International Journal of Engineering & Technology, *7 (3.27) (2018) 556-560*

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Direct Modeling of Chemical Processes in Conditions of Uncertainty of Initial Data

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Abstract

The paper studies the influence of uncertainty in kinetic parameters on the results of solving the direct problem of chemical kinetics. The direct problem of chemical kinetics is a calculation of multicomponent reacting-mix composition and speed of reaction on the basis of the set mathematical model with known parameters. Kinetic data are represented in intervals and are considered as objects of interval analysis. The computational experiment was carried out for the reactions proceeding without the change of reaction volume (reaction of reception of phthalic anhydride) and taking into account its change (reaction of oligomerization of α-methylstyrene). On the basis of methods of interval analysis the boundaries of solution of the direct problem of chemical kinetics caused by interval representation of kinetic parameters are obtained. In the example of reaction of oligomerization of α-methylstyrene, during which there is a change of the number of moles of a reaction mixture, and reaction of reception of phthalic dioxide flowing with constant reaction volume, various ways of construction are considered in interval expansion of the right parts of the differential equations that determine the type of kinetic model of the reactions studied.

Keywords: *interval analysis, kinetic parameters, optimal two-sided solution..*

1. Introduction

The kinetic model is the initial level in the mathematical modeling of chemical processes. The kinetic model determines the speed of reaction and generally turns on the reaction mechanism, equations of speed of separate stages, kinetic parameters of the model (rate constants and activation energies) and some additional simplifying regulations on a role of separate stages. Substance concentration change dynamics can be described by kinetic curves of an expenditure or formation of reaction reagents and products. For this purpose it is required to solve a direct kinetic problem. The direct problem of chemical kinetics is a calculation of multicomponent reacting-mix composition and speed of reaction on the basis of the set mathematical model with known parameters.

The paper studies the influence of uncertainty in kinetic parameters on the results of solving the direct problem of chemical kinetics. Kinetic data are represented in intervals and are considered as objects of interval analysis. A modified method of interval sensitivity analysis was used to solve the direct kinetic problem [1], [2], [3]. The main idea of this method is to analyze partial derivatives of the parameter solution. For the implementation of this method the technique of interval analysis is used.

In work [1] it is shown that the problem of not uniqueness of the solution of the inverse problem of determination of kinetic parameters can be solved by reduction of the generally accepted statement of the given problem, to a kind according to which the area becomes the solution, arbitrary variation of kinetic constants of speeds in which the demanded quality of the description of experiment is kept. One of the approaches to determine the desired area is based on the application of the computational apparatus of interval analysis to calculate the uncertainty intervals of kinetic parameters [2].

2. Methods

The kinetic model of a reaction proceeding without a change in the reaction volume has the form of a system

$$\frac{dx_i}{dt} = F_i(t,x,k) = f_i(t,x,k)\text{, } i=1,\ldots,n, \qquad (1)$$

with initial conditions at t=0: $x_i(0) = x_i^0$, i=1,…,n, где $t \in [0;l]$ – reaction time (hour); $x = (x_1,\ldots,x_n)^T$ – vector of component concentrations (mole fractions); $k = (k_1,\ldots,k_m)^T$ – vector of parameters – kinetic rate constants of the j-th reaction. The right sides of the ordinary differential equation of the system (1) are formed according to the law of mass action based on a pattern specified reaction steps [4].

While working out a mathematical description of a reaction, taking into account the changes of the mole number in its process (a conclusion on an inconsistent reaction volume is made on the basis of an analysis of the matrix stoichiometric reaction coefficients) [5], the ODE system can be given as

$$\frac{dx_i}{dt} = \frac{F_i - x_i F_n}{N} = f_i(t,x,k),\ i=1,\ldots,n,\ \frac{dN}{dt} = F_N = f_{n+1}(t,x,k) \qquad (2)$$

,

with initial conditions, $x_i(0)=x_i^0,\, i=1,\ldots,n,\ N(0)=1$.

