

Wave Model for Longitudinal Dispersion: Application to the Laminar-Flow Tubular Reactor

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The wave model for longitudinal dispersion, published elsewhere as an alternative to the commonly used dispersed plug-flow model, is applied to the classic case of the laminar-flow tubular reactor. The results are compared in a wide range of situations to predictions by the dispersed plug-flow model as well as to exact numerical calculations with the 2-D model of the reactor and to other available methods. In many practical cases, the solutions of the wave model agree closely with the exact data. The wave model has a much wider region of validity than the dispersed plug-flow model, has a distinct physical background, and is easier to use for reactor calculations. This provides additional support to the theory developed elsewhere. The properties and the applicability of the wave model to situations with rapidly changing concentration fields are discussed. Constraints to be satisfied are established to use the new theory with confidence for arbitrary initial and boundary conditions.

Introduction

In a recent article by Westerterp et al. (1995a) a new one-dimensional model for the residence time distribution in flowthrough contactors and chemical reactors has been developed as an alternative to the commonly used dispersed plug-flow model, also called the standard dispersion model (SDM). A qualitative analysis of the proposed wave model has been made in a second article (Westerterp et al., 1995b). The wave model differs fundamentally from the SDM and is not afflicted with the physical contradictions of the SDM. In contrast to the SDM, which works only with an average concentration, the wave model contains a second independent state variable, the dispersion flux, characterizing the deviation from plug-flow conditions. The equation relating the dispersion flux to the area mean concentration has the same form as Maxwell's constitutive law for viscoelastic fluids. From a mathematical point of view the wave model appeared to be simpler than the SDM for many practical purposes. The wave model gives the same results as the SDM for slow processes, although not for all of them. For rapidly varying concentration fields, where the SDM definitely produces wrong results, the wave model gives a qualitatively correct description of the phenomena. The wave model correctly predicts the reversibility of longitudinal dispersion with respect to a change

in the flow direction and distinguishes between apparent and real backmixing. The essential advantage of the wave model—if compared to other known alternatives to the SDM—is that it does not depend on the type of equipment under consideration. These features of the new model and its simplicity are an essential advantage for a wide class of problems, if compared to the Fickian dispersion models. However, the quantitative accuracy of the wave model for rapid processes has not been checked in the papers just mentioned, nor has its ability to represent adequately actual multidimensional phenomena occurring in the case of rapidly varying concentration fields, as in reactors with rapid chemical reactions. Therefore, in the present article we will test quantitatively the applicability of the wave model over a wide range of conditions. This can be done, of course, by comparing experimental reactor data with the model predictions. Eventually, this is probably the best approach, but because of the many experimental problems in obtaining accurate kinetics, in many cases it is difficult to achieve a high precision. In other words, it is often difficult to decide whether discrepancies are because of the model or the data. As an alternative a mathematical comparison between the wave model, the SDM, and more precise multidimensional calculations presents itself.

The laminar-flow tubular reactor is considered in this article in order to test certain concepts regarding the wave model.

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This application has the great virtues of mathematical tractability and practical experimental execution. The predictions of the theory can be compared with numerical solutions of the exact multidimensional equation and with numerous results obtained by other methods. It is the most investigated reactor problem and is often used as a test example for simplifying approaches to reactor modeling. The problem is also of practical interest, particularly for high-viscosity fluids. Moreover, this relatively simple problem is also of interest because it contains many of the essential features of dispersion in various flowing systems and provides a considerable insight into the effect of velocity shear on axial dispersion.

After the initial work by Taylor (1953), Aris (1956), and Cleland and Wilhelm (1956), diffusion with or without a chemical reaction when there is a fully developed laminar flow in a straight tube has been the subject of a large number of theoretical investigations. Numerical steady-state solutions for the case of a homogeneous first-order chemical reaction have been reported, among others, by Cleland and Wilhelm (1956), Vignes and Trambouze (1962), and Bailey and Gogarty (1962). Exact series solutions of the same problem have been presented by Hsu (1965), Dang and Steinberg (1977), and Dang (1978).

Different analytical approaches to the residence time distribution during laminar flow in a tube have been reported by Farrel and Leonard (1963), Philip (1963), Gill (1967), Chatwin (1970), Gill and Sankarasubramanian (1970, 1971, 1972), Whitaker (1971), Tseng and Besant (1970, 1972), Fife and Nicholes (1975), DeGance and Johns (1980), Smith (1981, 1987a,b), Barton (1983), Yamanaka (1983), Shankar and Lenhoff (1989), and Stokes and Barton (1990). Short-time asymptotic solutions to the pulse-input problem have been proposed by Lighthill (1966), Chatwin (1977) and Vrentas and Vrentas (1988). Numerical solutions of the same problem have been utilized by Ananthkrishnan et al. (1965), Gill and Ananthkrishnan (1967), Mayock et al. (1980), Yu (1981), Wang and Stewart (1983, 1989) and Takahashi et al. (1990). Dynamic behavior of a tubular reactor with a first-order reaction has been analyzed by Subramanian et al. (1974) and Nigam and Vasudeva (1976). The laminar-flow tubular reactor with a first-order homogeneous reaction was used as an example to examine the applicability of the SDM to the otherwise two-dimensional situation by a number of investigators (Bischoff, 1968; Wissler, 1969; Mashelkar, 1973; Kulkarni and Vasudeva, 1976; Carbonell and McCoy, 1978).

Experimental results have been presented by Cleland and Wilhelm (1956), Vignes and Trambouze (1962), Nigam and Vasudeva (1976), and Korenaga et al. (1989).

Publications with respect to the investigation of the nonlinear systems are quite scarce. Houghton (1962) and Wan and Ziegler (1970) investigated the conditions under which Taylor diffusion can be applied with steady systems in the presence of a reaction with a power-law rate equation. An analysis of the propagation of an injected pulse through a system in which a second-order chemical reaction takes place, has been made by Barton (1986) and Smith (1989). A diffusional type of equation for the area averaged concentration with an effective flow velocity, which depends on the concentration, for systems involving weak nonlinear reactions was recently derived by Yamanaka and Inui (1994) on the basis of the projection operator technique.

In this article the accuracy of the wave model is examined over the whole range of reaction rates for the steady-state behavior of a laminar flow reactor, in which a homogeneous reaction with first- or second-order irreversible kinetics takes place. The transient behavior of the reactor is investigated only for a first-order irreversible reaction. The first three spatial moments of the concentration—mean, variance, and skewness, as well as the mean and the variance of the residence time distribution—for uniform and nonuniform pulse injections are calculated for arbitrary moments of time. The theoretical predictions are compared to numerical, exact, and experimental results and to the predictions with the SDM and plug flow model. Many different theoretical approaches can be used to explore the laminar flow reactor (see the papers just cited). We engage in the comparison of two of them: the generalized dispersion theory of Gill and Sankarasubramanian (1970, 1972) and the orthogonal collocation method as frequently used for the analysis of various convective diffusion problems. It will be shown for a rather wide variety of problems that the wave model provides a good approximation to the more exact, but also more complicated two-dimensional equations. For instance, the maximum error in the calculated bulk concentrations for arbitrary values of the reaction constants and a conversion of 99% as determined with the exact solution does not exceed 8.7% in the case of a steady-state reactor with a first-order chemical reaction and 16.7% for a second-order reaction.

The examples considered also demonstrate that the wave model, having a clear physical significance and being more general, is simpler from the mathematical point of view and has a much wider region of validity for reactor calculations than a Fickian-type dispersed plug-flow model.

For the application considered an explanation is given for why the wave model with parameters as obtained in Westertep et al. (1995a) for asymptotic conditions is also applicable to rapid processes.

It was found that the wave model gives results close to those of the collocation method when used to handle the radial gradients in a reactor. The model corresponds to the two-point collocation that, as shown by Wang and Stewart (1983, 1989), in many cases closely approximates the fine-grid computations. This well-known procedure may serve as an additional justification of the wave model. It also provides a useful approach to obtain a one-dimensional equation.

The wave model fails when the radial concentration distribution at the reactor inlet or at the initial moment of time is essentially nonuniform. Restrictions to the value of the dispersion flux are derived in order that this theory can be used with confidence for arbitrary initial and boundary conditions.

