This procedure is illustrated in Figure 2 in which the center of the area of uncertainty remaining after block 3 is indicated by the square marked 3′. The first pilot experiment, marked by a circle 4, gives a yield of 92%, the same as at 3. Since this suggests immediately that there must be a high point in the portion between 3 and this experiment, the fourth block is located at point 4. Since there are in this case only two independent variables, the new contour tangent is a line, identical with that between 3 and 3′. The pilot experiment, shown as point 5, gives an increase (93%), indicating the need for a second, indicated by a triangle. Its yield being also 93% there must be a high point between these two pilot experiments. Block 5 is located arbitrarily at the first.

CONCLUSIONS

The contour tangent search method is an elimination technique of the Kiefer-Johnson type rather than a climbing method of the sort proposed by Box and Wilson. The proposed method can be modified so that it will climb, or at least not descend. Fundamental to the practical success of the contour tangent method is that the response surface be strongly unimodal as defined in the article and that the experimental error be small. The technique is not affected by the scales of measurement selected, and the need for extrapolation is avoided by exploiting the global property of strong unimodality.

NOTATION

$A_i(x_i)$ = hyperarea (element of integration)
a, b = fixed points in experimental region
m_i = ith slope coefficient
r = point on response surface
r^* = summit of response surface
s_i = minimum value of ith independent variable
t_i = maximum value of ith independent variable
$v(x)$ = maximum hypervolume
$v(x^m)$ = minimax hypervolume
V = hypervolume
x = variable point in experimental region
$x^{\cdot}$ = midpoint
x^m = minimax point
$\hat{x}$ = center of volume
$\bar{x}$ = centroid
y = dependent variable

LITERATURE CITED

1. Kiefer, J., *Proc. Am. Math. Soc.*, **4**, 502 (1953).
2. Johnson, S. M., "Rand Corporation Report P-856," Santa Monica, California (1956).
3. Box, G. E. P., and K. B. Wilson, *J. Roy. Stat. Soc.*, **B13**, 1 (1951).
4. Hooke, R., and T. A. Jeeves, *J.A.C.M.*, 8, 2, 212-229 (April, 1961).
5. Box, G. E. P., *Biometrics*, **10**, 16 (1954).
6. Wilde, D. J., "Advances in Chemical Engineering," Vol. 3, pp. 286-292, T. B. Drew, J. W. Hoopes, and T. Vermeulen, ed., Academic Press, New York (1962).
7. Buehler, R. J., B. V. Shah, and O. Kempthorne, "Statistical Laboratory Technical Report No. 1," Office of Naval Research Contract Nonr-530(05) NR-042-207, Iowa State Univ., Ames, Iowa (April, 1961).
8. *Ibid.*, Report No. 2 (April, 1961).
9. *Ibid.*, Report No. 3 (September, 1961).

Manuscript received January 2, 1962; revision received July 25, 1962; paper accepted July 30, 1962. Paper presented at A.I.Ch.E. Los Angeles meeting.

Dispersion in Laminar Flow by Simultaneous Convection and Diffusion

M. A. FARRELL and E. F. LEONARD
Columbia University, New York, New York

Recent interest in residence time distributions has developed from a recognition of the effects which these distributions can have on the performance of chemical reactors and contacting units. Efficient operation of such equipment often requires that the holding times be confined to a narrow range. Knowledge of the way in which established fluid-mechanical conditions affect residence time distributions is needed for improvement of current design methods.

This paper considers one of a class of residence time distribution function models which has not previously received attention, multidimensional diffusion-convection models which cannot be simplified to equivalent one-dimensional models. The specific model chosen for study is the transient convection-diffusion encountered during laminar flow in round pipes, but the method of treatment is applicable to any flow-diffusion situation in ducts of constant cross section through which a fluid is flowing with a known, steady velocity profile. The attack differs from earlier residence time distribution function studies in retaining the inherent two-dimensional nature of the diffusion-convection process. The results, unlike those of previous studies, are not always equivalent to simple one-dimensional models, and they are capable of explaining differences between observed residence time distribution functions in similar systems and the predictions of these simple models.

The residence time or holding time distribution function is perhaps best defined as the fraction of material introduced into a system at a time $t = 0$ which appears at the outlet of the system between t and $t + dt$ (*8*). The residence time distribution function may also be regarded as a probability distribution or as the response of a flow system to a unit impulse input. When a system is not unidimensional, the fraction of material leaving the system at any time must generally be determined by integration over a surface normal to the direction of outflow as indicated in Equation (1):

$$f(t) = \frac{\int_A [V(A)C(A) - D_m \nabla C] dA}{Q} = \frac{\overline{V} A C_{mo}}{Q} \quad (1)$$

