

Approximate Solution to the Diffusion-Reaction Problem with Nonlinear Kinetics in Transient Systems

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ABSTRACT

A method to obtain the approximate solution to the diffusion-reaction problem with nonlinear kinetics in transient systems is presented. The analytical solution to the equation that governs the process is based on the linearization of the kinetics expression through the Taylor series expansion above the surface particle concentration of the key component, which includes a critical radius to avoid negative concentration values. The present results for the average concentration were compared with the numerical solution of the exact problem and the error was less than ten percent for the power-law and Monod kinetics equation.

Key words: Approximate method, Diffusion-reaction problem, Linearization, Critical radius, Dead zone.

I. INTRODUCTION

The evaluation of the global reaction rate is important for the analysis, design and simulation of heterogeneous chemical reactors. However, it is a difficult and/or lengthy task due to the interaction between the transport phenomena and the kinetics that are present in this kind of systems [1].

In fact, the representation of the global rate of reaction is only possible when the simplicity of the kinetics allow it. In that case, the problem can be solved by employing analytical expressions. However, for reactions of industrial interest it is not common to represent the process with kinetics models as simple as the irreversible first order one. Therefore, analytical expressions to evaluate the global reaction rate are not available and numerical methods need to be used for most of the cases, for whose evaluation requires a lot of the computation time.

A great amount of time spent on numerical operations can be saved if a simplified method to evaluate the global rate of reaction were available. In this direction, some authors have obtained approximate solutions to the diffusion reaction problem with nonlinear kinetics. One way to simplify a model is by replacing a partial differential equation (PDE) for mass balance in the pellet by a proper ordinary differential equation (ODE). This idea is the basis of the methods proposed in References [2, 3, 4]. There are other ways to simplify the problem. Several authors [5, 6, 7, 8, 9, 10] have developed a

method based on the Taylor series expansion for the reaction rate expression above the surface particle concentration for the key component. Their methodology has proven to be satisfactory for low values of the Thiele modulus, but the error grows when the Thiele modulus is increased due to the presence of the zero order term in the mass balance in the pellet as a consequence of the linealization process. The nonhomogeneous term can lead to spurious solutions, such as the presence of negative concentration values. To avoid this drawback, the proposed linear boundary-value problem is equipped with a nonactive region. Numerical results show that such a modification increases the prediction capacity of the analytical expressions.

II. THEORY

The average equation that governs the mass transport in a catalytic pellet for the isothermal case in transient systems is given by:

$$\frac{\partial U_A}{\partial \tau} = \frac{1}{\xi^m} \left[\frac{\partial}{\partial \xi} \left(\xi^m \frac{\partial U_A}{\partial \xi} \right) \right] - \Phi^2 \mathcal{R}_A \quad (1)$$

Equation 1 is subjected to the following boundary conditions:

At the pellet center

$$\frac{\partial U_A}{\partial \xi} = 0 \quad \text{at } \xi = \xi_c \quad \text{for } \tau > 0 \quad (2)$$

At the pellet surface:

$$U_A = U_{in} \quad \text{at } \xi = 1 \quad \text{for } \tau > 0 \quad (3)$$

And the initial condition is:

$$U_A = U_0 \quad \text{for } 0 \leq \xi \leq 1 \quad \text{when } \tau = 0 \quad (4)$$

In (1) – (4), U_A is the dimensionless concentration for the key component, Φ^2 is the Thiele modulus, ξ_c is the critical radius (position in the particle where the reactant becomes exhausted in the particle), and m indicates the geometrical shape parameter that takes the value: 0 for slab, 1 for cylindrical, and 2 for spherical geometry.

The boundary condition given by (2) is included in order to consider the case where the reactant concentration can become depleted at some intermediate position in the particle when the reaction rate is fast enough. On the other hand, critical radius

is a function of the time [10, 11], but in this work we considered it a constant.

III. LINEALIZATION

To develop an analytic solution, we use the Taylor series to expand the reaction term for the surface concentration in the pellet:

$$\mathfrak{R}_A = \mathfrak{R}_A|_{\xi=1} + \frac{\partial \mathfrak{R}_A}{\partial U_A} \bigg|_{\xi=1} (U_A - U_A|_{\xi=1}) \quad (5)$$

