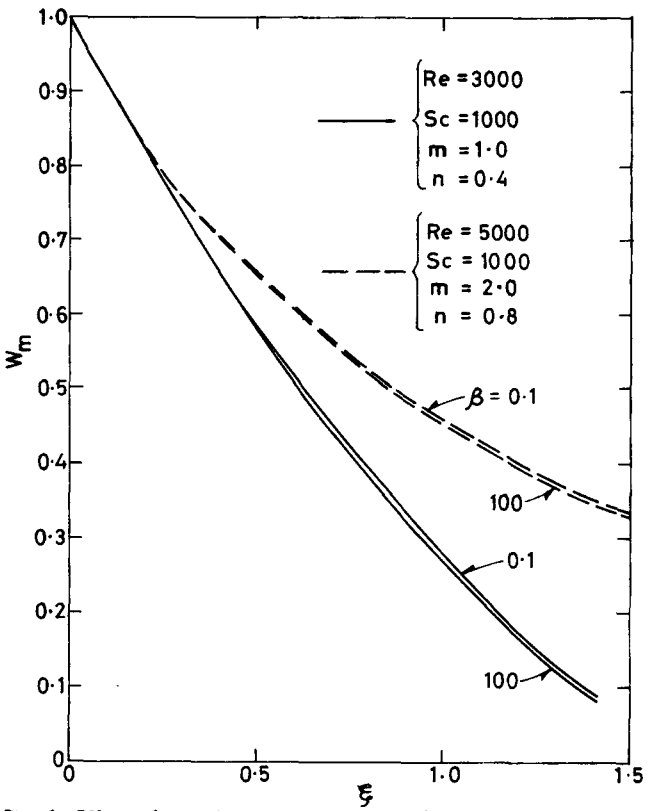

Fig. 3. Effect of reaction parameter β on the cup-mixing concentration.

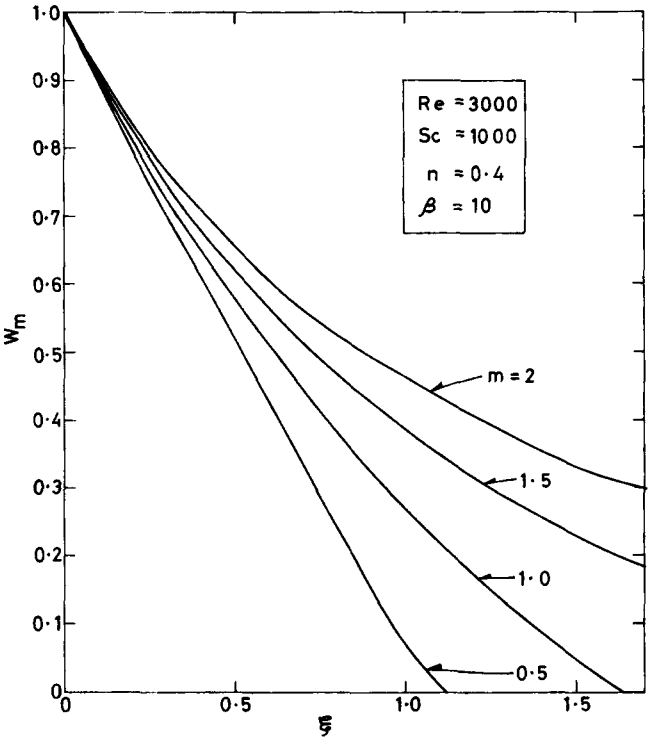

Fig. 4. Effect of reaction order on the cup-mixing concentration.

Typical variations of the dimensionless cup-mixing concentration with axial position are shown in Figures 1 to 4 for variations in the Reynolds number, the flow behavior index n, the reaction parameter β, and the reaction order m. Figures 1 and 2 reveal that the dimensionless cup-mixing concentration is essentially unaffected by variations in the Reynolds number and the flow behavior index. This is because the velocity profile $u/\langle u \rangle$ changes only by less than 10% for variations in Reynolds number from 3000 to 50000 and the flow behavior index from 0.4 to 2.0.

Since the reaction parameter β is incorporated in defining the dimensionless axial distance, and the plot of cup-mixing concentration vs. axial distance in Figure 3 shows no appreciable difference for values of β from 0.1 to 100, we may conclude that the reactor length for a given conversion is inversely proportional to the reaction parameter β for all reaction orders.

The effect of the reaction order on the conversion is shown in Figure 4. It is seen that the dimensionless cup-mixing concentration is significantly influenced by the reaction order, the conversion being larger for reactions of lower order. A plot of the concentration profile with Schmidt number as the parameter showed that the conversion was insensitive to variations in Schmidt number for values of Sc ranging from 10 to 10^6. From the above results, it can be concluded that non-Newtonianism has very little influence on the conversion for turbulent flow in a tubular reactor despite the fact that significant differences in axial dispersion coefficients exist as reported by Krantz and Wasan (1974). Further, irrespective of the values of Reynolds number, the flow behavior index, and the Schmidt number, the results in Figure 4 can be used to predict the conversions for any given values of the reaction parameter β and reaction order m. Again, the results of the present work are important from the fact that even for the turbulent Newtonian flow situation, theoretical predictions of the conversion for homogeneous non-linear reactions with Neumann boundary conditions have been reported for the first time.