PREVIOUS RESIDENCE TIME DISTRIBUTION FUNCTION STUDIES

Studies of the relationship between fluid mechanical conditions and the residence time distribution function have taken two opposite points of view: either known fluid mechanical conditions have been used to predict the residence time distribution function, experimental measurements of which have been used to confirm the analysis, or residence time distribution function measurements have been used to suggest fluid mechanical models for complex systems. Only a few studies appear to have taken the point of view first mentioned; of these studies the most important seem to be those of Taylor and others who favored his approach. In Taylor's first paper on this subject, dispersion of a soluble tracer during laminar flow in an open tube was studied (*16*). Variation of the axial velocity with radial position and radial transport of material by molecular diffusion were assumed to be the dominant dispersion mechanisms as indicated in Equation (2):

$$D_m\left[\frac{\partial^2 C}{\partial r^2}+\frac{1}{r}\frac{\partial C}{\partial r}\right]-U_o\left[1-\frac{r^2}{R^2}\right]\frac{\partial C}{\partial Z}=\frac{\partial C}{\partial t} \quad (2)$$

Taylor offered limited solutions for Equation (2) when the effect of either the velocity profile or the molecular diffusion could be neglected. When the time for convective transport to effect a change in concentration was long compared with the time for decay of radial concentration gradients by molecular diffusion, Taylor assumed that the tracer concentration could be considered dependent only on axial position and time. The criterion for this assumption was expressed semiquantitatively as in Equation (3):

$$\frac{L^*}{U_o}>>\frac{R^2}{(3.8)^2 D_m};\ \frac{4L^*D_m}{U_oR^2}>>0.277 \quad (3)$$

When the decay of radial concentration gradients could be considered complete, Equation (2) was found to be equivalent to Fick's law for molecular diffusion in a moving coordinate system:

$$K\frac{\partial^2 C_{mc}}{\partial Z_1^2}=\frac{\partial C_{mc}}{\partial t} \quad (4)$$

In Equation (4), Z_1 is the axial distance relative to a plane moving at the mean fluid velocity, and K, the virtual coefficient of diffusion, is a function of tube radius, center-line velocity, and molecular diffusivity:

$$K=R^2U_o^2/192D_m \quad (5)$$

The solution of Equation (4) for introduction of a unit impulse at time equal to zero was well known from molecular diffusion studies (*7*):

$$C_{mc}\pi R^2=\frac{1}{(4\pi Kt)^{1/2}}\exp\left[-\left(Z-\tfrac{1}{2}U_ot\right)^2/4Kt\right] \quad (6)$$

Spatial concentration distribution was a Gaussian with mean at the distance traveled at the average velocity between zero time and the instant under consideration. The residence time distribution however is defined as the variation of outlet concentration with time at a fixed point and could appear as a symmetric Gaussian curve only when the spatial distribution did not change appreciably while passing the measurement point, as noted by Levenspiel and Smith (*12*).

The assumption that material transport by axially-directed molecular diffusion is negligible compared with axial transport by convection is inherent in Equation (2) and consequently, limits the applicability of Equations (5) and (6). Taylor considered this problem in a subsequent paper (*17*) and showed that his derivation was valid when the molecular diffusivity was sufficiently small compared with K, the virtual diffusion coefficient. Aris (*1*) removed this restriction by demonstrating theoretically that Equation (6) was valid whenever the criterion of Equation (3) was satisfied if the virtual diffusion coefficient was defined as the sum of K and the molecular diffusivity. During a study of liquid dispersion in long capillary tubes Blackwell (*2*) obtained virtual diffusion coefficients which agreed with those defined by Aris.

For situations in which the minimum residence time (for example L/U_o) was sufficiently short Taylor (*16*) showed molecular diffusion to have no appreciable effect on the radial concentration gradients, and the molecular diffusion term in Equation (2) could be neglected. The residence time distribution function for this case can be calculated from only the laminar velocity profile, as noted by Bosworth (*3*); it is dependent upon the residence time and minimum residence time:

$$\begin{aligned} f(t)&=0 && t<t_o\\ f(t)&=2t_o^2/t^3 && t\geqq t_o \end{aligned} \quad (7)$$

When both diffusion and convection are equally important in effecting dispersion, the limiting residence time distribution functions of Equations (6) and (7) cannot be utilized, and instead a solution of the general diffusion-convection equation [Equation (2)] is required.

In a later paper Taylor (*18*) applied the method of analysis used for laminar flow to turbulent flow through open tubes and showed experimentally that the observed dispersion could be described by an effective axial diffusion mechanism superimposed on plug flow. Several investigators (*4, 9, 13, 14*) have used this model for studying dispersion in packed units. Inability to reproduce the degree of skew of the experimental residence time distribution functions has been the mode of failure of the effective diffusion model in these applications (*4*). Since dispersion in these complex systems is the result of coupled axial convection and radial diffusion and not axially-directed diffusion as the mathematical model states, a two-dimensional model might be able to explain the skewness of experimental residence time distribution functions better than the more limited unidimensional model.

