

# MODIFIED PARABOLIC PROFILE APPROXIMATION OF INTRAPARTICLE CONCENTRATION FOR CATALYTIC CHEMICAL REACTION AND ADSORPTION

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## Introduction

The parabolic profile approximation, which is equivalent to the widely used linear driving-force model<sup>5)</sup>, is not valid for the initial stage of adsorption upon a step change<sup>3)</sup>. Several efforts have been made to reduce the error at the initial stage of adsorption. Intraparticle concentration profile was approximated by a quartic function<sup>3)</sup>,  $n$ -th order function<sup>4)</sup>, or higher-order polynomial<sup>7)</sup>. Although these models increased the accuracy, the drawback was a loss of simplicity in the rate equation.

The heterogeneous catalytic reaction which accompanies both reaction and diffusion in catalyst particles is an important field for the application of this kind of approximation. The catalyst effectiveness factor calculated by the parabolic profile model has large error when the Thiele modulus is large<sup>6)</sup>. Therefore, there is no simple approximation that is valid for small time or large Thiele moduli.

The purpose of this work is to develop a simple approximation model for (1) a solid catalyzed reaction, and (2) an adsorption in particles suitable for small time or large Thiele moduli. Since the parabolic profile has negative values for these cases, we propose to modify the parabolic profile model by integrating the intraparticle concentration only over the positive region of the parabolic profile.

## 1. Theoretical Development

### 1.1 Fundamental equations

1) Reaction system The mass balance of the diffusing reactant within a catalyst particle can be written in terms of dimensionless variables for irreversible first-order kinetics.

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

The initial and boundary conditions for  $y(\theta, \xi)$  are

$$y(\theta=0) = 0 \quad (2)$$

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$$\frac{\partial y}{\partial \xi} = 0 \quad \text{at} \quad \xi = 0 \quad (3)$$

$$y = y_b = 1 \quad \text{at} \quad \xi = 1 \quad (4)$$

The diffusivity-based dimensionless time  $\theta$  can be converted to reaction-based dimensionless time ( $kt$ ) as used in our previous paper<sup>6</sup> when it is divided by  $9\phi^2$ .

2) **Adsorption system** The mass balance of the diffusing adsorbate can be written as

$$\frac{\partial y}{\partial \theta} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial y}{\partial \xi} \right) \quad (5)$$

It is evident from comparison of Eq. (1) with Eq. (5) that the adsorption system corresponds to the extreme of the reaction system with negligibly small Thiele modulus.

### 1.2 Exact solution

1) **Reaction system** The intraparticle concentration profile solved by Laplace transformation is given as a function of time as

$$y(\theta, \xi) = \frac{\sinh 3\phi\xi}{\xi \sinh 3\phi} + \frac{2\pi}{\xi} \times \sum_{n=1}^{\infty} \frac{n(-1)^n \sin(n\pi\xi) \exp\{-(n\pi)^2 + 9\phi^2\}\theta\}}{(n\pi)^2 + 9\phi^2} \quad (6)$$

The volume-averaged concentration is

$$y_{av}(\theta) = 3 \int_0^1 y(\theta, \xi) \xi^2 d\xi = \frac{1}{\phi \tanh 3\phi} - \frac{1}{3\phi^2} - 6 \sum_{n=1}^{\infty} \frac{\exp\{-(n\pi)^2 + 9\phi^2\}\theta\}}{(n\pi)^2 + 9\phi^2} \quad (7)$$

Note that the average concentration inside the particle is identical to the catalyst effectiveness factor at the transient state.

