Linear Driving Force Formulas for Unsteady-State Diffusion and Reaction in Slab, Cylinder and Sphere Catalyst

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Introduction

The unsteady-state diffusion, adsorption and reaction in a catalyst particle is described by a partial differential equation (PDE). The PDE involves the space coordinate in the particle as an independent variable. In reactor modeling, the PDE is coupled with another PDE describing the mass balance of each component in the fluid phase flowing through the reactor. The complexity of the solution is often commensurate with the number of independent variables in the model. In this respect, to have an approximation of the PDE that does not involve the space variable in the particle is desirable to simplify reactor modeling.

There have been proposed several approximations for spherical catalysts,[1–3] slab and cylinder catalysts.[4] The approximations are of different accuracy and forms. With increasing order of approximation, the approximation becomes more accurate but has more terms and coefficients to be evaluated.[1,3] Even high-order approximations, however, make the reactor model much more tractable than the model with the PDE for the catalyst. On the other hand, among approximations of similar mathematical forms, approximations with higher accuracy and simple coefficients are preferred in the reactor modeling. In this respect, new approximations with simple coefficients for spherical, cylindrical and slab catalysts are developed in this study for unsteady-state diffusion, a linear adsorption and a first-order reaction. As the unsteady mass transfer will also depend on the surface to volume ratio of the catalyst, the approximations are separately developed for each catalyst geometry.

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Previous approximations

The approximations are based on a dimensionless mass balance for unsteady-state intraparticle diffusion, a linear adsorption and a first-order reaction in a catalyst. For a spherical catalyst particle, the balance equation is

$$\frac{\partial c}{\partial \tau} = \frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2\frac{\partial c}{\partial x}\right) - \phi^2 c \tag{1}$$

At the catalyst surface $c(1,\tau) = f(\tau)$, a time-varying concentration. In the absence of the reaction, $\phi = 0$, Glueckauf[5] proposed the well-known linear driving force (LDF) formula for a spherical adsorbent:

$$d\bar{c}/d\tau = 15(f - \bar{c}) \tag{2}$$

Here $\bar{c}$ is the average concentration in the catalyst particle, defined by

$$\bar{c}(\tau) = 3\int_0^1 c(x,\tau)x^2 dx \tag{3}$$

For $\phi \geq 0$, Kim[1] proposed for a spherical catalyst particle:

$$\frac{d\bar{c}}{d\tau} = \frac{s_1}{s_2}(s_1 f - \bar{c}) \tag{4}$$

where

$$s_1 = \sum_{n=1}^{\infty}\frac{6}{(\phi^2 + n^2\pi^2)}, \quad s_2 = \sum_{n=1}^{\infty}\frac{6}{(\phi^2 + n^2\pi^2)^2} \tag{5}$$

As $\phi \to 0$, it has been shown that $s_1 \to 1$ and $s_2 \to 1/15$, and hence Eq. 4 becomes the LDF formula, Eq. 2, in the absence of reaction.

Later Szukiewicz[2] proposed an approximation for a spherical catalyst:

$$\frac{\partial \overline{c}}{\partial \tau} = 3\Psi_2(f - \overline{c}) - \phi^2 \overline{c}$$
$$\text{where } \Psi_2 = \frac{\phi^2(\phi\cosh\phi - \sinh\phi)}{\phi^2\sinh\phi - 3(\phi\cosh\phi - \sinh\phi)} \tag{6}$$