Therefore the reasons for seeking a generalized solution of Taylor's flow-diffusion problem extend beyond the need for predicting residence time distribution functions for only laminar flow situations; the conclusions drawn from this study may be applied qualitatively to turbulent flow through open and packed tubes, the method of solution may be extended to velocity profiles other than the laminar one, and the main characteristics of two-dimensional residence time distribution function models may be delineated.

OUTLINE OF THE MATHEMATICAL DEVELOPMENT

Equation (2) describes the variation of tracer concentration with time at a point in a cylindrical pipe. Molecular diffusion in the radial direction and convection in the axial direction are taken to be the methods of material transport. Angular symmetry is assumed, and the diffusion coefficient is considered to be independent of the tracer concentration:

$$D_m\left[\frac{\partial^2 C}{\partial r^2}+\frac{1}{r}\frac{\partial C}{\partial r}\right]-U_o\left[1-\frac{r^2}{R^2}\right]\frac{\partial C}{\partial Z}=\frac{\partial C}{\partial t} \quad (2)$$

Dimensionless groups are introduced in Equation (8) for r, and Z:

$$\frac{\partial^2 C}{\partial \xi^2}+\frac{1}{\xi}\frac{\partial C}{\partial \xi}-4\,(1\cdot-\xi^2)\cdot\frac{\partial C}{\partial \zeta}=\frac{\partial C}{\partial t}\frac{R^2}{D_m} \quad (8)$$

Initial and boundary conditions for a unit impulse input in concentration are given in Equation (9):

$$\begin{aligned} &C(t=0,\xi,\zeta>0)=0 \\ &\overline{U}\pi R^2\,C(t,\xi,\zeta=0)=\delta(t) \end{aligned} \qquad \left.\frac{\partial C}{\partial \xi}\right|_{\xi=0}=\left.\frac{\partial C}{\partial \xi}\right|_{\xi=1}=0 \quad (9)$$

By taking the Laplace transform of Equations (8) and (9) one can replace the independent variable time by a parameter s. The dimensionless transformed point concentration is denoted by $\overline{C}$, while gamma represents the dimensionless Laplace parameter:

$$\gamma = sR^2/4D_m \qquad (10)$$

$$\frac{\partial^2 \overline{C}}{\partial \xi^2} + \frac{1}{\xi}\frac{\partial \overline{C}}{\partial \xi} - 4(1-\xi^2)\cdot \frac{\partial \overline{C}}{\partial \zeta} = 4\gamma\overline{C} \qquad (11)$$

$$\frac{\partial \overline{C}}{\partial \xi}\Bigg|_{\xi = 0} = 0; \frac{\partial \overline{C}}{\partial \xi}\Bigg|_{\xi = 1} = 0$$

$$\overline{U}\pi R^2\overline{C}\ (\gamma, \xi, \zeta = 0) = 1 \qquad (12)$$

Separation of variables is applied to Equation (11) to obtain $\overline{C}$ as a function of ξ, ζ, and the dimensionless parameter γ:

$$\overline{C}(\gamma, \xi, \zeta) = \sum_{n=1}^{\infty} B_n \cdot \exp(-b_n^2\zeta)\ E_n(\gamma, \xi) \qquad (13)$$

The eigen function $E_n(\gamma, \xi)$ has the form

$$E_n(\gamma, \xi) = \exp\left(-b_n\xi^2\right)\sum_{k=0}^{\infty} a_{k,n}\,\xi^{2k} \qquad (14)$$

where $a_{o,n}$ equals 1, and successive coefficients are calculated by use of Equation (15):

$$a_{k,n} = a_{(k-1),n}\left[2b_nk - (b_n^2 + b_n - \gamma)\right]/k^2 \qquad (15)$$

Coefficients of eigen function terms which contain odd powers of ξ are found to be zero by applying the boundary condition at the center line.

This eigen value expansion was suggested by Lauwerier (*11*) in his study of the mathematical functions which arise in problems involving diffusion and chemical reaction during laminar flow. It is used in this solution because of the rapid convergence which it offers in comparison with the convergence of an ordinary power series expansion.

The *n*th eigen value b_n must satisfy the boundary condition at the pipe wall:

$$\frac{\partial E_n(\gamma, \xi)}{\partial \xi}\Bigg|_{\xi = 1} = 0 = -b_n\sum_{k=0}^{\infty} a_{k,n} + \sum_{k=0}^{\infty} k\,a_{k,n} \qquad (16)$$

Eigen constants B_n are evaluated from the axial boundary condition $\overline{U}\pi R^2\overline{C}(\gamma, \xi, \zeta = 0) = 1$ and the orthogonality property of the eigen functions:

$$B_n = \frac{1}{\overline{U}\pi R^2}\,\frac{\int_0^1 \xi(1-\xi^2)E_n(\gamma, \xi)\,d\xi}{\int_0^1 \xi(1-\xi^2)E_n^2(\gamma, \xi)\,d\xi} \qquad (17)$$

Integration of the point concentration in accordance with Equation (18) for constant zeta yields the Laplace transform of the residence time distribution function $\overline{C}_o$:

$$\overline{C}_o = \overline{U}\pi R^2\overline{C}_{mc}(\gamma, \zeta = \zeta_1) = \sum_{n=1}^{\infty} B_n \cdot \left[\exp(-b_n^2\zeta_1)\right]\frac{\int_0^1 \xi(1-\xi^2)E_n\ (\gamma, \xi)\,d\xi}{\int_0^1 \xi(1-\xi^2)\,d\xi} \qquad (18)$$

Inversion of Equation (18) to obtain the residence time distribution function requires the use of a long calculation procedure. Actually the inversion is unnecessary, since parameters which characterize the residence time distribution function can be obtained directly from the transformed equation. These parameters are the moments about the mean or central moments.

