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NUMERICAL IDENTIFICATION OF THE CHEMICAL REACTION RATE CONSTANT IN THE IDEAL DISPLACEMENT MODEL

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Abstract. A chemical-technological process of a second-order reaction in a chemical reactor of an ideal displacement, described by a nonlinear partial differential equation of the first order has been considered. Within the framework of the proposed model, the inverse problem of determining the rate constant of a chemical reaction was defined. In this case, an additional condition was set regarding the reagent concentration at the outlet from the reactor. To solve the inverse problem, its discrete analogue was constructed and a special representation was proposed for solving the resulting system of linear algebraic equations. As a result, an explicit formula for determining the approximate value of the rate constant of a chemical reaction was obtained. The possibilities of the proposed numerical method were illustrated by numerical calculations on model problems.

Keywords: chemical reactor of ideal displacement, chemical reaction rate constant, identification problem, coefficient inverse problem

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ЧИСЛЕННАЯ ИДЕНТИФИКАЦИЯ КОНСТАНТЫ СКОРОСТИ ХИМИЧЕСКОЙ РЕАКЦИИ В МОДЕЛИ ИДЕАЛЬНОГО ВЫТЕСНЕНИЯ

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Аннотация. Рассматривается химико-технологический процесс реакции второго порядка в химическом реакторе идеального вытеснения, описываемый нелинейным дифференциальным уравнением в частных производных первого порядка. В рамках предложенной модели поставлена обратная задача по определению константы скорости химической реакции. При этом задается дополнительное условие относительно концентрации реагента на выходе из реактора. Для решения поставленной обратной задачи строится ее дискретный аналог и предлагается специальное представление для решения полученной системы линейных алгебраических уравнений. В результате получена явная формула для определения приближенного значения константы скорости химической реакции. Возможности предложенного численного метода иллюстрируются численными расчетами на модельных задачах.

Ключевые слова: химический реактор идеального вытеснения, константа скорости химической реакции, задача идентификации, коэффициентная обратная задача

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Introduction

The main element in any chemical engineering system is the chemical reactor where chemical processes occur to obtain a specific reagent with the given properties. Diverse types of chemical reactors with widely different designs are used in chemical engineering [1–3]. However, the kinetics of the process occurring in the reactor is mainly determined by the flow regime of the reaction medium and the thermal conditions in the reactor. For this reason, chemical reactors are classified by based on critical flow regimes: perfect displacement and perfect mixing in isothermal, adiabatic or polythermal conditions.

Mathematical modeling methods are widely used to study the operation of chemical reactors [4–6]. An important step in modeling the processes running in chemical reactors is to provide the models with the necessary quantitative information, i.e., identifying the parameters of mathematical models.

In general, the parameters of a mathematical model quantitatively characterize certain properties of a chemical engineering process. Notably, the parameters of all mathematical models of chemical engineering processes are mainly determined based on experimental studies, which can be complicated for a number of reasons. Statements and techniques for solving inverse problems [7–9] are therefore introduced to identify the parameters of mathematical models in chemical engineering processes.

This paper proposes a numerical method based on solving the inverse problem of perfect displacement in a chemical reactor to identify the rate constant of a second-order chemical reaction.

Problem statement and solution method

Consider a chemical reactor with perfect displacement, which is a tubular apparatus with a large ratio of the length of the tube to its diameter. Reagents are continuously supplied to the reactor, and the resulting flow moves in full displacement mode in a single direction along the length of the reactor. It is assumed that the reaction medium is not mixed along the reactor, as well as along its cross-section, and the parameter values of the reaction medium along the cross-section are the same. The reactor operates in isothermal mode, and a second-order reaction occurs when a certain distribution of reagent concentrations participating in the reaction is established along the length of the reactor.

