The Reaction-Independence of Mixing Coefficients in Fixed-Bed Reactors

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Both the dispersion model and the cell model have been employed in the analysis of fixed-bed processes, particularly for fixed-bed reactors. In the dispersion model the dispersive flux supposed to be proportional to the concentration gradient is superimposed upon the convective flow, while in the cell model the packing is considered to form a net-like arrangement of cells in each of which the fluid is well mixed. It is usual to measure dispersion coefficients or mixing lengths in the absence of chemical reaction, simply because such experiments can be more easily carried out.

The question of whether mixing coefficients are changed by the occurrence of a chemical reaction has been raised, but not resolved by several authors including Wakao et al. (1978) and Aris (1965). In this paper we introduce a transformation that affords a proof of the reaction independence of the mixing coefficients.

Aris and Amundson (1957) have shown, by considering the impulse response of a fixed bed without chemical reaction, that if the diameter of a particle is taken as the mixing length the cell and dispersion models give the same first and second moments of the distribution when the axial Peclet group is 2. They did not consider chemical reaction in formulating the equivalence relation, and it is a matter of interest to enquire whether this also holds for the case of flow combined with chemical reaction.

We show that the same equivalence relation holds for systems of first-order reactions.

Dispersion Model for Systems of Isothermal First-Order Reactions

At high Reynolds number, experimental measurements show that dispersion coefficients become independent of molecular diffusivity (Gunn, 1987) so that the dispersion coefficient is the same for each component. The differential equation for a particular component is

$$\frac{\partial c_i}{\partial t} + V\frac{\partial c_i}{\partial x} = D_L\frac{\partial^2 c_i}{\partial x^2} - f_i(k_\ell c_j) \quad i = 1, 2 \ldots m \tag{1}$$

where $f_i(k_\ell c_j)$ represents the expression for the chemical reaction rate as a linear set of terms each of the form $k_\ell c_j$ with the k_ℓ as reaction velocity constants. For the irreversible first-order reaction $f_i(k_\ell c_j)$ is simply kc.

For simplicity, we consider the doubly-infinite bed. The transformation,

$$c_i = \phi_i \frac{\exp\left(-\dfrac{(x - Vt)^2}{4D_L t}\right)}{\sqrt{(4\pi D_L t)}} = \phi_i A \tag{2}$$

is now introduced into Eq. 1 where ϕ_i is a function of t only. On substituting Eq. 2 into Eq. 1, we obtain

$$\phi_i\left(\frac{\partial A}{\partial t} + V\frac{\partial A}{\partial x} - D_L\frac{\partial^2 A}{\partial x^2}\right) + A\partial\frac{\phi_i}{\partial t} + f_i(k_\ell c_j) = 0 \tag{3}$$

But as

$$A = \frac{\exp\left(-\dfrac{(x - Vt)^2}{4D_L t}\right)}{\sqrt{4\pi D_L t}}$$

is a solution to Eq. 1 with $f_i(k_\ell c_j) = 0$, the expression within the lefthand bracket of Eq. 3 is zero, and this equation reduces to,

$$\frac{\partial \phi_i}{\partial t} = f_i(k_\ell \phi_j) \quad i = 1, 2 \ldots \tag{4}$$

For the linear system, Eq. 4 may be placed in the matrix form,

$$\phi^1 = -\boldsymbol{K}\phi \tag{5}$$

where ϕ is the column vector $(\phi_1\ \phi_2 \ldots \phi_r)$, ϕ^1 is the derivative of ϕ with respect to time, and $\boldsymbol{K}$ is the $r \times r$ matrix of reaction velocity constants where r is the dimension of the maximum set of independent linear rate expressions in Eq. 4.

The solution to Eq. 1 may therefore be expressed as

$$C_R = C_o A \exp(-\boldsymbol{K}t) \tag{6}$$

where C_R is the vector of concentration, C_o is the vector of initial concentration, and A is given by Eq. 2. The solution to Eq. 1 without chemical reaction is simply,

$$C_{NR} = C_o A \tag{7}$$

Dispersion Coefficients with and without Chemical Reaction

When considering dispersion without chemical reaction, the amount of each component injected, the velocity V, and the dispersion coefficient D_L may be estimated from the zeroth, first and second moments (Aris and Amundson, 1957). The moment of order s is

$$\mu_s = \int_{-\infty}^{\infty} c x^s \, dx \tag{8}$$

The general forms of the concentration distributions (Eqs. 6 and 7) are related

$$C_R = \exp(-\boldsymbol{K}t) C_{NR} \tag{9}$$

The moment of order of the concentration distribution with reaction is therefore,

$$\mu_{s(R)} = \int_{-\infty}^{\infty} \exp(-\boldsymbol{K}t) C_{NR} x^s \, dx \tag{10}$$

and as the matrix $\boldsymbol{K}$ is independent of x,

$$\mu_{s(R)} = \exp(-\boldsymbol{K}t) \int_{-\infty}^{\infty} C_{NR} x^s \, dx = \exp(-\boldsymbol{K}t) \mu_{s(NR)} \tag{11}$$

In the presence of chemical reaction, the zeroth moment is not constant with time because of chemical transformation, but a particular consequence of Eq. 11 is that the normalized moments, with and without reaction, are equal.

$$\frac{\mu_{s(R)}}{\mu_{o(R)}} = \frac{\mu_{s(NR)}}{\mu_{o(NR)}} \tag{12}$$

The first dimensionless moment of the impulse response is Vt/d and the second moment is $2D_L t/d^2$ in the absence of chemical reaction. Thus,

$$\frac{\mu_{2(NR)}}{\mu_{1(NR)}} = \frac{2D_L}{Vd} = \frac{2}{Pe} = \frac{\mu_{2(R)}}{\mu_{1(R)}} \tag{13}$$

and therefore the dispersion coefficient in a fixed bed with chemical reaction is equal to the dispersion coefficient found without chemical reaction, since the normalized moments are equal when all other conditions are the same.