Van der Laan (*19*) showed that the moments about the origin could be found by evaluating derivatives of the Laplace transform with respect to *s* at *s* equal to zero, as indicated in Equation (19):

$$(-1)^n\alpha_n = (-1)^n\int_0^\infty t^n f(t)\,dt$$

$$(-1)^n\int_0^\infty t^n e^{-st}\ \ f(t)\,dt\,\Big|_{s = 0}$$

$$= \frac{\partial^n f(s)}{\partial s^n}\Bigg|_{s = 0}$$

$$= \frac{\partial^n \overline{C}_o}{\partial (st_o)^n}\Bigg|_{st_o = 0} t_o^n \qquad (19)$$

Central moments can be evaluated from the moments about the origin and the value of the mean. Expressions for the second and third central moments are given in Equation (20) (*6*):

$$\mu_2 = \alpha_2 - \alpha_1^2$$
$$\mu_3 = \alpha_3 - 3\alpha_1\alpha_2 + 2\alpha_1^3 \qquad (20)$$

Because gamma appears as a parameter in the expression for the eigen function, eigen values and eigen constants are evaluated for different values of gamma. At a fixed axial position the transformed residence time distribution function value is expressed numerically by a series of gamma values and corresponding $\overline{C}_o$ values. The equation describing the steady state concentration variation due to first-order reaction and diffusion in laminar flow under isothermal conditions is identical with Equation (11) when *s* is replaced by the reaction rate constant. This problem was solved by means of finite difference techniques by Cleland and Wilhelm (*5*) for boundary conditions which in the present study correspond to introduction of a unit impulse. Since the number of gamma values used by Cleland was insufficient for the purposes of this study, an I.B.M.-650 electronic data processing machine was programmed to perform the necessary calculations. Wissler and Schechter (*20*) have also developed a program similar to the one written for this study. Published concentration values for their program corresponded to the same gamma values covered by Cleland.

Moments about the origin are obtained by evaluating the coefficients of a polynomial fitted to curves of the transformed residence time distribution function as a function of the gamma-zeta product $(\gamma\cdot\zeta)$ or the equivalent expression st_o:

$$\overline{C}_o(st_o, \zeta_1) = \overline{C}_o(0, \zeta_1) + \frac{\partial \overline{C}_o}{\partial (st_o)}\Bigg|_{st_o = 0} \cdot\ st_o + \ldots\ldots\ldots\ldots \frac{\partial^n \overline{C}_o}{\partial (st_o)^n}\Bigg|_{st_o = 0} \cdot \frac{(st_o)^n}{n!} + \ldots\ldots\ldots \qquad (21)$$

Values of both the minimum residence time t_o and the diffusion parameter zeta are needed to specify the moments about the origin and central moments found from Equation (21). The dependence of the central moments on the minimum residence time can be eliminated by dividing the *n*th central moment by the mean residence time α_1 raised to the *n*th power:

$$\hat{\mu}_2 = \mu_2/\alpha_1^2;\ \hat{\mu}_n = \mu_n/\alpha_1^n \qquad (22)$$

These dimensionless central moments depend only on zeta.

RESULTS

The computer output consisted of values of the Laplace transform of the residence time distribution function $\overline{C}_o(st_o)$ for gamma values between 0.05 and 11 with zeta as parameter ranging from 0.01 to 8.0. Four eigen functions were used to determine the transformed residence time distribution function values. Since the fourth eigen function was found to contribute 1.8% or less to $\overline{C}_o(st_o)$ for the zeta range of interest, calculation of a fifth eigen function was considered unnecessary.

