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Applications of high-order approximate models for unsteady-state diffusion and reaction in a catalyst

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Abstract−The partial differential equation for unsteady-state diffusion, adsorption and a first-order reaction in a catalyst is often approximated to ordinary differential equations for reduced computational loads. Very high-order models obtained by the continued fraction expansion method are accurate for a wide range of the Thiele modulus and the changing frequency of surface concentration. In addition, they are numerically well-conditioned. However, due to their high dimensionalities, they will not have merits over other low-order models. Here, high-order models based on the continued fraction expansion method are shown to be used to obtain various practical models. With the Taylor series obtained from high-order models, Pade approximations are easily obtained regardless of the Thiele modulus and the shape of catalyst. Low-order models by applying the balanced truncation method to a high-order model can also be obtained, providing better approximations than the well-known Pade models.

Key words: Adsorption Dynamics, Pore Diffusion Model, Fractional Order System, Linear Driving Force Model, Convolution

INTRODUCTION

Dynamic mass transfer in a particle is important to describe behaviors of gas separation processes and catalytic reactors accurately. It is represented by a parabolic partial differential equation known as the pore diffusion model. Practical packed bed processes involve mass balance equations of the bulk flow through the beds in addition to this pore diffusion model. These coupled partial differential equations are rather complicated and the pore diffusion model needs be approximated for reduced computational loads [1,2].

By assuming that the mass transfer rate is proportional to the difference between the surface concentration and the average concentration in a particle, Glueckauf [3] proposed a first-order ordinary differential equation named the linear driving force (LDF) model to approximate the unsteady-state diffusion and adsorption in a spherical adsorbent. This simplification is very effective in reducing computational loads and its usages are expanded widely in practice [4-7]. The LDF model is valid only when the surface concentration in the particle changes slowly. To improve the approximation accuracies, Lee and Kim [4] proposed high-order differential equation models approximating the pore diffusion model accurately by applying the Pade approximation method to the exact Laplace domain solution. In the Pade approximation method, the Taylor series of Laplace domain solution is used. Since obtaining high-order terms in the Taylor series is quite involved, it is not simple to obtain a high-order approximation by the Pade method, especially when the reaction term is included [9].

Recently, as a useful alternative to the Pade method, an approximation method based on the continued fraction of the Laplace domain solution has been developed [8]. The continued fraction method unifies approximations for slab, cylinder and sphere adsorbents. The resulting time-domain differential equations approximating the pore diffusion model are systematic and do not require any involved operation. However, when the reaction term is included, low-order models based on the continued fraction method are less accurate than the same order Pade approximations.

The pore diffusion model is an infinite dimensional system, and hence each finite dimensional model has its own valid region. For wide valid regions, very high-order models are required. Actually, it is not difficult to obtain high-order models by the continued fraction method. However, they are not preferred for the purpose of reducing computational loads. Here, applications of high-order models based on the continued fraction expansion are studied. High-order models which are accurate but inconvenient for the practical use are used to obtain frequency responses and Taylor series effectively. With the Taylor series computed from high-order models, Pade approximations are easily obtained regardless of the Thiele modulus and the catalyst shape. By applying the model reduction method based on the balanced truncation method to high-order models, low-order models showing better accuracies than the well-known Pade models can also be obtained. Simulations illustrating these applications are given.

LAPLACE DOMAIN SOLUTION AND EXPANSIONS

Consider the dimensionless mass balance equation for a linear adsorption and a first-order reaction in a catalyst,

$$\frac{\partial q}{\partial t} = \frac{1}{x^{\zeta}}\frac{\partial}{\partial x}\left(x^{\zeta}\frac{\partial q}{\partial x}\right) - \phi^2 q = \frac{\zeta}{x}\frac{\partial q}{\partial x} + \frac{\partial^2 q}{\partial x^2} - \phi^2 q$$

$$q(x, 0)=0 \qquad (1)$$

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

Here x and t are dimensionless position and time variables, respectively. q(x, t) is the dimensionless concentration and f(t) is a time-varying concentration at the surface. ϕ is the Thiele modulus. The shape factor ζ is 0 for the infinite slab, 1 for the infinite cylinder and 2 for the sphere. Detailed definitions of variables can be found in Kim [1]. The volume-average concentration, $\bar{q}(t)=(\zeta+1)\int_0^1 x^{\zeta} q(x,t)dx$, is of the main interest because the mass exchange rate between the adsorbent and its surrounding can be conveniently expressed as $d\bar{q}(t)/dt$.

