R&D NOTE

Linear Driving-Force Model for Diffusion and Reaction with Interphase Partitioning

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The linear driving-force (LDF) model is a useful simplification of diffusion mathematics that continues to attract considerable attention (Başağaoğlu et al., 2000; Szukiewicz, 2000; Sircar and Hufton, 2000). Once the LDF expression is formulated for a single particle, the approximation can be used when such particles are in a well-mixed compartment or embedded in a periodic porous medium with fluid convection and hydrodynamic dispersion. LDF has mostly been applied to *reversible* adsorption processes, but its use would greatly simplify the interpretation of diffusion in *irreversible* adsorption or reaction processes. The motivation behind the LDF approximation is to replace the spatial-point dependence of the concentration, $y(\xi, \theta)$, with a particle volume-averaged concentration, $y_{\text{avg}}(\theta)$, which converts the second-order diffusion differential, $\nabla^2 y(r, t)$, into the LDF expression, $\kappa_{\text{LDF}}(1 - y_{\text{avg}})$. The LDF coefficient, κ_{LDF}, in general depends on coefficients for reaction rate, effective intraparticle diffusion, and external mass transfer. The resulting ordinary differential equation in time is much more tractable for analytical or numerical solution than the partial differential equation with its diffusion differential.

Szukiewicz (2000) recently proposed an interesting approximation of this type for treating time-dependent diffusion-reaction problems with infinite Biot number, *Bi*. The approach assumes that the diffusion-reaction mathematics can be approximated by long-time behavior, which is combined with the accumulation term (time derivative of concentration) to solve the unsteady-state problem. We will show that this approach is (1) equivalent to applying the steady-state effectiveness factor to the unsteady-state problem, (2) that it amounts to an assumption of a sinh form of the concentration profile for spherical particles (rather than the usual parabolic profile usually associated with the LDF), and (3) that near the steady-state limit the approximation is much more accurate than the usual LDF approach with a parabolic profile.

Goto et al. (1990) utilized the customary parabolic profile approximation to formulate a LDF model for isothermal, irreversible, first-order chemical reactions when the reactant diffuses into the particle where it reacts, such as a catalytic reaction. The work also provided, without approximation, a Laplace transform solution for the particle average concentration vs. time. By comparing with the exact unsteady-state solution for the catalytic first-order reaction including intraparticle diffusion and external mass transfer, it was demonstrated that the parabolic profile model becomes less accurate at high values of the Biot number, *Bi*, and Thiele modulus, ϕ. The steady-state result was then interpreted as a global effectiveness factor that also became less accurate for large *Bi* and ϕ. The conclusions were explained as the effect of increased diffusion resistance at large ϕ, causing the approximate treatment of diffusion to distort the true behavior. The results of Goto et al. (1990) contrasted with the work of Kim (1989), who claimed for the infinite *Bi* case and for large ϕ the LDF result became more accurate.

The Laplace transform solution to the reaction-diffusion equation is complicated, which might cause some hesitation in referring to the results of Goto et al. (1990). Therefore, we undertook an independent confirmation by numerical analysis. To add a level of generality in the current study, we consider that a porous particle with inert-matrix solid fraction, 1-β, has its pores filled with a fluid that is immiscible with the bulk fluid. This was the case (with no chemical reaction) addressed by Peker et al. (1992) for the supercritical CO_2 extraction of caffeine from nearly spherical, porous coffee beans saturated with water. For such a physical extraction, the LDF expression for the mass-transfer coefficient contained the equilibrium partition coefficient for caffeine distributed between water and supercritical CO_2.

With the definitions listed in the Notation section, the dimensionless partial differential equation that describes parti-

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tioning, diffusion, and first-order reaction is

$$\frac{\partial y}{\partial \theta} = \frac{1}{9\phi^2}\frac{1}{\xi^2}\frac{\partial}{\partial \xi}\left(\xi^2 \frac{\partial y}{\partial \xi}\right) - y, \tag{1}$$

with initial and boundary conditions

$$y(\theta = 0) = 0 \tag{2}$$

$$\partial y/\partial \xi = 0 \qquad \text{at } \xi = 0 \tag{3}$$

$$\partial y/\partial \xi = Bi(1 - Ky) \qquad \text{at } \xi = 1. \tag{4}$$

Here K is the equilibrium partition coefficient at the surface of the particle (ratio of external to intraparticle concentration at the particle surface). The effectiveness factor is a steady-state representation of the relative influence of diffusion on reaction inside particles. For Eqs. 1–4 the global and local effectiveness factors are

$$\eta_G = (K/3\phi^2)\,(dy/d\xi)_{\xi=1} \qquad \text{and}$$

$$\eta = (dy/d\xi)_{\xi=1}/3\phi^2 y_{\xi=1}, \tag{5}$$

so that $\eta_G = \eta K y_{\xi=1}$. The steady-state solution to Eq. 5 is

$$y(\xi) = y_{\xi=1}\sinh(3\phi\xi)/[\xi\sinh(3\phi)]. \tag{6}$$

Taking the derivative of the preceding concentration profile and substituting into Eq. 5 yields

