

# High-order approximations for unsteady-state diffusion and reaction in slab, cylinder and sphere catalyst

Dong Hyun Kim<sup>†</sup> and Jitae Lee

Department of Chemical Engineering, Kyungpook National University, Daegu 702-701, Korea  
 (Received 26 February 2011 • accepted 3 May 2011)

**Abstract**—High-order approximations for unsteady-state diffusion, a linear adsorption and a first-order reaction in a slab, cylinder and sphere catalyst are developed. The approximations are based on a first-, a second-, a third- and a fifth-order approximation of the Laplace domain solutions of the exact model for the catalyst of three geometries. The coefficients in the approximations are functions of Thiele modulus of the respective geometry and easy to determine. The accuracy of the approximation is shown to increase markedly with the approximation order.

Key words: Mathematical Modeling, Simulation, Approximation, LDF Formula, Transient Response

## INTRODUCTION

In modeling of unsteady-state packed-bed reactors or adsorbers, the basic element is the model for catalyst particles or adsorbent particles. The model for the particle is then coupled with the model for the flowing phase in the reactor or adsorber. The exact model for the particles is given in the form of a partial differential equation (PDE) to describe the transient concentration profile in the particle. The profile is then used to determine the mass exchange rate between the particle and the flowing fluid phase.

The exchange rate can also be expressed in terms of the average concentration in the particle. In this case, the reactor model does not involve the space variable in the particle and the resulting model is easier to solve, since the difficulty in the solution of the model is often commensurate with the number of independent variables in the model. The exact average concentration, however, can only be obtained from the exact concentration profile in the catalyst. This requires again the exact model in the form of PDE. But for approximate average concentrations, there have been developed many formulas without the space variable in the particle. For transient adsorption and diffusion in an adsorbent, Glueckauf [1] first proposed a formula that the mass exchange rate between the particle and its surrounding is proportional to the difference between the average concentration and the outside concentration of the particle. This type of equation has been called the LDF (linear driving force) equation. Later Kim [2] proposed LDF equations for transient diffusion, adsorption and reaction in catalyst particles. For cyclic adsorption processes such as pressure swing adsorption, approximation formulas are separately developed for adsorbents with monodisperse pore structures [3,4] and bidisperse pore structures [5]. More accurate high-order approximations have also been proposed [6-9]. All these approximations are for spherical adsorbents or spherical catalysts.

For other geometries such as an infinite slab and an infinite cylinder, approximations have been proposed recently. Patton et al. [10]

developed LDF approximations for slab and cylinder adsorbents. Szukiewicz [11] and Kim [12] obtained LDF approximations for adsorption and reaction in slab and cylinder catalysts. These LDF approximations for slab and cylinder are of first-order in the order of approximation and hence have a limited accuracy, being applicable to very slowly changing conditions. It has been shown that the accuracy of approximation increases significantly with the order of approximation [9]. To complement the first-order approximations, high-order approximations for adsorption and reaction in slab and cylinder catalysts are developed in this study. The new high-order approximations are shown to be highly accurate and as good as the exact model for pore diffusion in most practical applications.

## THEORY

The dimensionless unsteady-state mass balance for a linear adsorption and a first-order reaction in a catalyst is [12]

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial x^2} + \frac{S}{x} \frac{\partial c}{\partial x} - \phi^2 c \quad (1)$$

In the equation,  $\phi$  is the Thiele modulus. In the absence of reaction,  $\phi=0$ , Eq. (1) becomes the pore diffusion equation.  $S$  depends on the shape of the catalyst ( $S=0$  for an infinite slab,  $S=1$  for an infinite cylinder and  $S=2$  for a sphere). The boundary conditions at the external surface and at the center are

$$c(1, \tau) = f(\tau), \quad \left. \frac{\partial c}{\partial x} \right|_{x=0} = 0 \quad (2)$$

$f(\tau)$  is an arbitrary function of time. When Eq. (1) is coupled with the balance equation for the phase flowing through the reactor,  $f(\tau)$  becomes the concentration in the flowing phase. With a zero initial condition,  $c(x, 0)=0$ , Eq. (1) with Eq. (2) can be easily solved by the method of Laplace transform.