2) **Adsorption system** The exact solution by Crank<sup>2</sup>) is given by

$$y_{av} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp[-(n\pi)^2 \theta] \quad (8)$$

For small time ( $\theta < 0.1$ ) Eq. (8) is approximated by the following simplified expression<sup>1</sup>):

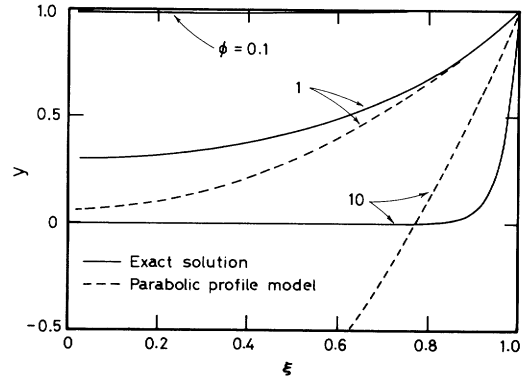
$$y_{av} = 6 \sqrt{\frac{\theta}{\pi}} - 3\theta \quad (9)$$

### 1.3 Solution with parabolic profile assumption (Linear driving-force model)

The intraparticle concentration profile is assumed to have a parabolic shape as

$$y(\theta, \xi) = a_0 + a_2 \xi^2 \quad (10)$$

With boundary condition Eq. (4), Eq. (10) leads to



**Fig. 1.** Concentration profiles of the reactant in a catalyst particle at steady state

$$\left. \frac{\partial y}{\partial \xi} \right|_1 = 5(y_b - y_{av}) \quad (11)$$

The intraparticle concentration profile is given by

$$y(\theta, \xi) = \frac{1}{2} (5y_{av} - 3y_b) + \frac{5}{2} (y_b - y_{av}) \xi^2 \quad (12)$$

1) **Reaction system** When the governing diffusion Eq. (1) is volume-averaged, one obtains the following rate equation after substitution of Eq. (11):

$$\frac{dy_{av}}{d\theta} = 15(y_b - y_{av}) - 9\phi^2 y_{av} \quad (13)$$

The rate equation, Eq. (13), corresponds to a linear driving-force expression of Eq. (1). With the initial condition,  $y_{av}(\theta = 0) = 0$ , the solution is given by

$$y_{av}(\theta) = \{1 - \exp[-3(5 + 3\phi^2)\theta]\} \frac{5y_b}{5 + 3\phi^2} \quad (14)$$

**Figure 1** shows the concentration profile of the reactant developed in a catalyst particle at the steady state. When Thiele modulus  $\phi$  is small, the profile approaches unity and the parabolic profile model agrees well with the exact solution. When the Thiele modulus is large, the profile for the parabolic profile model differs from the exact one. The reactant distributes only near the surface of the particle when  $\phi > 10$ , because the reactant is consumed quickly before it can diffuse into the interior of the particle. The parabolic profile model cannot properly describe the profile for that situation and the reactant concentration has even negative value.

2) **Adsorption system** The rate equation in the form of a linear driving-force expression is

$$\frac{dy_{av}}{d\theta} = 15(y_b - y_{av}) \quad (15)$$

which yields by integration

$$y_{av} = y_b [1 - \exp(-15\theta)] \quad (16)$$

The concentration profiles in a particle at various times are analogous to Fig. 1 with replacement of  $\phi$  by  $\theta$  as a parameter. At the beginning of the adsorption the profile has a shape similar to that of the curve for a reaction system with large  $\phi$ . The concentration within a particle approaches unity as the adsorption proceeds and the adsorbent particle becomes saturated for the adsorption system, while the gradient of the concentration profile exists even at steady state for the reaction system.

#### 1.4 Modified parabolic profile model

The concentrations in the interior have negative values for the parabolic profile model as mentioned above when the Thiele modulus is large or at small time. The error in the parabolic profile approximation in these region is mainly due to the negative values of the concentration. The application of the parabolic profile model is consequently restricted to the situation with small Thiele moduli and at large time.