We shall seek the solution of the systems (1), (2) in the form $x=(x_1,\ldots,x_n)^T \in \mathbf{x}$, where $x_i=[x_i]=\{x_i \in R \mid \underline{x}_i \le x_i \le \overline{x}_i\}$, $\underline{x}_i$, $\overline{x}_i$ - are the lower upper bounds of the components of the unknown vector, respectively [6]. The vector of constants of reaction rates $k=(k_1,\ldots,k_m)^T \in \mathbf{k}$ is characterized by a similar representation. We use the concepts of isotonicity and monotonicity of the function on variables in the construction of an algorithm for interval solution of the Cauchy problem with given initial conditions [7]. Then when the conditions are met

$$\frac{\partial f_i}{\partial x_j} \ne 0,\ i \ne j,\ i,j=1,\ldots,n, \tag{3}$$

$$sign\frac{df_i}{dk_j}=const,\ j: wid(\mathbf{k}_j)\ne 0, \\ \forall k \in \mathbf{k},\ \forall x \in \mathbf{x},\ i=1,\ldots,n, \\ j=1,\ldots,m \tag{4}$$

The system (1) can be rewritten as follows

$$\underline{x}'=f(t,\underline{x},k^1),\ \overline{x}'=f(t,\overline{x},k^2), \\ \underline{x}(0)=\underline{x}_0,\ \overline{x}(0)=\overline{x}_0, \tag{5}$$

Where $wid(\mathbf{k}_j)$ - width of interval value, $k^i \in \mathbf{k}$; $\underline{x}$ and $\overline{x}$ - some particular solutions of the original system. For the ordinary differential equation system (1), the following expressions are valid for the entire reaction time interval $sign\dfrac{\partial f_i}{\partial k_j}=const$, $i=1,\ldots,n$, $j=1,\ldots,m$ and $sign\dfrac{\partial f_i}{\partial x_j}=const$, $i,j=1,\ldots,n$, $i\ne j$. Then the system (1) can be represented through two independent subsystems with initial conditions $\underline{x}_i(0)=\underline{x}_{i0}$, $\overline{x}_i(0)=\overline{x}_{i0}$, the parallel solution of one of which gives the lower, the other – the upper boundaries of the two-sided solution of the system (1) with known initial conditions

For the reactions accounting for the mole number changes, the direct problem solution based on the above given estimation of the private derivative right parts of the ODE according to the variable and kinetic parameters is impossible [8], [9]. Let's apply another algorithm to search for an interval solution. To estimate $\overline{x}^{(i)}$ - upper boundary of $\mathrm{x}(t)$ on i coordinate, $\overline{x}^{(i)} \ge x_i$ - let's study the system

$$\tilde{x}'=f(t,\tilde{x},\tilde{k}),\ \tilde{x}\in\tilde{\mathrm{x}},\ \tilde{k}\in\tilde{\mathrm{k}}, \\ \tilde{x}(0)=\tilde{x}_0\in\tilde{\mathrm{x}}_0, \text{ where} \tag{6}$$

$$\mathrm{k}_j=\begin{cases}\overline{k}_j, & \text{если } \mathrm{x}_{ij}^k(t)\le 0,\\ \underline{k}_j, & \text{если } \mathrm{x}_{ij}^k(t)\ge 0,\\ \mathrm{k}_j, & \text{если } 0\in \mathrm{x}_{ij}^k(t),\end{cases} \tag{7}$$

$$\mathrm{x}_0=\begin{cases}\overline{x}_{0j}, & \text{если } \mathrm{x}_{ij}^0(t)\le 0,\\ \underline{x}_{0j}, & \text{если } \mathrm{x}_{ij}^0(t)\ge 0,\\ \mathrm{x}_0, & \text{если } 0\in \mathrm{x}_{ij}^0(t),\end{cases} \tag{8}$$