In reactor simulations, the mass exchange rate between the catalyst particle and its surrounding is more important than the concentration profile in the catalyst. The exchange rate can be expressed in terms of  $d\bar{c}/d\tau + \phi^2 \bar{c}$ , where  $\bar{c}$  is the volume-average concentration, determined by

<sup>†</sup>To whom correspondence should be addressed.  
 E-mail: dhkim@knu.ac.kr

**Table 1. Slab catalyst (S=0). Transfer function and coefficients**

$G(s) = \frac{\tanh \sqrt{\phi^2 + s}}{\sqrt{\phi^2 + s}}, \quad \phi = L_s \sqrt{\frac{k}{D_e}}$
$A_0 = \frac{Z}{\phi}$
$A_1 = \frac{1-Z^2}{2\phi^2} - \frac{Z}{2\phi^3}$
$A_2 = -\frac{Z(1-Z^2)}{4\phi^3} - \frac{3(1-Z^2)}{8\phi^4} + \frac{3Z}{8\phi^5}$
$A_3 = \frac{(1-Z^2)(3Z^2-1)}{24\phi^4} + \frac{Z(1-Z^2)}{4\phi^5} + \frac{5(1-Z^2)}{16\phi^6} - \frac{5Z}{16\phi^7}$
$A_4 = \frac{(1-Z^2)(2Z-3Z^2)}{48\phi^5} + \frac{5(1-Z^2)(1-3Z^2)}{96\phi^6} - \frac{15Z(1-Z^2)}{64\phi^7}$ $- \frac{35(1-Z^2)}{128\phi^8} + \frac{35Z}{128\phi^9}$
$A_5 = \frac{(1-Z^2)}{480\phi^6} (15Z^4 - 15Z^2 + 2) + \frac{(1-Z^2)}{32\phi^7} (Z^3 - 2Z)$ $+ \frac{7(1-Z^2)}{128\phi^8} (3Z^2 - 1) + \frac{7Z(1-Z^2)}{32\phi^9} + \frac{63(1-Z^2)}{256\phi^{10}} - \frac{63Z}{256\phi^{11}}$
$Z = \tanh(\phi)$

$$\bar{c}(\tau) = (S+1) \int_0^1 c(x, \tau) x^S dx \quad (3)$$

The solution in the Laplace domain can be integrated with respect to  $x$  as in Eq. (3) to have the Laplace domain solution for  $\bar{c}(\tau)$ . The solution for  $\bar{c}(\tau)$  can be expressed as  $G(s)F(s)$ , where  $F(s)$  is the Laplace transform of  $f(t)$ .  $G(s)$  is usually called the transfer function.  $G(s)$  for the three geometries is listed in Table 1 (slab), 2 (cylinder) and 3 (sphere).

To develop approximations of  $G(s)$ , we need the Taylor expansion of  $G(s)$ .

**Table 3. Sphere catalyst (S=2). Transfer function and coefficients**

$G(s) = 3 \left( \frac{\coth \sqrt{\phi^2 + s}}{\sqrt{\phi^2 + s}} - \frac{1}{\phi^2 + s} \right), \quad \phi = R_s \sqrt{\frac{k}{D_e}}$
$A_0 = 3 \left( \frac{Y}{\phi} - \frac{1}{\phi^2} \right)$
$A_1 = -\frac{3Y^2-1}{2\phi^2} - \frac{3Y}{2\phi^3} + \frac{3}{\phi^4}$
$A_2 = -\frac{3Y(1-Y^2)}{4\phi^3} - \frac{9(1-Y^2)}{8\phi^4} + \frac{9Y}{8\phi^5} - \frac{3}{\phi^6}$
$A_3 = \frac{1(1-Y^2)(3Y^2-1)}{8\phi^4} + \frac{3Y(1-Y^2)}{4\phi^5} + \frac{15(1-Y^2)}{16\phi^6} - \frac{15Y}{16\phi^7} + \frac{3}{\phi^8}$
$A_4 = \frac{1(1-Y^2)(2Y-3Y^3)}{16\phi^5} + \frac{5(1-Y^2)(1-3Y^2)}{32\phi^6} - \frac{45Y(1-Y^2)}{64\phi^7}$ $- \frac{105(1-Y^2)}{128\phi^8} + \frac{105Y}{128\phi^9} - \frac{3}{\phi^{10}}$
$A_5 = \frac{(1-Y^2)}{160\phi^6} (15Y^4 - 15Y^2 + 2) + \frac{(1-Y^2)}{32\phi^7} (8Y^3 - 6Y)$ $+ \frac{(1-Y^2)}{128\phi^8} (63Y^2 - 21) + \frac{31Y(1-Y^2)}{32\phi^9}$ $+ \frac{189(1-Y^2)}{256\phi^{10}} - \frac{189Y}{256\phi^{11}} + \frac{3}{\phi^{12}}$

$$Y = \coth(\phi)$$

sion of  $G(s)$ .

