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# ANALYTICAL SOLUTION TO A MODEL FOR THE STARTUP PERIOD OF FIXED-BED REACTORS



# YIZHOU ZHENG and TINGYUE GU\*

Department of Chemical Engineering, Ohio University, Athens, OH 45701, U.S.A.

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Abstract—A mathematical model for the startup period of a fixed-bed reactor with first-order reaction kinetics, axial dispersion and film mass transfer resistance was formulated and solved analytically using Laplace transform. The solution can be used to correlate or predict the reactant concentration profiles in the effluent of the reactor. The effects of both the Peclet number and Biot number on the effluent concentration profiles were studied. As an example, the approximate analytical solution was applied to experimental data of lactic acid fermentation in a fixed-bed fermentor with immobilized *Lactobacillus delbriieckii* cells. Copyright © 1996 Elsevier Science Ltd.

Keywords: fixed-bed, reactor, startup period, lactic acid, immobilized cells.

## INTRODUCTION

Fixed-bed is a widely used reactor type in fluidsolid catalytic reactions either with chemical catalysts or with biocatalysts. Efforts have been made in studying the reaction kinetics, the mass transfer mechanism, and the mathematical model of fixed-bed reactors. Most researchers focused on steady-state operations (Smith, 1981; Hill, 1977; Bailey and Ollis, 1986). Recently, interests in the mathematical modeling of unsteady-state operations have increased significantly because of their importance in fixed-bed reactor design and process control. Monbouquetle et al. (1990) applied an intrinsic unstructured model to describe the startup dynamics of a continuous Ca-alginateimmobilized Zymomonas mobilis fermentation. Gencer and Mutharasan (1983)studied ethanol fermentation in a whole cell immobilized tubular fermentor with either a transient or steady-state operation. A dynamic model of an immobilized cell reactor with simultaneous diffusion, reaction, and cell growth was suggested by Nakasaki and Mukeji (1989). Because of the complexity of the dynamic operation of a fixedbed reactor, the mathematical model has to be solved numerically. Chen and Hsu (1989), and Hsu and Dranoff (1987) developed a technique in which numerical inversion of Laplace transform by direct application of the fast Fourier transform algorithm was used to solve fixed-bed problems.

This work was undertaken to achieve a better understanding of the startup period of a fixed-bed reactor with first-order kinetics, axial dispersion and film mass transfer resistance. The main objectives were to establish a mathematical model and to obtain its analytical solution. The effects of the reaction kinetics and operating conditions on the startup period were then studied using the solution. As a practical example, the startup period of lactic acid fermentation in an immobilized-cell tubular reactor was presented to verify the solution.

## MATHEMATICAL MODEL AND ITS SOLUTION

For one-dimensional axial flow, the mass balance equation for a fixed-bed tubular reactor with axial dispersion can be written as

$$\frac{\partial C}{\partial t} = D_z \frac{\partial^2 C}{\partial Z^2} - v \frac{\partial C}{\partial Z} - \frac{1-\varepsilon}{\varepsilon} R \tag{1}$$

where R is the consumption rate of the reactant. When pore diffusion resistance can be neglected, the global kinetics for a first-order reaction can be expressed by

$$R = \frac{\partial C_i}{\partial t} = kC_i \tag{2}$$

where  $C_i$  is the reactant concentration at the fluid– solid interface. Intraparticle diffusion resistance is ignored here. The mass transfer rate across the fluid film can be expressed by the linear-driving-force model

$$R = \frac{\partial C_i}{\partial t} = k_L (C - C_i). \tag{3}$$

Combining eqs (2) and (3), the reactant consumption rate becomes

$$R = KC \tag{4}$$

where K is the apparent reaction rate constant of a first-order reaction with film mass transfer resistance. K can be calculated by the following equation:

$$K = kk_L/(k+k_L). \tag{5}$$

<sup>\*</sup> Corresponding author.