where $\mathrm{x}_{ij}^k(t)$ and $\mathrm{x}_{ij}^0(t)$ - are interval extensions $\partial x_i/\partial k_j$ and $\partial x_i/\partial x_{0j}$ correspondingly the interval functions $\mathrm{x}_{ij}^k(t)$, $\mathrm{x}_{ij}^0(t)$ can be defined solving system (6) and systems simultaneously [10]:

$$x_{ij}^{k\,\prime}=\sum_{l=1}^{n}\frac{\partial f_i}{\partial x_l}(t,x,k)x_{lj}^k+\frac{\partial f_i}{\partial k_j}(t,x,k),\ x_{ij}^k(0)=0, \\ i=1,\ldots,6,\ j=1,\ldots,12, \tag{9}$$

$$x_{ij}^{0\,\prime}=\sum_{l=1}^{n}\frac{\partial f_i}{\partial x_{x_l}}(t,x,k)x_{lj}^0,\quad x_{ij}^0(0)=\delta_{ij}, \\ i,j=1,\ldots,6, \tag{10}$$

Where δ_{ij} - Kronecker symbol.

To solve systems (9)-(10) an integral interval extension is based on the following principle. The interval variables are checked cyclically, their width is not zero. Let's make a change of an interval value for a value of its lower and upper boundaries according to the private derivative sign for the variables which helped to define zero "not introduction" into the interval. The cycle is continued till the condition of zero "not introduction" remains efficient for at least once on one of the variables and the interval narrowing takes place [11], [12]. If the intervals $\mathrm{x}_{ij}^k(t)$, $\mathrm{x}_{ij}^0(t)$ don't contain zero then system (6) doesn't contain interval parameters and can be solved by a two-sided method with a certain accuracy. Otherwise, a natural widening of right parts of the system can be observed.

Meeting the conditions $0\notin\dfrac{\partial f_i}{\partial x_{k_j}}(0,\mathrm{x}^0,\mathrm{k})$, $0\notin\dfrac{\partial f_i}{\partial x_{x_k}}(0,\mathrm{x}^0,\mathrm{k})$, we can speak about such time intervals t_0 when $0\notin \mathrm{x}_{ij}^k(t)$, $0\notin \mathrm{x}_{ij}^0(t)$. Till time interval t_0 the boundaries of the solutions are considered efficient.

3. Results and Discussion

The computational experiment was carried out for the reactions proceeding without the change of reaction volume (reaction of reception of phthalic anhydride) and taking into account its change (reaction of oligomerization of α-methylstyrene).

We will carry out the sensitivity analysis on the example of the reaction of receiving phthalic anhydride proceeding, without the change of reaction volume. It should be noted that the technique given here is applicable to the reactions proceeding with change of reaction environment mole number. We will enter the following designations: A_1 - naphthalene (initial substance), A_2 - naphthoquinone, A_3 - target product - phthalic anhydride, A_4 - carbon dioxide, A_5 - maleic anhydride. A set of the chemical transformations describing the reaction taking into account the entered designations is represented the following scheme of stages:

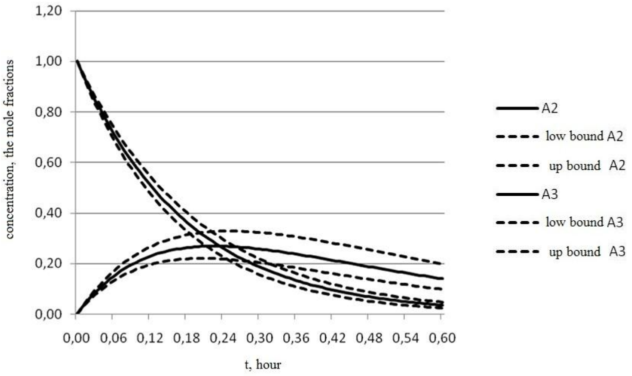
$$A_1 \to A_2,\qquad A_2 \to A_4,\qquad A_1 \to A_3,$$
$$A_1 \to A_4,\qquad A_2 \to A_3,\qquad A_3 \to A_5.$$