The following model is developed to defeat this restriction. The parabolic expression Eq. (10) is rewritten as

$$y(\theta, \xi) = a_2(\xi^2 - a_3^2) \quad (17)$$

where  $a_3 = (-a_0/a_2)^{1/2}$ . When the Thiele modulus is large or at small time,  $a_0$  has a negative value and then  $y(\theta, \xi)$  is negative in the range of  $\xi < a_3$ . The average concentration in a particle is obtained by integrating the concentration from its center to its surface. For the parabolic profile model the integration is carried out over the entire range including the negative values. As a result, the parabolic profile model underestimates the average concentration.

We expected that the integration limited to the positive region would provide a more accurate approximation. The volume-averaged concentration is then obtained by integration from  $a_3$  to 1 in terms of  $\xi$  instead of zero to 1.

$$\begin{aligned} y_{av}(\theta) &= 3 \int_{a_3}^1 y(\theta, \xi) \xi^2 d\xi \\ &= 3a_2 \left( \frac{2}{15} a_3^5 - \frac{1}{3} a_3^2 + \frac{1}{5} \right) \end{aligned} \quad (18)$$

For large Thiele moduli or small time,  $a_3$  is close to unity because reactants or adsorbates distribute only near the surface. By expanding Eq. (18) in terms of  $(1 - a_3)$  and neglecting terms higher than second order on  $(1 - a_3)$ , Eq. (18) is approximated to the following expression on the assumption of  $1 - a_3 \ll 1$ :

$$y_{av} = 3a_2(1 - a_3)^2 \quad (19)$$

By applying the parabolic expression Eq. (10) to the boundary conditions Eqs. (3) and (4) and eliminating  $a_3$  with Eq. (19), the following equation can be derived.

$$\left. \frac{\partial y}{\partial \xi} \right|_1 = \frac{(y_{av} + 3y_b)^2}{6y_{av}} \quad (20)$$

1) Reaction system The rate equation corresponding to Eq. (13) is given by

$$\frac{dy_{av}}{d\theta} = \frac{(y_{av} + 3y_b)^2}{2y_{av}} - 9\phi^2 y_{av} \quad (21)$$

which can be solved to yield

$$\begin{aligned} &\left[ \frac{(a-9)y_{av}}{3(a-3\sqrt{a})y_b} + 1 \right]^{3-\sqrt{a}} \left[ \frac{(a-9)y_{av}}{3(a+3\sqrt{a})y_b} + 1 \right]^{3+\sqrt{a}} \\ &= \exp[6(a-9)\phi^2\theta] \end{aligned} \quad (22)$$

where  $a = 1/(2\phi^2)$ . When  $a \ll 1$ , that is, Thiele modulus  $\phi$  is sufficiently large, the above equation is simplified to the explicit expression in terms of  $y_{av}$ .

$$y_{av} = \frac{3ay_b}{9-a} \left[ 1 + \sqrt{1 + \frac{9-a}{a} \{1 - \exp[-2(9-a)\phi^2\theta]\}} \right] \quad (23)$$

2) Adsorption system The rate equation corresponding to Eq. (15) is given by

$$\frac{dy_{av}}{d\theta} = \frac{(y_{av} + 3y_b)^2}{2y_{av}} \quad (24)$$

which yields the solution as

$$-\frac{y_{av}}{y_{av} + 3y_b} + \ln\left(\frac{y_{av} + 1}{3y_b}\right) = \frac{1}{2} \theta \quad (25)$$

#### 1.5 Catalyst effectiveness factor

The steady-state behavior is practically important for the design and analysis of catalytic reactors. The steady-state effectiveness factor in terms of dimensionless concentrations is defined as

$$\eta = \lim_{\theta \rightarrow \infty} \frac{y_{av}}{y(\xi=1)} = y_{av} \quad (26)$$

The effectiveness factor is then given as follows.

$$\eta = \frac{1}{\phi} \left( \frac{1}{\tanh 3\phi} - \frac{1}{3\phi} \right) \quad (\text{exact solution})$$

$$\eta = \frac{1}{1 + 3\phi^2/5} \quad (\text{parabolic profile approximation})$$

$$\eta = \frac{1}{\sqrt{2}\phi - 1/3} \quad (\text{modified parabolic profile approximation})$$