Thus, eq. (1) can be rewritten as

$$\frac{\partial C}{\partial t} = D_z \frac{\partial^2 C}{\partial Z^2} \qquad \frac{\partial C}{\partial Z} \qquad 1 - KC. \tag{6}$$

For the startup period of a fixed-bed reactor, the initial and boundary conditions are:

$$C(0,Z) \tag{7}$$

$$C(t,0) = C_0 \tag{8}$$

$$\left. \frac{\partial C(t, Z)}{\partial Z} \right|_{Z=L} = 0.$$
<sup>(9)</sup>

The Laplace transform can be used to solve eqs (6)-(9)The result is as follows:

$$\frac{\tilde{C}}{C_0} = \frac{\exp\left[(Pe/2) \cdot (Z/L)\right]}{s}$$

$$\frac{\cosh\left[\lambda(L-Z)\right] + \sinh\left[\lambda(L-Z)\right] \cdot (Pe/2\lambda L)}{\cosh\left(\lambda L\right) + \sinh\left(\lambda L\right) \cdot (Pe/2\lambda L)}$$
(10)

where the overhead sign  $\sim$  indicates Laplace transform, s is the Laplace transform parameter.  $C_0$  is the inlet concentration of the reactant. *Pe* and *Bi* are Peclet number and Biot number defined below, respectively,

$$Pe = vL/D_z$$
,  $Bi = KL^2/D_z$ ,  $(lla, llb)$ 

Also,

$$\lambda L = \left[ \left[ \frac{Pe}{2} \right]^2 + \frac{1-\varepsilon}{\varepsilon} Bi + \frac{Bi}{K} s \right]^{1/2}.$$
 (12)

The direct inverse Laplace transform of eq. (10) seems impossible. Therefore, a series expansion technique was used to solve the problem. The hyperbolical functions, sinh() and cosh() in eq. (10) can be expanded as Taylor's series. After rearrangement, eq. (10) can be expressed as

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The following equations can be easily proved by the method of mathematical induction:

$$\sum_{n=0}^{\infty} \left[ \frac{1}{2n!} + \frac{1}{(2n+1)!} \cdot \frac{Pe}{2} \right] (\lambda L)^{2n} = \prod_{n=1}^{\infty} \left[ a_n + b_n (\lambda L)^2 \right]$$
(15)

$$\frac{1}{\prod_{n=1}^{\infty} [a_n + b_n (\lambda L)^2]} = \sum_{n=1}^{\infty} \frac{c_n}{d_n + e_n (\lambda L)^2} \quad (16)$$

Combining eqs (12) and (14)-(16), eq. (14) can be expressed as a function of s:

$$\frac{\tilde{C}_L}{C_0} = \exp\left(\frac{Pe}{2}\right) \cdot \frac{1}{s} \cdot \sum_{n=1}^{\infty} \frac{f_n}{g_n + h_n s}.$$
 (17)

In eqs (15)–(17),  $a_n$ ,  $b_n$ ,  $c_n$ ,  $d_n$ ,  $e_n$ ,  $f_n$ ,  $g_n$ , and  $h_n$  are functions of the parameters Pe and Bi.

After the inverse Laplace transform of eq. (17), we obtain the dimensionless reactant concentration at the exit of a fixed-bed reactor with first-order kinetics, axial dispersion and film mass transfer resistance:

$$\frac{C_L}{C_0} = \begin{cases} \exp(Pe/2) \sum_{n=1}^{\infty} (1/\alpha_n) [1 - \exp(-\beta_n \tau)] & (\tau > 0) \\ 0 & (\tau \le 0) \end{cases}$$

(18)

where

$$\tau = K\left(t - \frac{L}{v}\right). \tag{19}$$

The parameters a, and  $\beta_n$  are functions of the dimensionless parameters Pe and Bi. The parameters a, can be determined from the steady-state solution to eq. (6) as follows. As steady state, eq. (6) can be expressed as

$$D_z \frac{\mathrm{d}^2 C}{\mathrm{d}Z^2} - v \frac{\mathrm{d}C}{\mathrm{d}Z} - \frac{1-\varepsilon}{\varepsilon} KC = 0. \tag{20}$$

The analytical solution to eq. (20) at the reactor exit (Z = L) is

$$\frac{\tilde{C}}{C_{0}} = \exp\left[\frac{Pe}{2} \cdot \frac{Z}{L}\right] \left\{ \frac{1}{s \sum_{n=0}^{\infty} \left[ \left(\frac{1}{2n!} + \frac{Pe}{2 \cdot (2n+1)!}\right) (\lambda L)^{2n} \right]} + \frac{(Pe/2) \cdot \left[ (L-Z)/L \right]}{s \sum_{n=0}^{\infty} \left[ \left(\frac{1}{2n!} + \frac{Pe}{2 \cdot (2n+1)!}\right) (\lambda L)^{2n} \right]} + \frac{\sum_{n=1}^{\infty} \left[ \left(\frac{1}{2n!} + \frac{1}{(2n+1)!} \cdot \frac{Pe}{2} \cdot (L-Z) \right) [\lambda (L-Z)]^{2n} \right]}{s \sum_{n=0}^{\infty} \left[ \left(\frac{1}{2n!} + \frac{1}{(2n+1)!} \cdot \frac{Pe}{2} \right) (\lambda L)^{2n} \right]} \right\}.$$
(13)