The Laplace transformation method can be applied to the above partial differential equation [10] and we have a solution in the form of transfer function, $\bar{Q}(s)=G_{\zeta}(s+\phi^2)F(s)$, as

$$G_{\zeta}(s+\phi^2) = \frac{(\zeta+1)I_{(\zeta+1)/2}(\sqrt{s+\phi^2})}{\sqrt{s+\phi^2}\,I_{(\zeta-1)/2}(\sqrt{s+\phi^2})} \tag{2}$$

Here s is the Laplace variable, $\bar{Q}(s)$ and F(s) are Laplace transforms of $\bar{q}(t)$ and f(t), respectively, and $G_{\zeta}(s+\phi^2)$ is the transfer function relating the volume-average concentration $\bar{q}(t)$ and the surface concentration f(t). The function $I_{\alpha}(z)$ in Eq. (2) is the modified Bessel function [10,11].

It is difficult to solve the partial differential equation of Eq. (1) when it is coupled with other balance equations in the form of partial differential equations. There have been many approximate equations to reduce the computational loads. They are all closely related with the transfer function $G_{\zeta}(s+\phi^2)$. The linear driving force (LDF) model [3] for the sphere catalyst without reaction (ϕ=0), $\dot{\bar{q}}(t)=15(f(t)-\bar{q}(t))$, is equivalent to the first-order transfer function of $G_{\zeta=2}(s)=15/(s+15)$ which is the simplest Pade approximation of $G_{\zeta}(s)$. This simple LDF model is extended to equations with reaction and other geometries [7]. This simple LDF model is very useful in spite of its poor approximation accuracies.

High-order approximations for equations without reaction are available [4]. Kim and Lee [9] derived models based on the Pade approximation for equations with reaction up to the second order. For this, the following Taylor expansion is used:

$$\begin{aligned}
&G_{\zeta}(s+\phi^2) = g_0 + g_1 s + g_2 s^2 + \cdots \\
&g_0 = G_{\zeta}(\phi^2) = \frac{\zeta+1}{\phi}\Theta \\
&g_1 = G'_{\zeta}(\phi^2) = \frac{\zeta+1}{2\phi^3}(\phi - (\zeta+1)\Theta - \phi\Theta^2) \\
&g_2 = \frac{1}{2!}G''_{\zeta}(\phi^2) = -\frac{(\zeta+1)}{8\phi^5}((\zeta+3)\phi \\
&\quad + (2\phi^2 - (\zeta+1)(\zeta+3))\Theta - 3(\zeta+1)\phi\Theta^2 - 2\phi^2\Theta^3) \\
&\cdots \\
&\Theta = \frac{I_{(\zeta+1)/2}(\phi)}{I_{(\zeta-1)/2}(\phi)}
\end{aligned} \tag{3}$$

From this Taylor series expansion, Pade approximations can be obtained. Here, $\text{Pade}_{[m,n]}(s+\phi^2)$ is used to represent the Pade approximation whose numerator and denominator orders are m and n, respectively. Equations for the Taylor series of Eq. (3) are rather involved when the number of terms increases [9].

Approximate models can also be obtained from the continued fraction expansion of $G_{\zeta}(s+\phi^2)$. It is given as [11]

$$G_{\zeta}(s+\phi^2) = \cfrac{\zeta+1}{\zeta+1+\cfrac{s+\phi^2}{\zeta+3+\cfrac{s+\phi^2}{\zeta+5+\cfrac{s+\phi^2}{\zeta+7+\cdots}}}} \tag{4}$$

The continued fraction is more systematic and will be easy to remember. By truncating Eq. (4), we can obtain approximate models. We call this $CF_{[n]}(s+\phi^2)$ where n is the order of approximate model. The truncated continued fraction $CF_{[n]}(s+\phi^2)$ can be realized as (see Appendix A; Chen and Shieh [12])

$$\begin{aligned}
&\dot{x}(t) = Ax(t) + bf(t) \\
&\bar{q}(t) = cx(t) \\
&A = -\begin{pmatrix}
(\zeta+1)(\zeta+3) & (\zeta+1)(\zeta+7) & \cdots & (\zeta+1)(\zeta+4n-1) \\
(\zeta+1)(\zeta+3) & (2\zeta+6)(\zeta+7) & \cdots & (2\zeta+6)(\zeta+4n-1) \\
\vdots & \vdots & & \vdots \\
(\zeta+1)(\zeta+3) & (2\zeta+6)(\zeta+7) & \cdots & (n\zeta+2n^2-n)(\zeta+4n-1)
\end{pmatrix} \\
&\quad -\phi^2 I \\
&b = (\zeta+1)(1, 1, \cdots 1)^T \\
&c = (\zeta+3, \zeta+7, \cdots \zeta+4n-1)
\end{aligned} \tag{5}$$

When ϕ=0, $CF_{[n]}(s)$ is equivalent to $\text{Pade}_{[n-1,n]}(s)$ for $G_{\zeta}(s)$ [11]. For example, the first truncation $G_{\zeta=2}(s)=3/(3+s/5)$ is equivalent to the LDF for the sphere without reaction (ϕ=0). For a nonzero ϕ, $CF_{[n]}(s+\phi^2)$ of Eq. (4) is not the same as $\text{Pade}_{[n-1,n]}(s+\phi^2)$ obtained from the Taylor series of Eq. (3). For a low order of n, the approximation performance of $CF_{[n]}(s+\phi^2)$ will be poor for a large ϕ. However, as n increases, $CF_{[n]}(s+\phi^2)$ approaches to $G_{\zeta}(s+\phi^2)$ and its approximation accuracy becomes excellent. Here, $CF_{[n]}(s+\phi^2)$ with a large n as high as 121 is considered.