Previous investigators had proposed one-dimensional models for the laminar flow residence time distribution function appropriate when the action of either the velocity profile (*3*) or molecular diffusion (*16*) determined the extent of fluid mixing. Comparison of the general solution with these one-dimensional models was sought to ascertain that the general solution represented a plausible transition of the

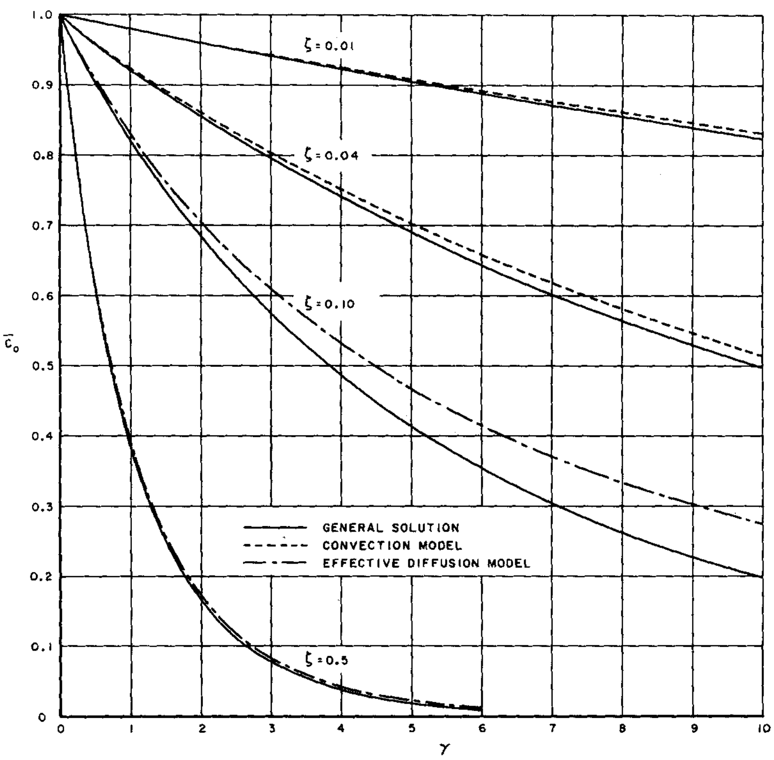

Fig. 1. Comparison of transformed residence time distribution function-gamma function for the two-dimensional solution with limiting one-dimensional models. At zetas of 0.01 and 0.04 the one-dimensional residence time distribution function depends only on the velocity profile; at zetas of 0.1 and 0.5 the effective axial diffusion model is the one-dimensional form.

laminar flow residence time distribution function between these limiting cases.

When the minimum residence time is short compared with the time for decay of radial gradients by diffusion, zeta is small. For this condition the velocity profile is the determining dispersion mechanism and the convection model [Equation (7)] represents the laminar residence time distribution function. In Figure 1 the Laplace transform of this function and the general solution are seen to converge as zeta decreases from 0.04 to 0.01. The convection model predicts transformed residence time distribution function values within 1% of the general solution values at a zeta of 0.01 and within 3.5% at zeta equal to 0.04.

For checking the general solution at large zeta the transform of the solution to the uniaxial effective diffusion equation shown in Equation (23) was obtained for introduction of a unit impulse at the inlet of a semi-infinite pipe [Equation (24)]:

$$D_e \frac{\partial^2 C_a}{\partial Z^2} - \bar{U} \frac{\partial C_a}{\partial Z} = \frac{\partial C_a}{\partial t} \quad (23)$$

$$\pi R^2 \bar{U} C_a(Z = 0, t) = \delta(t) \quad (24)$$

Taylor's expression for the virtual diffusion coefficient for laminar flow ($K = R^2 U_o^2 / 192 D_m$) was substituted for D_e to permit expression of the transformed residence time distribution function [Equation (25)] in terms of gamma and zeta, the variables used in the general solution:

$$\bar{f}(s) = \bar{C}_a \pi R^2 \bar{U} = \exp\left[4\zeta\left(3 - \sqrt{3(3 + \gamma)}\right)\right] \quad (25)$$

In Figure 1 the general solution is seen to approach the effective diffusion model [Equation (25)] at zeta values near 0.5. Values of the transformed residence time distribution function predicted by the effective diffusion model are within 1% of the general solution values at zetas exceeding 0.7.

Thus it is seen that the general solution represents the residence time distribution function during laminar flow for the extreme cases of dispersion controlled by convection or molecular diffusion, as well as for conditions when both dispersion mechanisms merit consideration.

Any statement of the zeta range for which the general solution must be employed depends on the extent of agreement between the general solution and simple models required for acceptance of the simpler model. For example if the one-dimensional models are considered adequate when they predict transformed residence time distribution function values within 1% of the $\bar{C}_o(st_o)$ values, the general solution must be used to represent the laminar residence time distribution function for zetas between 0.01 and 0.7.

Moments

At constant zeta moments of the residence time distribution function about the origin were found by fitting a polynomial to the $\bar{C}_o - st_o$ function in accordance with Equation (21). Curve fitting was accomplished with the Gregory-Newton interpolation procedure *(10)* for evenly-spaced abscissas. For zeta values between 0.01 and 2.0 the number of points employed for fitting varied from twelve to nine; in general, only six points were available for calculations at larger values of zeta.

