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Mathematical Modeling of the Catalyst Deactivation Process inside a Grain Using Mathcad

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Abstract—The problem of the mathematical modeling of the catalyst deactivation process inside a spherical grain with a parallel first-order deactivation mechanism has been solved in the work [9] by the finite difference method. This paper presents a simpler method for the solution of this problem. It is shown that the set of nonlinear partial differential equations for planar, cylindrical, and spherical grains can be reduced to a boundary problem for two ordinary differential equations with respect to the spatial variable, where time is a parameter. The obtained equations are solved by the shooting method using Mathcad functions. For illustration, the profiles of relative catalyst activity and dimensionless reagent concentration are calculated for a spherical grain at a Thiele parameter of 5 and different time moments, together with the dependence of the degree of internal grain surface utilization on dimensionless time. Some asymptotic dependences are proposed for these parameters over a long time period.

Keywords: catalyst deactivation modeling

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INTRODUCTION

Catalyst deactivation is an undesirable phenomenon, which diminishes the activity of a catalyst and requires its periodic regeneration or replacement. A loss in the activity of a catalyst remains a serious problem for a number of chemical oil refining and biomass conversion processes, such as pyrolysis, cracking, dehydrogenation, reforming, and deoxygenation. The problems of deactivation are considered in a number of monographs [1–5], reviews [6–8], and original papers, in which the reasons for this phenomenon are studied, and different models describing the mechanism of deactivation and method of its reduction are proposed.

One theoretical model with a parallel deactivation mechanism is considered in [9]. This model, which is also called the model of deactivation with an initial compound [3], can be illustrated by the following scheme of reactions:

$$\mathrm{A} \xrightarrow{k_\mathrm{B}} \mathrm{B}, \qquad \text{(I)}$$

$$\mathrm{A} \xrightarrow{k_\mathrm{C}} \mathrm{C}. \qquad \text{(II)}$$

Reagent A participates in two parallel and irreversible first-order reactions. The first reaction is the formation of the main product B with the reaction rate constant k_B, and the second reaction is the formation of the catalytic poison C with the reaction rate constant k_C. The catalytic poison precipitates onto a catalyst to deactivate its active sites. It is assumed that the relative activity of a catalyst is linearly related to the amount of the formed catalytic poison, and this process is isothermic. In this case, the time dependence of the catalyst activity (a) has the form

$$a = 1 - \beta\int_0^t k_\mathrm{C} c a \mathrm{d}t, \qquad (1)$$

where a is the relative activity of a catalyst, β is a constant (coefficient of proportionality), c is the reagent concentration, and t is the time. Equation (1) can be written in differential form as

$$\frac{\partial a}{\partial t} = -\beta k_\mathrm{C} c a. \qquad (2)$$

In the quasi-homogeneous model, the change in the reagent's concentration inside a catalyst grain, taking the deactivation into consideration is described as

$$D_\mathrm{eff}\left(\frac{\partial^2 c}{\partial x^2} + \frac{n}{x}\frac{\partial c}{\partial x}\right) = kca, \qquad (3)$$

where D_eff is the effective diffusion coefficient of a reagent in a grain, n is a parameter ($n = 0$ for a planar grain, $n = 1$ for a cylindrical grain, and $n = 2$ for a spherical grain), x is the longitudinal coordinate of a grain (the distance from a selected grain point to the central plane for a planar grain, to the axis of a cylindrical grain, and to the center of a spherical grain), $0 \le x \le b$, where b is the distance from the center to the boundary of a grain, and $k = k_B + k_C$. In Eq. (3), it is implied that deactivation is slower than the chemical reaction and represents a diffusion process, which results in the concentration profile in a grain at each time moment being determined by the relative catalyst activity profile.

The boundary conditions defined for the functions $c(t, x)$ and $a(t, x)$ are

$$\frac{\partial c}{\partial x}(t,0) = 0, \quad c(t, b) = c_0, \quad a(0, x) = 1, \tag{4}$$

where c_0 is the reagent concentration at the boundary of a grain.

Hence, the deactivation process in a catalyst grain even in such a relatively simple model is described by two nonlinear partial differential equations, whose solution requires the application of numerical methods. This problem has been solved for a spherical grain in the work [9] by the finite difference method. The relative catalyst activity and reagent concentration profiles inside a grain and the degree of the internal grain surface utilization were calculated depending on the time and the Thiele parameter.