$$G(s) = A_0 + A_1 s + A_2 s^2 + A_3 s^3 + A_4 s^4 + A_5 s^5 \cdots \quad (4)$$

The coefficients  $A_0 \cdots A_5$  are all functions of  $\phi$  and listed in Tables 1-3 for the three geometries. The approximations of  $G(s)$  are in the form of rational functions which correspond to simple expressions in the time domain. The approximations developed in the present

**Table 2. Cylinder catalyst (S=1). Transfer function and coefficients**

$G(s) = \frac{2I_1(\sqrt{\phi^2 + s})}{(\sqrt{\phi^2 + s})I_0(\sqrt{\phi^2 + s})}, \quad \phi = R_c \sqrt{\frac{k}{D_e}}$
$A_0 = \frac{2I_1(\phi)}{\phi I_0(\phi)}$
$A_1 = \frac{1}{\phi^2} \left( 1 - \frac{I_1(\phi)^2}{I_0(\phi)^2} \right) - \frac{2I_1(\phi)}{\phi^3 I_0(\phi)}$
$A_2 = \frac{\phi^2 I_1(\phi)^3 + 3\phi I_0(\phi) I_1(\phi)^2 - (\phi^2 - 4) I_0(\phi)^3 I_1(\phi) - 2\phi I_0(\phi)^3}{2\phi^5 I_0(\phi)^3}$
$A_3 = \frac{-1}{12\phi^7 I_0(\phi)^4} \left( 3\phi^3 I_1(\phi)^4 + 12\phi^2 I_0(\phi) I_1(\phi)^3 + (22\phi^2 - 4\phi^3) I_0(\phi)^2 I_1(\phi)^2 \right)$ $+ (24 - 10\phi^2) I_0(\phi)^3 I_1(\phi) + (\phi^3 - 12\phi) I_0(\phi)^4$
$A_4 = \frac{1}{48\phi^9 I_0(\phi)^5} \left( 6\phi^4 I_1(\phi)^5 + 30\phi^2 I_0(\phi) I_1(\phi)^4 + (70\phi^2 - 10\phi^4) I_0(\phi)^2 I_1(\phi)^3 \right)$ $+ (100\phi - 35\phi^3) I_0(\phi)^3 I_1(\phi)^2 + (96 - 52\phi^2 + 4\phi^4) I_0(\phi)^4 I_1(\phi)$ $+ (7\phi^3 - 48\phi) I_0(\phi)^5$
$A_5 = \frac{1}{240\phi^{11} I_0(\phi)^6} \left( -15\phi^5 I_1(\phi)^6 - 90\phi^4 I_0(\phi) I_1(\phi)^5 + (30\phi^5 - 255\phi^3) I_0(\phi)^2 I_1(\phi)^4 \right)$ $+ (135\phi^4 - 450\phi^2) I_0(\phi)^3 I_1(\phi)^3 + (-17\phi^5 + 271\phi^3 - 548\phi) I_0(\phi)^4 I_1(\phi)^2$ $+ (-47\phi^4 + 308\phi^2 - 480) I_0(\phi)^5 I_1(\phi) + (2\phi^5 - 47\phi^3 + 240\phi) I_0(\phi)^6$

study are

$$G_1(s) = \frac{b_{10}}{a_{10} + s}, G_2(s) = \frac{b_{20} + b_{21}s}{a_{20} + s}, G_3(s) = \frac{b_{30} + b_{31}s}{a_{30} + a_{31}s + s^2} \text{ and} \\ G_5(s) = \frac{b_{50} + b_{51}s + b_{52}s^2}{a_{50} + a_{51}s + a_{52}s^2 + s^3} \quad (5)$$

**Table 4. The first-order approximation**

Approximate transfer function:
$G_1(s) = \frac{b_{10}}{a_{10} + s}$
Coefficients:
$a_{10} = -\frac{A_0}{A_1}$
$b_{10} = -\frac{A_0^2}{A_1}$
Approximation formula:
$\frac{d\bar{c}}{d\tau} = -a_{10}\bar{c} + b_{10}f$

**Table 5. The second-order approximation**

Approximate transfer function:
$G_2(s) = \frac{b_{20} + b_{21}s}{a_{20} + s}$
Coefficients:
$a_{20} = -\frac{A_1}{A_2}$
$b_{20} = -\frac{A_0A_1}{A_2}$
$b_{21} = A_0 - \frac{A_1^2}{A_2}$
Approximation formula:
$\frac{d\bar{c}}{d\tau} = -a_{20}\bar{c} + b_{20}f + b_{21}\frac{df}{d\tau}$