The effectiveness factors  $\eta$  approach the following asymptotic values when  $\phi$  is large ( $\phi \gg 1$ ).

$$\eta = \frac{1}{\phi} \quad (\text{exact solution})$$

$$\eta = \frac{5}{3\phi^2} \quad (\text{parabolic profile approximation})$$

$$\eta = \frac{1}{\sqrt{2}\phi} \quad (\text{modified parabolic profile approximation})$$

## 2. Results and Discussion

### 2.1 Transient behavior

1) Reaction system The average concentrations of the approximate models are compared with the exact solution in **Fig. 2** for different values of Thiele modulus  $\phi$ . At the initial stage (smaller time  $\theta$ ) the parabolic profile model is not accurate for any value of  $\phi$ . The modified parabolic profile model gives a much better approximation than the parabolic profile model at small time independent of  $\phi$ . Equation (23) is obviously applicable only to larger  $\phi$  ( $\phi > 10$ ) as expected from its derivation.

When the reaction proceeds and approaches the steady state, the accuracy of two models becomes dependent on  $\phi$ . When  $\phi$  is small, that is, intraparticle diffusion is less important, the parabolic profile model gives an accurate approximation for larger time. However, it does not give good approximation for large  $\phi$ , and is no longer valid for  $\phi > 3$  even at steady state. On the other hand, the modified model gives a much better approximation for large  $\phi$  over the entire region of time. As can be expected by the derivation from Eq. (18) to Eq. (19), the modified parabolic model is not suitable for small  $\phi$  except for small time.

The valid regions of these models are approximately given as follows. The parabolic profile model is valid for:

$$\phi < 1.2 \quad \text{and} \quad \theta > 0.082\phi + 0.070 \quad (\text{error } 10\%)$$

$$\phi < 1.6 \quad \text{and} \quad \theta > 0.016\phi + 0.033 \quad (\text{error } 20\%)$$

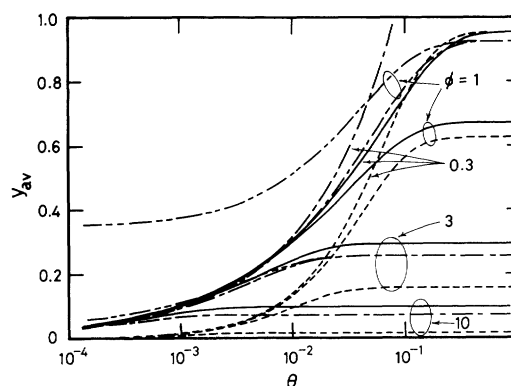
The modified parabolic profile model is valid for:

$$\phi > 1.4 \quad \text{or} \quad \theta < 0.015\phi + 0.012 \quad (\text{error } 10\%)$$

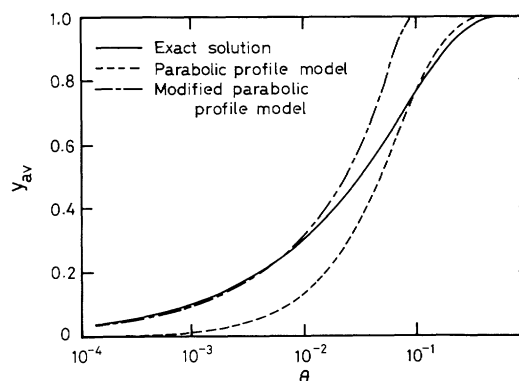
$$\phi > 1.2 \quad \text{or} \quad \theta < 0.053\phi + 0.013 \quad (\text{error } 20\%)$$

2) Adsorption system The comparison for the average concentration by the approximate models with the exact solution is shown in **Fig. 3**. This corresponds to the small  $\phi$  asymptote of Fig. 2, because the adsorption system is identical to the reaction system with negligibly small Thiele modulus. The parabolic profile model coincides with the exact solution for longer time, because the concentration profile approaches unity as the adsorption proceeds.