$$1/\eta_G = 1/\eta + 3\phi^2/KBi, \tag{7}$$

where

$$\eta = [1/\tanh(3\phi) - 1/3\phi]/\phi. \tag{8}$$

Equation 8 is the usual expression for the local effectiveness factor, and Eq. 7 reduces to the usual global effectiveness factor (Froment and Bischoff, 1990) when $K = 1$. Volume averaging Eq. 1 for the steady-state yields

$$(1/3\phi^2)(dy/d\xi)_{\xi=1} = y_{\text{avg}} = \eta_G/K. \tag{9}$$

The LDF approximation to Eqs. 1–4 in terms of volume-averaged concentrations is

$$dy_{\text{avg}}/d\theta = \kappa_{\text{LDF}}(1 - Ky_{\text{avg}}) - y_{\text{avg}}, \tag{10}$$

where κ_{LDF} is the LDF coefficient. According to Szukiewicz (2000), κ_{LDF} is formulated by the steady-state form of Eq. 10, so that with Eq. 9, we have

$$\kappa_{\text{LDF}} = \eta_G/[K(1 - \eta_G)]. \tag{11}$$

It is not difficult to show that Eq. 11 reduces to the Szukiewicz coefficient when $K = 1$, $Bi \gg 1$, and the reaction-diffusion modulus identity ($\phi = \Phi/3$) are applied. Szukiewicz (2000) uses this steady-state value of κ_{LDF} in the unsteady-state Eq. 10. The solution to Eq. 10 is a simple expression that illustrates the benefit of the LDF approach

$$y_{\text{avg}} = \frac{\{1 - \exp[-(\kappa_{\text{LDF}}K + 1)\theta]\}}{(1/\kappa_{\text{LDF}} + K)}. \tag{12}$$

The relationship of the preceding approximation to the parabolic concentration profile is readily established. When $\sinh(3\phi\xi)$ in Eq. 6 is expanded to second order for $3\phi\xi \ll 1$, the dimensionless, spatially varying concentration is approximated as

$$y(\xi) \approx \frac{3\phi y_{\xi=1}}{\sinh(3\phi)}\left(1 + \frac{3(\phi\xi)^2}{2}\right) \tag{13}$$

With a time-varying parabolic concentration profile, such as Eq. 13 (Goto et al., 1990), the LDF coefficient is

$$\kappa_{\text{LDF}} = Bi/[3\phi^2(1 + KBi/5)], \tag{14}$$

which can also be derived by expanding $1/\tanh(3\phi)$ in Eq. 8 to three terms, substituting into Eq. 9, and combining with Eq. 11. Equation 14 reduces to the case considered by Goto et al. (1990) when $K = 1$ (same fluid in the pores and external to the particle). The LDF coefficient also reduces to a combined mass-transfer coefficient investigated by Peker et al. (1992) where the reaction rate is zero. Obviously, the power-series expansions for $\sinh(3\phi\xi)$ and $\coth(3\phi\xi)$ apply only when $\phi < 1$, which is the range of validity discussed by Goto et al. (1990).

A numerical simulation model is formulated using the finite difference (FD) approximation (Crank-Nicolson) with $\alpha = 0.5$ (a weighting parameter between the implicit and explicit FD approximations) to ensure that the solution is unconditionally stable. In the FD scheme, there are N nodes and $(N-1)$ intervals with a length of $\Delta\xi$ such that $\Delta\xi = \xi/(N-1)$, and with the grid coordinates of $\xi_i = (j-1)\Delta\xi$, in which j represents the node number along the radial distance away from the center of the particle. The total simulation period is $\theta_n = n\Delta\theta$, in which $\Delta\theta$ is the time increment and n is the time-step index. The FD approximation can easily be written for all nodes except where $\xi = 0$. At the center of the spherical particle ($j = 1$), $\xi = 0$ is a singular point for the radial diffusion model. However, the FD approximation can still be written using L'Hopital's rule (Özişik, 1989) for $y_1^n = y_1(\xi_j, \theta_n)$

$$b_1 y_1^{n+1} + c_1 y_2^{n+1} = d_1 y_1^n - e_1 y_2^n, \tag{15}$$

in which

$$b_1 = \frac{6\alpha}{9\phi^2(\Delta\xi)^2} + \frac{1}{\Delta\theta} + \alpha$$

$$d_1 = \frac{-6(1-\alpha)}{9\phi^2(\Delta\xi)^2} + \frac{1}{\Delta\theta} - (1-\alpha) \tag{16a}$$

$$c_1 = \frac{-6\alpha}{9\phi^2(\Delta\xi)^2} \qquad e_1 = \frac{-6(1-\alpha)}{9\phi^2(\Delta\xi)^2}. \tag{16b}$$

The FD formulation was solved by the Thomas algorithm for temporal concentrations at each grid node over the entire domain. Once the nodal concentrations were computed, the volume-averaged concentrations were then calculated by weighting the nodal concentrations with their representative volumes. We found that the FD solution matched the Laplace-transform solution by Goto et al. (1990) precisely.