**Table 6. The third-order approximation**

Approximate transfer function:
$G_3(s) = \frac{b_{30} + b_{31}s}{a_{30} + a_{31}s + s^2}$
Coefficients:
$a_{30} = \frac{A_0A_2 - A_1^2}{A_1A_3 - A_2^2}$
$a_{31} = \frac{-A_0A_3 + A_1A_2}{A_1A_3 - A_2^2}$
$b_{30} = A_0a_{30}$
$b_{31} = \frac{2A_0A_1A_2 - A_0^2A_3 - A_1^3}{A_1A_3 - A_2^2}$
Approximation formula:
$\frac{d\bar{c}}{d\tau} = -a_{31}\bar{c} + b_{31}f + u$
$\frac{du}{d\tau} = -a_{30}\bar{c} + b_{30}f$

The coefficients in  $G_1, \dots, G_5$  are determined by matching the series expansions of the approximations and Eq. (4). The number of matching terms in the expansions depends on the number of coefficients in the approximations. For example,

$$G_1(s) = \frac{b_{10}}{a_{10} + s} = \frac{b_{10}}{a_{10}} - \frac{b_{10}}{a_{10}^2}s + \dots \quad (6)$$

By matching the first two terms in Eq. (4) and Eq. (6),  $a_{10}$  and  $b_{10}$  of  $G_1(s)$  can be determined in terms of  $A_0$  and  $A_1$ , ie.

$$a_{10} = -\frac{A_0}{A_1}, b_{10} = -\frac{A_0^2}{A_1} \quad (7)$$

As  $G_1$  is accurate to the first-order term,  $A_1s$ , in the series expansion, it can be called a first-order approximation of  $G$ . Similarly, since  $G_5(s)$  is made to be exact up to the sixth term, from  $A_0$  to  $A_5s^5$ , it is a fifth-order approximation. As the number of matching terms increases, the accuracy of the approximate functions of  $G(s)$  increases

**Table 7. The fifth-order approximation**

Approximate transfer function:
$\frac{b_{50} + b_{51}s + b_{52}s^2}{a_{50} + a_{51}s + a_{52}s^2 + s^3}$
Coefficients:
$a_{50} = (A_1^2A_4 - A_0A_2A_4 - 2A_1A_2A_3 + A_2^3 + A_0A_3^2)/\Gamma$
$a_{51} = (-A_1^2A_5 + A_1A_2A_4 + A_1A_3^2 - A_2^2A_3 - A_0A_3A_4 + A_0A_2A_5)/\Gamma$
$a_{52} = [A_0(A_4^2 - A_3A_5) + A_1(A_2A_5 - A_3A_4) + A_2(A_3^2 - A_2A_4)]/\Gamma$
$b_{50} = A_0a_{50}$
$b_{51} = [A_0^2(A_2A_5 - A_3A_4) + A_1^2(A_1A_4 - 2A_2A_3 - A_0A_5) + A_2^2(A_1A_2 - A_0A_3) + 2A_0A_1A_3^2]/\Gamma$
$b_{52} = [A_0^2(A_4^2 - A_3A_5) + A_1^2(2A_2A_4 - A_1A_5) + A_2^2(A_2^2 - 2A_0A_4 - 3A_1A_3) + A_3^2(A_1^2 + 2A_0A_2) + 2A_0A_1(A_2A_5 - A_3A_4)]/\Gamma$
Where $\Gamma = -A_1A_4^2 + A_1A_3A_5 + 2A_2A_3A_4 - A_2^2A_5 - A_3^3$
Approximation formula:
$\frac{d\bar{c}}{d\tau} = -a_{52}\bar{c} + b_{52}f + u$
$\frac{du}{d\tau} = -a_{51}\bar{c} + b_{51}f + v$
$\frac{dv}{d\tau} = -a_{50}\bar{c} + b_{50}f$

**Table 8. Taylor series coefficients of the transfer function  $G(s)$  for  $\phi=0$**

	Slab, S=0	Cylinder, S=1	Sphere, S=2
$A_0$	1	1	1
$A_1$	$-\frac{1}{3}$	$-\frac{1}{8}$	$-\frac{1}{15}$
$A_2$	$\frac{2}{15}$	$\frac{1}{48}$	$\frac{2}{315}$
$A_3$	$-\frac{17}{315}$	$-\frac{11}{3072}$	$-\frac{1}{1575}$
$A_4$	$\frac{62}{2835}$	$\frac{19}{30720}$	$\frac{2}{31185}$
$A_5$	$-\frac{1382}{155925}$	$-\frac{473}{4423680}$	$-\frac{1382}{212837625}$

markedly. This type of approximation is called the Pade approximation [6]. The time domain approximation formulas and the coefficients of  $G_1$ ,  $G_2$ ,  $G_3$  and  $G_5$  are listed in Tables 4-7, respectively.

