A Method of Solution for Mass Transfer with Chemical Reaction Under Conditions of Viscous Flow in a Tubular Reactor

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Prediction of the concentration field in a tubular reactor where diffusion and chemical reaction occurs simultaneously constitutes one of the fundamental problems in reactor design. Under practical flow conditions, nonuniform distribution of residence time caused by the transverse velocity pattern can create radial concentration gradients, which, in turn, tend to be smoothed out by diffusion and, at times, by convection. Theoretical means of predicting the concentration field in such processes are of value both from theoretical and practical points of view.

Specifically, for laminar flow with first-order chemical reaction taking place, the problem reduces to finding the solution to the following partial differential equation:

$$u_m\left[1-\left(\frac{r}{r_o}\right)^2\right]\frac{\partial c}{\partial z}= D\left[\frac{\partial^2 c}{\partial r^2}+\frac{1}{r}\frac{\partial c}{\partial r}\right]-kc \qquad (1)$$

with the initial and boundary conditions

$$\begin{aligned}&\text{at } z=0 \quad c=c_o\\ &\text{for } z>0\\ &\frac{\partial c}{\partial r}=0 \text{ at } r=0 \text{ and } r=r_o\end{aligned} \qquad (2)$$

Steady state, constant physical properties, no volume change due to chemical reaction, as well as negligible axial diffusion, are assumed. A rigorous analytical solution of the above equation does not seem to have been obtained. The only approximate solutions reported are those by Cleland and Wilhelm (*1*), who solved the partial differential equation numerically by finite difference method. Their methods are summarized in reference 2. In fact, it is possible to solve Equation (1) analytically by using the separation-of-variables technique. The purpose of this communication is to illustrate the mathematical scheme for such an approach.

It is convenient to change the variables in Equations (1) and (2) by letting $C = c/c_o$, $\xi = r/r_o$, and $\alpha = D/kr_o^2$. Thus, one obtains

$$(1-\xi^2)\frac{\partial C}{\partial z}=\frac{1}{N_{Sc}\,N_{Re}\,r_o}\left[\frac{\partial^2 C}{\partial \xi^2}+\frac{1}{\xi}\frac{\partial C}{\partial \xi}-\frac{C}{\alpha}\right] \qquad (3)$$

with

$$\begin{aligned}&\text{at } z=0, \quad C=1\\ &\text{for } z>0\\ &\frac{\partial C}{\partial \xi}=0 \text{ at } \xi=0 \text{ and } \xi=1\end{aligned} \qquad (4)$$

By separation of variables, Equation (3) can be reduced to a pair of ordinary differential equations, one of which constitutes the eigenvalue problem of the "Sturm-Liouville" system. The analytical solution of Equations (3) and (4) can thus be written

$$C=\sum_{n=1}^{\infty}A_nY_n(\xi)\exp\left[-\frac{\beta_n^2 z}{\alpha N_{Sc}\,N_{Re}\,r_o}\right] \qquad (5)$$

where β_n and Y_n are the eigenvalues and eigenfunctions, respectively, of the following characteristic equation:

$$\frac{d^2Y_n}{d\xi^2}+\frac{1}{\xi}\frac{dY_n}{d\xi}-\frac{1}{\alpha}[1-\beta_n^2(1-\xi^2)]\,Y_n=0 \qquad (6)$$

satisfying the boundary conditions

$$\frac{dY_n}{d\xi}=0 \text{ at } \xi=0 \text{ and } \xi=1 \qquad (7)$$

Clearly, for each preassigned value of the parameter α, it is possible to find a set of eigenvalues and eigenfunctions satisfying both Equations (6) and (7). An expression for the coefficients of series expansion A_n, appearing in Equation (5), can be obtained by utilizing the orthogonal properties of the eigenfunctions, as

$$A_n=\frac{\int_0^1 \xi(1-\xi^2)Y_n d\xi}{\int_0^1 \xi(1-\xi^2)Y_n^2 d\xi} \qquad (8)$$