The reaction proceeds without a change in reaction volume, as evidenced by the last row of the matrix. Then the differential equation system describing the reaction kinetics is of the form:

$$\frac{dx_i}{dt} = f_i(t,\mathrm{x},\mathrm{k}),\quad t\in[0;0.6], \qquad (11)$$
$$x_i(0) = x_i^0,\ i=\overline{1,5}.$$

In the first case, the calculating experiment was held at the initial substance concentrations $x_1(0)=1$, $x_i(0)=0$, i=2,…,5, the reaction period $t\in[0;0,6]$ hours and temperature T=347 °C. The kinetic constants for this process have the form (12). The variation of kinetic constants was carried out within 10% when constructing the boundaries of the two-way solution of the system (1). The graphic two-sided solution of the direct problem for the considered reaction is presented in pic. 1. Variation of kinetic constants results in an interval value of substance concentration with an accuracy for an exact solution of the direct problem: A_1 - 34,43%, A_2 - 36,43%, A_3 - 26,82%, A_4 - 25,99%, A_5 - 32,63%.

$$\begin{aligned} \boldsymbol{k}_1 &= [3.19324;\ 3.39076] \\ \boldsymbol{k}_2 &= [0.61789;\ 0.65611] \\ \boldsymbol{k}_3 &= [1.78577;\ 1.89623] \\ \boldsymbol{k}_4 &= [0.48209;\ 0.51191] \\ \boldsymbol{k}_5 &= [2.71309;\ 2.88091] \\ \boldsymbol{k}_6 &= [0.03589;\ 0.03811] \end{aligned} \qquad (21)$$

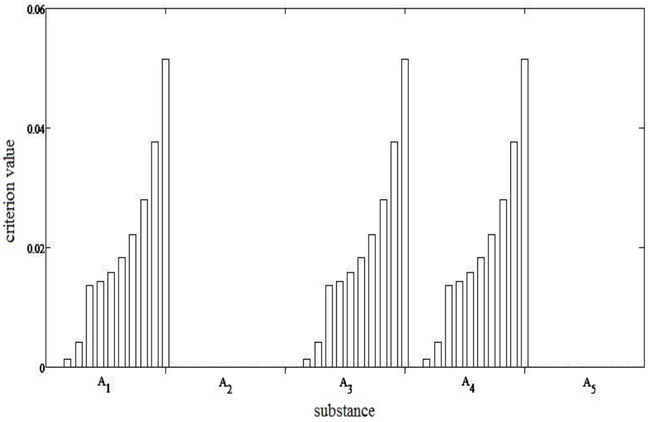


Pic. 1:. Changing of the concentration of naphthalene and naphthoquinone

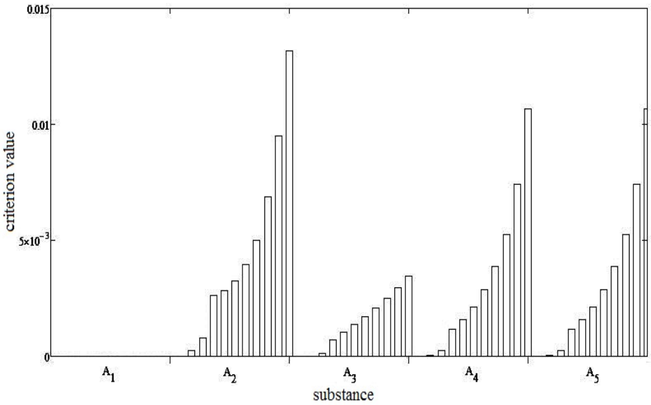
Also in this study we analyzed the influence of variation in values of constant reaction concentrations preparation of phthalic anhydride.

Analysis shows that the concentration of the reaction products A_2, A_5 are insensitive to changes in the parameter k_1, thus influence of its change in limits of the considered uncertainty interval on concentration of substances A_1, A_3, A_4 occurs practically equally. The greatest influence_of the rate constant k_2 is happening in relation to changes in the concentration of substance A_2, and only one of the five substances A_1 is independent of its variation. The rate constant k_3 does not affect the concentration A_2, but retains influence on the dynamics of the remaining reagents.