APPLICATIONS OF HIGH-ORDER CONTINUED FRACTION MODELS

1. Computations of Frequency Responses

Accurate low-order models for the cyclic operations [4] can be obtained from frequency responses of $G_{\zeta}(j\omega+\phi^2)$, where ω is the angular frequency. Non-cyclic time domain responses can also be computed from frequency responses by methods such as the fast Fourier transformation (FFT) method [13]. Routines for evaluations of $G_{\zeta}(j\omega+\phi^2)$ are needed. If routines for Bessel functions are not available, the above continued fraction model of Eq. (5) with a large n can be used effectively to compute $G_{\zeta}(j\omega+\phi^2)$. Since

$$CF_{[n]}(s+\phi^2) = c(sI-A)^{-1}b \approx G_{\zeta}(s+\phi^2) \tag{6}$$

$G_{\zeta}(j\omega+\phi^2)$ will be $c(j\omega I-A)^{-1}b$. In the next section, Eq. (6) can be better for $G_{\zeta}(s+\phi^2)$ even when routines for Bessel functions are available.

2. Pade Approximations

Usefulness of the Pade approximation was proved in various applications [4]. The Pade approximation is based on the Taylor series of Eq. (3). As shown in Eq. (3), the Taylor series expansion is rather complex when the number of expansion terms increases. A simpler method to compute the Taylor series is proposed.

The Taylor series expansion for $CF_{[n]}(s+\phi^2)$ is

$$CF_{[n]}(s+\phi^2)=c(sI-A)^{-1}b=-c(I-A^{-1}s)^{-1}A^{-1}b$$
$$=-c(I+A^{-1}s+A^{-2}s^2+\cdots)A^{-1}b=-cA^{-1}b-cA^{-2}bs-cA^{-3}bs^2-\cdots \quad (7)$$

Hence, when n is large enough to approximate $G_\zeta(s+\phi^2)$, the coefficients for the Taylor series expansion of Eq. (3) are

$$g_k=-cA^{-(k+1)}b\approx G^{(k)}(\phi^2)/k! \quad (8)$$

From the Taylor series expansion of Eq. (8), we can obtain the Pade approximation [4]. The accuracies of Eq. (8) according to n are given in the next section. The matrix multiplications in Eq. (8) can be done without numerical difficulties because the matrix A is well-conditioned.

It requires solving a system of linear equations to obtain the Pade approximation from the Taylor series expansion of Eq. (7). The problem becomes ill-conditioned as the approximation order n increases and this numerical difficulty can be relieved by the continued fraction method as

$$CF_{[n]}(s+\phi^2)=g_0+g_1s+g_2s^2+\cdots=\cfrac{1}{\cfrac{1}{g_0+g_1s+g_2s^2+\cdots}}$$
$$=\cfrac{1}{\cfrac{1}{g_0}+\cfrac{-\frac{g_1}{g_0}s-\frac{g_1}{g_0}s^2-\cdots}{g_0+g_1s+g_2s^2+\cdots}}=\cfrac{h_0}{h_1+\cfrac{s}{h_2+\cfrac{s}{h_3+\cdots}}} \quad (9)$$

A very simple method to obtain (h_0, h_1, h_2 ⋯) from (g_0, g_1, g_2 ⋯) is in Appendix B. The truncated continued fraction results in the Pade approximation [12]. It can also be realized to a state equation easily (see Appendix A).

3. Reduced Order Models with the Balanced Truncation

Reduced order models obtained by applying a model reduction method to accurate high-order models can be better than models by the Pade approximation method. This opportunity is investigated