Table 1. Eigenvalues, Eigenfunctions, and the Coefficients ($\alpha = 0.1$)

n	β_n^2	$Y_n(1)$	A_n
1	1.6858	0.35308	1.4340
2	4.5968	−0.42904	−0.60647
3	10.425	0.38165	0.25596
4	19.446	−0.34110	−0.13117
5	31.676	0.31190	0.078204
6	47.112	−0.29011	−0.051596
7	65.752	0.27314	0.036501
8	87.596	−0.25942	0.027154
9	112.64	0.24804	0.020979
10	140.89	−0.23888	−0.016690
11	172.34	0.23005	0.013593
12	206.99	−0.22275	−0.011284

The integrals appearing in the numerator and denominator of Equation (8) can be written in the alternative forms, respectively

$$\int_0^1 \xi(1-\xi^2)Y_n^2 d\xi = \frac{\alpha}{2\beta_n}\left[\frac{\partial Y}{\partial \beta}\frac{\partial Y}{\partial \xi}-Y\frac{\partial^2 Y}{\partial\beta\partial\xi}\right]_{\substack{\beta=\beta_n\\ \xi=1}} = -\frac{\alpha Y_n(1)}{2\beta_n}\left(\frac{\partial^2 Y}{\partial\beta\partial\xi}\right)_{\substack{\beta=\beta_n\\ \xi=1}} \qquad (9)$$

and

$$\int_0^1 \xi(1-\xi^2)Y_n d\xi = \frac{1}{\beta_n^2}\int_0^1 \xi Y_n d\xi \qquad (10)$$

For the present study, however, the form of Equation (8) was retained for actual computation.

The first twelve eigenvalues and eigenfunctions of the system composed of Equations (6) and (7) have been determined for the case of $\alpha = 0.1$. Equation (6) was solved numerically and the eigenvalues β_n were determined so that they satisfy both the characteristic equation, Equation (6), and the boundary condition, Equation (7). The coefficients A_n are then evaluated from Equation (8). The entire computation was carried out with the aid of an IBM 7094 computer, by using double precision statements. The twelve eigenvalues and the important quantities are tabulated in Table 1.

Of practical interest are the concentration of reactant at the reactor wall and the average reactant concentration based upon the volumetric flow rate C_{av}. An expression for the former can be obtained by letting $\xi = 1$ in Equation (5), namely

$$C_w = \sum_{n=1}^{\infty} A_n Y_n(1) \exp\left[-\frac{\beta_n^2 z}{\alpha N_{Sc} N_{Re} r_o}\right] \tag{11}$$

The latter can be found through the relationship

$$C_{av} = \frac{\int_0^{r_o} r\left[1-\left(\frac{r}{r_o}\right)^2\right] C\,dr}{\int_0^{r_o} r\left[1-\left(\frac{r}{r_o}\right)^2\right] dr} = 4\int_0^1 \xi(1-\xi^2)C\,d\xi = 4\sum_{n=1}^{\infty} A_n \exp\left[-\frac{\beta_n^2 z}{\alpha N_{Sc} N_{Re} r_o}\right] \int_0^1 \xi(1-\xi^2)\,Y_n\,d\xi \tag{12}$$

Information required for calculating C_w can be found in Table 1. The eigenfunctions needed to calculate the local concentration in general, $C(\xi, z)$, and the average concentration, C_{av}, are listed in Table 2, at intervals of 0.1 from $\xi = 0$ to $\xi = 1$. By using the twelve eigenvalues, eigenfunctions, and the relevant constants determined in this study, the average concentration C_{av} has been calculated from Equation (12) for various values of λ $(= z/\alpha N_{Sc} N_{Re} r_o)$. Simpson's rule was used to evaluate the integral appearing in Equation (12). Comparison of the author's calculations with those reported by Cleland and Wilhelm (*1*) showed that they agree well with each other. Figure 1 illustrates the longitudinal variation of average concentration and the concentration at the reactor axis ($\xi = 0$) as well as at the reactor wall ($\xi = 1$).