Different Approaches for the Investigation of the Laminar-Flow Reactor

Exact description—the problem chosen for comparison

We assume that the concentration variation in the laminar-flow tubular reactor can be described by the two-dimensional convective diffusion equation:

$$\frac{\partial c}{\partial t} + 2\bar{u}\left(1 - \frac{r^2}{a^2}\right)\frac{\partial c}{\partial x} + q(c) = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r}\right) \quad (1)$$

along with the following initial

$$t = 0, \quad c = \zeta_{\text{init}}(x, r) \quad (2)$$

and boundary conditions

$$x = 0, \quad c = \zeta_0(r, t); \quad r = 0 \quad \text{and} \quad a, \quad \frac{\partial c}{\partial r} = 0. \quad (3)$$

The molecular diffusion coefficient D in Eq. 1 is considered to be independent of the solute concentration. We have neglected the molecular diffusion in the axial direction on the assumption that the longitudinal mixing is completely dominated by the combined effects of the nonuniform convection and transverse diffusion.

Standard dispersion model

The commonly encountered one-dimensional model for chemical reactors is the longitudinally dispersed plug-flow model. We also call it the standard dispersion model (SDM). The model equation is usually written as:

$$\frac{\partial \bar{c}}{\partial t} + \bar{u} \frac{\partial \bar{c}}{\partial x} + q(\bar{c}) = D_e \frac{\partial^2 \bar{c}}{\partial x^2} \quad (4)$$

with the boundary conditions known from Danckwerts (1953):

$$x = 0, \quad \bar{u} \bar{\zeta}_0 = \bar{u} \bar{c} - D_e \frac{\partial \bar{c}}{\partial x}; \quad x = L, \quad \frac{\partial \bar{c}}{\partial x} = 0. \quad (5)$$

Here and throughout this article an overbar on a quantity denotes its cross-sectionally averaged value as defined for an axisymmetrical problem in a tube by

$$\overline{(\dots)} = \frac{2}{a^2} \int_0^a (\dots) r dr.$$

The value of the dispersion coefficient for laminar flow in a circular tube is well known from Taylor (1953) as being $D_e = a^2 \bar{u}^2 / 48D$. The peculiarity of this model is the presence of an additional parameter—the reactor length L —that is absent in the multidimensional model of Eqs. 1–3. The appearance of this parameter is due to the description of the hydrodynamical axial dispersion by an equation of the parabolic type. Thus, the application of the SDM is burdened with the uncertainty of choosing the reactor length L . Different recommendations are known at this point. To be concrete we will assume the reactor is infinitely long as often recommended—see, for example, Wissler (1969) and Subramanian et al. (1974)—so $L \rightarrow \infty$.

Convective dispersion theory of Gill and Sankarasubramanian

This theory, later called the G-S theory, is frequently used for the analysis of different convective diffusion equations. It gives the solution of multidimensional convective diffusion equations—in our case Eq. 1 with $q = 0$ —in terms of an area-averaged concentration $\bar{c}_I(x, t)$, when the concentration

is specified at the initial moment of time $t = 0$ in the form of $\zeta_{\text{init}}(x, r) = \psi(x)Y(r)$, see Gill and Sankarasubramanian (1970, 1971). For practical reasons the shortened two-term approximation of this theory is used, and the previously mentioned solution is found from the equation:

$$\frac{\partial \bar{c}_I}{\partial t} = K_1(t) \frac{\partial \bar{c}_I}{\partial x} + K_2(t) \frac{\partial^2 \bar{c}_I}{\partial x^2}, \quad (6)$$

where $K_1(t)$ and $K_2(t)$ are known functions of time that also depend on the initial transverse concentration distribution $Y(r)$.

For the solution of linear problems with other initial and boundary conditions different variants of the superposition technique have been developed using the solution of the basic equation Eq. 6 (Gill and Sankarasubramanian, 1972; Subramanian et al., 1974).

Wave model

This model has been proposed as an alternative to the SDM. A quasi-linear hyperbolic system of two first-order equations for the average concentration \bar{c} and the dispersion flux j was obtained (Westerterp et al., 1995a):

$$\frac{\partial \bar{c}}{\partial t} + \bar{u} \frac{\partial \bar{c}}{\partial x} + \frac{\partial j}{\partial x} + q(\bar{c}) = 0 \quad (7)$$

$$[1 + \tau q'(\bar{c})]j + \tau \frac{\partial j}{\partial t} + \tau(\bar{u} + u_a) \frac{\partial j}{\partial x} = -D_e \frac{\partial \bar{c}}{\partial x} \quad (8)$$

with the following initial and boundary conditions:

$$t = 0, \quad \bar{c} = c_{\text{init}}(x) = \bar{\zeta}_{\text{init}}(x), \quad j = j_{\text{init}}(x) = \overline{(u - \bar{u}) \zeta_{\text{init}}} \quad (9)$$

$$x = 0, \quad \bar{c} = c_0(t) = \bar{\zeta}_0(t), \quad j = j_0(t) = \overline{(u - \bar{u}) \zeta_0}. \quad (10)$$

Here the prime indicates the derivative with respect to c , so $q' = \partial q / \partial c$. The dispersion flux—the second unknown variable—is defined as

$$j = \overline{(u - \bar{u})c}. \quad (11)$$

The wave model contains three parameters—the longitudinal dispersion coefficient D_e ; the relaxation time τ ; and the parameter of velocity asymmetry u_a . In Eqs. 7 and 8 the dispersion coefficient D_e is the Taylor dispersion coefficient, the same as in the SDM. For laminar flow in a tube the parameters of the wave model were calculated in an earlier article by Westerterp et al. (1995a), and are

$$D_e = \frac{a^2 \bar{u}^2}{48D}; \quad \tau = \frac{a^2}{15D}; \quad u_a = \frac{\bar{u}}{4}. \quad (12)$$

For nonlinear chemical reaction rates more refined equations may be used instead of Eqs. 7 and 8 (Westerterp et al., 1995a):

$$\frac{\partial \bar{c}}{\partial t} + \bar{u} \frac{\partial \bar{c}}{\partial x} + \frac{\partial j}{\partial x} + q(\bar{c}) + \frac{1}{2} q''(\bar{c}) \frac{\tau}{D_e} j^2 = 0 \quad (13)$$

$$\left(1 + \tau q'(\bar{c}) + \frac{1}{2} j \frac{\tau}{v} q''(\bar{c})\right) j + \tau \frac{\partial j}{\partial t} + \tau(\bar{u} + u_a) \frac{\partial j}{\partial x} = -D_e \frac{\partial \bar{c}}{\partial x} \quad (14)$$

This system compared to Eqs. 7 and 8 contains an additional parameter v , which is equal to $7\bar{u}/1,558$ for laminar flow in a round tube. For a linear reaction rate $q''(c) = 0$, and Eqs. 13 and 14 coincide with Eqs. 7 and 8. Equations 13 and 14 contain a more exact representation of the averaged reaction rate, or take into account that $\bar{q}(c) \neq q(\bar{c})$ for nonlinear chemical reactions.

Orthogonal collocation technique

The well-known orthogonal collocation technique with two interior radial nodes will also be involved in the comparison, according to the variant given by Wang and Stewart (1983).

Application of the Different Approaches to the Laminar Flow Reactor

In this section we consider some typical examples showing the capabilities of the different approaches.