Table 1. Approximations for ϕ=0

ζ	n	Pade ($Pade_{[m,n]}(s)$)	Continued fraction with order reduction ($CFR_{[n]}(s)$)
0	1	$\frac{3}{s+3}$	
		$\frac{s+15}{6s+15}$	$\frac{s/17.963+1}{s/2.6045+1}$
	2	$\frac{10s+105}{s^2+45s+105}$	
		$\frac{s^2+105s+945}{15s^2+420s+945}$	$\frac{s/11.107+1}{s/2.4880+1}\frac{s/208.60+1}{s/38.942+1}$
	3	$\frac{21s^2+1260s+10395}{s^3+210s^2+4725s+10395}$	
		$\frac{s^3+378s^2+17325s+135135}{28s^3+3150s^2+62370s+135135}$	$\frac{s/10.248+1}{s/2.4724+1}\frac{s/77.311+1}{s/27.609+1}\frac{s/1473.8+1}{s/268.71+1}$
1	1	$\frac{8}{s+8}$	
		$\frac{s+24}{4s+24}$	$\frac{s/33.752+1}{s/6.6897+1}$
	2	$\frac{24s+384}{s^2+72s+384}$	
		$\frac{s^2+144s+1920}{9s^2+384s+1920}$	$\frac{s/18.135+1}{s/5.9720+1}\frac{s/352.26+1}{s/67.486+1}$
	3	$\frac{48s^2+3840s+46080}{s^3+288s^2+9600s+46080}$	
		$\frac{s^3+480s^2+28800s+322560}{16s^3+2400s^2+69120s+322560}$	$\frac{s/22.886+1}{s/5.8394+1}\frac{s/171.03+1}{s/43.272+1}\frac{s/3408.5+1}{s/427.51+1}$
2	1	$\frac{15}{s+15}$	
		$\frac{3s+105}{10s+105}$	$\frac{s/55.708+1}{s/12.447+1}$
	2	$\frac{42s+945}{s^2+105s+945}$	
		$\frac{s^2+189s+3465}{7s^2+420s+3465}$	$\frac{s/27.292+1}{s/10.522+1}\frac{s/545.77+1}{s/106.37+1}$
	3	$\frac{81s^2+8316s+135135}{s^3+378s^2+17325s+135135}$	
		$\frac{s^3+594s^2+45045s+675675}{12s^3+2310s^2+90090s+675675}$	$\frac{s/22.886+1}{s/10.096+1}\frac{s/171.03+1}{s/63.689+1}\frac{s/3408.5+1}{s/635.73+1}$

here. There are many methods to reduce model orders [14]. Studies about model reduction methods are beyond the scope of this research. We just use a commercial program given in the MATLAB package [15].

Consider a high-order system in the state equation form of $\dot{x}(t)=Ax(t)+bf(t)$, $\bar{q}(t)=cx(t)+df(t)$. We separate the state vector x in two parts as

$$\begin{pmatrix}\dot{\bar{x}}\\ \dot{\tilde{x}}\end{pmatrix}=\begin{pmatrix}A_{11} & A_{12}\\ A_{21} & A_{22}\end{pmatrix}\begin{pmatrix}\bar{x}\\ \tilde{x}\end{pmatrix}+\begin{pmatrix}b_1\\ b_2\end{pmatrix}f(t)$$
$$\bar{q}(t)=(c_1 \;\; c_2)\begin{pmatrix}\bar{x}\\ \tilde{x}\end{pmatrix}+df(t) \tag{10}$$

When the state variable $\tilde{x}$ does not affect the output $\bar{q}(t)$ much, we can remove the state $\tilde{x}$ with assuming its time derivative be zero (it is called 'quasi steady-state').

$$0=A_{21}\bar{x}+A_{22}\tilde{x}+b_2f(t) \tag{11}$$

Then $\tilde{x}=-A_{22}^{-1}A_{21}\bar{x}-A_{22}^{-1}b_2f(t)$ and

$$\begin{aligned}\dot{\bar{x}}&=A_{11}\bar{x}+A_{12}\tilde{x}+b_1f(t)=(A_{11}-A_{12}A_{22}^{-1}A_{21})\bar{x}\\&\quad+(b_1-A_{12}A_{22}^{-1}b_2)f(t)\equiv A_r\bar{x}+b_rf(t)\\ \bar{q}(t)&=c_1\bar{x}+c_2\tilde{x}+df(t)=(c_1-c_2A_{12}A_{22}^{-1})\bar{x}\\&\quad+(d-c_2A_{12}A_{22}^{-1}b_2)f(t)=c_r\bar{x}+d_rf(t)\end{aligned} \tag{12}$$

The performance of the above model reduction is highly dependent on the form of the system matrix A. Therefore, before applying the above model reduction, it is usually needed to reformulate A by applying the similarity transformation of $\hat{x}=Tx$:

$$\begin{aligned}\dot{\hat{x}}(t)&=T\dot{x}(t)=T(Ax(t)+bf(t))=TAT^{-1}\hat{x}(t)+Tbf(t)\\ \bar{q}(t)&=cx(t)+df(t)=cT^{-1}\hat{x}(t)+df(t)\end{aligned} \tag{13}$$

If the transformation matrix T is composed of eigenvectors of A, this similarity transformation makes the system matrix TAT^{-1} be diagonal. For the system matrix with diagonal and negative real elements with ascending order in absolute values, the above model reduction is just to ignore the fast modes. Here a recent method based on the balanced state equation is used. First, by applying the similarity transformation, we obtain the balanced state equation [14] and apply the above model reduction. Routines for this balanced model reduction are available in the Control System Toolbox for MATLAB [15]. The routines to reduce the order of system (A, b, c, d) are as follows:

```
sa=ss(A, b, c, d);          %(a, b, c, d): CF model
n=2;                        %approximation order
[sb, g]=balreal(sa);        % compute balanced realization
elim=(g<g(n)/1.001);        % eliminate small entries of g
sc=modred(sb, elim);        % remove negligible states
[Ar, br, cr, dr]=ssdata(sc); %(Ar, br, cr, dr): CFR model
```

Model order can be changed by changing the number n.