Cell Model for Systems of Isothermal First-Order Reaction

The differential equation for a particular component in cells numbered 0, 1, 2 . . . n is

$$qc_{i,n-1} - qc_{i,n} = \epsilon d \frac{\partial c_i n}{\partial t} + \epsilon d f_i(k_\ell c_{j,n}), \quad i = 1, 2 \ldots m \tag{14}$$

$$qc_{i,f}(t) - qc_{i,o} = \epsilon d \frac{\partial c_{i,o}}{\partial t} + \epsilon d f_i(k_\ell c_{j,o})\ i = 1, 2 \ldots m \tag{15}$$

With $c_{i,n} = 0$, $t < 0$ as the initial condition and $c_{i,f}(t)$ representing a unit impulse function.

Consider the transformation introducing α as $(qt/\epsilon d)$,

$$c_{i,n} = \psi_i \frac{\alpha^n e^{-\alpha}}{n!} \tag{16}$$

where ψ_i is a function of t only and not of n. On substituting this equation into Eq. 14

$$\psi_i \left(q \frac{\alpha^{n-1} e^{-\alpha}}{(n-1)!} - q \frac{\alpha^n e^{-\alpha}}{n!} - \epsilon d \frac{\partial}{\partial t} \frac{\alpha^n e^{-\alpha}}{n!} \right) = \epsilon d \frac{\alpha^n e^{-\alpha}}{n!} \frac{\partial \psi_i}{\partial t} + \epsilon d f_i(k_\ell \psi_i) \frac{\alpha^n e^{-\alpha}}{n} \tag{17}$$

and as the expression in brackets on the lefthand side is zero by virtue of $\alpha^n e^{-\alpha}/n!$ being a solution to Eq. 14 with $f_i = 0$, Eq. 17 reduces to,

$$\psi^1 = -\boldsymbol{K}\psi \tag{18}$$

where ψ is the column vector $(\psi_1\ \psi_2 \ldots \psi_r)$. The solution to this equation has the same form as the solution to Eq. 5. Indeed, for the same initial conditions it is clear that $\psi = \phi$ and the full form of the solution is

$$C_{n(R)} = C_o \exp(-\boldsymbol{K}t) \frac{\alpha^n e^{-\alpha}}{n!} \tag{19}$$

and therefore Eqs. 11 and 12 also apply to the cell model.

Discussion

In the several years since the appearance of early work on mixing in fixed beds such as that of McHenry and Wilhelm (1957), most experimental studies have been directed to the dispersion model, partly because the model is compatible with the low velocity condition of diffusion-dominated dispersion and because experiments designed to test the hypothesis of complete mixing in the interstices of particles in a fixed bed have not substantiated that hypothesis (Gunn and Pryce, 1969). However, irrespective of which model is favored, our analysis supports the characterization of mixing in fixed-bed reactors by experiments carried out under nonreacting conditions.

Aris and Amundson (1957) set equivalence between the dispersion and cell models by separately equating the first moments and the second moments of the impulse responses for each model. When the mixing length of the cell model was taken as the particle diameter d, they found the Peclet group to be equal to 2. As Eq. 12 holds for both models, it follows that the equivalence condition is the same when there is a system of isothermal first-order reactions occurring in the bed.

The appeal of this result in its simplicity is all the greater because the value of the Peclet group in beds of spheres at high Reynolds number is about 2 (McHenry and Wilhelm, 1957; Gunn and Pryce, 1969). Aris and Amundson's result is based on the hypothesis of one particle diameter for the mixing length. It is of interest to note that another compulsive hypothesis for a different theoretical approach leads to the same result.

In a study of convective mixing in fixed beds, Gunn (1969) considered the probability of axial displacement of a fluid particle placed within a small group of solid, fixed particles in the bed. If p is the probability of axial displacement he showed that the axial Peclet group is

$$Pe = \frac{2p}{1-p} \tag{20}$$

If the probability of axial displacement of the fluid particle is equal to the probability of the particle remaining stationary, Eq. 20 gives Pe to be 2.

Notation

A = defined by Eq. 2
$c, c_i, c_{i,n}$ = concentration vector and components
C_0 = initial concentration vector
d = particle diameter
D_L = coefficient of axial dispersion
f_i = linear reaction function
k, k_ℓ = first-order reaction velocity constant
$\boldsymbol{K}$ = matrix of first order reaction velocity constants
n = cell number
r = order of matrix $\boldsymbol{K}$
p = probability of axial displacement
Pe = axial Peclet group Vd/D_L
q = volumetric flowrate through unit cross-section
t = time
V = velocity, interstitial
x = axial coordinate

Greek letters

$\alpha = qt/\epsilon d$
ϵ = porosity
ϕ, ψ = reaction velocity functions
μ_s = moment of order s defined by Eq. 8

Subscripts

f = inlet
L = axial
n = cell number = 0, 1, 2...
NR = without reaction
R = with reaction

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Errata

Equation 16 of the paper titled "Effects of Osmotic Pressure and Adsorption on Ultrafiltration of Ovalbumin" (June 1990, p. 911) should read:

$$Sh = 1.62 \left(\frac{Re\ Sc\ d_h}{L} \right)^{1/3} \tag{16}$$