Steady-state reactor performance

We restrict ourselves to a simple but practical problem, namely, the reactor with a constant and uniform inlet concentration. In this case the boundary condition at the reactor inlet for Eq. 1 is

$$x = 0 \quad c = \zeta_0 = c_0 = \text{constant} \quad (15)$$

We present the results in the form of the area average concentration \bar{c} and bulk concentration c_b that is defined as

$$c_b = \frac{4}{\bar{u}a^2} \int_0^a \bar{u} \left(1 - \frac{r^2}{a^2}\right) cr \, dr = \bar{c} + \frac{j}{\bar{u}}$$

The solution of the SDM is well known. The dispersion flux is related to the concentration by $j = -D_e \partial \bar{c} / \partial x$. The G-S theory is applicable only for a first-order reaction with $q = k_1 c$ and is described by Subramanian et al. (1974). In this case the two coefficients $K_1(t)$ and $K_2(t)$ of Eq. 6 should be found for the initial transverse concentration distribution $Y(r) = 1 - r^2/a^2$ and the solution of Eq. 6 should be obtained for the initial condition $t = 0$, $\bar{c}_I = c_0 \bar{u} \delta(x)$, where $\delta(x)$ is a Dirac delta function. The bulk average concentration is calculated as (Gill, 1975)

$$c_b(x) = -\frac{1}{\bar{u}} \int_0^\infty \left(K_1(t') \bar{c}_I(x, t') + K_2(t') \frac{\partial \bar{c}_I(x, t')}{\partial x} \right) e^{-k_1 t'} dt'$$

This is a rather tedious procedure especially at small distances from the reactor inlet and for high reaction rates, be-

cause of singular behavior of $\bar{c}_I(x, t)$ at $x = 0$ and the slow convergence of the series for $K_1(t)$ and $K_2(t)$.

The equations of the wave model for the problem considered are

$$\bar{u} \frac{d\bar{c}}{dx} + \frac{dj}{dx} + q(\bar{c}) = 0 \quad (16)$$

$$[1 + \tau q'(\bar{c})] j + \tau(\bar{u} + u_a) \frac{dj}{dx} = -D_e \frac{d\bar{c}}{dx} \quad (17)$$

with the following boundary conditions:

$$x = 0, \quad \bar{c} = \bar{\zeta}_0 = c_0, \quad j = \overline{(u - \bar{u}) \zeta_0} = 0 \quad (18)$$

For a first-order chemical reaction with $q = k_1 c$ and a position-independent rate constant k_1 , Eqs. 16 and 17 can be combined to one equation of the second order for the average concentration

$$\left(\tau \bar{u}^2 + \tau \bar{u} u_a - D_e\right) \frac{d^2 \bar{c}}{dx^2} + (\bar{u} + k_1 \tau (2\bar{u} + u_a)) \frac{d\bar{c}}{dx} + k_1 (1 + k_1 \tau) \bar{c} = 0 \quad (19)$$

with boundary conditions:

$$x = 0, \quad \bar{c} = c_0, \quad \frac{d\bar{c}}{dx} = -\frac{\tau(\bar{u} + u_a) k_1 c_0}{\tau \bar{u}(\bar{u} + u_a) - D_e} \quad (20)$$

which follows from Eqs. 16–18. The bulk concentration in this case also obeys Eq. 19 but with different boundary conditions:

$$x = 0, \quad c_b = c_0, \quad \frac{dc_b}{dx} = -k_1 c_0 \quad (21)$$

For a first-order chemical reaction the analytical solutions of the SDM and the wave model are straightforward. The general properties of these solutions have been considered in a previous article (Westerterp et al., 1995b). Both these solutions are much simpler than the G-S solution. In the case of a nonlinear chemical reaction rate the numerical solution of the wave model can easily be obtained by “marching” numerically through the reactor from the inlet to the end, as for the simple plug-flow model, whereas in this case the SDM needs iterative calculations.

The dimensionless area-mean concentration \bar{c}/c_0 for a first-order reaction as a function of the dimensionless axial distance $X_1 = k_1 x / \bar{u}$ is presented in Figure 1. The ratio of the bulk concentration calculated by different approximate methods to the numerical solution of the steady-state form of Eq. 1 with the inlet boundary condition of Eq. 15 is given in Figures 2 and 3 for the values $\alpha_1 = k_1 a^2 / D = 100$ and $\alpha_2 = k_2 c_0 a^2 / D = 100$. For a second-order reaction with $q = k_2 c^2$ the results calculated with Eqs. 13 and 14 are also given in Figure 3.

It is seen that the agreement between the wave model and the two-dimensional equation Eq. 1 is far better than ob-

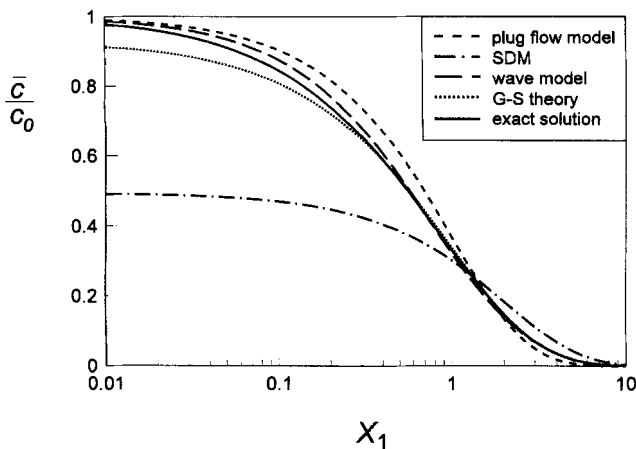


Figure 1. Steady-state area-mean concentrations for a first-order reaction as a function of $X_1 = k_1 x / \bar{u}$ and for $k_1 a^2 / D = 100$.

tained with conventional models. In spite of the wide variation of yield values, the magnitude of the ratio $c_b / c_{b,exact}$ remains within narrow limits along the reactor. It is noteworthy that the wave model also gives satisfactory results in the case of no diffusion in the radial direction or of infinitely fast chemical reactions with $\alpha_{1,2} \rightarrow \infty$, that is for purely convective mass transfer. The maximum absolute error in c_b for the wave model does not exceed 16.7%, when the concentration changes from 1 to 0.01—over a hundredfold concentration change—and for arbitrary reaction rates. The SDM gives adequate results only if $\alpha_{1,2} \leq 15$, as is well known. On the contrary, we would like to point out that for high reaction rates the SDM becomes even less accurate than the plug-flow model, which is a simplest variant of the wave model. Despite the large error the plug-flow model, in contrast to the Fick-

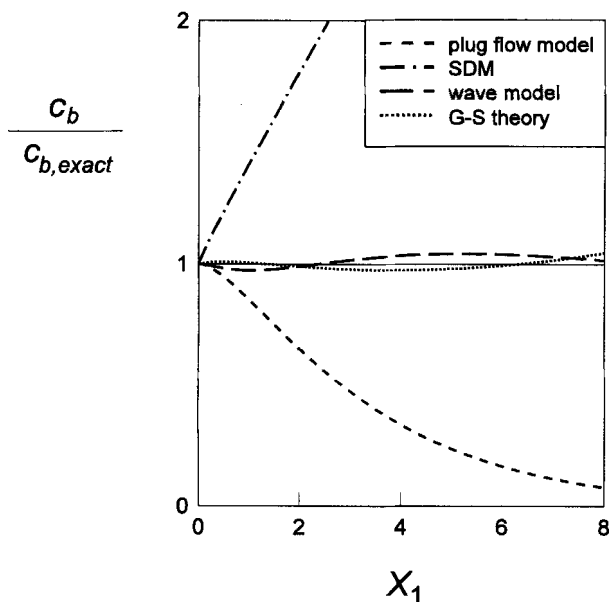


Figure 2. Values of $c_b / c_{b,exact}$ for a first-order reaction as a function of $X_1 = k_1 x / \bar{u}$ and for $k_1 a^2 / D = 100$.