He assumed this form to have a similarity with Eq. 1 in terms of accumulation, diffusion and reaction and obtained Ψ from the solution of Eq. 1 in the Laplace-Carson transform. Szukiewicz also proposed approximations for other catalyst geometries such as slab and cylinder with external mass transfer resistances.[4] In the absence of external mass transfer resistances, the approximation for a spherical catalyst is the same as Eq. 6, and the approximations for slab and cylinder catalyst are

$$\frac{\partial \overline{c}}{\partial \tau} = \frac{\phi^2\sinh\phi}{\phi\cosh\phi - \sinh\phi}(f - \overline{c}) - \phi^2\overline{c} \quad \text{for slab} \tag{7}$$

$$\frac{\partial \overline{c}}{\partial \tau} = \frac{2\phi^2 I_1(\phi)}{\phi I_0(\phi) - 2I_1(\phi)}(f - \overline{c}) - \phi^2\overline{c} \quad \text{for cylinder} \tag{8}$$

Recently Kim[3] proposed three approximations of different accuracy from a series expansion of the Laplace-domain solution of Eq.1. Among the three, the approximation which has the same mathematical form as Eq. 4 is

$$\frac{d\overline{c}}{d\tau} = -\frac{A_0}{A_1}(A_0 f - \overline{c}) \tag{9}$$

where

$$A_0 = 3\left(\frac{\coth\phi}{\phi} - \frac{1}{\phi^2}\right),$$
$$A_1 = -\frac{3}{2}\frac{(\coth\phi)^2 - 1}{\phi^2} - \frac{3}{2}\frac{\coth\phi}{\phi^3} + \frac{3}{\phi^4} \tag{10}$$

It has been shown $A_0 = s_1$ and $A_1 = -s_2$, and thus Eq. 9 is identical to Eq. 4.

Theory

The unsteady-state mass balance for a linear adsorption and a first-order reaction in a catalyst is

$$\varepsilon_p \frac{\partial C_p}{\partial t} + \frac{\partial Q}{\partial t} = \frac{D_e}{L^2}\left(\frac{\partial^2 C_p}{\partial x^2} + \frac{S}{x}\frac{\partial C_p}{\partial x}\right) - kC_p,$$

$$C_p(x,0) = 0,\ C_p(1,t) = F(t),\ \left.\frac{\partial C_p}{\partial x}\right|_{x=0} = 0. \tag{11}$$

When $S = 0$, 1, and 2, Eq. 11 is the mass balance equation for a catalyst with the geometry of an infinite slab, an infinite cylinder and a sphere, respectively. x is the dimensionless position variable in the catalyst ($x = 0$ at center and $x = 1$ at external surface); L is the characteristic length of the catalyst; ε_p is the void fraction in the catalyst particle; Q is the adsorbed phase concentration in the catalyst, $Q = KC_p$; and D_e is the effective diffusivity. For the slab $L = L_S$, half of the slab thickness; for the cylinder $L = R_c$, the radius of the cylinder; and for the sphere $L = R_S$, the radius of the sphere. The dimensionless mass balance equation is

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial x^2} + \frac{S}{x}\frac{\partial c}{\partial x} - \phi^2 c,$$
$$c(x,0) = 0, c(1,\tau) = f(\tau),\ \left.\frac{\partial c}{\partial x}\right|_{x=0} = 0. \tag{12}$$

where $c = C_p/C_0$ (C_0 is a reference concentration) and

$$\tau = \frac{t}{\frac{L^2}{D_e}(\varepsilon_p + K)} \tag{13}$$

The Thiele modulus is

$$\phi = L_S\sqrt{\frac{k}{D_e}} \text{ for } S = 0,$$
$$\phi = R_C\sqrt{\frac{k}{D_e}} \text{ for } S = 1, \text{ and } \phi = R_S\sqrt{\frac{k}{D_e}} \text{ for } S = 2 \tag{14}$$

Equation 12 is denoted as the exact model in this study. For each catalyst shape, Eq. 12 can be solved by the method of Laplace transform. The Laplace-domain solution can be integrated with respect to x to obtain the volume-average solution in the Laplace domain, which can be expressed as $G(s)H(s)$. Here s is the Laplace domain variable, and $H(s)$ is the Laplace transform of $f(\tau)$. $G(s)$ is often called the transfer function.