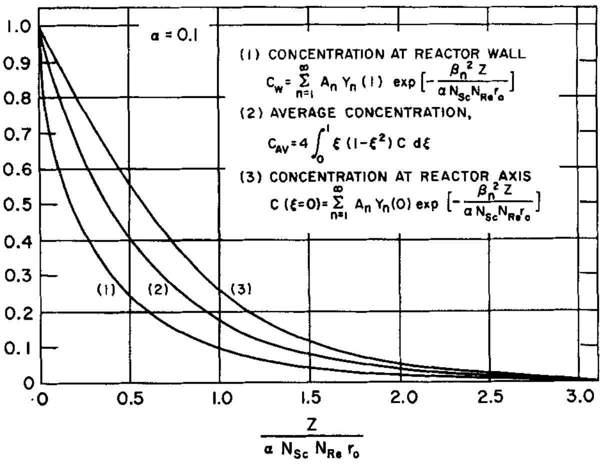

Fig. 1. Reactant concentration vs. axial distance variable.

The mathematical scheme illustrated above can be conformed to obtain the analytical solution corresponding to any arbitrary value of the diffusion parameter, $\alpha = D/kr_o^2$. It should be emphasized that the principal advantage of the present method of solution lies in the fact that it is possible to express the reactant concentration in an explicit form, such as Equation (5). Thus, once the eigenvalues, eigenfunctions, and the constants are determined, the reactant concentration at any axial position can be readily calculated using this equation. By the method of numerically solving the partial differential equation, however, the solution is obtained through implicit difference equations. Furthermore, the numerical method must fulfill the criteria of both convergence and stability, which need not be considered in the present method. Since the proposed method, in effect, transfers the numerical work required in the solution of a partial differential equation to that for an ordinary differential equation, it might be called a *quasi-analytic* method. The computational problems of the latter are usually less severe than those of the former.

TABLE 2. FIRST EIGHT EIGENFUNCTIONS ($\alpha = 0.1$)

ξ	Y_1	Y_2	Y_3	Y_4
0	1.00000	1.00000	1.00000	1.00000
0.1	0.98303	0.91236	0.77847	0.59030
0.2	0.93421	0.67514	0.26345	−0.14455
0.3	0.85938	0.35475	−0.21881	−0.40254
0.4	0.76714	0.031661	−0.41539	−0.082407
0.5	0.66738	−0.22840	−0.29984	−0.27342
0.6	0.56991	−0.39273	−0.026904	0.26867
0.7	0.48335	−0.46378	0.22245	0.0019389
0.8	0.41468	−0.46868	0.35690	−0.24209
0.9	0.36950	−0.44475	0.38812	−0.33661
1.0	0.35308	−0.42904	0.38165	−0.34110

ξ	Y_5	Y_6	Y_7	Y_8
0	1.00000	1.00000	1.00000	1.00000
0.1	0.36944	0.14122	−0.068998	−0.23905
0.2	−0.38034	−0.36881	−0.15972	0.10717
0.3	−0.11968	0.23715	0.26780	−0.011661
0.4	0.30327	0.083249	−0.24784	−0.081249
0.5	0.079109	−0.26140	0.089214	0.16883
0.6	−0.25505	0.065892	0.13636	−0.21232
0.7	−0.16010	0.23120	−0.21505	0.13207
0.8	0.13631	−0.041413	−0.039783	0.10421
0.9	0.29522	−0.26011	0.22878	−0.19985
1.0	0.31190	−0.29011	0.27313	−0.25942

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NOTATION

A_n = coefficients of series expansion in Equation (5)
C = dimensionless local concentration of reactant
C_{av} = dimensionless integral average concentration of reactant
C_w = dimensionless reactant concentration at reactor wall
D = molecular diffusivity
N_{Re} = $2r_o u_{av}\rho/\mu$, Reynolds number
N_{Sc} = $\mu/\rho D$, Schmidt number
$Y_n(1)$ = eigenfunction of Equations (6) and (7) at $\xi = 1$
Y_n = eigenfunction of Equations (6) and (7)
c = local concentration of reactant
c_o = concentration of reactant at reactor inlet
k = reaction velocity constant, first order
r = radial distance
r_o = reactor radius
u_{av} = average fluid velocity

u_m = maximum fluid velocity
z = axial distance coordinate

Greek Letters

α = D/kr_o^2, a diffusion parameter
β_n = eigenvalues of Equations (6) and (7)
λ = $z/\alpha N_{Sc} N_{Re} r_o = kz/u_m$, axial distance variable
μ = viscosity of fluid
ξ = r/r_o, dimensionless radial distance
ρ = density of fluid

LITERATURE CITED

1. Cleland, F. A., and R. H. Wilhelm, *A.I.Ch.E. J.*, 2, No. 4, 489 (1956).
2. Lapidus, Leon, "Digital Computation for Chemical Engineers," p. 181, McGraw-Hill, New York (1962).