Here the 121-st-order model $CF_{[121]}(s+\phi^2)$ based on Eq. (5) is constructed and then its orders are reduced. Numerator and denominator orders of this reduced order model will be both n and we call it $CFR_{[n]}(s+\phi^2)$. Tables 1 and 2 show reduced order models in the form of transfer function.

Table 2. Approximations for ϕ=10

ζ	n	Pade ($Pade_{[m,n]}(s)$)	Continued fraction with order reduction ($CFR_{[n]}(s)$)
0	1	$\frac{20}{s+200}$	
		$\frac{s+400}{30s+4000}$	$0.1\frac{s/795.40+1}{s/171.52+1}$
	2	$\frac{s^2+1200.1s+160022.6}{50.003s^2+20002s+1600226}$	$0.1\frac{s/328.26+1}{s/138.95+1}\frac{s/6070.5+1}{s/1110.0+1}$
	3	$\frac{s^3+2404.3s^2+802469s+46260856}{70.067s^3+56133s^2+11237740s+642608566}$	$0.1\frac{s/240.60+1}{s/127.38+1}\frac{s/1660.2+1}{s/578.93+1}\frac{s/32185+1}{s/5871.2+1}$
1	1	$\frac{40.189}{s+211.83}$	
		$\frac{s+404.31}{15.331s+2131.1}$	$0.18972\frac{s/823.55+1}{s/181.58+1}$
	2	$\frac{s^2+1218.4s+164849}{25.444s^2+10524s+868908}$	$0.18972\frac{s/337.27+1}{s/145.52+1}\frac{s/6324.0+1}{s/1166.6+1}$
	3	$\frac{s^3+2463.9s^2+841748s+68915207}{35.720s^3+29690s^2+6151582s+363246997}$	$0.18972\frac{s/246.16+1}{s/132.69+1}\frac{s/1719.8+1}{s/604.98+1}\frac{s/33513+1}{s/6137.7+1}$
2	1	$\frac{60.75}{s+225}$	
		$\frac{s+411.43}{10.476s+1523.8}$	$0.27\frac{s/856.95+1}{s/192.82+1}$
	2	$\frac{s^2+1247.8s+172763}{17.332s^2+7465.4s+639863}$	$0.27\frac{s/348.47+1}{s/152.95+1}\frac{s/6620.5+1}{s/1231.5+1}$
	3	$\frac{s^3+2550.3s^2+900862s+76164857}{24.395s^3+21227s^2+4590267s+282092061}$	$0.27\frac{s/253.38+1}{s/138.75+1}\frac{s/1791.2+1}{s/635.43+1}\frac{s/35078+1}{s/6448.5+1}$

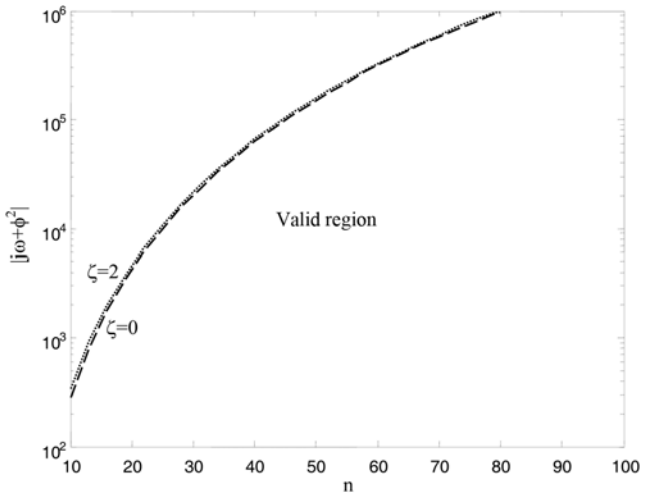

Fig. 1. Regions that the absolute relative errors of $CF_{[n]}(j\omega+\phi^2)$ are less than 1×10^{-8}.