$G(s)$ can be expanded as

$$G(s) = A_0 + A_1 s + A_2 s^2 + \ldots \tag{15}$$

According to Kim[3] an approximation of $G(s)$ that is correct to the first order in its expansion is

$$G_1(s) = \frac{-A_0^2/A_1}{s - A_0/A_1} \tag{16}$$

The corresponding time-domain expression for $G_1(s)$ is

$$\frac{d\overline{c}}{d\tau} = -\frac{A_0}{A_1}(A_0 f - \overline{c}) \tag{9}$$

where the volume-average concentration is

$$\overline{c} = (S+1)\int_0^1 c(x,\tau)x^S dx \tag{17}$$

Table 1 lists $G(s)$, A_0 and A_1 for the three catalyst shapes. As Eq. 4 is an approximation, approximating the coefficient $(-A_0/A_1)$ may be allowed if it can be further simplified. In this regard, the asymptotic behavior of the coefficient $(-A_0/A_1)$ when ϕ is small or large is examined, and the asymptotes are listed in Table 1. The asymptotes for small ϕ consist of a constant and a ϕ^2 term, and those for large ϕ are commonly $2\phi^2$.

Table 1. Transfer Function, Expansion Coefficients, Asymptotes and LDF Formulas for Slab, Cylinder and Sphere Catalyst

	Slab ($S = 0$)	Cylinder ($S = 1$)	Sphere ($S = 2$)
ϕ	$L_S\sqrt{\frac{k}{D_e}}$	$R_C\sqrt{\frac{k}{D_e}}$	$R_S\sqrt{\frac{k}{D_e}}$
$G(s)$	$\frac{\tanh\sqrt{\phi^2+s}}{\sqrt{\phi^2+s}}$	$\frac{2I_1(\sqrt{\phi^2+s})}{(\sqrt{\phi^2+s})I_0(\sqrt{\phi^2+s})}$	$3\left(\frac{\coth\sqrt{\phi^2+s}}{\sqrt{\phi^2+s}}-\frac{1}{\phi^2+s}\right)$
A_0	$\frac{\tanh\phi}{\phi}$	$\frac{2I_1(\phi)}{\phi I_0(\phi)}$	$3\left(\frac{\coth\phi}{\phi}-\frac{1}{\phi^2}\right)$
A_1	$\frac{1-(\tanh\phi)^2}{2\phi^2}-\frac{\tanh\phi}{2\phi^3}$	$\frac{\phi I_0(\phi)^2-2I_0(\phi)I_1(\phi)-\phi I_1(\phi)^2}{\phi^3 I_0(\phi)^2}$	$-\frac{3}{2}\frac{(\coth\phi)^2-1}{\phi^2}-\frac{3}{2}\frac{\coth\phi}{\phi^3}+\frac{3}{\phi^4}$
$-\frac{A_0}{A_1}$, $\phi\to 0$	$3+\frac{7}{5}\phi^2$	$8+\frac{5}{3}\phi^2$	$15+\frac{13}{7}\phi^2$
$-\frac{A_0}{A_1}$, $\phi\to\infty$	$2\phi^2$	$2\phi^2$	$2\phi^2$
β	$3+2\phi^2$	$8+2\phi^2$	$15+2\phi^2$
LDF formula	$\frac{d\bar{c}}{d\tau}=(3+2\phi^2)(A_0f-\bar{c})$	$\frac{d\bar{c}}{d\tau}=(8+2\phi^2)(A_0f-\bar{c})$	$\frac{d\bar{c}}{d\tau}=(15+2\phi^2)(A_0f-\bar{c})$

An approximation of $(-A_0/A_1)$ valid for all ϕ may be obtained by combining the asymptote at small and large ϕ.

$$-\frac{A_0}{A_1}\approx\beta=\begin{cases}3+2\phi^2 & \text{for slab}\\ 8+2\phi^2 & \text{for cylinder}\\ 15+2\phi^2 & \text{for sphere}\end{cases} \tag{18}$$