Goto et al. (1990) showed that the traditional LDF approximation (parabolic profile) for the transient diffusion-reaction equation is accurate only for $Bi < 1$ and $\phi < 1$. They also noted for larger Bi and ϕ, the customary LDF approximation yields large errors and cannot match the steady-state limits. To correct for this shortcoming, Goto and Hirose (1993) modified the parabolic profile approximation by a weighting method. Szukiewicz's (2000) alternative model, however, is based on the steady-state limit. To analyze the performance of this new model, we solved it first for $\phi = 10$, $K = 1$ and for Bi ranging from 0.1 to 1,000, and then compared the results to numerical solutions in Figure 1. Even for large ϕ, the new model results matched the FD solutions very well for $Bi \leq 1$. This result is similar to the findings of Goto et al. (1990), in which the same problem was solved for $\phi = 1$. For larger Bi numbers, however, the new LDF solution deviated from the FD solutions significantly at small times. As expected, the new model matched the steady-state limits exactly for all Bi and ϕ.

We also analyzed the concentration histories for different values of K at large Bi and ϕ. Dimensionless volume-averaged concentrations decrease with increased K due to a smaller concentration gradient across the particle boundary (Eqs. 9 and 10). For large Bi and ϕ, steady-state limits (Figure 2) were exact, and deviations between the new approximate and the FD model solutions decrease as K gets smaller. In sum, the new approximate model and the customary parabolic profile approximation predict concentration profiles sufficiently accurately at all times for small Bi and ϕ ($Bi < 1$ and $\phi < 1$). On the other hand, for large Bi and ϕ, both models fail to predict the concentration profile precisely at shorter times; however, unlike the customary parabolic profile approximation, the new approximation model predicts concentration profiles at longer times, near the steady-state limit, accurately. Thus, the new LDF model is an improvement over the parabolic approximation for combined mass transfer, intraparticle diffusion, and chemical reaction, particularly as the solution approaches steady-state.

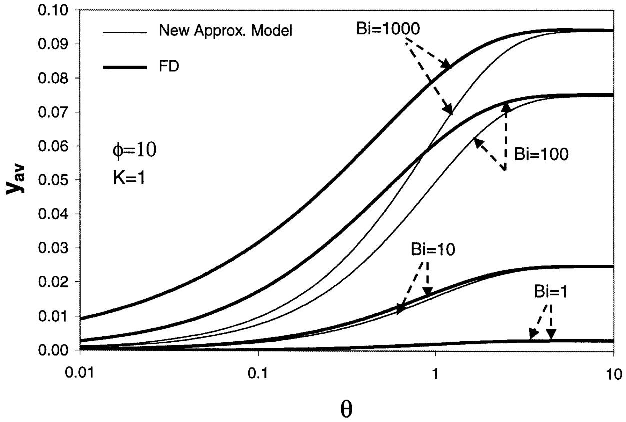

Figure 1. Concentration histories for the diffusing reactant with $\phi = 10$, $K = 1$.

The new approximate model is compared to the FD solution.

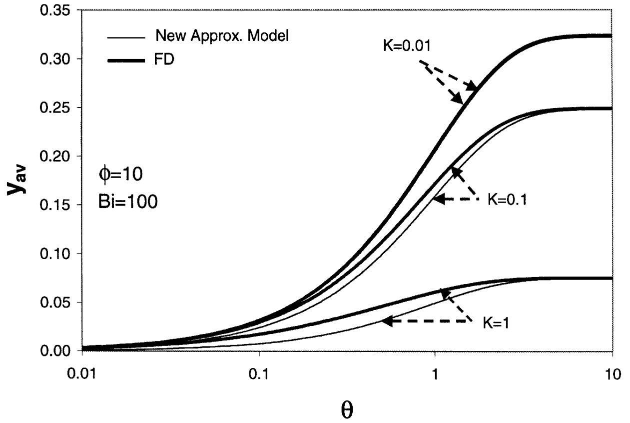

Figure 2. Concentration histories for the diffusing reactant with $Bi = 100$, $\phi = 10$.

The new approximate model is compared to the FD solution.

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Notation

j = node number index
k = reaction rate constant, L/T
k_f = mass-transfer coefficient, L/T
n = dimensionless time index
r = radial distance, L
r_0 = radius of the spherical particle, L
y = dimensionless intraparticle concentration, c_i/c_b
Bi = Biot number, $k_f r_0/D$
$D = D = D_i/\beta$
D_i = intraparticle diffusion coefficient, L^2/T
K = equilibrium partition coefficient at the surface of the particle
N = total number of grid points

Greek letters

α = weighting parameter between the implicit and explicit finite difference approximations
β = porosity
ϕ = Thiele modulus, $(r_0/3)(\sqrt{k/D})$
Φ = Thiele modulus (Szukiewicz), $r_0(\sqrt{k/D})$
η = effectiveness factor
η_G = global effectiveness factor
κ_{LDF} = LDF coefficient given in Eq. 11
θ = dimensionless time, kt
ξ = dimensionless radial distance, r/r_0
$\Delta\xi$ = nodal space along the radius of a spherical particle
$\Delta\theta$ = dimensionless time step

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