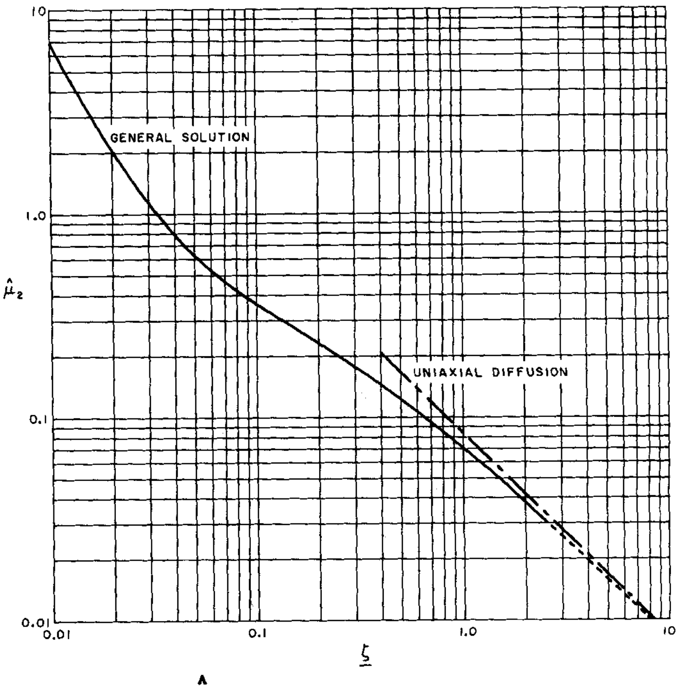

Fig. 2. Variation of $\hat{\mu}_2$ with zeta for the two-dimensional residence time distribution function.

Two tests were made to check the accuracy of the moments determined by interpolation. In a study of continuous flow systems Spalding (*14*) demonstrated theoretically that the mean residence time was equal to the volume between the inlet and outlet divided by the volumetric flow rate when no diffusion occurred across the inlet and outlet planes. Hence one can conclude for the present case that the first moment about the origin should be twice the minimum residence time, or the coefficient of the linear term in a polynomial fit to the $\overline{C}_o - st_o$ function should equal -2. Values of the linear coefficient differed from (-2) by less than 1% at twenty-four zeta values between 0.032 and 8.0; at zetas of 0.01, 0.016, and 0.024 the calculated coefficients deviated from the predicted value by less than 3%.

As a second test two different sets of $\overline{C}_o(st_o)$ values were fitted at zetas of 0.2, 0.3, 0.4, and 0.5. At each zeta second moments about the origin were found to be in agreement within 1% of the smaller value. Third moments agreed within 2.5% at zetas of 0.2 and 0.3 and within 10 and 4% at zetas of 0.4 and 0.5 respectively.

These tests indicated that the interpolation procedure provided first and second moments of sufficient accuracy for the zeta range in which the general solution is applicable; however uncertainties in the third moment could limit the usefulness of the interpolation procedure as zeta increased. For this reason, and because fewer points were used for curve fitting at high zetas, only third moments for zetas less than 0.5 were considered in developing the following discussion.

Figure 2 presents the dimensionless variance $\hat{\mu}_2$ as a function of zeta for the two-dimensional diffusion-convection solution. When zeta is large, the figure shows that the one-dimensional diffusion model and the general solution yield equivalent results. This agreement is expected from the approach of the $\overline{C}_o - \gamma$ function for the general solution to that of the effective diffusion model as zeta increases (Figure 1). Comparison of the general solution with the variance-zeta function of the convection model [Equation (7)] was not made because this model predicts infinite values of all moments greater than the first. In previous investigations (*4*, *9*) the mean and second central moment of a measured residence time distribution function have been used to determine the parameters of simple, one-dimensional models proposed to represent fluid mixing in the experimental system. The primary indication that simple models such as the series perfect mixer and effective diffusion models are inadequate has been their inability to predict the high skewness of the residence time distribution functions for some systems to which they have been applied (*4*). The third central moment of any distribution is a measure of skewness, having a value of zero for symmetric distributions and positive values for residence time distribution function curves exhibiting tails.

In Figure 3 dimensionless third central moments $\hat{\mu}_3$ are plotted against dimensionless second central moments for three cases: the general solution developed in this paper and the two simple models just mentioned. (For the solution developed in this paper $\hat{\mu}_2$ values between 0.2 and 8.0 correspond to values of zeta between 0.5 and 0.01 respectively.) The $\hat{\mu}_3 - \hat{\mu}_2$ function was chosen for presentation to stress differences between the residence time distribution functions of the general solution and those predicted by the one-dimensional cases, on the assumption that the appropriateness of a given model is to be judged by matching the first and second moments of the observed residence time distribution function to the two free parameters of either simple model and then comparing the observed skewness with that predicted.

For large values of $\hat{\mu}_2$ (corresponding to short systems) the skewness of the generalized solution exceeds by an order of magnitude those of the one-dimensional models. At intermediate values of $\hat{\mu}_2$ (increasing values of ζ) $\hat{\mu}_3$ for the generalized solution remains much larger than the one-dimensional values but begins to approach them. At low values of $\hat{\mu}_2$ the uncertainty in the computations reported here is greatest, but the third central moments clearly show little absolute difference. In view of the close correspondence of the $\overline{C}_o - \gamma$ functions for uniaxial diffusion and the generalized solution under conditions of large zeta, it seems likely that the $\hat{\mu}_3$'s for these two cases coincide in the limit.