At the reactor exit we have Z = L. Thus, the second and third terms in eq. (13) vanish. Therefore, eq. (13) becomes

$$\frac{\widetilde{C}}{C} = \exp\left(\frac{Pe}{2}\right) \frac{l}{s \sum_{n=0}^{\infty} \left[ \left(\frac{1}{2n!} + \frac{l}{(2n+1)!} \cdot \frac{Pe}{2}\right) (\lambda L)^{2n} \right]}.$$
(14)

 $\frac{C_L}{C_0} - \frac{\exp(Pe/2)}{\cosh(\gamma L) + (Pe/2\gamma L)\sinh(\gamma L)}$ (21)

where

$$\gamma L = \left[ \left( \frac{Pe}{2} \right)^2 + \frac{1-\varepsilon}{\varepsilon} Bi \right]^{1/2}.$$
 (22)

When  $\tau$  is infinite, eq. (18) becomes the solution for steady-state operation, since it is no longer

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time-dependent. It is simplified to

$$\frac{C_L}{C_0} = \exp\left(\frac{Pe}{2}\right) \cdot \sum_{n=1}^{\infty} \frac{1}{\alpha_n}$$
(23)

Combining eqs (21) and (23), we have

$$\sum_{n=1}^{\infty} \frac{1}{\ddot{a}_{n}} = \frac{1}{\cosh\left(\gamma L\right) + \left(\frac{Pe}{2\gamma L}\right)\sinh\left(\gamma L\right)}.$$
 (24)

Equation (18) is the solution to the unsteady-state startup period of the reactor. However, it is difficult to use since a general explicit expression for  $\beta_n$  is not available. Instead, we can use eq. (10) if only a limited number of terms are taken in the Taylor's series expansions of the hyperbolic functions in eq. (10). For example, if only the first two or three terms are considered in the Taylor's series expansions, the respective approximate analytical solution can be expressed as follows:

$$\frac{C_L}{C_0} = \frac{\exp\left(Pe/2\right)}{a_0 + a_1 q} \left[ 1 - \exp\left(-\frac{q + a_0/a_1}{Bi}\tau\right) \right]$$
(25)

and

$$\frac{C_L}{C_0} = \frac{\exp(Pe/2)}{a_0 + a_1q + a_2q^2} \left\{ 1 - \left[ \frac{b_1 + q}{b_1 - b_0} \exp\left( -\frac{q + b_0}{Bi} \tau \right) - \frac{b_0 + q}{b_1 - b_0} \exp\left( -\frac{q + b_1}{Bi} \tau \right) \right] \right\}$$
(26)

where

$$a_0 = 1 + \frac{Pe}{2} \tag{27a}$$

$$a_1 = \frac{1}{2!} + \frac{Pe}{2} \cdot \frac{1}{3!} \tag{27b}$$

$$a_2 = \frac{1}{4!} + \frac{Pe}{2} \cdot \frac{1}{5!} \tag{27c}$$

$$q = \left(\frac{Pe}{2}\right)^2 + \frac{1-\varepsilon}{\varepsilon} Bi \qquad (27d)$$

$$b_0 + b_1 = \frac{a_1}{a_2}$$
(27e)

$$b_0 \cdot b_1 = \frac{a_0}{a_2} \tag{27f}$$

Hence, by comparing eq. (23) with eqs (25) and (26) at  $\tau = +\infty$  (i.e., at steady state), we obtain the following approximate relationships:

$$\sum_{n=1}^{\infty} \frac{1}{\alpha_n} = \frac{1}{a_0 + a_1 q}$$
(20)

(From two term Taylor's series expansions) (28)

$$\sum_{n=1}^{\infty} \frac{1}{\alpha_n} = \frac{1}{a_0 + a_1 q + a_2 q^2}$$

(From three term Taylor's series expansions). (29)