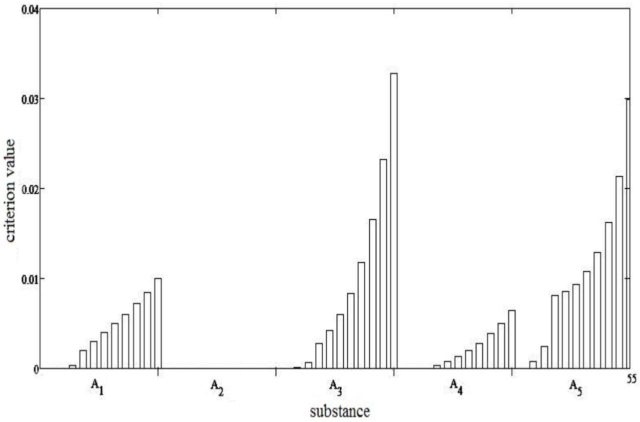
The rate constant k_4 is the only parameter whose change doesn't remain traceless at reaction course, though extent of its influence on concentration is rather small. The rate constant k_5 makes the maximum impact on substance A_2, not affecting the output A_4, A_5. The rate constant k_6 has the least impact on the course of the reaction. Change of concentration of a target product depends on degree of variation of all constants at the same time, thus, as expected, the rate constants k_1, k_2 and k_4 have the greatest impact.



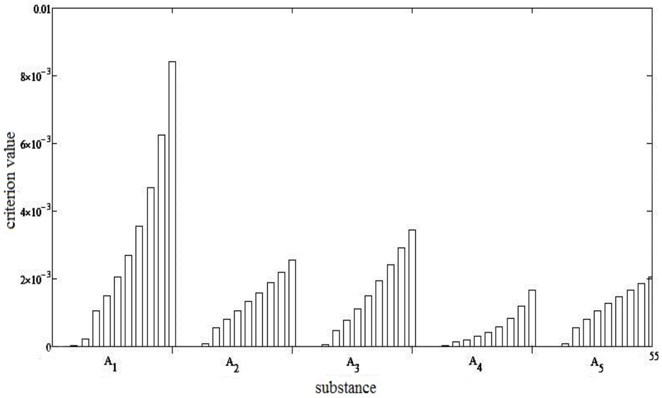
Pic. 2:. Sensitivity of reagent and product concentrations of phthalic anhydride to kinetic parameters k_1



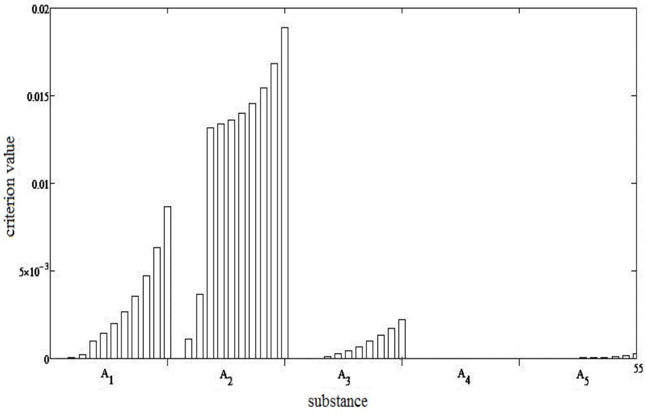
Pic. 3:. Sensitivity of reagent and product concentrations of phthalic anhydride to kinetic parameters k_2.