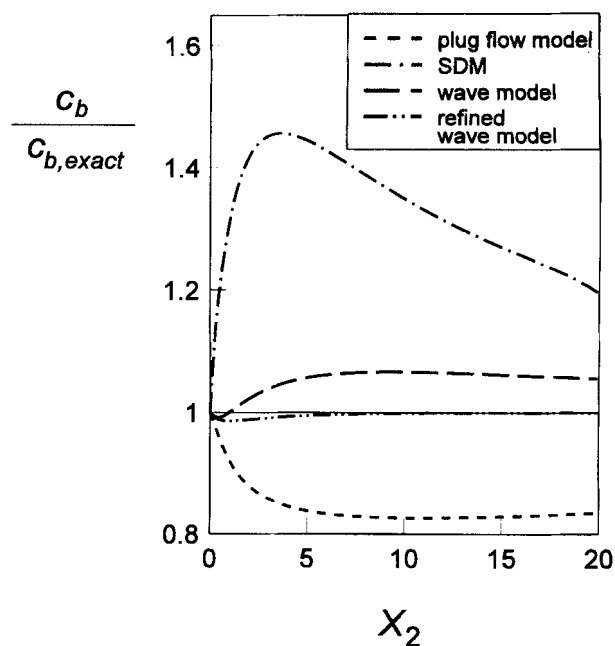


Figure 3. Values of $c_b / c_{b,exact}$ for a second-order reaction as a function of $X_2 = k_2 c_0 x / \bar{u}$ and for $k_2 c_0 a^2 / D = 100$.

ian dispersion model, remains qualitatively correct, whereas the SDM completely fails in the limiting cases of $\alpha_{1,2} \rightarrow \infty$ and fixed values of $X_{1,2}$. This also shows an inherent weakness of the SDM for reactor calculations. Agreement between the one-dimensional Fickian-type equation and the exact two-dimensional model can be reached only with an empirical reaction-dependent dispersion coefficient (Kulkarni and Vasudeva, 1976) or through empirical manipulation with the boundary conditions.

Spatial moments

The spatial moments of the concentration distribution of a solute injected into a stream can directly be calculated by means of the wave model for arbitrary methods of the solute injections. Examples of the application of the wave model for the calculations of the moments are presented in Westerterp et al. (1995b). The analytical calculation of the moments using the SDM is only possible for infinite and semi-infinite media. Besides that the analytical solutions are not available for all initial and boundary conditions (Kreft and Zuber, 1978).

For convenience we define the following dimensionless quantities:

$$C = \frac{c}{c_r}, \quad J = \frac{j}{\bar{u}c_r}, \quad \theta = \frac{tD}{a^2}, \quad X = \frac{xD}{\bar{u}a^2}, \quad \rho = \frac{r}{a},$$

where c_r is a reference concentration; its value is not important.

In order to test the accuracy of the wave model for the calculation of the first spatial moments we will consider two initial distributions of tracer material:

Table 1. Second Spatial Moments $1,000m_2$ for the Initial Condition $G = \delta(X)$ at Different Moments of Time θ

θ	Exact	Wave Model	Collocation	SDM
0.01	0.03121	0.02974	0.03162	0.4166
0.05	0.6296	0.6177	0.6493	2.083
0.10	2.024	2.009	2.088	4.167
0.20	5.702	5.694	5.835	8.333
0.40	13.90	13.90	14.07	16.67
1.00	38.89	38.89	39.06	41.67

$$\theta = 0 \quad C = G(X, \rho) = \begin{cases} \delta(X) & \text{case A} \\ 2\rho^2\delta(X) & \text{case B.} \end{cases}$$

These particular initial distributions have been used as examples by Chatwin (1977) and Wang and Stewart (1983) and represent situations where the initial distribution is uniform in case A or increasing monotonically from the axis to the wall in case B. The expressions of the first three spatial moments of the mean, variance, and skewness for the wave model are presented in Westerterp et al. (1995b).

The simple and accurate calculations of the moments for developed laminar flow of a Newtonian fluid can be made by means of the orthogonal collocation method with as few as two radial collocation points, as shown by Wang and Stewart (1983). These computations as well as the predictions of the SDM and G-S procedure are also included in the comparison.

We present the spatial moments around the mean as defined by

$$m_0 = \int_{-\infty}^{\infty} \bar{C} dX, \quad m_1 = \frac{\int_{-\infty}^{\infty} X\bar{C} dX}{m_0},$$

$$m_n = \frac{\int_{-\infty}^{\infty} (X - m_1)^n \bar{C} dX}{m_0}, \quad n = 2, 3.$$

In the important case A the second and third central spatial moments m_2 and m_3 are compared to the exact solutions derived by Aris (1956), Chatwin (1977), and Barton (1983). The first moment m_1 in this case is equal to 1 according to all approaches. Table 1 and Figure 4 show the spatial variance and skewness as a function of dimensionless time θ .

In case B the calculation of the first moment is also of interest. Table 2 shows the calculated mean and variance for the nonuniform initial solute distribution in comparison to

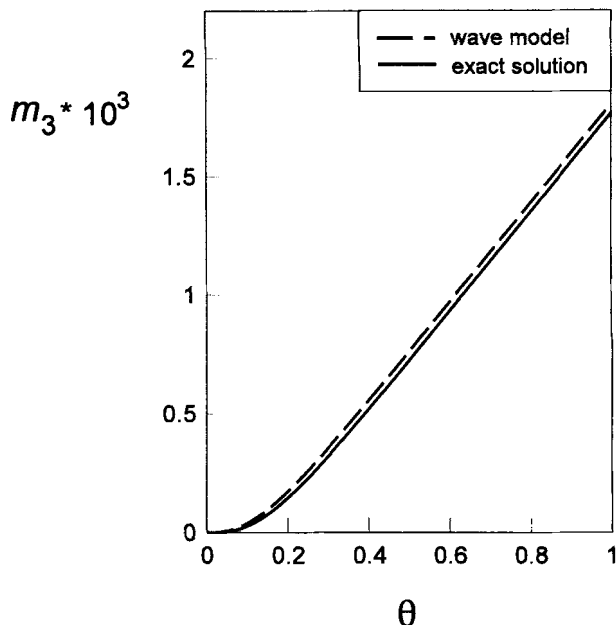


Figure 4. $m_3(\theta)$: predicted by the wave model vs. the exact solution by Barton (1983).

the exact results given by Chatwin (1977) and Barton (1983). The moments by the collocation method differ from the ones of Wang and Stewart (1983) who presented the exact value of the second moment in a coordinate system moving with the mean fluid velocity and not relative to the center of gravity of the pulse. Moreover, we use the mean velocity as the reference velocity, whereas Wang and Stewart used the maximum velocity.

The SDM cannot handle any initial radial concentration distribution— $m_1 = \theta$ and $m_2 = \theta/24$ for arbitrary initial transverse concentration distributions—and is not valid for the initial period before the equalization of the concentration over the cross section has been attained. The SDM, of course, gives $m_3 = 0$ whatever θ is. The truncated two-term dispersion equation, Eq. 6, has the remarkable property that two of the spatial moments are exact. However, it predicts a symmetric distribution around the center of gravity of the tracer and the third central moment is zero. Thus there is a need to retain higher-order terms in the application of the generalized dispersion theory, in order to predict the results observed. The orthogonal collocation method used by Wang and Stewart (1983) gives $m_3 = 0$ independent of the initial concentration distribution. To our knowledge no results for the

Table 2. Spatial First Moments $100(m_1 - \theta)$ and Second Moments $1,000m_2$, Respectively, for the Initial Condition $G = 2\rho^2\delta(X)$ at Different Moments of Time θ

θ	$100(m_1 - \theta)$			$1,000m_2$		
	Exact	Wave Model	Collocation	Exact	Wave Model	Collocation
0.01	-0.3022	-0.3095	-0.3080	0.02035	0.02220	0.4167
0.05	-1.1082	-1.1725	-1.1472	0.4328	0.4893	2.083
0.10	-1.6172	-1.7264	-1.6627	1.517	1.681	4.167
0.20	-1.9760	-2.1116	-1.9984	4.794	5.101	8.333
0.40	-2.0776	-2.2167	-2.0799	12.79	13.17	16.67
1.00	-2.0834	-2.2222	-2.0833	37.76	38.15	41.67

skewness for the case of a nonuniform pulse have been presented in the literature, with which we can make a comparison. As pointed out by Barton (1983) "the calculation of the m_3 in the general case is very laborious and the resulting expression is too long and complicated to reproduce."

It is notable that the large-time asymptotic values of the first three moments given by the wave model are exact (Westertep et al., 1995b). The model does not correctly predict the time dependence of the third moment at $\theta \rightarrow 0$: according to the wave model $m_3 \sim \theta^3$ in this limit, whereas from the exact expression of m_3 as obtained by Barton (1983) $d^3m_3/d\theta^3 = 0$ should hold at $\theta = 0$. However, such a small difference hardly can be detected in an experiment. Note that at $\theta \rightarrow 0$ or if dispersion is caused by convection alone, we find $m_3 \sim \theta^3(u - \bar{u})^3$, but for the parabolic velocity profile we have $(u - \bar{u})^3 = 0$.