For the three catalyst shapes, $(-A_0/A_1)$ and β are compared in Figure 1, where close agreement between the two is observed for each catalyst geometry, showing that the simpler β can be used instead of $(-A_0/A_1)$ in approximation. Consequently the proposed approximations for Eq. 12 are

$$\frac{d\bar{c}}{d\tau}=(3+2\phi^2)(A_0f-\bar{c})\quad\text{for slab catalyst} \tag{19}$$

$$\frac{d\bar{c}}{d\tau}=(8+2\phi^2)(A_0f-\bar{c})\quad\text{for cylinder catalyst} \tag{20}$$

$$\frac{d\bar{c}}{d\tau}=(15+2\phi^2)(A_0f-\bar{c})\quad\text{for sphere catalyst} \tag{21}$$

It is again noted that A_0 as well as ϕ are different for each catalyst geometry and are listed in Table 1. If f is a constant, Eq. 12 and Eqs. 19–21 approach a steady state as $\tau\to\infty$. At the steady state, $\bar{c}=A_0f$ and hence A_0 can be obtained from the solution of the steady state mass balance, which is given by Eq. 12 with a constant f and $\partial c/\partial\tau=0$. For a first-order reaction, A_0 is independent of f and identical to the effectiveness factor for the respective catalyst geometry. It is noted that $A_0\to 1$ as $\phi\to 0$.

In the absence of reaction, the well-known LDF formula $d\bar{c}/d\tau=15(f-\bar{c})$ has been developed for spherical adsorbents, and for other adsorbent shapes, this study gives that

$$\frac{d\bar{c}}{d\tau}=3(f-\bar{c})\text{ for slab adsorbent} \tag{22}$$

$$\frac{d\bar{c}}{d\tau}=8(f-\bar{c})\text{ for cylinder adsorbent} \tag{23}$$

Discussion

For a unit step change in the outer surface concentration ($f(\tau)=1$ when $\tau>0$) and for each catalyst geometry, the response of the exact model, Eq. 12, and those of the approximations are compared in Figures 2a–c. For each catalyst geometry, the step response of the proposed approximation, Eqs. 19–21, is as good as the response of the first-order approximation, Eq. 9, demonstrating that the proposed approximations, Eqs. 19–21, are essentially first-order approximations. This is not unexpected in view of the close agreement between $(-A_0/A_1)$ and β in Figure 1. As τ increases, all the step responses approach the corresponding steady states, which are A_0f for the respective geometries. At the same ϕ value for the catalysts, the steady-state average concentrations are different among the three catalyst shapes, largely due to the difference in the volume to surface ratios of the catalyst geometries (L_S for an infinite slab, $R_c/2$ for an infinite cylinder and $R_S/3$ for a sphere). When compared to the proposed approximations in Figures 2a–c, Szukiewicz's approximations[2,4] show larger errors at small τ and approach the respective steady states somewhat faster for the cases of cylinder and sphere catalysts.

Each of Szukiewicz's approximations, Eqs. 6–8, have one characteristic coefficient and approaches the corresponding steady state as τ increases. Szukiewicz[2,4] obtained the coefficient from the complex solution of the unsteady-state balance

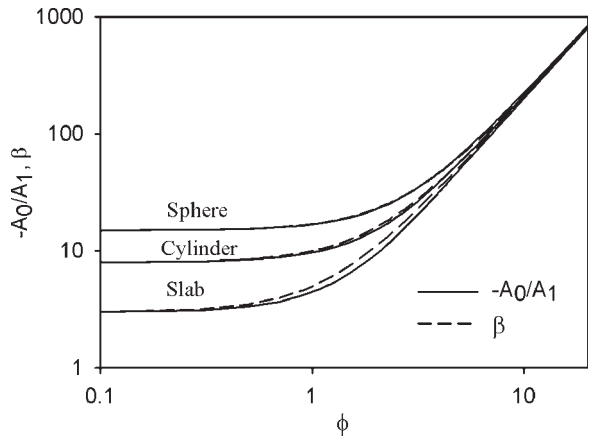

Figure 1. Comparison of the coefficient $(-A_0/A_1)$ and its approximation β for the three catalyst geometries.