A mathematical model for the transformation of one of the reagents as a result of a second-order chemical reaction occurring in a given chemical reactor with perfect displacement can be represented as a first-order nonlinear partial differential equation:

$$\frac{\partial C(x,t)}{\partial t} + v(t)\frac{\partial C(x,t)}{\partial x} + kC^2(x,t) = 0,\ 0 < x < l,\ 0 < t \le T, \tag{1}$$

where $C(x,t)$ is the concentration of the given reagent; $v(t)$ is the flow rate in the reactor; k is the rate constant of the chemical reaction; l is the length of the chemical reactor; x is the coordinate along which the reaction flow moves; t is the time.

Suppose that the initial and boundary conditions are given for Eq. (1)

$$C(x,0) = \varphi(x), 0 \le x \le l, \tag{2}$$

$$C(0,t) = p(t),\ 0 \le t \le T. \tag{3}$$

Evidently, if we set the functions $v(t)$, $\varphi(t)$, $p(t)$ and the value of the constant k, then by solving problem (1)–(3) we can find the function $C(x,t)$, i.e., the distribution of the reagent concentration along the length of the reactor.

Now let us assume the rate constant k is also unknown along with the function $C(x,t)$. Instead, an additional condition is set for the concentration of the reagent at the outlet of the reactor:

$$C(l,t) = r(t),\ 0 \le t \le T. \tag{4}$$

The problem consists in finding the function $C(x,t)$ and the parameter k satisfying Eq. (1) and conditions (2)–(4).

The formulated problem (1)–(4) belongs to the class of coefficient inverse problems of mathematical physics [9–11]. Notably, the existence of a solution and unique solvability of coefficient inverse problems for partial differential equations have been studied in [12, 13].

Assuming the existence of a solution and the unambiguous solvability of the coefficient inverse problem (1)–(4), we construct its discrete analogue by the method of difference approximation. For this purpose, we introduce a uniform space-time difference grid in a rectangular region $\{0 \le x \le l,\ 0 \le t \le T\}$

$$\overline{\omega} = \left\{(x_i, t_j) : x_i = i\Delta x,\ t_j = j\Delta t,\ i = 0,1,2,...,n,\ j = 0,1,2,...,m\right\},$$

where $\Delta x = l/n$ is the step of the difference grid with respect to the variable x, $\Delta t = T/m$ is the step of the difference grid with respect to time t.

A linear difference problem as a discrete analogue of problem (1)–(4) is obtained using explicit-implicit time approximations. To do this, the convective term in Eq. (1) is approximated implicitly, and the nonlinear term $kC^2(x,t)$ describing the course of the chemical reaction is approximated explicitly over time. As a result, we obtain the following system:

$$\frac{C_i^j - C_i^{j-1}}{\Delta t} + v^j \frac{C_i^j - C_{i-1}^j}{\Delta x} + k(C_i^{j-1})^2 = 0, \quad i = 1,2,...,n-1, \tag{5}$$

$$C_0^j = p^j, \tag{6}$$

$$C_n^j = r^j, \quad j = 1,2,...,m, \tag{7}$$

$$C_i^0 = \varphi_i, \tag{8}$$

where $C_i^j \approx C(x_i, t_j)$, $\nu^j = \nu(t_j)$, $p^j = p(t_j)$, $\varphi_i = \varphi(x_i)$, $r^j = r(t_j)$.

Apparently, the discrete analogue of problem (1)–(4) is a system of linear algebraic equations where the unknowns are the rate constant of the chemical reaction k and C_i^j, $i = 1, 2, ..., n - 1$, $j = 1, 2, ..., m$, i.e., the approximate values of the required function $C(x,t)$ in the nodes of the difference grid ω.

To solve the resulting system of equations (5)–(8), we introduce decomposition of this system into mutually independent subsystems, each of which can be solved independently of the other subsystem [9, 12]. Then the solution of the system of equations (5)–(8) for each fixed value of $j = 1, 2, ..., m$ can be represented as

$$C_i^j = U_i^j + kW_i^j, \quad i = 0,1,2,...,n, \tag{9}$$

where U_i^j, W_i^j and k are unknown variables.