#### DISCUSSION OF THE ANALYTICAL SOLUTION

# (1) Relationship between the steady-state solution and

# the approximate unsteady-state solution

It is desirable to evaluate eqs (25) and (26) to see whether the first two or three terms in the Taylor's series expansions are sufficiently accurate. This is partially achieved by comparing the exact value of  $\Sigma(1/\alpha_n)$  (appearing in the exact unsteady-state solution, eq. (18)) obtained from eq. (24) and its approximate value obtained from eqs (28) and (29). The results are shown in Fig. 1. It is obvious that at lower Pe and Bi values (e.g.  $Pe \leq 4$ ,  $Bi \leq 5$ ), the exact value of  $\Sigma(1/\alpha_n)$  obtained from eq. (24) is in good agreement with those obtained from eqs (28) and (29). At higher Pe and Bi values, more terms are needed in the Taylor's series expansions for accuracy. Figure 1 shows that three term Taylor series expansions are much better than two term expansions in terms of the accuracy of  $\Sigma(1/\alpha_n)$ . In the following discussions, we will only use eq. (29), which is the approximate solution to eq. (6) using the first three terms in the Taylor series expansions of the hyperbolical functions in eq. (10).

# (2) The effects of Pe and Bi values

Figures 2 and 3 show the effects of the dimensionless parameters Pe and Bi on the fixed-bed effluent concentration history in the startup period. Both figures are calculated from eq. (26). Figure 2 indicates that when the value of Pe is kept constant and the value of Bi is increased, the effluent concentration levels off to the steady-state value more slowly and the reactant conversion ratio ( $x = 1 - C_L/C_0$ ) at steadystate is higher. When the value of Bi approaches infinity (i.e., the apparent reaction rate constant, K, approaches infinity) the reactant concentration in the effluent approaches zero, and the conversion ratio approaches unity. A very small value of Bi indicates that the apparent reaction rate constant is very small. This makes the conversion ratio close to zero.

When Bi is a constant, increasing Pe value means the increase of flow rate if the length of fixed bed is kept unchanged. The effluent concentration will be faster to reach the steady-state value after the startup period, but the conversion ratio will be lower at the steady state. If Pe approaches infinite, the effluent concentration history will be a step change and the conversion ratio will be zero. From Figs 2 and 3, it is obvious that a higher value of Bi and a lower value of Pe are preferred to obtain a higher conversion ratio at the steady state, but a longer time will be required to reach the steady state.

# (3) The effect of axial dispersion on the conversion ratio

When the axial dispersion in the fixed bed can be neglected, which is equivalent to assuming plug flow, the mass balance equation, eq. (1), is reduced to

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial Z} + \frac{1 - \varepsilon}{\varepsilon} R = 0.$$
(30)

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Fig. 1. The comparison between exact and approximate values of  $\Sigma(1/\alpha_n)$ . [(-----) calculated from eq. (24), in which the  $\gamma L$  values are evaluated from eq. (22) with  $\varepsilon = 0.4$ ; (- -) calculated from eq. (28); (- . --) calculated from eq. (29)].



Fig. 2. The effect of parameter Bi on the effluent conversion ratio when Pe = 1.0 and Pe = 0.5 in the startup period. [(----) Pe = 1.0, (---) Pe = 0.5].

Combining the initial and boundary conditions, the effluent concentration in the startup period can be obtained using Laplace transform

$$\frac{C_L}{C_0} = \begin{cases} \exp\left(-\left[(1-\varepsilon)/\varepsilon\right] \cdot (KL/v) & (\tau > 0) \\ 0 & (\tau \le 0) \end{cases} \right) \end{cases}$$
(31)

Equation (31) indicates that the conversion ratio of the fixed-bed reactor with first-order kinetics in the startup period will be a step change when plug flow is assumed.

It is obvious that eq. (31) is the limit of eq. (18) when  $D_z$  is infinite. Due to the counteracting effect of Pe and



Fig. 3. The effect of parameter Pe on the effluent conversion ratio when  $\mathbf{E}i = 1.0$  and  $\mathbf{E}i = 2.0$  in the startup period. [(----)  $\mathbf{E}i = 1.0, (---) \mathbf{E}i = 2.0$ ].

*Bi* on the conversion ratio shown in Figs 2 and 3, there should be an optimal value of  $D_z$  to reach the largest conversion ratio ( $\mathbf{x} = 1 - C_L/C_0$ ) for a certain fixed-bed reactor.

# A PRACTICAL EXAMPLE

Since the fixed-bed structure, reaction kinetics, and flow pattern are the same in both the startup period and the steady-state period, the dimensionless parameters Pe and Bi will remain the same. Therefore, the Pe and Bi values, correlated from the steady-state experimental data based on eq. (21), can be used to predict the conversion ratio in the startup period.

