TAYLOR DISPERSION MODELS INVOLVING NONLINEAR IRREVERSIBLE REACTIONS

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Introduction

The axial dispersion model originated by Taylor[3] provides a useful technique for process control and process design in complex convective diffusion systems. One of the authors has derived extended Taylor dispersion equations in systems including heterogeneity in the radial direction by an averaging method based on the projection operator technique[4]. The result has been further extended to systems involving linear reactions[5]. Extended Taylor dispersion equations involving linear reactions or adsorption have been derived by various averaging techniques[1, 2]. However, it is difficult to extend the Taylor dispersion model to nonlinear systems. In this paper, we derive an approximate Taylor dispersion equation for systems involving weak nonlinear irreversible reactions.

1.   The Basic Equations

We consider unsteady mass transfer in a circular tube surrounded by an impermeable wall of radius R. The system may be composed of multiple axi-symmetric strata of fluid and solid phases. The reaction is assumed to take place in strata containing catalysts. The concentration of reactant $C(r, z, t)$ at radial distance r, axial distance z and time t is determined by the following mass balance equation.

$$\frac{\partial C}{\partial t} = L_0 C + M_1 [C] \tag{1}$$

$$L_0 C = \frac{1}{r} \frac{\partial}{\partial r} \left\{ r S(r) D(r) \frac{\partial}{\partial r} \left(\frac{C}{S(r)} \right) \right\} \tag{2}$$

$$M_1 [C] = D(r) \frac{\partial^2 C}{\partial z^2} - v(r) \frac{\partial C}{\partial z} - \rho(r) K[C] \tag{3}$$

$$\left. \frac{\partial}{\partial r} \left(\frac{C}{S(r)} \right) \right|_{r=0, R} = 0 \tag{4}$$

where the partition coefficient S, the diffusion coefficient D, the axial flow velocity v and the catalyst distribution function ρ are functions of the radial distance r. The reaction rate K is an arbitrary nonlinear function of the concentration. The linear operator L_0 indicates radial

sorption and diffusion. The operator M_1 stands for axial diffusion and convection, and nonlinear reaction. The expressions $K[C]$ and $M_1[C]$ denote operations nonlinear to C. The basic Eqs. (1)-(4) are similar to that treated in previous papers[4, 5], except for the nonlinear reaction term.

The Taylor dispersion model is valid under the condition that the radial diffusion rate is much faster than the axial mass transfer rate. We assume that L_0 is a primary operator in Eq. (1) and that M_1 can be treated as a small perturbation; the reaction rate is assumed to be sufficiently small. Explicit conditions for the perturbation approximation have been obtained in work described in previous papers[4, 5]. The concentration C approaches the equilibrium distribution of L_0:

$$C \to \frac{S}{\langle S \rangle} \langle C \rangle \tag{5}$$

where $\langle \ \rangle$ denotes the area average in the cross section:

$$\langle C \rangle = \frac{1}{\pi R^2} \int_0^R 2 \pi r \, C \, dr \tag{6}$$

We define a projection operator[4, 5] P as follows.

$$PC = \frac{S}{\langle S \rangle} \langle C \rangle \; ; P^2 = P \tag{7}$$

Equation (7) shows that PC is the asymptotic concentration distribution indicated in Eq. (5). The projection operator decomposes the concentration into two parts:

$$C = PC + (1 - P) C \tag{8}$$

Under the approximation condition, $(1-P) C$ is a sufficiently small term in comparison with PC. Then the reaction rate can be approximated up to the first-order term as follows.

$$K[C] = K[PC] + \frac{\partial K}{\partial C} [PC] (1 - P) C \tag{9}$$

Substituting Eqs. (8) and (9) into Eq. (1), we derive

$$\frac{\partial C}{\partial t} = M_1 [PC] + \left\{ L_0 + \frac{\partial M_1}{\partial C} [PC] \right\} (1 - P) C \tag{10}$$

where

$$\frac{\partial M_1}{\partial C}[PC] = D(r)\frac{\partial^2}{\partial z^2} - v(r)\frac{\partial}{\partial z} - \rho(r)\frac{\partial K}{\partial C}[PC] \qquad (11)$$

To derive Eq. (10), we used the following identity[4, 5]:

$$PL_0 = L_0 P = 0 \qquad (12)$$

The approximate mass balance Eq. (10) reduces to a quasi-linear equation for $(1-P)C$. Then we can apply the projection operator technique to Eq. (10) as described in the following section.