Substituting (5) in the mass balance, we can obtain the following linear PDE:

$$\frac{\partial U_A}{\partial \tau} = \frac{1}{\xi^m} \left[\frac{\partial}{\partial \xi} \left(\xi^m \frac{\partial U_A}{\partial \xi} \right) \right] - \beta - \gamma^2 U_A \quad (6)$$

where:

$$\beta = \Phi^2 \left[\mathfrak{R}_A|_{\xi=1} - \frac{\partial \mathfrak{R}_A}{\partial U_A} \bigg|_{\xi=1} U_A|_{\xi=1} \right] \quad (7)$$

$$\gamma^2 = \Phi^2 \frac{\partial \mathfrak{R}_A}{\partial U_A} \bigg|_{\xi=1} \quad (8)$$

It should be noticed that β is a zero order reaction term, and if the approximate problem is solved, as a result of the presence of this term, negative values of the concentration might be obtained. It is clear that this situation will be predicted from the model at the starting of the reaction when the pellets are reagent depleted. To avoid this, a nonreaction zone is introduced in the analysis

IV. APPROXIMATE SOLUTION

After that the Laplace Transform has been applied, the solution for (6) with the boundary conditions given by (2) and (4) for the three geometrical shapes, given by m , are shown in Table 1.

The constants and some of the details behind these equations are described in Appendix.

The averaged particle concentration is obtained by using [12]:

$$\langle U_A \rangle = (m+1) \int_{\xi_c}^1 U_A \xi^m d\xi \quad (9)$$

In (9), we only considered the region where the reactant is present, which can be seen in the integration limits.

The average concentration was obtained by substituting the profiles concentration in (9). The results are shown in Table 2.

To find the critical radius, an additional boundary condition must be included, and it is given by

$$U_A = 0 \quad \text{en } \xi = \xi_c \quad (10)$$

By substituting the Equations given in Table 1 in (10), we obtain an expression to calculate the critical radius. The results are presented in Table 3.

Table 1. Approximate concentration profile for the key component, for different pellets shapes: slab ($m=0$), cylinder ($m=1$) and sphere ($m=2$)

$m = 0$	$U_A(\xi, \tau) = \frac{\beta}{\gamma^2} \left(\frac{\text{Cosh}[\gamma(\xi - \xi_c)]}{\text{Cosh}[\gamma(1 - \xi_c)]} - 1 \right) + \sum_{n=1}^{\infty} \frac{2 \text{Cos}[\mu_n(\xi - \xi_c)]}{(1 - \xi_c) \text{Sen}[\mu_n(1 - \xi_c)]} e^{-(\mu_n^2 + \gamma^2)\tau} \left[\frac{\beta + U_0(\mu_n^2 + \gamma^2)}{\mu_n(\mu_n^2 + \gamma^2)} + \mu_n I_{in} \right] \quad (11)$
$m = 1$	$U_A(\xi, \tau) = \left(U_0 + \frac{\beta}{\gamma^2} \right) \left(1 - \frac{\ln(\xi_c / \xi)}{\ln(\xi_c)} \right) e^{-\gamma^2 \tau} + \frac{\beta}{\gamma^2} \left(\frac{I_0(\gamma \xi) K_1(\gamma \xi_c) + K_0(\gamma \xi) I_1(\gamma \xi_c)}{I_0(\gamma) K_1(\gamma \xi_c) + K_0(\gamma) I_1(\gamma \xi_c)} - 1 \right) + 2 \sum_{n=1}^{\infty} \frac{[Y_0(\mu_n \xi) J_1(\mu_n \xi_c) - J_0(\mu_n \xi) Y_1(\mu_n \xi_c)] e^{-(\mu_n^2 + \gamma^2)\tau}}{B(\mu_n, \xi_c)} \left[\frac{\beta + U_0(\mu_n^2 + \gamma^2)}{\mu_n(\mu_n^2 + \gamma^2)} + \mu_n I_{in} \right] \quad (12)$
$m = 2$	$U_A(\xi, \tau) = \frac{\beta}{\gamma^2} \left(\frac{1}{\xi} \left\{ \frac{\xi_c \gamma \text{Cosh}[\gamma(\xi - \xi_c)] + \text{Senh}[\gamma(\xi - \xi_c)]}{\xi_c \gamma \text{Cosh}[\gamma(1 - \xi_c)] + \text{Senh}[\gamma(1 - \xi_c)]} \right\} - 1 \right) + \frac{2}{\xi} \sum_{n=1}^{\infty} \frac{(\xi_c \mu_n \text{Cos}[\mu_n(\xi - \xi_c)] + \text{Sen}[\mu_n(\xi - \xi_c)])}{\text{Sen}[\mu_n(1 - \xi_c)]} e^{-(\mu_n^2 + \gamma^2)\tau} \left[\frac{A_n}{D_n} + \frac{1}{C_n} I_{in} \right] \quad (13)$