Temporal moments

The most common approach in experimental work is based on measuring the distribution of residence times as a function of the axial distance, that is, on the measurement of the concentration variations as a function of time at fixed locations. Therefore, as a further test of the wave model, we will calculate the temporal moments of the residence time distribution. Such calculations can also be made directly by the wave model for arbitrary tracer injections (Westertep et al., 1995b). The results available for comparison are given by Houseworth (1984). This author has analyzed the residence time distribution in laminar flow in a tube with a Monte Carlo method, based on an analytical solution of the diffusion equation over the tube cross section.

We consider, as Houseworth did, the case of an instantaneous injection of a small amount of tracer arbitrarily distributed over the cross section of the tube at the point $X = 0$, whereas at the initial moment $\theta = 0$ the concentration is zero all over the tube. The initial and boundary conditions for the two-dimensional equation, Eq. 1, in our case can be written in dimensionless form as

$$\theta = 0, \quad C = 0; \quad X = 0, \quad C = F(\rho)\delta(\theta),$$

where the function $F(\rho)$, describing the concentration distribution over the inlet cross section, has been normalized such that $\bar{F} = 1$. These boundary conditions describe the problem of tracer injection proportional to the fluid flux along a given streamline rather than introducing the material uniformly over the cross section, as we did for the calculation of the spatial moments. The corresponding initial and boundary conditions for the wave model of Eqs. 7 and 8 with no reaction or $q = 0$ in dimensionless form are

$$\theta = 0, \quad \bar{C} = 0, \quad J = 0; \quad X = 0, \quad \bar{C} = \delta(\theta), \\ J = w\delta(\theta),$$

where $w = \overline{(u - \bar{u})F}/\bar{u}$. Let:

$$\mu_n = \int_0^\infty \theta^n \bar{C}(X, \theta) d\theta, \quad n = 0, 1, 2$$

be the temporal moments of the residence time distribution of the solute in the tube. The calculation of the first moments with the wave model gives the following results:

$$\mu_0 = 1 + w(1 - e^{-\gamma}) \\ \mu_1 = \gamma\alpha^{-1}[(1 + w)y + w\beta(1 - e^{-\gamma} - ye^{-\gamma}) \\ + (\beta - \alpha - w(1 + \alpha))(1 - e^{-\gamma})] \\ \mu_2 = \gamma^2\alpha^{-2}\{(1 + w)y^2 - w\beta^2y^2e^{-\gamma} \\ + 4[\beta - \alpha + w(\beta - \alpha - 1/2)](y - 1 + e^{-\gamma}) \\ + 2[\beta(\beta - \alpha) + w(\alpha + \beta(\beta - \alpha - 2))](1 - e^{-\gamma} - ye^{-\gamma})\},$$

where

$$\alpha = \frac{\bar{u}^2\tau}{(\bar{u} + u_a)\bar{u}\tau - D_e}, \quad \beta = \frac{\bar{u}^2\tau + D_e}{(\bar{u} + u_a)\bar{u}\tau - D_e} \\ \gamma = \frac{\tau D}{a^2} \quad \text{and} \quad y = \frac{X\alpha a^2}{D\tau}.$$

Using these expressions we can calculate the mean ν_1 and the variance σ_t^2 of the residence time distribution, which are

$$\nu_1 = \frac{\mu_1}{\mu_0}, \quad \sigma_t^2 = \frac{\int_0^\infty (\theta - \nu_1)^2 \bar{C}(X, \theta) d\theta}{\mu_0} = \frac{\mu_2}{\mu_0} - \nu_1^2.$$

For a tracer input uniform over the cross section $w = (u - \bar{u})F/\bar{u} = 0$ and the variance can be represented in the form:

$$\sigma_t^2 = 2\gamma^2\alpha^{-2}(\beta - \alpha)\{(2 - \beta)y \\ + [(\beta - 1)y - (2 - \beta)](1 - e^{-\gamma}) - (1/2)(\beta - \alpha)(1 - e^{-\gamma})^2\}.$$

Note that there are some errors in the same formula in the earlier article by Westertep et al. (1995b). In order to illustrate the theory we consider two special forms for $F(\rho)$, the distribution of the tracer over the inlet cross section: the first one where the inlet distribution is uniform or $F(\rho) = 1$, and the second where the tracer is supplied through a point source situated in the tube axis or $F(\rho) = \delta(\rho)/(2\rho)$. Tables 3 and 4 show the mean ν_1 and variance σ_t^2 of the residence time distribution for the two inlet conditions obtained by Houseworth (1984), the wave model and the SDM. For the SDM the following boundary conditions were used:

$$X = 0, \quad \bar{C} - \frac{1}{48} \frac{\partial \bar{C}}{\partial X} = \delta(\theta); \quad X \rightarrow \infty, \quad \bar{C} \rightarrow 0.$$

From Table 3 we see that the wave-model solution is accurate in the case of a uniform radial distribution and not too close to the inlet. The predictions of the SDM are independent of the inlet concentration distribution and therefore they are not shown in Table 4. A point source is an extreme case of a nonuniform inlet concentration and it is evident

Table 3. Mean $100\nu_1$ and Variance $1,000\sigma_t^2$ of the Residence Time Distribution as a Function of $X = xD/a^2\bar{u}$ for the Inlet Condition $F(\rho) = 1$

X	100ν ₁			1,000σ _t ²		
	Monte Carlo	Wave Model	SDM	Monte Carlo	Wave Model	SDM
0.01	0.9813	1.308	3.083	0.04706	0.03413	1.687
0.05	4.920	6.147	7.083	0.6995	0.7169	3.225
0.10	9.978	11.66	12.08	2.117	2.307	5.148
0.20	19.96	21.99	22.08	5.534	6.299	8.994
0.30	29.97	32.07	32.08	9.631	10.48	12.84
0.50	50.06	52.08	52.08	18.35	18.84	20.53

that a one-dimensional reactor model cannot be a suitable tool for the investigation of such a problem. This case is included in Table 4 to explore the region of applicability of the wave model. The unrealistic negative values of the variance for small distances as predicted by the wave model is explained later.

Transient behavior of the reactor

Consider the problem of a tubular reactor where the reacting component enters at the inlet of the tube with a constant uniform concentration c_0 . Initially, the tube contains no reactant. If the reaction is of the first order with a rate constant k_1 , the concentration of reactant satisfies the equation:

$$\tau \frac{\partial^2 \bar{c}}{\partial t^2} + \tau(2\bar{u} + u_a) \frac{\partial^2 \bar{c}}{\partial x \partial t} + (\tau\bar{u}^2 + \tau\bar{u}u_a - D_e) \frac{\partial^2 \bar{c}}{\partial x^2} + (1 + 2k_1\tau) \frac{\partial \bar{c}}{\partial t} + (\bar{u} + k_1\tau(2\bar{u} + u_a)) \frac{\partial \bar{c}}{\partial x} + k_1(1 + k_1\tau)\bar{c} = 0. \quad (22)$$

The initial and boundary conditions to be applied are

$$t = 0 \quad \bar{c} = 0, \quad \frac{\partial \bar{c}}{\partial t} = 0; \quad x = 0 \quad \bar{c} = c_0 H(t), \quad \frac{\partial \bar{c}}{\partial x} = - \frac{\tau(\bar{u} + u_a)(\delta(t) + k_1 H(t))}{\tau\bar{u}(\bar{u} + u_a) - D_e} c_0, \quad (23)$$

where $H(t)$ is the Heaviside unit step function. These conditions are the direct consequence of the Eqs. 7 and 8 and their initial and boundary conditions:

$$t = 0 \quad c = 0, \quad j = 0; \quad x = 0 \quad c = c_0 H(t), \quad j = 0.$$

The solution of Eq. 22 can be written as

$$\bar{c} = c_0 e^{-k_1 x/\bar{u}} \int_0^t E(x, t') dt',$$

where $E(t)$ is the solution of Eq. 22 for an instantaneous source of unit strength injected at time zero at the reactor inlet, that is for the initial and boundary conditions:

$$t = 0 \quad E = 0, \quad \frac{\partial E}{\partial t} = 0; \quad x = 0 \quad E = \delta(t), \quad \frac{\partial E}{\partial x} = - \frac{\tau(\bar{u} + u_a)}{\tau\bar{u}(\bar{u} + u_a) - D_e} \delta'(t).$$