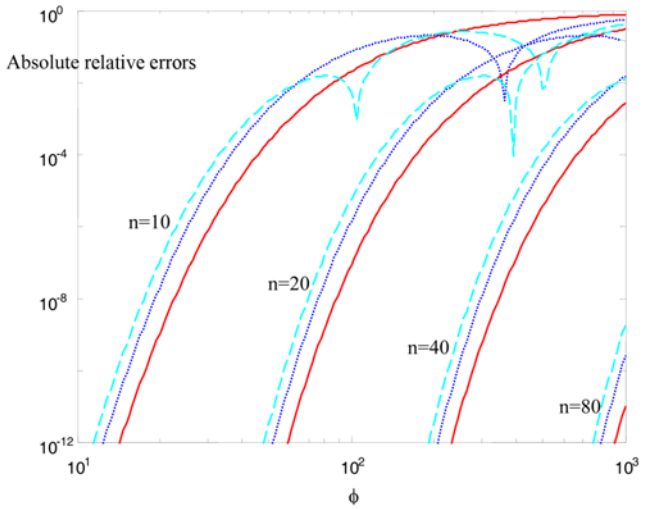

Fig. 2. Absolute relative errors of the first 3 coefficients in the Taylor series of $CF_{[n]}(s+\phi^2)$ for ζ=2 (solid line: g_1, dotted line: g_2, dashed line: g_3).

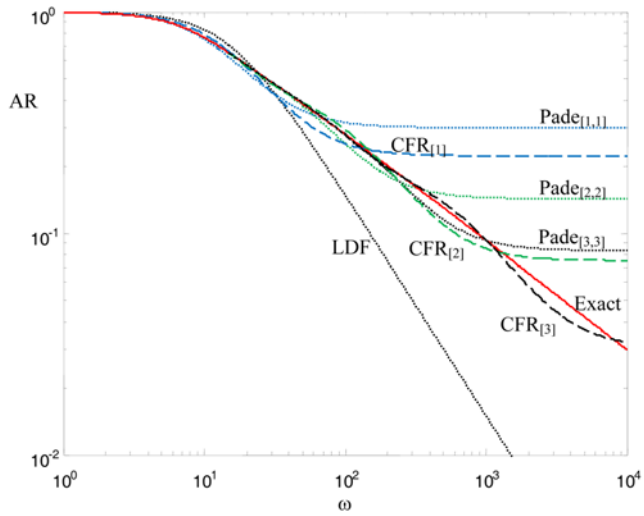

Fig. 3. Amplitude ratio (AR) plots for ϕ=0 and ζ=2.

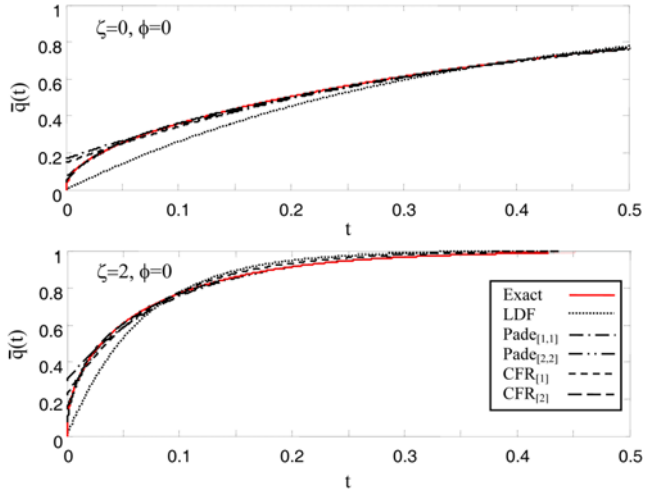

Fig. 4. Step responses without reaction (ϕ=0).

DISCUSSION

First, accuracies of $CF_{[n]}(j\omega+\phi^2)$ are examined. They are dependent closely on the size of $|j\omega+\phi^2|$ and Fig. 1 shows the region such that $|CF_{[n]}(j\omega+\phi^2)-G_\zeta(j\omega+\phi^2)|/|G_\zeta(j\omega+\phi^2)|<1\times10^{-8}$. Regions are very similar for ζ=0 and 2. As n increases, valid regions for the frequency ω and the Thiele modulus ϕ increase much. The order n can be increased as large as 121 without computational problems. With such n, we can use $CF_{[n]}(s+\phi^2)$ without worrying about its accuracy. On the other hand, the function $\sqrt{s}$ for $G_{\zeta=0}(s)$ fails to provide values when s is greater than 10^6. The proposed $CF_{[n]}(s+\phi^2)$ may be used preferably instead of Bessel functions.

Fig. 2 shows errors in the coefficients of Taylor series obtained with Eq. (8). We can see that the approximation order n around 30 will be sufficient for a practical range of Thiele modulus.

Table 1 shows low-order models based on the Pade method and the balanced truncation method for ϕ=0. Fig. 3 shows the amplitude ratio plots of $G_\zeta(s)$ and its approximations. For ϕ=0, the Pade approximation models are equal to those of low-order models by the continued fraction method, $CF_{[n]}(s)$. Reduced order models $CFR_{[n]}(s)$ are obtained from $CF_{[121]}(s)$. Fig. 4 and Table 3 show step responses and their integral of squared errors (ISE), respectively. We can see that $CFR_{[1]}(s)$ has similar performance compared to $Pade_{[1,1]}(s)$ having the same complexity. The performance is improved more and more as the order n increases.