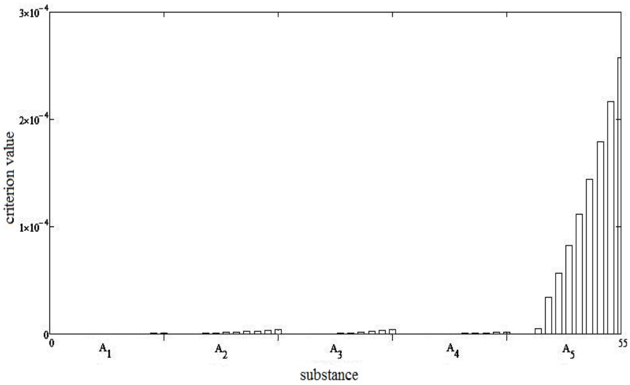
Pic. 4:. Sensitivity of reagent and product concentrations of phthalic anhydride to kinetic parameters k_3



Pic. 5:. Sensitivity of reagent and product concentrations of phthalic anhydride to kinetic parameters k_4.

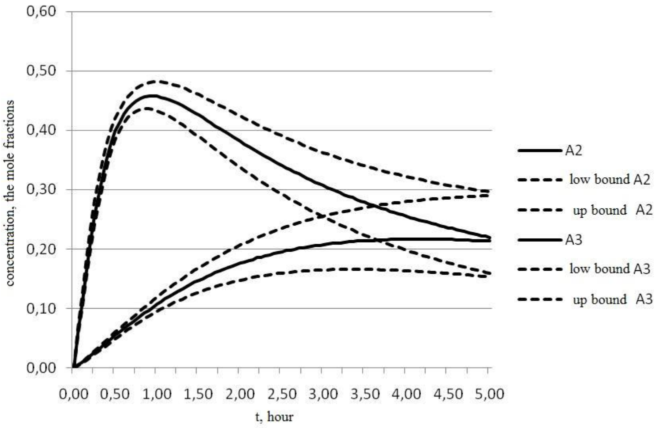


Pic. 6:. Sensitivity of reagent and product concentrations of phthalic anhydride to kinetic parameters k_5.



Pic. 7:. Sensitivity of reagent and product concentrations of phthalic anhydride to kinetic parameters k_6.

In the second case, the calculating experiment was held at the initial substance concentrations $x_1(0)=1$, $x_i(0)=0$, i=2,…,5, $x_N(0)=1$ and the reaction period $t\in[0;5]$ hours. When solving the direct problem with an interval method of responsive analysis numeric values of kinetic constants were used, obtained by the solution of an inverse kinetic problem based on the mathematical description of the process and experimental data obtained in the temperature-controlled laboratory reactor equipped with a discontinuous mixer at 80 °C and 10% catalyzer "Ceocar-10" concentration [13]. Picture 8 demonstrates a graphic solution of the direct kinetic problem. Variation of kinetic constants results in an interval value of substance concentration with an accuracy for an exact solution of the direct problem: A_1 - 10,16%, A_2 - 30,95%, A_3 - 31,85%, A_4 - 22,47%, A_5 - 18%. Till the time interval t0=0,45 hours, the solution can be considered efficient.



Pic. 8:. Changing of the concentration 4-methyl-2,4 diphenylpenten-1 and 4-methyl-2,4 diphenylpenten

4. Summary

Analyzing the results obtained by changing the porosity of the kinetic parameters in the range from 5% to 10%, we can assume that the variation of the kinetic data is not the crew dynamics grid, while the output of the main products is sensitive to porosity on average by no more than 16% -33% - for the first, 15% -30% - for the second reaction. In addition, increasing the error in the kinetic parameters reduces the time interval at which it is possible to build the optimal boundaries of the set of solutions of the direct problem by the method of interval sensitivity analysis.

5. Conclusions

Thus, on the basis of the interval analysis methods the boundaries of the chemical kinetics direct problem solution were obtained. The result analysis gained under the accuracy measurement of kinetic parameters in the range of 5% to 10% lets us conclude that kinetic data variations do not influence the dynamics of the curves, while the basic product yield is sensitive to the accuracy of not more than 15%-30% in average. Besides, when increasing the accuracy in kinetic parameters the time interval decreases. It gives an opportunity to model efficient boundaries of a number of direct problem solutions with the interval response analysis method.

Acknowledgements

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University and the study was funded by RFBR according to the research project №17-47-020068 and project №18-38-00255.

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