## DISCUSSION

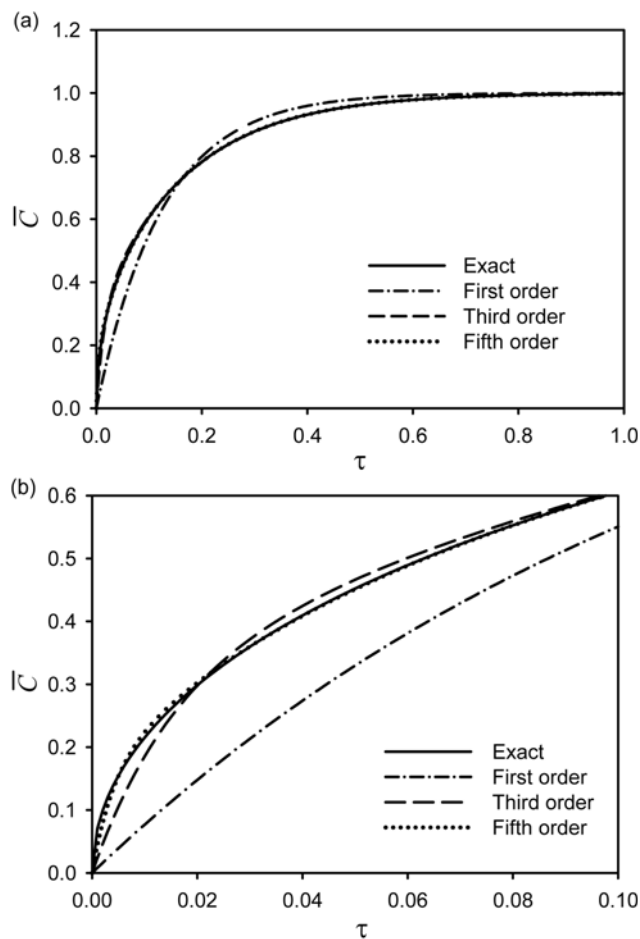
### 1. Approximations in the Absence of Reaction ( $\phi=0$ )

The coefficients in Eq. (4) become constants, which are listed in

Table 8 for the three geometries. The resulting approximations are listed in Table 9. Previous approximations have been developed mainly for spherical geometry. Eq. (T9) in Table 9 is the well-known linear driving force (LDF) formula, first proposed by Glueckauf [1]. Eq. (T10) is a second-order approximation, proposed by Kim [2]. The third-order and the fifth-order approximation, Eqs. (T11) and T(12), were developed by Lee and Kim [6]. Recently, Patton et al. [10] and Kim [12] developed Eq. (T1) and Eq. (T5) for slab