Substituting relation (9) into Eq. (5), we obtain:

$$\frac{U_i^j + kW_i^j - C_i^{j-1}}{\Delta t} + \nu^j \frac{U_i^j + kW_i^j - U_{i-1}^j - kW_{i-1}^j}{\Delta x} + k(C_i^{j-1})^2 = 0,$$

or

$$\left[\frac{U_i^j - C_i^{j-1}}{\Delta t} + \nu^j \frac{U_i^j - U_{i-1}^j}{\Delta x}\right] + k\left[\frac{W_i^j}{\Delta t} + \nu^j \frac{W_i^j - W_{i-1}^j}{\Delta x} + (C_i^{j-1})^2\right] = 0.$$

Furthermore, substituting relation (9) into Eq. (6), we obtain

$$U_0^j + kW_0^j = p^j.$$

Since the variables U_i^j, W_i^j are arbitrary, we obtain the following independent systems of linear algebraic equations with respect to the variables U_i^j, W_i^j from the last two relations:

$$\frac{U_i^j - C_i^{j-1}}{\Delta t} + \nu^j \frac{U_i^j - U_{i-1}^j}{\Delta x} = 0, \quad i = 1,2,...,n, \tag{10}$$

$$U_0^j = p^j; \tag{11}$$

$$\frac{W_i^j}{\Delta t} + \nu^j \frac{W_i^j - W_{i-1}^j}{\Delta x} + (C_i^{j-1})^2 = 0, \quad i = 1,2,...,n, \tag{12}$$

$$W_0^j = 0, \quad j = 1,2,...,m \tag{13}$$

Evidently, the solutions to the system of linear equations (10), (11) and (12), (13) can be found by the recurrent formulas

$$U_i^j = \frac{C_i^{j-1} + U_{i-1}^j \nu^j \Delta t / \Delta x}{1 + \nu^j \Delta t / \Delta x}, \quad i = 1,2,...,n,\ U_0^j = p^j; \tag{14}$$

$$W_i^j = \frac{W_{i-1}^j \nu^j \Delta t / \Delta x - (C_i^{j-1})^2 \Delta t}{1 + \nu^j \Delta t / \Delta x}, \quad i = 1,2,...,n,\ W_0^j = 0,\ j = 1,2,...,m. \tag{15}$$

Substituting relation (9) into additional condition (7) produces the following equality:

$$U_n^j + kW_n^j = r^j.$$

We then obtain a formula for calculating the value of the parameter k for each fixed value of $j = 1, 2, ..., m$:

$$k = \frac{r^j - U_n^j}{W_n^j}. \tag{16}$$

Thus, the variables k and C_i^j ($i = 1, 2, ..., n-1$, $j = 1, 2, ..., m$) from the system of linear algebraic equations (5)–(8) are determined by constructing the following computational algorithm.

Step 1. Solutions of a system of linear algebraic equations (10), (11) and (12), (13) are determined for a fixed value of the time layer j by recurrent formulas (14) and (15).

Step 2. The approximate value of the required parameter k is determined by Eq. (16).

Step 3. The values of variables C_i^j, $i = 1, 2, ..., n$ are calculated by Eq. (9).

Step 4. This calculation technique is repeated in each subsequent layer.

Results of numerical calculations

The proposed numerical method was tested with various simulation problems to establish its practical applicability. Numerical experiments were carried out by the following algorithm.

I. The solution of the system of linear algebraic equations (5)–(8) is determined for the given values of the variables k, v^j, p^j, φ_i:

$$C_i^j = \frac{C_i^{j-1} + C_{i-1}^j v^j \Delta t / \Delta x - k(C_i^{j-1})^2 \Delta t}{1 + v^j \Delta t / \Delta x},$$
$$i = 1, 2, .., n,\ j = 1, 2, ..., m,$$
$$C_i^0 = \varphi_i,\ C_0^j = p^j.$$

II. The values of the variable r^j, defined as $r^j = C_n^j$, are taken as input data to reconstruct the value of the parameter k by the proposed computational algorithm.