Table 2 shows low-order models based on the Pade method and the balanced truncation method for ϕ=10. Fig. 5 shows the amplitude ratio plots of $G_\zeta(s+\phi^2)$ and its approximations. Reduced order models $CFR_{[n]}(s+\phi^2)$ are obtained from $CF_{[121]}(s+\phi^2)$. Fig. 6 and Table 3 show step responses and their integral of squared errors, respectively. Similar conclusions can be drawn as for ϕ=0. Since ϕ is large, the performances of $CF_{[n]}(s+\phi^2)$ are somewhat worse.

CONCLUSION

High-order models in the form of state equations that can substi-

Table 3. Integral of squared errors (ISE)

System order	Model	ϕ=0 (t=[0, 1], Sampling time=0.0001)			ϕ=10 (t=[0, 0.1], Sampling time=0.00001)		
		ζ=0	ζ=1	ζ=2	ζ=0	ζ=1	ζ=2
1	LDF	2.0E-3	1.7E-3	1.2E-3	9.0E-7	3.3E-6	6.5E-6
	$Pade_{[1, 1]}$	1.9E-4	2.5E-4	2.3E-4	3.1E-7	1.1E-6	2.3E-6
	$CF_{[1]}$				4.8E-4	1.3E-3	1.9E-3
	$CFR_{[1]}$	1.5E-4	1.9E-4	1.6E-4	1.5E-7	5.5E-7	1.1E-6
2	$Pade_{[1, 2]}$	1.9E-5	3.2E-5	3.5E-5	7.5E-8	2.8E-7	5.8E-7
	$Pade_{[2, 2]}$	5.4E-6	1.1E-5	1.3E-5	4.4E-8	1.7E-7	3.4E-7
	$CF_{[2]}$				6.4E-5	1.1E-4	1.1E-4
	$CFR_{[2]}$	2.9E-6	5.6E-6	6.4E-6	1.0E-8	3.7E-8	7.7E-8
3	$Pade_{[3, 3]}$	5.1E-7	1.3E-6	1.9E-6	1.2E-8	4.6E-8	9.5E-8
	$CF_{[3]}$				1.8E-6	2.8E-6	2.9E-6
	$CFR_{[3]}$	1.9E-7	4.3E-7	5.7E-7	1.3E-9	4.9E-9	1.0E-8
4	$Pade_{[4, 4]}$	9.4E-8	2.9E-7	4.8E-7	4.8E-9	1.8E-8	3.6E-8
	$CF_{[4]}$				9.5E-8	2.4E-7	3.6E-7
	$CFR_{[4]}$	2.2E-8	5.5E-8	8.0E-8	2.4E-10	9.2E-10	1.9E-9

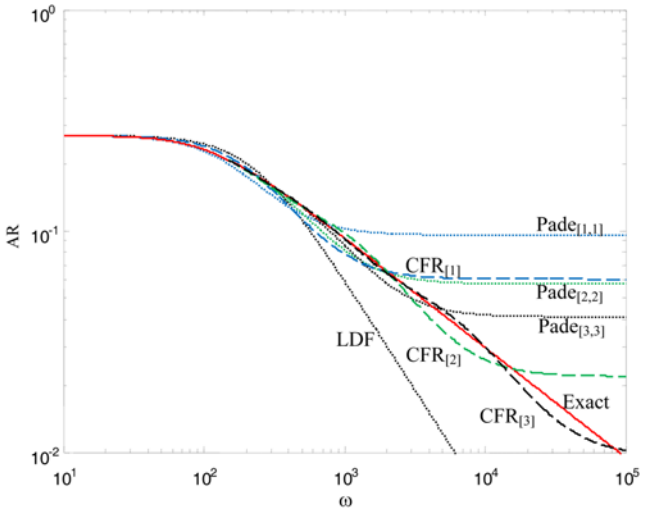

Fig. 5. Amplitude ratio (AR) plots for ϕ=10 and ζ=2.

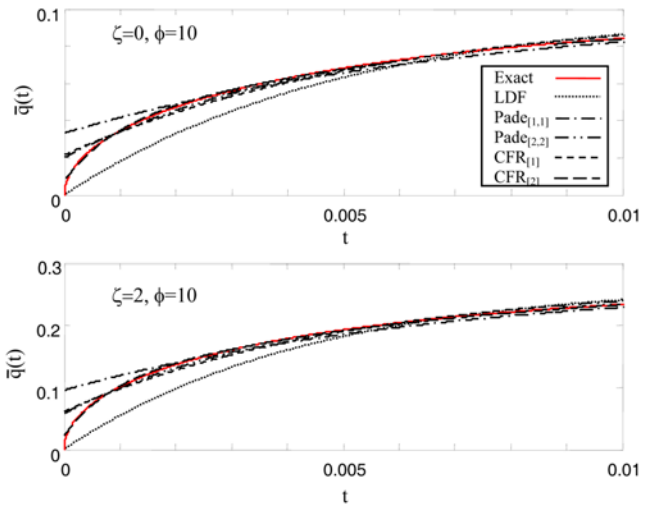

Fig. 6. Step responses with reaction (ϕ=10).

tute the exact partial differential equations for unsteady-state diffusion, adsorption and a first-order reaction in a catalyst are available. Although very high-order models obtained by the continued fraction expansion method are accurate and valid for wide range of the Thiele modulus, they will not be used in practice due to their dimensionalities. Here, it is shown that these high-order models can be used positively to relieve complexities in evaluating frequency responses, obtaining Pade approximations and better reduced order models.