After the advent of applied mathematical software, and in particular, Mathcad, the solution of many problems became feasible not only for qualified applied mathematicians but also for students skilled in working with such software. The objective of this work was to demonstrate how some mathematical transformations and the Mathcad applied mathematical software can be used to solve the problem of catalyst deactivation in planar, cylindrical, and spherical grains for the deactivation model described above in a simpler way than in the work [9] and to obtain the asymptotic dependences of the basic parameters on the time and the spatial variable over a long time period.

DERIVATION OF EQUATIONS AND METHOD OF SOLUTION

Let us introduce the dimensionless variables $y = c/c_0$, $\xi = x/b$, and $\tau = c_0\beta k_C t$, with which Eqs. (2) and (3) and boundary conditions (4) take the from

$$\frac{\partial^2 y}{\partial \xi^2} + \frac{n}{\xi}\frac{\partial y}{\partial \xi} = \psi^2 y a, \tag{5}$$

$$\frac{\partial a}{\partial \tau} = -ya, \tag{6}$$

$$\frac{\partial y}{\partial \xi}(\tau,0) = 0, \quad y(\tau,1) = 1, \quad a(0,\xi) = 1, \tag{7}$$

where $\psi = b\sqrt{\frac{k}{D_{\text{eff}}}}$ is the Thiele parameter.

The integration of Eq. (6) at $\xi = 1$ with the use of $y(\tau, 1) = 1$ allows us to find a at the external boundary of a grain as

$$a(\tau,1) = \mathrm{e}^{-\tau}. \tag{8}$$

From Eqs. (5) and (6) it follows that

$$\frac{\partial^2 y}{\partial \xi^2} + \frac{n}{\xi}\frac{\partial y}{\partial \xi} + \psi^2 \frac{\partial a}{\partial \tau} = 0. \tag{9}$$

Equation (6) gives the relationship between y and a

$$y = -\frac{1}{a}\frac{\partial a}{\partial \tau} = \frac{\partial}{\partial \tau}\ln\frac{1}{a}. \tag{10}$$

Substituting Eq. (10) into Eq. (9), we obtain that

$$\frac{\partial^2}{\partial \xi^2}\frac{\partial}{\partial \tau}\ln\frac{1}{a} + \frac{n}{\xi}\frac{\partial}{\partial \xi}\frac{\partial}{\partial \tau}\ln\frac{1}{a} + \psi^2\frac{\partial a}{\partial \tau} = 0, \tag{11}$$

$$\frac{\partial}{\partial \tau}\left(\frac{\partial^2}{\partial \xi^2}\ln\frac{1}{a} + \frac{n}{\xi}\frac{\partial}{\partial \xi}\ln\frac{1}{a} + \psi^2 a\right) = 0. \tag{12}$$

Equation (12) is integrated over time to find that

$$\frac{\partial^2}{\partial \xi^2}\ln\frac{1}{a} + \frac{n}{\xi}\frac{\partial}{\partial \xi}\ln\frac{1}{a} + \psi^2 a = f(\xi). \tag{13}$$

The integration results in the function $f(\xi)$ determined by considering Eq. (13) at $\tau = 0$ using $a(0, \xi) = 1$, i.e.,

$$f(\xi) = \psi^2. \tag{14}$$

Substituting the explicit form of $f(\xi)$ into Eq. (13), we find that

$$\frac{\partial^2}{\partial \xi^2}\ln\frac{1}{a} + \frac{n}{\xi}\frac{\partial}{\partial \xi}\ln\frac{1}{a} = \psi^2(1-a). \tag{15}$$

In Eq. (15), all the partial derivatives were replaced by ordinary ones, as the time is not incorporated into it in explicit form and is present only as a parameter in boundary condition (8) at $\xi = 1$.

By introducing the function $w = \ln\frac{1}{a}$, it is possible to write Eq. (15) in a form which is more convenient for calculations. In this case, the relative catalyst activity will be expressed through the function w as $a = \mathrm{e}^{-w}$. When a is varied from 1 (the maximally active catalyst) to 0 (total deactivation), w is changed from 0 to ∞. As a result of such a replacement, Eq. (15) takes the form

$$\frac{\mathrm{d}^2 w}{\mathrm{d}\xi^2} + \frac{n}{\xi}\frac{\mathrm{d}w}{\mathrm{d}\xi} = \psi^2\left(1 - \mathrm{e}^{-w}\right). \tag{16}$$

The boundary conditions for the function w will be

$$\frac{\mathrm{d}w}{\mathrm{d}\xi}(0) = 0, \quad w(1) = \tau, \tag{17}$$

where the dependence of w on τ is omitted for short.