Numerical experiments were carried out on a space-time difference grid with steps $\Delta t = 1$ s, $\Delta t = 5$ s, $\Delta x = 0.04$ m for the following exact values of the rate constant: $k = 0.25$, 0.55 m^3/(kg·s).

The following data were used for the remaining parameters of model (1)–(4):

$$\varphi(x) = 0.1 \text{ kg/m}^3,\ p(t) = 0.8 \text{ kg/m}^3,\ v = 0.4 \text{ m/s},\ l = 2 \text{ m}.$$

Perturbed input data were also used along with unperturbed input data in the numerical experiments.

The following ratio was used to perturbate the input data r^j

$$\tilde{r}^j = r^j + \delta \xi^j r^j,$$

where ξ^j is a random variable modeled with a random number sensor; δ is the error level of the input data ($\delta = 0.02$ was used).

The results of numerical experiments conducted with unperturbed and perturbed input data are given in Table.

Analyzing the results, we can conclude that the value of the required rate constant is reconstructed exactly if unperturbed input data are used, regardless of the time step of the difference grid Δt, (second and third columns in Table). However, perturbed input data where the error is random affect the accuracy of reconstructing the value of the required constant (the remaining columns in Table). The reconstruction error of the required rate constant value depends on the time step of the difference grid Δt. It follows from the data in Table that the relative reconstruction errors of $k_e = 0.25$ and 0.55 m^3/(kg·s) exceed 10% and 6.5%, respectively, for the time step $\Delta t = 1$ s. However, the maximum relative reconstruction errors of $k_e = 0.25$ and 0.55 m^3/(kg·s) do not exceed 3.5 and 2.2%, respectively, for the step $\Delta t = 5$ s.

Table

Numerical search for value of rate constant k with variable input data

t, s	Calculated k, $m^3/(kg \cdot s)$, with different input data					
	Unperturbed		Perturbed			
	$k_e = 0.25$ $m^3/(kg \cdot s)$	$k_e = 0.55$ $m^3/(kg \cdot s)$	$k_e = 0.25$ $m^3/(kg \cdot s)$		$k_e = 0.55$ $m^3/(kg \cdot s)$	
			$\Delta t = 1$ s	$\Delta t = 5$ s	$\Delta t = 1$ s	$\Delta t = 5$ s
5	0.250	0.550	0.235	0.250	0.532	0.545
10			0.245	0.250	0.543	0.544
15			0.276	0.242	0.584	0.545
20			0.261	0.247	0.563	0.542
25			0.249	0.247	0.548	0.546
30			0.266	0.244	0.570	0.542
35			0.226	0.246	0.515	0.540
40			0.263	0.248	0.579	0.544
45			0.225	0.246	0.515	0.544
50			0.246	0.246	0.542	0.538

Preset parameters: k_e is the exact value of the constant k, t is the time, Δt is the step on the space-time difference grid.

The results of numerical experiments indicate that the time step of the difference grid Δt acts as a regularization parameter (self-regularization) [8, 9], so that the reconstruction accuracy of the required constant increases with increasing Δt.

Analysis of the obtained results confirms that self-regularization can be used to reduce the influence of the error in the input data on the reconstruction accuracy of the required rate constant, therefore making the proposed computational algorithm more robust against input data errors.

Conclusion

We considered the problem of identifying the rate constant of a second-order chemical reaction occurring in a perfect displacement reactor. We adopted a numerical method based on discretization and special decomposition to solve the resulting system of linear algebraic equations. This method allows to determine the rate constant of a chemical reaction with a sufficiently high accuracy. The proposed numerical method can also be used to identify the hydrodynamic parameters of the flow in a perfect displacement chemical reactor.

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