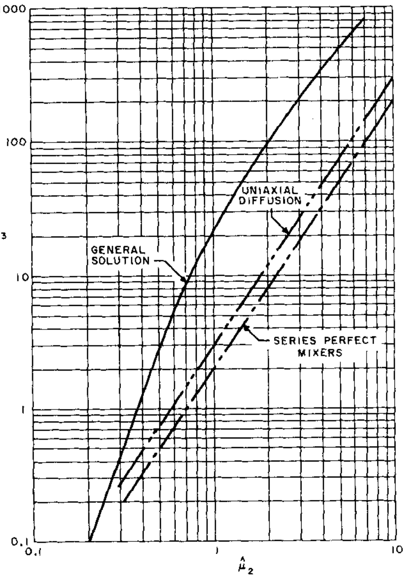

Fig. 3. Dimensionless third central moment $\hat{\mu}_3$ as a function of the dimensionless variance $\hat{\mu}_2$ for the general solution and two one-dimensional models.

The distinguishing characteristic of the general solution appears to be its ability to predict more highly skewed residence time distribution functions than either one-dimensional model of equal mean and variance. Since failure of one-dimensional models to reproduce experimental residence time distribution functions has taken just this form, one may conclude, at least for some systems, that consideration of dispersion mechanisms which represent the simultaneous, distributed effects of convection and diffusion will explain fluid mixing better than effective one-dimensional dispersion mechanisms. The ability to represent residence time distribution functions exhibiting long tails is expected of solutions of the two-dimensional convection-diffusion equation for other radially dependent velocity profiles.

Figure 3 also suggests comparison of third moments for a measured residence time distribution function and dispersion models of equal variance to determine the model which best represents the physical system. When such a comparison is made at a variance value for which the third central moments differ greatly, as for $\hat{\mu}_2$ values between 1 and 10 in this study, the best model may be readily distinguished.

Effect of Axial Diffusion on the Transformed Residence Time Distribution Function

In the solution of the general diffusion-convection equation transport in the axial direction due to molecular diffusion was considered to be negligible compared with transport due to convection. To estimate the experimental conditions for which this assumption is valid an axial diffusion term was introduced into the two-dimensional equation [Equation (2)]. The Laplace transform of the residence time distribution function for this expanded convection-diffusion equation was found to be equal to the expression given in Equation (26) for any value of zeta:

$$f(\gamma) = -\frac{D_m{}^2 4^2}{U_o{}^2 R^2} \cdot \int_o^1 \left[\frac{\partial \overline{C}}{\partial \zeta} \bigg|_{\zeta = \zeta_1} - \frac{\partial \overline{C}}{\partial \zeta} \bigg|_{\zeta = 0} \right] \xi d\xi + 4 \int_o^1 (1 - \xi^2) \overline{C} \xi d\xi \quad (26)$$

The second term on the right-hand side had been evaluated in accordance with Equation (18). Equation (13) was used to calculate the integral portion of the first term on the right-hand side. The value of the dimensionless group $\overline{U}R/D_m$ which made the axial integral term equal to 0.001 was assumed to define the limiting physical conditions for which the solution presented in this paper is valid.

The axial diffusion integral attained a maximum value of 47.0 for the gamma and zeta range employed in this study, whence axial diffusion could be considered negligible if the parameter $\overline{U}R/D_m$ assumed a minimum value of 434.

When one uses this dimensionless specification on the diffusional behavior of the system in conjunction with the requirement on the fluid mechanical behavior of the system, $2\overline{U}R/\nu < 2{,}000$, the condition for ignoring axial diffusion can be given as a limit on the Schmidt group $\nu/D_m > 0.434$. For liquids and most gases at atmospheric and higher pressures this condition is met.

SUMMARY

1. A solution has been developed for the two-dimensional convection-diffusion equation for laminar flow which makes no assumption concerning the relative importance of radial diffusion or axial convection as dispersion mechanisms. The general solution cannot be approximated by one-dimensional dispersion models for a definite range of operating conditions.

2. A method has been developed for determining the moments of the laminar residence time distribution function in its range of application. Use of the third central moment in determining the model which best predicts an experimental distribution has been demonstrated.

3. The solution of this paper has been shown to predict more skewed distributions than one-dimensional models of equal mean and variance, suggesting that these results may help in some cases to reconcile theory with experience.

4. The effect of the assumption of negligible axial diffusion has been considered, and the solution appears to be applicable for a wide range of liquid flow conditions; it is also acceptable for gas flow situations at atmospheric pressure and above.

ACKNOWLEDGMENT

The authors gratefully acknowledge use of computing facilities at the Watson Scientific Computing Laboratories and the Electronics Research Laboratories of Columbia University. The first named author wishes to acknowledge the financial assistance provided by a Seely W. Mudd Scholarship during part of the time this work was in progress.