This solution was presented in Westerterp et al. (1995b). It is not equal to zero for $u_2 t \leq x \leq u_1 t$, where u_1 and u_2 are the characteristic velocities of the hyperbolic system of Eqs. 7 and 8, which for laminar flow in a tube are

$$u_{1,2} = \bar{u} + \frac{u_a}{2} \pm \sqrt{\frac{u_a^2}{4} + \frac{D_e}{\tau}} = \bar{u} \left(1 \pm \frac{1 + \sqrt{2I}}{8} \right). \quad (24)$$

Figure 5 shows the bulk concentration as a function of the axial position as calculated by the different methods and for the parameter values used in the experiments of Nigam and Vasudeva (1976). The analytical solution of the unsteady-state SDM with a first-order reaction term probably has not yet been presented. Therefore the simplified boundary conditions of the form

$$x = 0 \quad \bar{c} = c_0, \quad x \rightarrow \infty \quad \bar{c} \rightarrow 0$$

have been used, as in the articles of Subramanian et al. (1974) and Nigam and Vasudeva (1976).

Breakthrough curve for a pulse input specified at the initial moment of time

The problem of dispersion in laminar flow through a straight tube for a pulse input specified at the initial moment has been the subject of a large number of theoretical investigations. Because the exact analytical solution of the partial differential equation is difficult to obtain, a number of inter-

Table 4. Mean $100\nu_1$ and Variance $1,000\sigma_t^2$ of the Residence Time Distribution as a Function of $X = xD/a^2\bar{u}$ for the Inlet Condition $F(\rho) = \delta(\rho)/(2\rho)$

X	100ν ₁		1,000σ _t ²	
	Monte Carlo	Wave Model	Monte Carlo	Wave Model
0.01	0.5052	0.4347	0.0000017	-0.02530
0.05	2.661	3.681	0.005200	0.09790
0.10	5.919	8.626	0.2061	0.9911
0.20	14.37	18.81	2.274	4.141
0.30	24.01	28.91	5.764	8.038
0.50	43.75	48.96	14.01	16.30

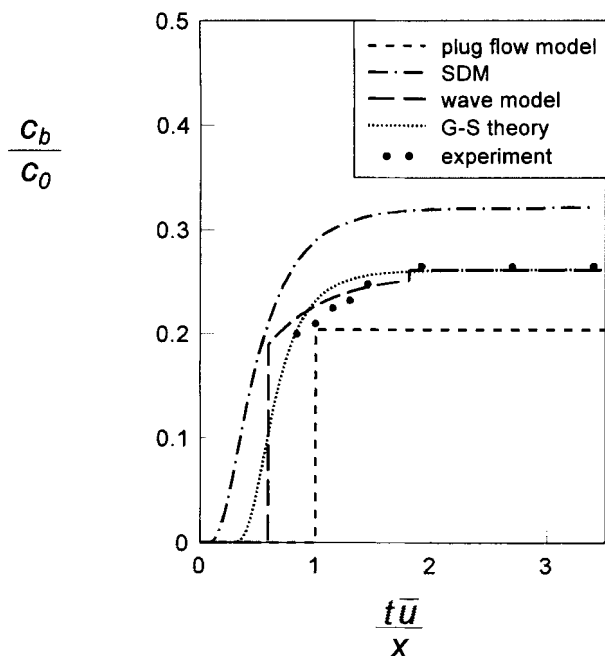


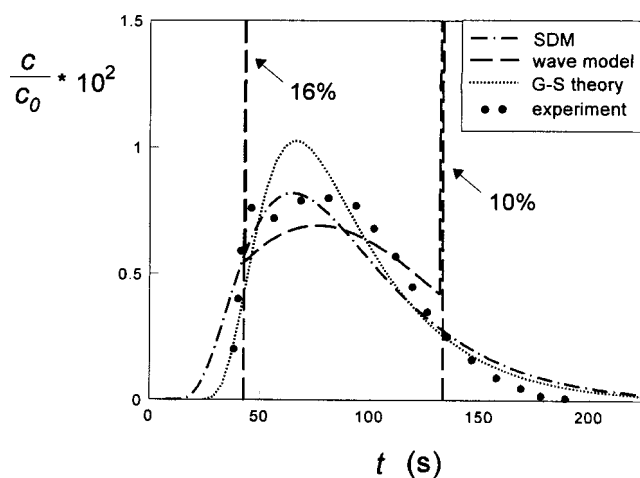
Figure 5. Breakthrough for a step change of the inlet concentration in a laminar flow reactor for $D/(k_1 a^2) = 0.037$ and $k_1 x/\bar{u} = 1.59$ calculated by different methods vs. experimental data of Nigam and Vasudeva (1976).

tigators have attempted to develop approximate analytical or numerical solutions. Comprehensive numerical calculations have been made by Yu (1981), Shankar and Lenhoff (1989) and by Takahashi et al. (1990). These numerical solutions agree very well with the experimental results by Korenaga et al. (1989) for a finite slug of a dye solution dispersed in water. The analytical solution of the wave model for the initial condition of the two-dimensional equation, Eq. 1, in the form:

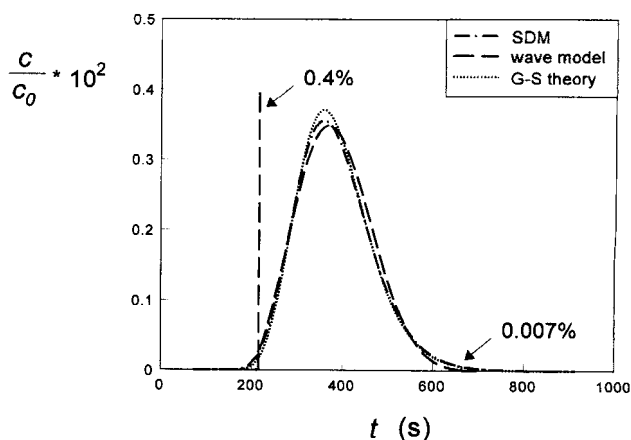
$$t = 0, \quad c = \frac{M}{\pi a^2} \delta(x)$$

is given in Westerterp et al. (1995b), where M is the amount of material injected. This solution can be used to handle problems with any radially uniform initial conditions through the conventional superposition integral similar to those as in the previous example. An example of the calculated breakthrough curve at a small distance from the inlet in the case of a rectangular, radially uniform initial concentration profile is presented in Figure 6a and compared to the experimental data of Korenaga et al. (1989) and to the predictions of the G-S theory and the SDM. For the small initial slug length used in the experiments of Korenaga et al. (1989) the solutions are very close to those with initial conditions approximated by the delta function.

The wave model predicts unrealistic concentration peaks that, however, correspond to the double-peaked behavior of the experimental breakthrough curves. These concentration spikes were observed only at an early stage of the dispersion for delta Dirac type or other sharp initial distributions. At a later stage in the dispersion process the area under the spikes



(a)



(b)

Figure 6. Breakthrough for an initial rectangular pulse calculated by different methods.