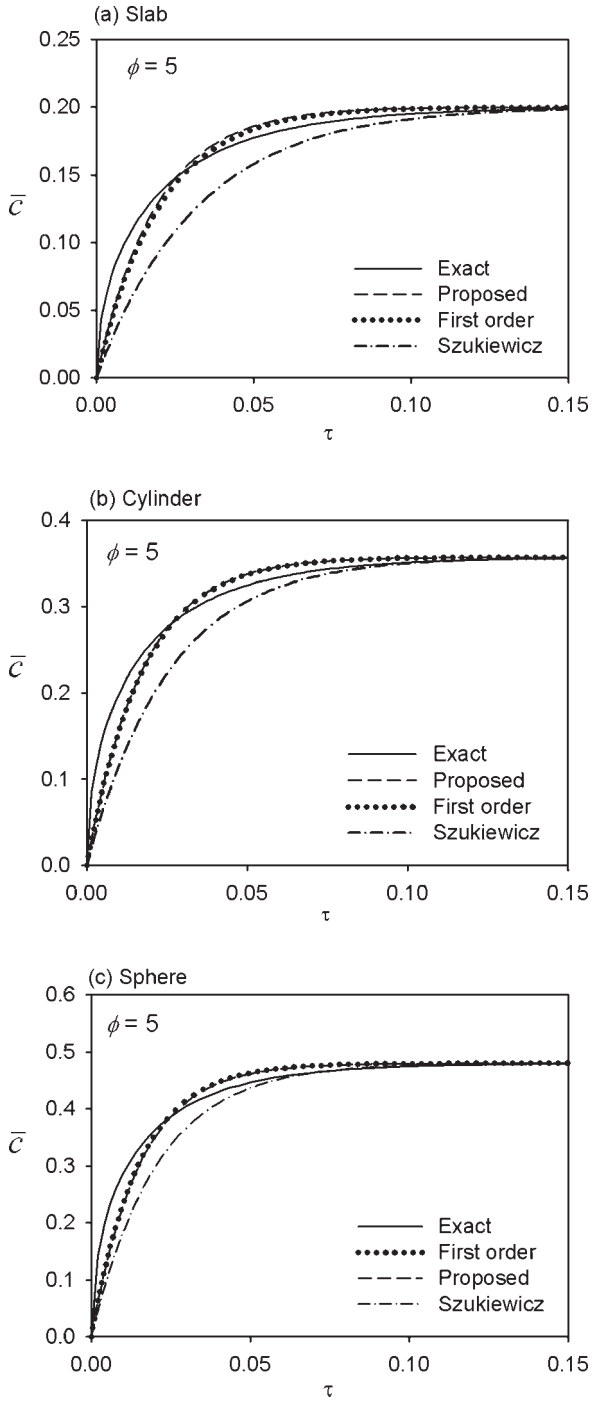

Figure 2. Comparison of the approximations for step responses of a catalyst. Catalyst geometry: (a) slab, (b) cylinder, and (c) sphere. $\phi = 5$.

equation Eq.12 by the method of Laplace-Carson transform. The coefficient, however, can be more easily determined from the solution of the steady-state mass balance equation, Eq. 12 with $\partial c/\partial\tau = 0$. At steady state, for example, the approximation for a sphere catalyst, Eq. 6, becomes

$$3\Psi_2(f - \bar{c}_s) - \phi^2\bar{c}_s = 0 \tag{24}$$

The steady-state concentration $\bar{c}_s$ for $f = 1$ is given by

$$\bar{c}_s = \frac{3\Psi_2}{3\Psi_2 + \phi^2} \text{ or } \Psi_2 = \frac{\bar{c}_s\phi^2}{3(1 - \bar{c}_s)} \tag{25}$$