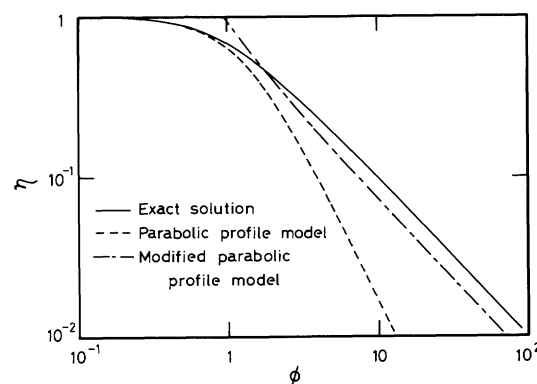
The parabolic profile model is valid for  $\theta > 0.05$  (error 10%) or  $\theta > 0.038$  (error 20%) and the error becomes large as time becomes smaller. On the other hand, the modified parabolic model approximates excellently for smaller time, and is valid for  $\theta < 0.018$



**Fig. 2.** Comparison of the average concentration histories for the reaction system [— exact solution, --- parabolic profile model, ---- modified parabolic profile model Eq. (22), - - - modified parabolic profile model Eq. (23)]



**Fig. 3.** Comparison of the average concentration histories for the adsorption system



**Fig. 4.** Catalyst effectiveness factors at steady state

(error 10%) or  $\theta < 0.033$  (error 20%).

### 2.2 Catalyst effectiveness factor

The effectiveness factors for the exact and approximate models are compared in **Fig. 4**. The slope of the line in  $\ln \eta$  versus  $\ln \phi$  plot is  $-1$  for both the exact solution and the modified parabolic profile model while it is  $-2$  for the parabolic profile model for larger Thiele moduli  $\phi$ . As can be expected from the asymptote values and the slopes of lines in Fig. 4, the effectiveness factor of the parabolic profile

model deviates significantly from the exact solution as  $\phi$  becomes large. However, the difference of the effectiveness factor between the modified parabolic profile model and exact solution does not increase with  $\phi$ . The error is only  $1/\sqrt{2}$  and is independent of Thiele modulus  $\phi$  except for smaller  $\phi$ . The irrational deviation of the effectiveness factor for the modified parabolic profile model for smaller  $\phi$  is due to the approximation made to derive Eq. (19) from Eq. (18). Therefore, it may be appropriate to use the parabolic profile model for smaller Thiele moduli and the modified parabolic profile model for larger Thiele moduli when we evaluate steady-state behavior. The catalyst effectiveness factor is approximated better by the parabolic model for  $\phi < 1.2$  and by the modified parabolic model for  $\phi > 1.2$ .

#### Nomenclature

$a$	= $1/(2\phi^2)$	[—]
$a_0, a_2, a_3$	= coefficients in approximate profile	[—]
$C$	= intraparticle concentration	[mol/m <sup>3</sup> ]
$C_b$	= bulk concentration	[mol/m <sup>3</sup> ]

$D$	= intraparticle effective diffusivity	[m <sup>2</sup> /s]
$k$	= first-order reaction rate constant	[1/s]
$r$	= radial distance from center of particle	[m]
$r_0$	= radius of particle	[m]
$t$	= time	[s]
$y$	= dimensionless concentration ( $= C/C_b$ )	[—]
$y_b$	= dimensionless bulk concentration ( $= 1$ )	[—]
$y_{av}$	= volume-averaged dimensionless concentration	[—]
$\eta$	= effectiveness factor	[—]
$\theta$	= dimensionless time ( $= Dt/r_0^2$ )	[—]
$\xi$	= dimensionless radial distance ( $= r/r_0$ )	[—]
$\phi$	= Thiele modulus ( $= (r_0/3)(k/D)^{1/2}$ )	[—]

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