(a) $x = 40$ cm, the calculated curves are compared to experimental data of Korenaga et al. (1989); (b) $x = 200$ cm. Other parameters are $a = 0.403$ mm; $\bar{u} = 0.545$ cm/s; $D = 3.78 \cdot 10^{-6}$ cm²/s; the initial slug length is 0.39 cm. The numbers near the spikes indicate the fractions of the amount of tracer under the spikes.

becomes relatively small and the solution of the wave model closely corresponds to the exact solution. The breakthrough curves at a long distance from the inlet calculated by the wave model, G-S theory, and by the SDM are presented in Figure 6b. All solutions are close to each other in the central part of the concentration cloud, but differ near the front and the end. In contrast to the other approximate solutions the solution of the wave model is permanently zero outside the region $x/u_1 \leq t \leq x/u_2$. For a smoother initial distribution, as in experimental work, the results of the hyperbolic model are not unrealistic anymore at any stage of dispersion. The solution of the wave model after a short period of time or at small distances is easily understood and has been explained in an earlier article by Westerterp et al. (1995b). One should realize that the prediction of the concentration profile of a solute initially injected into a stream over a short time is a very difficult problem. Although a number of special analyti-

cal and numerical approximations have been developed, there are only a few solutions that are valid for arbitrary moments of time, as was shown by Yu (1981).

Limitations of the Wave Model

In most practical systems molecular diffusion in the axial direction can be neglected and axial mass transport occurs due to convection. This results in restrictions to the value of the dispersion flux:

$$(u_{\min} - \bar{u})\bar{c} \leq j \leq (u_{\max} - \bar{u})\bar{c}, \quad (25)$$

where u_{\min} and u_{\max} are minimum and maximum values of the axial velocities. According to the SDM the dispersion flux is proportional to concentration gradient $-\partial\bar{c}/\partial x$ and can have arbitrary values, including $\pm\infty$. A signal can never travel faster than the velocity of the "fastest streamline" if molecular diffusion in the axial direction is negligible. This physical contradiction also exposes the shortcomings of the SDM and narrows the limits of its applicability. According to the wave model axial mass transport occurs by two convective flows with the velocities u_1 and u_2 of Eq. 24. Therefore the dispersion flux in the wave model can be represented as

$$j = u_1 c_1 + u_2 c_2 - \bar{u}\bar{c} = (u_1 - \bar{u})c_1 + (u_2 - \bar{u})c_2, \quad (26)$$

where c_1 and c_2 are the concentrations in the first and second wave and $c_1 + c_2 = \bar{c}$. Taking into consideration the inequalities $0 \leq c_1 \leq \bar{c}$ and $0 \leq c_2 \leq \bar{c}$, we conclude that the dispersion flux of the wave model must obey the constraints:

$$(u_2 - \bar{u})\bar{c} \leq j \leq (u_1 - \bar{u})\bar{c}. \quad (27)$$

So the wave model predicts confined values of the dispersion flux for any concentration gradient: this is as it should be. However, the restrictions of the wave model to the value of the dispersion flux as given in Eq. 27 are only approximations and narrower than the exact restrictions of Eq. 25; this leads to some limitations of the model. For laminar flow in a round tube $u_{\min} = 0$, $u_{\max} = 2\bar{u}$, and from Eq. 24 we have $u_1 = 1.698\bar{u}$ and $u_2 = 0.552\bar{u}$. So for the wave model:

$$-0.448\bar{u}\bar{c} \leq j \leq 0.698\bar{u}\bar{c}, \quad (28)$$

whereas allowed values of j are

$$-\bar{u}\bar{c} \leq j \leq \bar{u}\bar{c}. \quad (29)$$

The discrepancies of the constraints of Eqs. 28 and 29 may lead to physically unrealistic results: if j is higher than $0.698\bar{u}\bar{c}$ or lower than $-0.448\bar{u}\bar{c}$, the concentration in one of the waves will be negative, as follows from Eq. 26. Fortunately, such contradictions occur only in extreme situations with essentially nonuniform radial concentration profiles, where the application of a one-dimensional model obviously does not make sense. Such situations arise for example in the case of a point injection of solute in the center of the tube, where the initial or inlet value of the dispersion flux is equal to $\bar{u}\bar{c}$. This explains the negative values of the variance of the residence

time distribution for a point injection in the tube axis at short distances from the injection point with $X \ll 1$ or $x \ll \bar{u}\tau$; see Table 4. In the case of spatial moments such contradictions have not been observed even for point injections.

Unrealistic negative values of the variance of the residence time distribution are found due to an inconsistency of the approximate Eqs. 7 and 8 and the exact boundary condition for essentially nonuniform, inlet radial concentration profiles. The dispersion flux in the equations is approximate, whereas its boundary value is exact and can exceed the approximate constraints. A simple way to exclude this contradiction, whenever the exact values exceed the permissible limits, is to bring the boundary values of the dispersion flux in line with the model equations, that is to use the limiting values of the dispersion flux instead of its exact values.

The second reason for the decrease in the accuracy of Eqs. 7 and 8 is the approximate representation of the nonlinear consumption rate averaged over cross-section, through the mean concentration. The approximation used—where the consumption rate is represented through the first term only of a Taylor expansion about the mean concentration (Westerp et al., 1995a)—may be insufficient for nonlinear rapid chemical reactions with characteristic times lower than the relaxation time. In this case the transverse concentration profiles are very steep and a more refined cross-sectional averaging of the source term becomes necessary. This can be seen from Figure 2, which shows that for the second-order reaction, Eqs. 13 and 14 are considerably more accurate than Eqs. 7 and 8. Regrettably Eqs. 13 and 14 are not suitable to describe the reactor because of the additional parameter ν .

Discussion

We have tested the accuracy of the wave model by comparing it to known solutions of only certain standard problems for laminar flow in a circular tube. The results of the comparison show that the wave model gives a fair approximation to the exact solutions in a wide range of situations and is definitely preferable to the SDM. Similar results were obtained for many other problems of mass transfer in laminar flows of Newtonian and non-Newtonian fluids and for turbulent flows in tubes, between parallel plates, in Couette flow and in open channels.

The main parameters of the wave model—the dispersion coefficient D_e and relaxation time τ , which make it different from the SDM—must also be known for the application of the SDM. D_e is a parameter of the basic equation, Eq. 4, and τ is a measure for the applicability of the SDM. The SDM is only applicable if τ is much smaller than other characteristic times of the system, like the average residence time and the chemical reaction time constant. Therefore the beauty of the wave model is that it can be used on the basis of the same information as needed for the SDM. More precise determinations of τ and of the velocity asymmetry u_a are desirable but not absolutely necessary. In particular, many results presented in this article could be obtained, although with some loss of accuracy, using only the findings of Taylor (1953), who determined D_e and in fact introduced and estimated the relaxation time, called by him the "time of decay" being $a^2/[3.8)^2 D]$, and further the value of u_a in his case would have been set to zero.

It is important from the mathematical point of view that the more general wave model is simpler than the SDM for reactor calculations for all situations where the boundary conditions are important. For linear steady-state and unsteady-state problems the analytical solutions of the wave model can be obtained by standard methods and for arbitrary initial and boundary conditions. For nonlinear systems the solutions of the wave model can be obtained by "marching" through the reactor from the inlet to the outlet, whereas the SDM needs iterative calculations.

The parameters of the wave model in Eq. 12 were obtained on the basis of a modification of Taylor's (1953) analysis of the asymptotic behavior, where the concentration is approximately uniform over the cross section and varies only slowly with respect to both time and the axial coordinate. Therefore the wave model as well as Taylor's model is also asymptotic, only with different properties and it is not surprising that the hyperbolic model gives excellent quantitative results for slow processes and, for instance, gives the exact asymptotic values of the first three spatial moments. Moreover, the results presented here demonstrate that the model also gives reasonably accurate descriptions under conditions of rapidly changing concentrations. The moments of the concentration distribution, the predictions of the steady-state reactor behavior at high reaction rates or $k_1 a^2/D$, $k_2 c_0 a^2/D \rightarrow \infty$, and the description of the transient behavior of the reactor are examples of these. This is not obvious. Some considerations why the wave model with the asymptotic parameters gives good results over a wide range of situations are given below.