**Table 9. Approximations of  $G(s)$  and the corresponding approximation formulas for  $\phi=0$**

Catalyst shape	Approximation of $G(s)$	Approximation formula
Slab ( $S=0$ )	$\frac{3}{s+3}$	$\frac{d\bar{c}}{d\tau} = 3(f(\tau) - \bar{c})$ (T1)
	$\frac{s+15}{6s+15}$	$\frac{d\bar{c}}{d\tau} = \frac{5}{2}(f(\tau) - \bar{c}) + \frac{1}{6} \frac{df(\tau)}{d\tau}$ (T2)
	$\frac{10s+105}{s^2+45s+105}$	$\frac{d\bar{c}}{d\tau} = -45\bar{c} + u + 10f(\tau)$ $\frac{du}{d\tau} = 105(f(\tau) - u)$ (T3)
	$\frac{21s^2+1260s+10395}{s^3+210s^2+4725s+10395}$	$\frac{d\bar{c}}{d\tau} = -210\bar{c} + u + 21f(\tau)$ $\frac{du}{d\tau} = -4725\bar{c} + v + 1260f(\tau)$ $\frac{dv}{d\tau} = 10395(f(\tau) - \bar{c})$ (T4)
Cylinder ( $S=1$ )	$\frac{8}{s+8}$	$\frac{d\bar{c}}{d\tau} = 8(f(\tau) - \bar{c})$ (T5)
	$\frac{s+24}{4s+24}$	$\frac{d\bar{c}}{d\tau} = 6(f(\tau) - \bar{c}) + \frac{1}{4} \frac{df(\tau)}{d\tau}$ (T6)
	$\frac{24s+384}{s^2+72s+384}$	$\frac{d\bar{c}}{d\tau} = -72\bar{c} + u + 24f(\tau)$ $\frac{du}{d\tau} = 384(f(\tau) - u)$ (T7)
	$\frac{48s^2+3840s+46080}{s^3+288s^2+9600s+46080}$	$\frac{d\bar{c}}{d\tau} = -288\bar{c} + u + 48f(\tau)$ $\frac{du}{d\tau} = -9600\bar{c} + v + 3840f(\tau)$ $\frac{dv}{d\tau} = 46080(f(\tau) - \bar{c})$ (T8)
Sphere ( $S=2$ )	$\frac{15}{s+15}$	$\frac{d\bar{c}}{d\tau} = 15(f(\tau) - \bar{c})$ (T9)
	$\frac{3s+105}{10s+105}$	$\frac{d\bar{c}}{d\tau} = \frac{21}{2}(f(\tau) - \bar{c}) + \frac{3}{10} \frac{df(\tau)}{d\tau}$ (T10)
	$\frac{42s+945}{s^2+105s+945}$	$\frac{d\bar{c}}{d\tau} = -105\bar{c} + u + 42f(\tau)$ $\frac{du}{d\tau} = 945(f(\tau) - u)$ (T11)
	$\frac{81s^2+8316s+135135}{s^3+378s^2+17325s+135135}$	$\frac{d\bar{c}}{d\tau} = -378\bar{c} + u + 81f(\tau)$ $\frac{du}{d\tau} = -17325\bar{c} + v + 8316f(\tau)$ $\frac{dv}{d\tau} = 135135(f(\tau) - \bar{c})$ (T12)

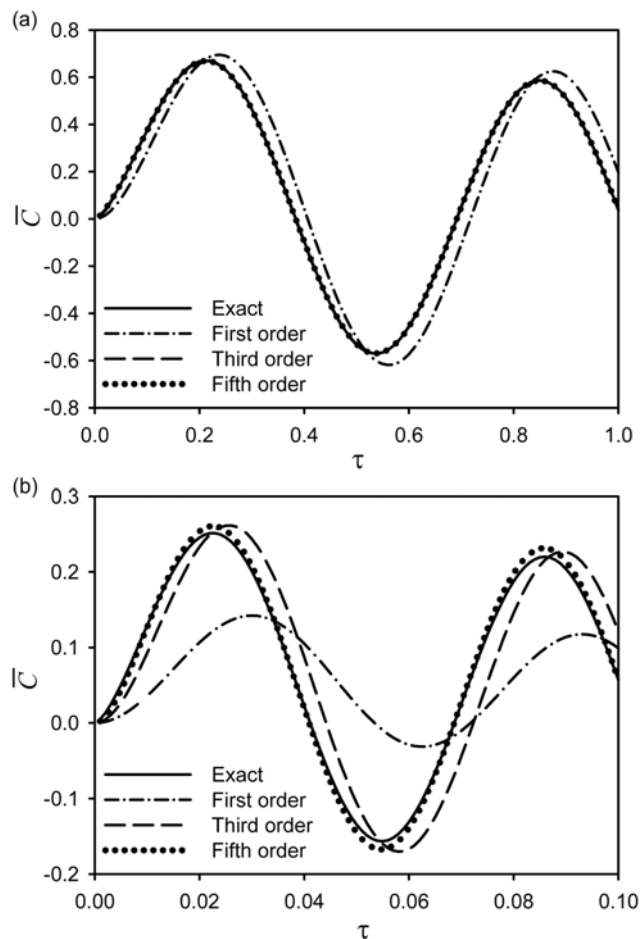


**Fig. 1. (a) Step responses of the approximations for a cylinder adsorbent. (b) Redrawing of the step responses in the time interval (0, 0.1).**

and cylinder adsorbents, respectively. The high-order approximations, Eqs. (T2)-(T4) and Eqs. (T6)-(T8), are new approximations developed in this study.

Fig. 1(a) compares the approximations for the case of unit step  $f(\tau)=1$  and cylinder geometry ( $S=1$ ). The exact response is obtained by numerical inversion of the Laplace transform  $G(s)/s$ . All the approximations approach the steady-state value  $\bar{c}=1$  as  $\tau$  increases. The first-order approximation, Eq. (T5), shows some deviation from the exact response, but the third-order and the fifth-order approximations, Eqs. (T7) and (T9), virtually coincide with the exact step response. It is seen that the accuracy of approximation considerably increases with the order of approximation. Fig. 1(b) is a magnification of Fig. 1(a) at small  $\tau$  values. Here the fifth-order approximation is seen to be as good as the exact model.