The steady-state solutions for the three catalyst geometries are well known.[6] For a first-order reaction, it is easy to show that for $f = 1$, $\bar{c}_s = \eta$, where η is the effectiveness factor. The effectiveness factor for the three geometries is also well known[6] and identical to A_0 in Table 1. It is thus seen that in Szukiewicz approximations, the coefficients are introduced to account for the respective steady states. Consequently Szukiewicz approximations are of zero order in approximation of the exact transfer function $G(s)$. This may be verified from the series expansion of the transfer function of Eq. 6:

$$\begin{aligned} G_s(S) &= \frac{3\Psi_2}{3\Psi_2 + \phi^2 + s} \\ &= \frac{3\Psi_2}{3\Psi_2 + \phi^2} - \frac{3\Psi_2}{(3\Psi_2 + \phi^2)^2}s + \cdots \\ &= A_0 - \frac{3\Psi_2}{(3\Psi_2 + \phi^2)^2}s + \ldots \end{aligned} \tag{26}$$

The series is correct to the zeroth-order term, the constant term, when compared with the expansion of $G(s)$. As Szukiewicz's approximations, Eq. 6–8, are zero-order approximations, they are bound to be less accurate than the first-order or the proposed approximations of this study. For a sphere catalyst, this can be seen in Figure 3 in terms of the total square error:

$$S_E = \int_0^\infty (\bar{c}_{exact} - \bar{c}_{approx})^2 d\tau \tag{27}$$

where $\bar{c}_{exact}$is the step response of the exact model, which can be obtained by numerically inverting the Laplace-domain solution for the unit step ($= G(s)/s$). It is seen that the errors of the approximations are decreasing with increasing ϕ, and the errors of the first-order approximation and the simpler proposed approximation give virtually the same errors, again

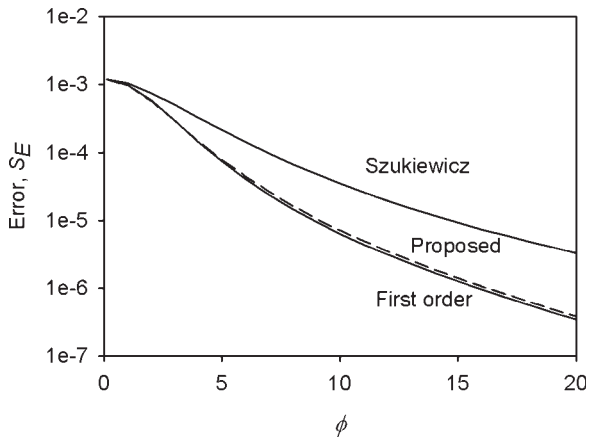

Figure 3. Comparison of errors of the approximations as computed by Eq. 27.