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APPENDIX A (REALIZATION OF TRANSFER FUNCTIONS)

From a system $\overline{Q}(s)=G(s)F(s)$ for the rational transfer function G(s), a set of first-order differential equations showing the same dynamics

$$\dot{x}(t)=Ax(t)+bf(t)$$
$$\overline{q}(t)=cx(t)+df(t) \tag{A1}$$

can be obtained. The system is defined by the system matrices of (A, b, c, d).

1. Rational Transfer Function

For the transfer function

$$G(s)=d_0+\frac{b_{n-1}s^{n-1}+\cdots+b_1s+b_0}{s^n+a_{n-1}s^{n-1}+\cdots+a_1s+a_0} \tag{A2}$$

The system matrices for Eq. (A1) are [16]

$$A=-\begin{pmatrix} -a_{n-1} & 1 & \cdots & 0 & 0 \\ -a_{n-2} & 0 & \cdots & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ -a_1 & 0 & \cdots & 0 & 1 \\ -a_0 & 0 & \cdots & 0 & 0 \end{pmatrix} \tag{A3}$$

$b=(b_{n-1}), b_{n-2}, \cdots b_1, b_0)^T$
$c=(1, 0, \cdots 0, 0)$
$d=d_0$

Pade approximations are given in the form of Eq. (A2) and we call them by $Pade_{[n-1,\,n]}(s)$ if $d_0=0$ and $Pade_{[n,\,n]}(s)$, otherwise.

2. Continued Fraction Transfer Function

Consider the truncated continued fraction

$$G(s)=\cfrac{h_0}{h_1+\cfrac{s}{h_2+\cfrac{s}{h_3+\cdots\cfrac{s}{h_{2n}}}}}\equiv\frac{h_0}{h_1+}\frac{s}{h_2+}\frac{s}{h_3+}\cdots\frac{s}{h_{2n}} \tag{A4}$$

The time-domain equation of G(s) is given by [12]

$$A=-\begin{pmatrix} h_1h_2 & h_1h_4 & h_1h_6 & \cdots & h_1h_{2n} \\ h_1h_2 & (h_1+h_3)h_4 & (h_1+h_3)h_6 & \cdots & (h_1+h_3)h_{2n} \\ h_1h_2 & (h_1+h_3)h_4 & (h_1+h_3+h_5)h_6 & \cdots & (h_1+h_3+h_5)h_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ h_1h_2 & (h_1+h_3)h_4 & (h_1+h_3+h_5)h_6 & \cdots & (h_1+h_3+\cdots+h_{2n-1})h_{2n} \end{pmatrix}$$
$$b=h_0(1, 1, 1\cdots 1)^T \tag{A5}$$
$$c=(h_2, h_4, h_6\cdots h_{2n})$$

G(s) is totally equivalent to the Pade approximation with the numerator and denominator polynomials of orders n−1 and n, respectively, which we call $CF_{[n]}(s)$.

APPENDIX B (ROUTH METHOD FOR THE CONTINUED FRACTION) [12]

Consider a rational transfer function

$$G(s)=\frac{a_{21}+a_{22}s+\cdots+a_{2,(n)}s^{n-1}}{a_{11}+a_{12}s+\cdots+a_{1,(n+1)}s^n} \tag{B1}$$

We find the equivalent transfer function in the continued fraction form:

$$G(s)=\cfrac{1}{h_1+\cfrac{s}{h_2+\cfrac{s}{h_3+\cdots}}} \tag{B2}$$

To find the continued fraction coefficients of (h_1, h_2, h_3 ⋯), first we construct the Routh table as

$$\begin{matrix} a_{11}, a_{12}, a_{13}, \cdots \\ a_{21}, a_{22}, a_{23}, \cdots \\ a_{31}, a_{32}, \cdots \\ a_{41}, \cdots \\ \cdots \end{matrix} \tag{B3}$$

where

$$a_{j,k}=\frac{a_{j-1,1}a_{j-2,k+1}-a_{j-2,1}a_{j-1,k+1}}{a_{j-1,1}}=j=3,4,\cdots,n+1,k=1,2,\cdots. \tag{B4}$$

Then

$$h_k=\frac{a_{k,1}}{a_{k+1,}},k=1,2,\cdots,2n \tag{B5}$$