As the approximations are based on the Taylor series expansion around  $s=0$ , the approximations are valid for slowly varying  $f(\tau)$ . This is examined for a sinusoidal change in the surface concentration ( $f(\tau)=\sin(\omega\tau)$ ). For  $f(\tau)=\sin(\tau)$ , the responses of all the approximations including the first-order approximation coincide with the exact model response (not shown). As the frequency increases, however, the approximation starts to become less accurate. Fig. 2(a) and Fig. 2(b) show the sinusoidal responses of the approximations and the exact model for  $f(\tau)=\sin(10\tau)$  and  $f(\tau)=\sin(100\tau)$ , respectively.



**Fig. 2. Sinusoidal responses of the approximations for a cylinder adsorbent. (a)  $f(\tau)=\sin(10\tau)$ , (b)  $f(\tau)=\sin(100\tau)$ .**

In Fig. 2(a), it is seen that the first-order approximation deviates considerably from the exact response, while the third-order and the fifth-order approximations are indistinguishable with the exact response. For  $f(\tau)=\sin(100\tau)$ , shown in Fig. 2(b), only the fifth-order approximation is shown to be valid. With increasing order of approximation, the applicable range of the approximation is extended to higher frequencies.

## 2. Approximations in the Presence of Reaction ( $\phi > 0$ )

Recently, simple first-order approximations for the three geometries were developed [12]:

$$\frac{d\bar{c}}{d\tau} = \{(S+2)^2 - 1 + 2\phi^2\} (A_0 f(\tau) - \bar{c}) \quad (8)$$

where  $S$  is the shape factor. The same equation can be derived from the present first-order approximation for each geometry by considering the asymptotes of  $A_0$  and  $A_1$  at small and large values of  $\phi$ . Eq. (8) gives an approximate time constant of the catalyst particle, which is

$$\tau_0 = \frac{1}{(S+2)^2 - 1 + 2\phi^2} \quad (9)$$

The time constant characterizes the response to a time-varying input. Physically, the constant represents the time it takes to reach 63.2% of its steady-state value after it receives a step input. A smaller time

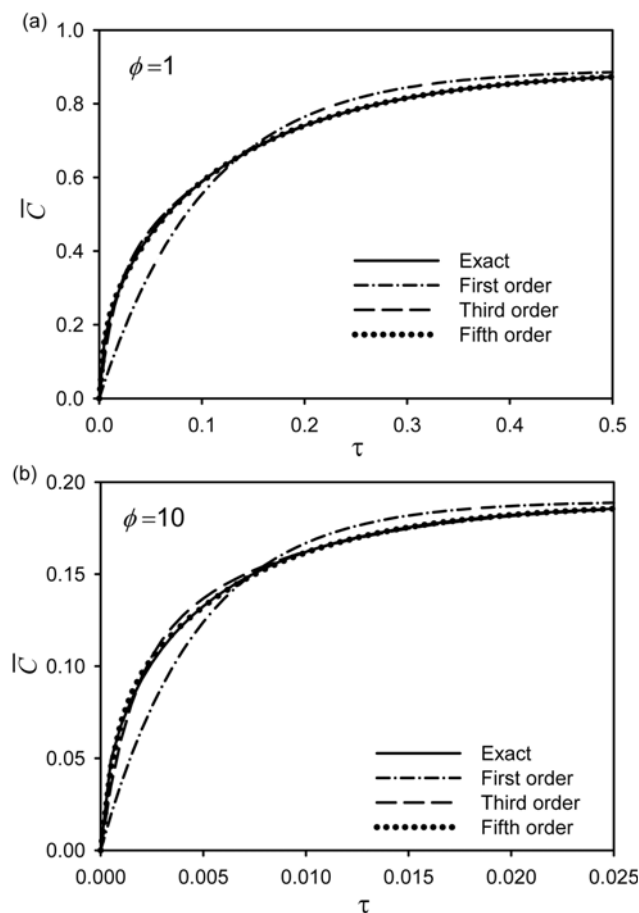


Fig. 3. Step responses of the exact model and the first-order approximation for a cylinder catalyst. (a)  $\phi=1$ , (b)  $\phi=10$ .

constant means a faster dynamic response. According to Eq. (9), the time constant is a function of  $\phi$  and decreases with increasing  $\phi$ .