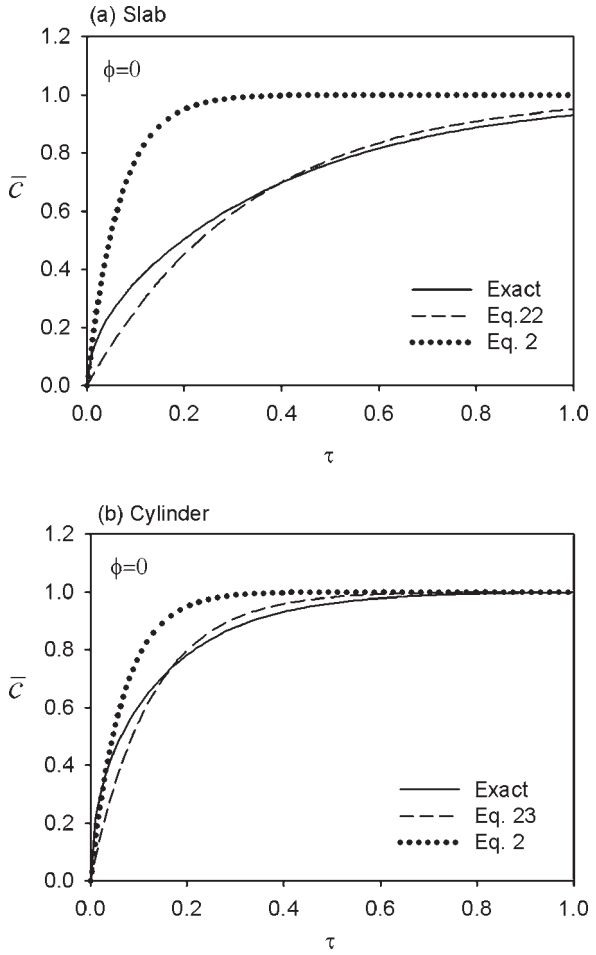

Figure 4. Step responses of the exact model and the approximations in the absence of reaction. Adsorbent geometry: (a) slab and (b) cylinder.

demonstrating that the simpler approximation can replace the first-order approximation.

The main area of application of the approximations is reactor modeling. The accuracy of the approximate reactor model would be dependent on the accuracy in the approximation of the mass balance equation for a catalyst, Eq. 12. Kim[3] has shown for a reactor packed with sphere catalysts that the accuracy of the approximate reactor model increases remarkably with increasing approximation order for catalyst. He has also shown that when the space time of the bulk flow through the reactor is greater than the diffusion time of the catalyst ($= R_S^2/D_e$), the pulse responses of the reactor model with the first-order approximation are in excellent agreement with those of the exact reactor model with Eq. 1. For reactors packed with slab or cylinder catalysts, similar results are expected and will be investigated in a separate study.

In the absence of reaction, the known first-order approximation has been the Glueckauf LDF formula, Eq. 2, for spherical adsorbents. Figure 4a,b demonstrate that the LDF formula is no longer applicable when the shape of the adsorbent is either slab or cylinder, and the proposed equations, Eqs. 22 and 23, are the correct approximations for the geometries.

It is noted that the approximations are based on Eq. 12 and hence, in principle, are not valid if the reaction in the catalyst is not a first-order reaction. When ϕ is small, however, the LDF equations may be used for nonlinear reaction rates because the effect of reaction on the transient concentration profile developed in catalyst would be small. An example of this is shown in Figure 5 for a second-order reaction. Figure 5a,b compares the step responses of the proposed approximation and the exact model for the case of $\phi = 1$ and 5, respectively. When $\phi = 1$, the approximation accuracy of the proposed equation is similar to the case of a first-order reaction, but when $\phi = 5$, the approximation becomes less accurate. For a second-order reaction, $\phi = R\sqrt{kC_0/D_e}$ and A_0 is different from those listed in Table 1 and obtained from the solution of the steady state equation for reaction:

$$\frac{d^2c}{dx^2} + \frac{S}{x}\frac{dc}{dx} - \phi c^2 = 0,\ c(1) = f, \frac{dc}{dx}\bigg|_{x=0} = 0. \qquad (28)$$

For Eq. 28, the numerical methods proposed by Kim and Lee[7,8] can be applied to obtain the steady-state concentration profile in the catalyst. With the concentration profile, the volume-average concentration at the steady state A_0 for the reac-