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NOTATION

c = local concentration
c_0 = inlet concentration
D = molecular diffusivity
f = Fanning friction factor
k = reaction rate constant
K = consistency index
m = reaction order
n = flow behavior index
r = radial coordinate
R = radius of the tube
Re = Reynolds number
Sc = Schmidt number
Sc_t = turbulent Schmidt number, ϵ/ϵ_D
u = time-averaged local axial velocity
u_* = friction velocity, $\sqrt{\tau_w/\rho}$
u^+ = dimensionless time averaged local axial velocity, u/u_*
U_4^+ = function defined by Equation (14)
U_5^+ = function defined by Equation (15)
$<u>$ = bulk average velocity
W = dimensionless concentration
x = axial coordinate
y = radial distance from the wall, $R - r$
z = dimensionless radial coordinate

Greek Letters

α = total diffusivity, $D + \epsilon_D$
β = reaction parameter, $kc_0^{m-1}R/<u>$
ϵ = eddy momentum diffusivity
ϵ_D = eddy mass diffusivity
ν = non-Newtonian viscosity
ρ = density
τ_w = wall shear stress
ψ = function defined by Equation (7)
ξ = dimensionless axial coordinate, $k\,c_0^{m-1}\,x/<u>$

LITERATURE CITED

Bogue, D. C., and A. B. Metzner, "Velocity Profiles in Turbulent Pipe Flow," *Ind. Eng. Chem. Fundamentals*, **2**, 143 (1963).

Cleland, F. A., and R. H. Wilhelm, "Diffusion and Reaction in Viscous-flow Tubular Reactor," *AIChE J.*, **2**, 489 (1956).

Dodge, D. W., and A. B. Metzner, "Turbulent Flow of Non-Newtonian Systems," *ibid.*, **5**, 189 (1959).

Homsy, R. V., and R. D. Strohman, "Diffusion and Chemical Reaction in a Tubular Reactor with Non-Newtonian Laminar Flow," *ibid.*, **17**, 215 (1971).

Hsu, C. J., "A Method of Solution for Mass Transfer with Chemical Reaction Under Conditions of Viscous Flow in a Tubular Reactor," *ibid.*, **11**, 938 (1965).

Krantz, W. B., and D. T. Wasan, "A Correlation for Velocity and Eddy Diffusivity for the Flow of Power-Law Fluids Close to a Pipe Wall," *Ind. Eng. Chem. Fundamentals*, **10**, 424 (1971).

———., "Axial Dispersion in the Turbulent Flow of Power-Law Fluids in Straight Tubes," *ibid.*, **13**, 56 (1974).

Lapidus, L., *Digital Computation for Chemical Engineers*, McGraw Hill, New York (1962).

Lauwerier, H. A., "A Diffusion Problem with Chemical Reaction," *App. Sci. Res., Sect. A*, **8**, 366 (1959).

Randhava, S. S., and D. T. Wasan, "Mass Transfer with Homogeneous Chemical Reaction in Turbulent Pipe Flow," *AIChE J.*, **17**, 664 (1971).

———., "Surface-Catalyzed Reactions in Turbulent Pipe Flows," *Adv. Chem. Ser.*, **109**, 564 (1972a).

———., "Homogeneous Reactions in Turbulent Pipe Flows—Tubular Non-catalytic Reactors," *Chem. Eng. J.*, **4**, 215 (1972b).

Solomon, R. L., and J. L. Hudson, "Heterogeneous and Homogeneous Reactions in a Tubular Reactor," *AIChE J.*, **13**, 545 (1967).

Vignes, J. P., and P. J. Trambouze, "Diffusion et réaction chimique dans un réacteur tubulaire en régime laminaire," *Chem. Eng. Sci.*, **17**, 73 (1962).

Von Rosenberg, D. U., *Method of Numerical Solution of Partial Differential Equations*, Elsevier, New York (1969).

Walker, R. E., "Chemical Reaction and Diffusion in a Catalytic Tubular Reactor," *Phys. Fluids*, **4**, 1211 (1961).

Wissler, E. H., and R. S. Schechter, "A Diffusion Problem with Chemical Reaction," *Appl. Sci. Res. Sect. A* **10**, 198 (1961).

———., "Turbulent Flow of Gas Through a Circular Tube with Chemical Reaction at the Wall," *Chem. Eng. Sci.*, **17**, 937 (1962).

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Kinetics of Solid Phase Reactions

The kinetics of isothermal transformations or decompositions of solids proceeding through nucleation and subsequent growth is treated in the spirit of Avrami, eliminating, however, some of the internal contradictions of his treatment. Universal solutions of the dimensionless integral equation are computed. The theory is extended to nonisothermal systems and the resulting integral equations are solved numerically for the adiabatic case. It is shown that two kinds of catastrophic behavior can occur: one is characterized by slopes approaching infinity in the conversion vs. time curve following a long period of quiescent behavior; the other is characterized by a very short time for total conversion and by milder slopes in the conversion vs. time curve throughout the course of reaction. In the first kind the nucleation is mainly responsible for the catastrophic behavior, while in the second kind the rate of growth is responsible.

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