2. The Dispersion Equation

Applying P and $(1-P)$ to Eq. (10), we derive a couple of equations for PC and $(1-P)C$:

$$\frac{\partial PC}{\partial t} = PM_1[PC] + P\frac{\partial M_1}{\partial C}[PC](1-P)C \qquad (13)$$

$$\frac{\partial(1-P)C}{\partial t} = (1-P)\left\{L_0 + \frac{\partial M_1}{\partial C}[PC]\right\}(1-P)C$$
$$+ (1-P)M_1[PC] \qquad (14)$$

Equation (14) can be simplified by neglecting $\partial M_1/\partial C$ in comparison to L_0. Then the solution of Eq. (14) is approximately expressed as[4]

$$(1-P)C = \int_0^t \exp[L_0(t-t')](1-P)M_1[PC(t')]\,dt'$$
$$+ \exp[L_0 t](1-P)C(r, z, 0) \qquad (15)$$

The second term in the r.h.s. of Eq. (15) is a transient term that is eliminated when the time t is sufficiently longer than the radial diffusion relaxation time τ. We can simplify the integral in the r.h.s. of Eq. (15) by the adiabatic approximation method[4,5], noticing that $PC(t)$ is a sufficiently slowly varying function in comparison with $\exp[L_0 t]$, which decays rapidly. As a result, the following expression is obtained for $t \gg \tau$.

$$(1-P)C = \left(\int_0^\infty \exp[L_0 t]\,dt\right)(1-P)M_1[PC(t)]$$
$$= -L_0^{-1}(1-P)M_1[PC(t)] \qquad (16)$$

In Eq. (16), we defined the inverse of L_0 operating to any function $(1-P)f(r)$ under the boundary condition (4) as follows.

$$F(r) = L_0^{-1}(1-P)f(r) \Leftrightarrow (1-P)f(r) = L_0 F(r) \qquad (17)$$

Substituting Eq. (16) into Eq. (13), we obtain a closed equation for PC.

$$\frac{\partial PC}{\partial t} = PM_1[PC] - P\frac{\partial M_1}{\partial C}[PC]L_0^{-1}(1-P)M_1[PC] \qquad (18)$$

The above equation is an abstract form of an extended Taylor dispersion equation. Equation (18) is transformed to the equation for the average concentration $<C>$ by a simple algebraic manipulation[4,5]. In the following, we assume for simplicity that axial diffusion is negligible in comparison with axial convection, and

that the partition coefficient of the strata containing catalysts is constant. Then Eq. (18) is transformed to

$$\frac{\partial\langle C\rangle}{\partial t} = D_e\frac{\partial^2\langle C\rangle}{\partial z^2} - v_e^*[\langle C\rangle]\frac{\partial\langle C\rangle}{\partial z} - K_e[\langle C\rangle] \qquad (19)$$

where

$$D_e = \frac{[v, v]}{\langle S\rangle} \qquad (20)$$

$$v_e^* = \frac{\langle Sv\rangle}{\langle S\rangle} - \frac{2}{\langle S\rangle}[\rho, v]\frac{\partial K}{\partial C}\left[\frac{S_K}{\langle S\rangle}\langle C\rangle\right] \qquad (21)$$

$$K_e = \langle\rho\rangle K\left[\frac{S_K}{\langle S\rangle}\langle C\rangle\right] - \frac{[\rho, \rho]}{S_K}K\left[\frac{S_K}{\langle S\rangle}\langle C\rangle\right]\frac{\partial K}{\partial C}\left[\frac{S_K}{\langle S\rangle}\langle C\rangle\right] \qquad (22)$$

where S_k is the partition coefficient of the catalyst phase. In the above expressions, we defined a binary form[5] for arbitrary functions $f(r)$ and $g(r)$ as

$$[f, g] = -\langle f L_0^{-1}(1-P)Sg\rangle$$
$$= \frac{1}{\pi R^2}\int_0^R\frac{2\pi}{rS(r)D(r)}\left\{\int_0^r r'S(r')\left(f(r') - \frac{\langle Sf\rangle}{S}\right)dr'\right\}$$
$$\times\left\{\int_0^r r'S(r')\left(g(r') - \frac{\langle Sg\rangle}{S}\right)dr'\right\}dr \qquad (23)$$

Equation (19) is an extended Taylor dispersion equation for systems involving nonlinear irreversible reactions. When nonlinear reactions are not involved, Eq. (19) is shown to be reduced to the previous results[4, 5]. The effective diffusion coefficient D_e, given by Eq. (20), is an extended form of the Taylor diffusion coefficient[3]. It is noticed that the effective quasi-flow velocity v_e^* given by Eq. (21) depends on the concentration $<C>$ when nonlinear reaction is involved. The effective reaction rate K_e is transformed from the basic reaction rate by Eq. (22). Equation (19) can be used as a process model of sorption beds involving nonlinear irreversible reactions or adsorption.

Nomenclature

C	=	concentration	[mol·m^{-3}]
D	=	diffusion coefficient	[m^2·s^{-1}]
K	=	reaction rate	[mol·m^{-3}·s^{-1}]
R	=	radius	[m]
r	=	radial distance	[m]
S	=	partition coefficient	[-]
t	=	time	[s]
v	=	flow velocity	[m·s^{-1}]
z	=	axial distance	[m]
ρ	=	catalyst distribution function	[-]
τ	=	radial diffusion relaxation time	[s]

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