Figs. 3(a) and 3(b) show step responses of a cylinder catalyst ( $S=1$ ) for  $\phi=1$  ( $\tau_0=0.1$ ) and  $\phi=10$  ( $\tau_0=0.0048$ ). The step response for

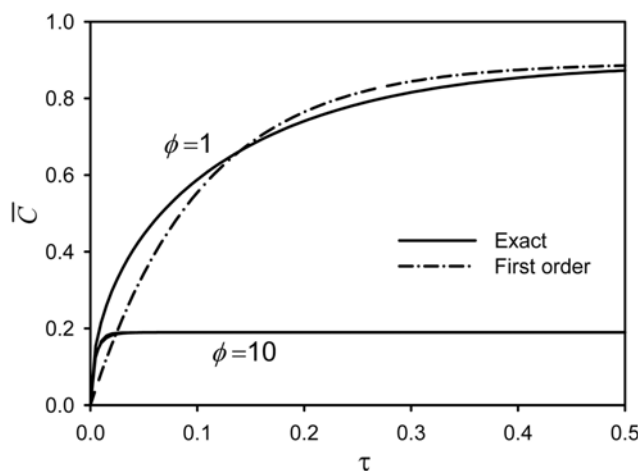


Fig. 4. Step responses of the exact model and the first-order approximation for  $\phi=1$  and  $\phi=10$ .

$\phi=10$  is around 20 times faster than the response for  $\phi=1$ . When plotted in the time range of  $0-5\tau_0$  ( $0-0.5$  for  $\phi=1$  and  $0-0.025$  for  $\phi=10$ ), the two figures look similar: the first-order approximation being least accurate and the high-order approximations being indistinguishable with the response of the exact model. If, however, the figures are plotted on the same time scale ( $0-0.5$ ) as shown in Fig. 4, it is seen that the first-order approximation is as good as the exact model when  $\phi=10$ . This is because the error in the small time span is not apparent if it is seen on the time scale much greater than the time constant of the particle, and also the particle responds very quickly to the external disturbances.

## CONCLUSION

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

## ACKNOWLEDGEMENT

This work was funded by Priority Research Centers Program through the National Research Foundation of Korea (NRF).

## NOMENCLATURE

- $A_i$  : i-th order coefficient in the series expansion of  $G(s)$
- $C_0$  : reference concentration [ $\text{mol m}^{-3}$ ]
- $C_p$  : concentration in catalyst [ $\text{mol m}^{-3}$ ]
- $c$  : dimensionless concentration in catalyst ( $=C_p/C_0$ )
- $\bar{c}$  : average concentration in catalyst, dimensionless
- $D_e$  : effective diffusivity in catalyst [ $\text{m}^2 \text{s}^{-1}$ ]
- $f$  : concentration at the outer surface of catalyst, dimensionless
- $G(s)$  : transfer function of catalyst
- $G_i$  : i-th order approximation of  $G(s)$
- $I_0, I_1$  : the zeroth- and first-order modified Bessel functions of the first kind
- $k$  : reaction rate constant [ $\text{s}^{-1}$ ]
- $L_s$  : half of slab thickness [m]
- $R_c$  : radius of cylindrical catalyst [m]
- $R_s$  : radius of spherical catalyst [m]
- $S$  : shape factor of catalyst, dimensionless
- $s$  : Laplace-domain variable
- $x$  : space variable in catalyst, dimensionless

## Greek Letters

- $\phi$  : Thiele modulus, defined in Table 1, 2 and 3
- $\tau$  : time, dimensionless

## REFERENCES

1. E. Glueckauf, *Trans. Farad. Soc.*, **51**, 1540 (1955).
2. D. H. Kim, *AIChE J.*, **35**, 343 (1989).
3. D. H. Kim, *Chem. Eng. Sci.*, **51**, 4137 (1996).
4. H.-K. Hsuen, *Chem. Eng. Sci.*, **55**, 3475 (2000).

5. D. H. Kim, *Chem. Eng. Sci.*, **52**, 3471 (1997).
6. J. Lee and D. H. Kim, *Chem. Eng. Sci.*, **53**, 1209 (1998).
7. D. H. Kim and J. Lee, *Korean J. Chem. Eng.*, **16**, 69 (1999).
8. P. Cruz, A. Mendes and F. D. Magalhaes, *Chem. Eng. Sci.*, **59**, 4393 (2004).
9. D. H. Kim, *AIChE J.*, **54**, 2423 (2008).
10. A. Patton, B. D. Crittenden and S. P. Perera, *Trans IChemE, Part A, Chem. Eng. Res. Design*, **82**, 999 (2004).
11. M. K. Szukiewicz, *AIChE J.*, **47**, 2131 (2001).
12. D. H. Kim, *AIChE J.*, **55**, 834 (2009).