NOTATION

A = outlet area
$a_{k,n}$ = kth coefficient of the expansion for the nth eigen function
b_n = nth eigen value
B_n = nth eigen constant
$C(A)$ = point concentration at outlet resulting from a tracer pulse input
∇C = concentration gradient perpendicular to outflow area
C = point concentration
C_a = area mean concentration
C_{mc} = mixing cup average concentration
$\overline{C}, \overline{C}_a, \overline{C}_{mc}$ = Laplace transforms of the corresponding concentrations
$\overline{C}_o = \overline{U}\pi R^2 \overline{C}_{mc}$ = Laplace transform of the two-dimensional residence time distribution function
D_m = molecular diffusivity
D_e = effective axial diffusivity
$E_n(\gamma,\xi)$ = nth eigen function
$f(t)$ = residence time distribution function
$f(t)dt$ = fraction of material leaving system between t and $t + dt$
$\overline{f}(s)$ = Laplace transform of the residence time distribution function
$K = R^2 U_o{}^2/(192 D_m)$ = effective axial diffusion coefficient for laminar flow as defined by Taylor
L^* = length of tracer distribution in tube
L = distance between tracer inlet and measurement point
Q = total quantity of material injected into system at $t = 0$
r = radial coordinate
R = tube radius
s = Laplace parameter
t = time measured from introduction of tracer
$t_o = L/U_o$ = minimum residence time for tracer
U_o = center-line velocity for laminar flow
$\overline{U} = U_o/2$ = average fluid velocity
$V(A)$ = point velocity perpendicular to outflow area
$\overline{V}$ = average velocity perpendicular to outflow area
Z = axial coordinate measured from tracer inlet
$Z_1 = Z - \frac{1}{2}(U_o t)$ = axial position relative to a coordinate system moving with the mean fluid velocity

Greek Letters

α_n = nth moment about the origin
α_1 = mean residence time
$\xi = \dfrac{r}{R}$ = dimensionless radial coordinate
$\delta(t)$ = Dirac delta function
$\zeta = \dfrac{4ZD_m}{U_o R^2}$ = dimensionless axial coordinate, or dispersion parameter
$\gamma = \dfrac{sR^2}{4D_m}$ = dimensionless Laplace parameter
μ_n = nth central moment
$\hat{\mu}_n = \dfrac{\mu_n}{\alpha_1{}^n}$ = dimensionless nth central moment
ν = kinematic viscosity

Subscripts

k,n = integers 0, 1, 2 . . . .

LITERATURE CITED

1. Aris, R. B., *Proc. Roy. Soc. (London)*, **A235**, 67 (1956).
2. Blackwell, R. J., Paper presented before the local section of the Am. Inst. Chem. Engrs., Galveston, Texas (Oct. 18, 1957).
3. Bosworth, R. C. L., *Phil. Mag. (London)*, **39**, Series 7, p. 847 (1948).
4. Carberry, J. J., and R. H. Bretton, *A.I.Ch.E. Journal*, **4**, 367 (1958).
5. Cleland, F. A., and R. H. Wilhelm, *ibid.*, **2**, 489 (1956).
6. Cramer, H., "The Elements of Probability Theory," p. 74, Wiley, New York (1955).
7. Crank, J., "The Mathematics of Diffusion," p. 10, Oxford University Press, London, England (1956).
8. Dankwerts, P. V., *Chem. Eng. Sci.*, **2**, 1 (1953).
9. Ebach, E. A., and R. R. White, *A.I.Ch.E. Journal*, **4**, 161 (1958).
10. Lanczos, C., "Applied Analysis," p. 306, Prentice Hall, Englewood Cliffs, New Jersey (1956).
11. Lauwerier, H. A., *Appl. Sci. Res.*, **A8**, 366 (1959).
12. Levenspiel, O., and W. K. Smith, *Chem. Eng. Sci.*, **6**, 227 (1957).
13. Liles, A. W., and C. J. Geankoplis, *A.I.Ch.E. Journal*, **6**, 591 (1960).
14. McHenry, K. W., Jr., and R. H. Wilhelm, *ibid.*, **3**, 83 (1957).
15. Spalding, D. B., *Chem. Eng. Sci.*, **9**, 74 (1958).
16. Taylor, G. I., *Proc. Roy. Soc. (London)*, **A219**, 186 (1953).
17. *Ibid.*, **A225**, 473 (1954).
18. *Ibid.*, **A223**, 446 (1954).
19. Van der Laan, E. T., *Chem. Eng. Sci.*, **7**, 187 (1958).
20. Wissler, E. H., and R. S. Schechter, *Appl. Sci. Res.*, **A10**, 198 (1961).

Manuscript received December 20, 1961; revision received August 2, 1962; paper accepted August 6, 1962. Paper presented at A.I.Ch.E. New York meeting.