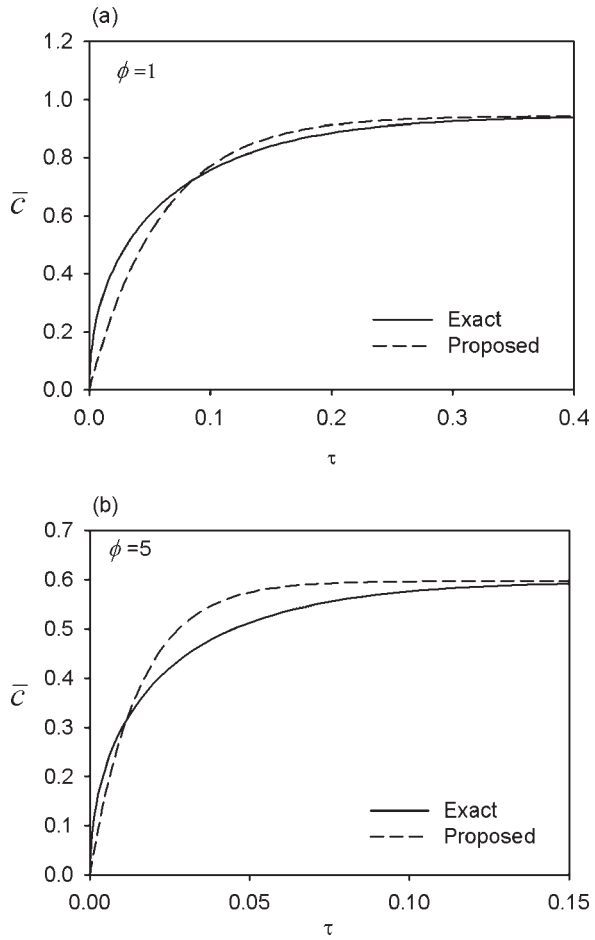

Figure 5. Step responses of the exact model and the approximation for a spherical catalyst and a second-order reaction. (a) $\phi = 1$ and (b) $\phi = 5$.

tion is obtained by Eq. 17. In modeling of a reactor for a nonlinear reaction, the ranges of f and ϕ for the catalyst may be estimated, and for the ranges of f and ϕ, the dependence of A_0 on ϕ and f can be determined prior to solution of the reactor model. For example, a grid in a 2D space of ϕ and f, covering the ranges, may be generated, and A_0 at the grid points is determined by solving the nonlinear steady state equation for the catalyst such as Eq.28. With these A_0 values, A_0 for any values ϕ and f in the ranges can be estimated by interpolation during solution of the approximate reactor model.

Conclusion

For the three typical geometries of catalysts (sphere, cylinder and slab), simple LDF formulas have been developed for unsteady-state diffusion, a linear adsorption and a first-order reaction in catalysts. Mathematically the formulas are time-domain equations of first-order approximations of the exact model in the Laplace domain. In reactor modeling, the approximations would be useful by removing the space variable in catalysts and making the resulting model more tractable.

Acknowledgments

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Notation

A_i = i-th order coefficient in the series expansion of $G(s)$
C_0 = reference concentration, mol m^{-3}
C_p = concentration in catalyst, mol m^{-3}
c = dimensionless concentration in catalyst ($=C_P/C_0$)
$\overline{c}$ = average concentration in catalyst, dimensionless
D_e = effective diffusivity in catalyst, m s^{-2}
F = concentration at the outer surface of catalyst, mol m^{-3}
f = concentration at the outer surface of catalyst, dimensionless
$G(s)$ = transfer function of catalyst
G_1 = transfer function of first-order approximation of $G(s)$
K = adsorption equilibrium constant, dimensionless
I_0, I_1 = the zeroth- and first-order modified Bessel functions of the first kind
k = reaction rate constant, s^{-1}
L_S = half of slab thickness, m
Q = concentration of adsorbed phase in catalyst, mol m^{-3}
R_C = radius of cylindrical catalyst, m
R_S = radius of spherical catalyst, m
S = shape factor of catalyst, dimensionless
s = Laplace-domain variable
t = time, s
x = length coordinate in catalyst, dimensionless

Greek letters

β = coefficient, defined in Eq. 20
ϕ = Thiele modulus, defined in Table 1
τ = time, dimensionless ($= tD_e/(L^2(\varepsilon_p + K))$

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