Hence, the relative catalyst activity profile at any time moment is determined by solving boundary

$\psi := 5 \qquad \tau := 0.4 \qquad n := 2 \qquad \varepsilon := 0.001$

Given

$$\frac{d^2}{d\xi^2}w(\xi) + \frac{n}{\xi}\cdot\frac{d}{d\xi}w(\xi) = \psi^2\left(1 - e^{-w(\xi)}\right) \qquad w'(\varepsilon) = 0 \qquad w(\varepsilon) = 0.0297$$

$w := \text{Odesolve}(\xi, 1.2) \qquad w(1) = 0.4 \qquad a(\xi) := e^{-w(\xi)}$

Given

$$\frac{d^2}{d\xi^2}y(\xi) + \frac{n}{\xi}\cdot\frac{d}{d\xi}y(\xi) = \psi^2\cdot y(\xi)\,a(\xi) \qquad y'(\varepsilon) = 0 \qquad y(\varepsilon) = 0.0816$$

$$y := \text{Odesolve}(\xi, 1) \qquad y(1) = 1 \qquad \eta := (n+1)\cdot\int_{\varepsilon}^{1} y(\xi)\cdot a(\xi)\cdot\xi^n d\xi = 0.401$$

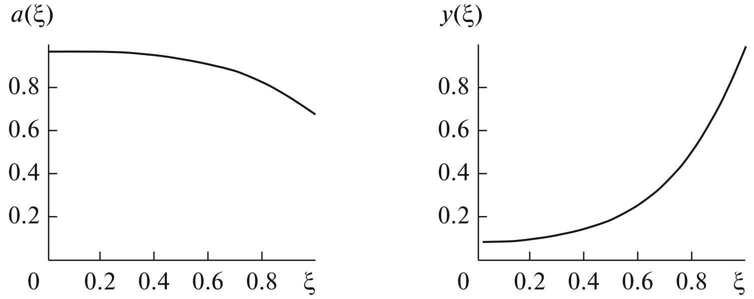

Fig. 1. Mathcad calculation of relative catalyst activity and reagent concentration profiles and degree of grain utilization at $\psi = 5$ and $\tau = 0.4$ for a spherical grain.

problem (16) and (17), which incorporates the boundary condition at the external boundary of a grain, for an ordinary differential equation.

In the limit case at great τ, the term e^{-w} in Eq. (16) may be neglected, and the solution for the functions w and a after integration of the simplified equation is

$$w = \tau - \frac{\psi^2}{2(n+1)}\left(1-\xi^2\right), \quad a = e^{\frac{\psi^2}{2(n+1)}\left(1-\xi^2\right)-\tau}. \tag{18}$$

At $\xi = 0$, Eqs. (5) and (16) for cylindrical and spherical grains have a peculiarity which can be overcome by transferring the boundary condition from the point $\xi = 0$ to the point $\xi = \varepsilon$, where ε is a small value, thus solving the boundary problem within the range $\varepsilon \le \xi \le 1$ with the boundary conditions $\frac{dw}{d\xi}(\varepsilon) = 0$ and $\frac{dy}{d\xi}(\varepsilon) = 0$ near the center of a grain.

The boundary problem for Eq. (16) was solved by the shooting method, fitting $w(\varepsilon)$ so as to meet the condition $w(1) = \tau$. In Mathcad, the Cauchy problem was solved using the function Given-Odesolve.

The concentration profile $y(\tau, \xi)$ was calculated based on Eq. (5) by the shooting method with the use of the Given-Odesolve function. At large τ, the concentration profile tends to unity, and the inner-diffusion resistance may be neglected.