The procedure used in a previous article by Westerterp et al. (1995a) to obtain Eqs. 7 and 8 with the parameters of Eq. 12 is the same closure procedure as that based on Taylor's (1953) original ideas: to find the expression relating the dispersion flux to the average concentration, some appropriate radial concentration distribution should be used. Instead of the radial concentration distribution used by Taylor, we have taken a more universal form of this distribution, namely:

$$c = \bar{c} - \frac{g_1}{D_e} j, \quad (30)$$

where

$$g_1 = -\frac{\bar{u}a^2}{4D} \left(\frac{1}{3} - \rho^2 + \frac{1}{2}\rho^4 \right), \quad \rho = \frac{r}{a}.$$

Such a simple modification of Taylor's procedure allows us to introduce the second state variable—the dispersion flux—and it leads to an essential change in the final result. It is obvious that Eq. 30 cannot be universally adequate, and sometimes a more refined approximation is necessary. To this end the concentration, as a continuous function, can be approximated uniformly by a polynomial:

$$c(x, r, t) = \sum_0^{\infty} a_n(x, t) \rho^{2n}, \quad (31)$$

where $\rho = r/a$ and $a_n(x, t)$, $n = 0, 1, 2, \dots$, are unknown functions of the axial position and time. This approximation satisfies the boundary condition in Eq. 3 at the reactor axis.

Also taking the boundary condition Eq. 3 at the reactor wall into account and introducing the concentration averaged over the cross section, Eq. 31 can be rewritten as

$$c(x, r, t) = \bar{c}(x, t) + 6\bar{u} \sum_{n=2}^{\infty} \frac{(n+1)(n+2)}{(n+1)(n+2)-6} \times \left(\frac{1}{2} - \frac{1}{n(n+1)} - \rho^2 + \frac{1}{n}\rho^{2n} \right) j_n(x, t), \quad (32)$$

where the unknown functions $j_n(x, t)$, with $n = 2, 3, \dots$, are normalized such that

$$j = \sum_{n=2}^{\infty} j_n, \quad (33)$$

and can be considered as the corresponding components of the dispersion flux in the series of Eq. 32 for the radial concentration distribution. If only the first term in the series in Eq. 32 is used we exactly have Eq. 30 again. The use of the exact representation of the concentration profile of Eq. 32 instead of Eq. 30 in the procedure described in Westerterp et al. (1995b) leads to a new equation instead of Eq. 8:

$$\sum_{n=2}^{\infty} (1 + \tau_n q'(\bar{c})) j_n + \sum_{n=2}^{\infty} \tau_n \frac{\partial j_n}{\partial t} + \sum_{n=2}^{\infty} \tau_n (\bar{u} + u_{an}) \frac{\partial j_n}{\partial x} = -D_e \frac{\partial \bar{c}}{\partial x}, \quad (34)$$

where D_e is the Taylor dispersion coefficient and parameters τ_n and u_{an} with $n = 2, 3, \dots$ are easily calculated through known formulas. It is remarkable that for laminar flow in a tube the values of τ_n change only from $a^2/15D$ to $a^2/16D$ and the values of u_{an} from $\bar{u}/4$ to $\bar{u}/8$ when n varies from 2 to ∞ . The same trends are also observed for other velocity profiles. Equation 33 and a weak dependence of the parameters of Eq. 34 on n may serve, at least on an intuitive basis, as a justification to use Eq. 8 instead of the exact Eq. 34 for processes with concentration fields rapidly changing with respect to time and coordinates: that is for those with a characteristic time of an order of magnitude of τ or lower. In addition, it easily can be checked that the use of any values of τ_n and u_{an} , $n = 2, 3, \dots$, instead of τ and u_a , does not influence essentially the steady-state concentration profiles calculated by Eqs. 16 and 17.

The comparisons presented earlier as well as other examples show that in many cases the results given by the wave model are in close agreement with those of the collocation method. This agreement can be easily explained.

In the case of two interior collocation points the application of the collocation procedure of Wang and Stewart (1983, 1989) to Eq. 1 with boundary conditions Eq. 3 gives rise to equations that can be rewritten as

$$\frac{\partial \bar{c}}{\partial t} + \bar{u} \frac{\partial \bar{c}}{\partial x} + \frac{\partial j}{\partial x} = 0$$

$$j + \frac{a^2}{16D} \left(\frac{\partial j}{\partial t} + \bar{u} \frac{\partial j}{\partial x} \right) = -\frac{a^2 \bar{u}^2}{48D} \frac{\partial \bar{c}}{\partial x}.$$

These equations are Eqs. 7 and 8 of the wave models, but with different parameter values:

$$D_e = \frac{a^2 \bar{u}^2}{48D}; \quad \tau = \frac{a^2}{16D}; \quad u_a = 0. \quad (35)$$

The relation $u_a = 0$ is a reason why the collocation method m_2 does not depend on the initial concentration distribution; see Tables 1 and 2, as well as $m_3 = 0$. These disadvantages can be avoided by using other collocation points than the zeros of the shifted Legendre polynomial. The collocation method does not tell us how to choose the "best" collocation points in the first approximations. However, this powerful method, as well as other variants of the method of weighted residuals (Finlayson, 1972), are very useful in obtaining the structure of one-dimensional equations that should be used for the description of longitudinal dispersion; see, as an example, Dil'man and Kronberg (1983). Thus, all these well-known procedures may serve as additional mathematical justifications of the wave model. For many calculations the difference between the parameters in Eqs. 12 and 35 is not very important.

Here we remark on a terminological contradiction in the work of Wang and Stewart (1983, 1989). It is generally assumed that the area averaging of multidimensional convective-diffusion equations gives rise to a diffusional-type one-dimensional equation. These authors oppose radial averaging and favor the collocation method; they stated that radially averaged equations have only a limited predictive power. But orthogonal collocation is also a way of averaging radially, which results in equations essentially different from the commonly used diffusional equations, and has a high predictive power.

We have neglected molecular diffusion in the axial direction in Eq. 1 because for most practical problems, including the laminar-flow reactor, the transport in the axial direction is dominated by shear dispersion and by other hydrodynamical mechanisms. For more complex problems than dispersion in laminar flow, we also have to consider the combined action of different hydrodynamical mechanisms through the application of the wave approach to each individual mechanism. The axial molecular diffusion, if necessary, can be incorporated into the wave model. This incorporation changes the type of governing equations and leads to mathematical complications. It should be noted that, as was shown by Wang and Stewart (1983), the solution of linear dispersion problems with axial molecular diffusion incorporated, and in an infinitely long tube with the concentration specified at the initial moment, can be obtained as a convolution of the concentration profile for the case where the axial molecular diffusion is neglected.

One should realize that the total variety of multidimensional situations cannot be represented only in terms of a few averaged characteristics, like the average concentration and the dispersion flux. Therefore there is no reason to expect that the wave model will predict arbitrary multidimensional distributions well. The wave model fails in the detailed description of processes with essentially nonuniform transverse concentration distributions. More complex models are needed to describe such complex situations. A more detailed repre-

sentation needs more one-dimensional equations—an infinite number of coupled equations for the exact representation—but such refinements can hardly be justified in reactor engineering practice because of the mathematical complexities and the many additional parameters, which cannot be evaluated in sufficient detail from experimental data in a way useful for design or scale-up purposes.

It should be stressed that the wave model should not be confused with a mathematical tool for the approximate solution of the partial differential equations, as it may seem from this article. First of all it should be considered as a simple alternative to the conventionally used dispersed plug-flow model or SDM and as a basic method for reactors with a complex flow behavior. This is an important difference of the wave approach in comparison to other known dispersion theories.

Conclusions

The validity of the wave model has been tested through a comparison with available solutions for the laminar-flow reactor. The results obtained provide additional support for the theory described in previous papers by Westerterp et al. (1995a,b) and clearly demonstrate the advantages of the wave model over the conventionally used standard dispersion model. The solutions of the wave model in a wide range of situations are in very reasonable agreement to the exact data. Hyperbolic-type equations are definitely preferable to parabolic ones for the description of hydrodynamical dispersion. If the necessary restrictions to the values of the dispersion flux are imposed the model can be used for almost all situations.

Notation

- a = tube radius
- k_2 = constant of second-order chemical reaction
- q = consumption rate of component per unit of reactor volume
- r = radial coordinate
- u = axial velocity
- x = axial coordinate
- X_2 = dimensionless axial coordinate, $k_2 c_0 x / \bar{u}$
- ζ = inlet or initial concentration

Subscript

- 0 = inlet, at $x = 0$

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