Effects of Solvent Purity on Non-Newtonian Viscosity

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Although variations in the rheology of non-Newtonian solutions have often been attributed to solvent characteristics, there have been no data available to show the magnitude of the changes produced. As a portion of a larger study program on the tube flow of non-Newtonian fluids, such data were obtained for a limited number of fluids common to the existing literature (*1* to *5*) and is presented herein.

By virtue of its simplicity, the power law (*6* to *9*), $\tau = a\left(\frac{du}{dy}\right)^n$, where τ is the shear stress and du/dy is the shear rate, is used to present the experimental data. In this paper the power law constants (coefficient and exponent) are determined from a straight line data fit over two orders of magnitude in the shear rate when the shear stress and shear rate are plotted logarithmically as in Figure 1. Despite the fact that the power law does not account for either the normal stresses or elasticity effects (*10* to *13*) thought necessary to describe these fluids, it can be assumed that any change in the power law constants is indicative of a change in the other rheological properties not independently measurable at this time.

It was not the intention of these experiments to provide quantitative data that others might use in their own research, but only to show that greater care must be taken before accepting viscosity data in the literature when the solvent analysis was omitted or comparing flow data taken with like concentrations of the same fluid (*6*, *9*).

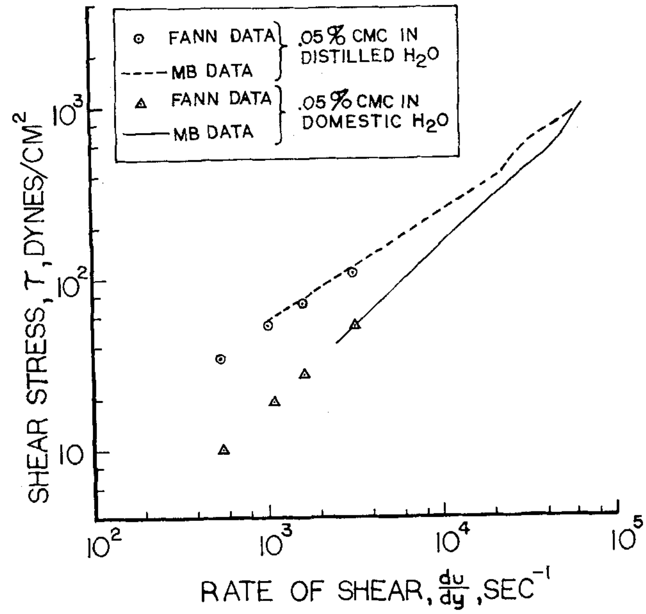

Fig. 1.

The fluids tested were 0.05% concentrations by weight of several polymer additives commonly used in basic research studies. The first is sodium carboxymethylcellulose (CMC 7HSP), which is essentially nonassociating, free draining, random coiling, and slightly anionic (*6*) in dilute solutions (less than 1%). Natrosol 250 (HHR) is a cellulose gum like the carboxymethylcellulose, but it differs in being nonionic and having a hydration inhibitor. The third polymer, J-2P, is basically a guar gum of galactomannan, consisting of a high molecular weight carbohydrate polymer having galactose branches. The solvents used were domestic water and high purity distilled water. No attempt was made to correlate the water properties with the observed effects. An analysis of each fluid solvent used is given in Table 1.

EXPERIMENTS

For each fluid sample to be tested, both the solvent (water) and the polymer ad-

TABLE 1. WATER ANALYSIS

Test	Domestic, p.p.m.	Distilled, p.p.m.
Total dissolved solids	1135.5	0.9
Chlorides as Cl	87	trace
Sulfates as SO_4	310	trace
Iron as Fe	0.1	trace
Calcium as Ca	2.0	trace
Magnesium as Mg	2.4	trace
Sodium as Na	271	trace
Carbonates as CO_3	17	trace
Bicarbonates as HCO_3	445	trace
Fluorides as F	trace	trace
Metaphosphates as PO_3	1	trace
*p*H value	8.4	6.8
Total hardness	14.8	