The degree of internal grain surface utilization η was calculated as

$$\eta = (n+1)\int_{\varepsilon}^{1} y(\xi)\,a(\xi)\,\xi^n d\xi. \tag{19}$$

At large τ, the dependence of the degree of internal grain surface utilization on τ and ξ has the form

$$\eta = e^{-\tau}(n+1)\int_{0}^{1} e^{\frac{\psi^2}{2(n+1)}\left(1-\xi^2\right)}\xi^n d\xi. \tag{20}$$

RESULTS AND DISCUSSION

The calculation of the relative catalyst activity, the dimensionless reagent concentration, and the internal grain surface utilization degree at $\psi = 5$ and $\tau = 0.4$ for a spherical grain with the Mathcad software is exemplified in Fig. 1. In the calculations, $\varepsilon = 0.001$ is accepted. It can be seen that the program, together with the plots, occupies less than half a page.

For illustration and comparison with the results [9], the calculated relative catalyst activity and reagent concentration profiles for a spherical grain at $\psi = 5$ and different time moments are plotted in Figs. 2 and 3. The calculated time dependence of the degree of the internal grain surface utilization at $\psi = 5$ is shown in Fig. 4. The

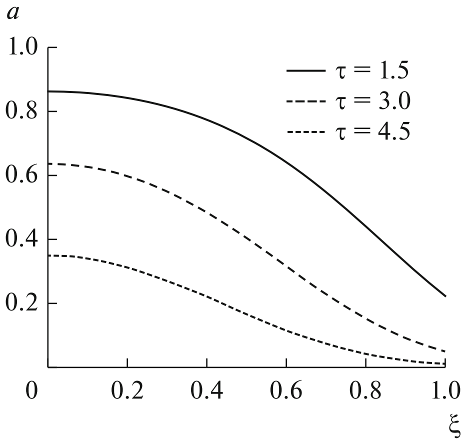

Fig. 2. Relative catalyst activity profiles at $\psi = 5$ and different time moments for spherical grain.

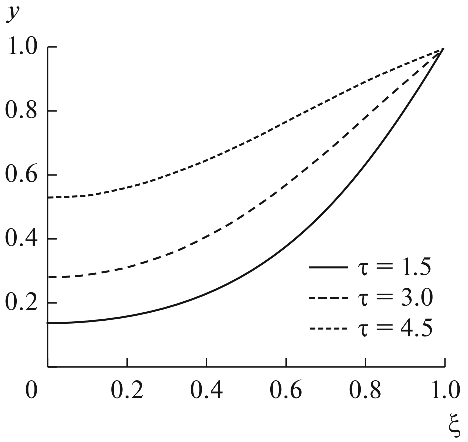

Fig. 3. Dimensionless reagent concentration profiles at $\psi = 5$ and different time moments for spherical grain.

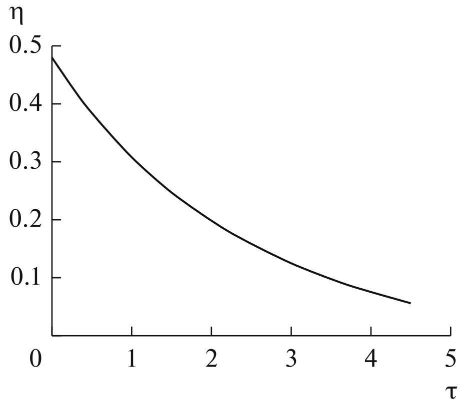

Fig. 4. Utilization degree of internal surface of spherical grain versus time at $\psi = 5$.

dependences presented in Figs. 2–4 completely coincide with the dependences obtained in the work [9].

The method proposed in this work gives a simple tool for the analysis of the catalyst deactivation process inside a grain, when the model with a parallel first-order deactivation mechanism is applicable. The applicability of this model can be verified based on the experiments with a small-size grain in the absence of diffusive resistance. The kinetic model parameters are determined from the analytical dependences given in [10] for a plug-flow reactor and [4] for a stirred-tank reactor.

CONCLUSIONS

Hence, a simpler method than the technique [9] for solving the problem of the mathematical modeling of the deactivation process inside a catalyst grain with a parallel first-order deactivation mechanism has been proposed in this work. It has been shown that the set of nonlinear partial differential equations for planar, cylindrical, and spherical grains can be reduced to the boundary problem for two ordinary differential equations with respect to the spatial variable, where time is a parameter. The obtained equations were solved by the shooting method using Mathcad functions. The relative catalyst activity and dimensionless reagent concentration profiles were calculated for a spherical grain at a Thiele parameter $\psi = 5$ and different time moments, together with the dependence of the utilization degree of the internal surface of a spherical grain on dimensionless time as an example. The asymptotic dependences of these parameters over a long time period were proposed.

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