In order to test the approximate analytical solution in this work, lactic acid fermentations with immobilized cells in a fixed-bed fermentor were studied. According to Donald (1984), the fermentation rate of lactic acid with immobilized cells observes first-order kinetics. Therefore, the system can be used to test the analytical solution.

#### (1) Experimental

A strain of *Lactobacillus delbriieckii* was used in the experiments. The cells were immobilized by the alginate calcium entrapment method. A fixed-bed col-

umn with an inner diameter of 0.28 m and a bed length of 0.37 m was used as a bioreactor. The void fraction of the bed was found to be  $\varepsilon = 0.4$ . The reaction temperature was controlled at 45°C. The composition of inlet fermentation medium was as follows (see Table 1).

At the beginning, the immobilized cells were cultured in the column with the fermentation medium. Then, the medium was wash<sup>1</sup> out with distilled water quickly until no glucose could be detected at the effluent to ensure that initial conditions had been established. After that, the fermentation medium was pumped into the column inlet at a constant flow rate. The glucose and lactic acid concentrations in the column effluent were analyzed to obtain the effluent concentration history in the startup period until steady-state operation was reached.

### (2) Results and discussion

The experimental data on glucose effluent concentrations at different flow rates are shown in Fig. 4. The dimensionless parameters Pe and Bi which were correlated from steady-state experimental data through nonlinear regression using eq. (21) are given in Table 2. The dynamic behavior in the startup

Table 1. Medium composition (wt%)

			-			
Glucose	Yeastextract	Peptone	KH <sub>2</sub> PO <sub>4</sub>	$MgSO_4 \cdot 7H_2O$	NaCl	рн
10.0%	2.0%	0.8%	0.2%	0.05%	0.01%	5.8-6.0



Fig. 4. The comparison between the experimental data and the predicated curves for effluent history in lactic acid fermentation with immobilized cells in the startup period: [(A) run 1 data points, (•) run 2 data points; (O)run 3 data points; (O)run 4 data points].

Table 2. The parameters Pe and Bi correlated from steady-state experimental data

Run no.	v (m/s)	Pe	Bi
1	$2.777 \times 10^{-5}  4.722 \times 10^{-5}  9.194 \times 10^{-5}  1.797 \times 10^{-4}$	0.220	0.355
2		0.289	0.251
3		0.305	0.200
4		0.380	0.132

period for the fixed-bed lactic acid fermentation was predicted based on the parameters listed in Table 2 and eq. (26). Figure 4 shows that the predicted curves using eq. (26) are in good agreement with the experimental data. With an increase in the flow rate, Pe will increase but Bi will decrease based on the steady-state data listed in Table 2, and at the same time, the conversion ratio of glucose will be reduced according to Fig. 4.

### CONCLUSIONS

An approximate analytical solution for the unsteady-state startup period of a fixed-bed reactor with first-order kinetics, axial dispersion, and film mass transfer resistance was obtained. The solution is capable of predicting the dynamic behavior during the startup period with parameters correlated from steady-state operations. A practical example using lactic acid fermentation successfully demonstrated that the approximate analytical solution provides a satisfactory fit of the experimental data.

#### NOTATION

Bi	Biot number defined in eq. (11b), dimension-				
	less				
С	concentration of reactant, mol/m <sup>3</sup>				
$D_z$	axial dispersion coefficient, m <sup>2</sup> /s				
k	first-order reaction rate constant, $s^{-1}$				
k <sub>L</sub>	fluid film mass transfer rate constant, s <sup>-1</sup>				
K	apparent reaction rate constant, $s^{-1}$				
L	length of the fixed-bed column, m				
Pe	Peclet number, dimensionless				
R	consumption rate of reactant, $mol/(m^3 s)$				
5	Laplace transform parameter				
t	time, s				
v	interstitial velocity, m/s				
x	reactant conversion ratio, dimensionless				
Z	column length axis starting from the inlet of				
	the fixed-bed reactor, m				

# Greek letters

α

parameter in eq. (18)

- parameter in eq. (18) parameter defined by eq. (22) β
- γ
- void fraction of the fixed-bed 3
- λ parameter defined by eq. (12)
- dimensionless time defined by eq. (19) τ

# Subscript

0 inlet

- L reactor exit
- 1, 2, 3 ... n

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