Program for modelling the kinetics of chemical reactions in a cascade of reactors

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Abstract. An algorithm for solving the direct kinetic problem in a cascade of reactors is developed, based on explicit and implicit numerical methods for solving the Cauchy problem. The program is implemented in Borland Delphi environment. There are ability to compile kinetic models of various catalytic processes based on the law of the acting masses in the software package. The software package can be used to simulate the kinetics of an industrial process in a cascade of reactors of ideal mixing of periodic action and ideal displacement.

1. Introduction

Mathematical modeling of chemical processes and reactors is a coherent system of concepts and methods, the application of which has already allowed solving a number of important scientific and technical problems in the development of technological processes and devices. The production of most chemical and petrochemical products is based on catalysis. Methodological bases for modeling catalytic processes were laid down in the works of Russian scientists - Academician G.K. Boreskov and Corresponding Member of the Russian Academy of Sciences M.G. Slinko, as well as foreign researchers N.A. Amundson, R. Aris. They are based on the general scheme of mathematical modeling formulated by Academician A.A. Samarsky.

The first level of modeling is the kinetic model, the construction of which can take place in various ways. Almost all catalytic reactions proceed with changes in reaction volume or number of reactive substance molecules. In the literature this fact, as a rule, is ignored that leads to model inaccuracy and necessity of model parameters correction at development of concrete industrial processes. As shown in the works of A.V. Balayev, S.A. Mustafina, S.I. Spivak, considering changes in the number of molecules, the model becomes more correct and the laws of heat and substance conservation are observed.

The information generated at each simulation level becomes an integral part of the following level: modeling of grain and layer of catalyst, reactor and the whole technological scheme.

At the present time the possibilities of increasing the productivity of reactors at the expense of increasing their sizes are practically over, in this case the task of intensification of catalytic processes at the expense of new ways of their conducting, which is realization of optimal managing is stated. A considerable number of works by G.K. Boreskov, M.G. Slinko, K. Denbig, A.I. Boyarinov, V.V. Kafarov, G.M. Ostrovsky, Y.M. Volin, V.I. Bykov, S.I. Spivak, S.A. Mustafina and others are devoted to the development of methods of catalytic processes optimization.
The task of optimizing the catalytic process is solved in two stages: at the first stage, the analysis of the kinetic model is performed and process limit values are determined; at the second stage, technological optimization is carried out by selecting the optimal design and operating parameters of reactors [1-3].

The problems of creating an exact mathematical formulation of the task of optimal control, search of an effective way of solving the task, creation of program shells for conducting computational experiments remain actual.

2. Problem formulation

The basis of the kinetic equations of chemical reactions is the provision on the independence of elementary reactions, i.e. a chemical reaction can be written in the form of

$$\sum_{i=1}^{m} v_j X_i = 0, \quad j = 1, n,$$

(1)

where $X_i$ - reactive substances, $v_j$ - stoichiometric ratio at the component $X_i$ in $j$-stage, $m$ - number of substances, $n$ - number of elementary stages.

According to the law of active masses, the reaction rate is proportional to the product of reagent concentrations in the degrees of their stoichiometric coefficients:

$$r_j = k^+ \prod_{i=1}^{N_j^A} C_i^{v_{ij}^+} - k^- \prod_{i=1}^{N_j^B} C_i^{v_{ij}^-},$$

(2)

where $C_i$ - molar concentrations $X_i$; $N_j^A$ - source numbers of stage $j$ (index $A$ stands for multiple inputs); $N_j^B$ - product numbers of stage $j$ (index $B$ stands for multiple substances in the reaction products); $k^+$, $k^-$ - kinetic constants of forward and backward reaction rates respectively, which are determined by the Arrhenius equation

$$k = k^0 e^{-\frac{E}{RT}},$$

(3)

where $k^0$ - preexponential factor; $E$ - activation energy for the appropriate stage, $R$ - universal gas constant; $T$ - reaction temperature.

The reaction speed for the $i$-component is expressed by changing the quantity of this component in a unit of time in a unit of reaction space ($V$).

$$\omega_i = \frac{1}{V} \frac{dN_i}{dt}.$$

(4)

By means of the ratio

$$N_i = VC_i,$$

(5)

reaction speed can be rewritten as

$$\omega_i = \frac{1}{V} \frac{d(VC_i)}{dt} = \frac{1}{V} \frac{C_i dV + VdC_i}{dt},$$

(6)

and if the volume of the reaction mixture in the process of the chemical reaction is virtually unchanged ($dV=0$) speed takes shape

$$\omega_i = \frac{dC_i}{dt}.$$

(7)

This definition is widely spread in the literature, but cannot serve as a general definition of speed, because the $dC_i/dt$ value is related not only to the number of acts of chemical transformation, but also to the law by which the volume of the system changes. And it can be done in an arbitrary form. For
example, when a reaction is realized in a cylinder with a piston, the system volume can be arbitrarily changed out of any connection with the chemical transformation.

In practice, in the process of gas reactions there are cases when the number of molecules in the reaction changes and the system pressure is kept constant. That’s why at development of mathematical description of complex process it's necessary to take into account change of number of molecules in reaction mixture [4].

To determine whether such a change exists, the matrix of stoichiometric coefficients determines the components of the vector \( \delta \)

\[
\delta_j = \sum_{i=1}^{m} v_{ij}, \quad j = 1, n,
\]

if at least one of them is different to zero, the change happens.

According to the law of mass preservation, the total material balance for the variant where the total concentration \( C = \sum_{i=1}^{m} C_i \) changes over time is as follows

\[
\frac{dC_i}{dt} = \sum_{j=1}^{n} v_{ij} r_j, \quad i = 1, m,
\]

Let’s move on to the concentrations of substances in molar fractions \( x_i = \frac{C_i}{C} \) and supplement the system with the condition of normalization of the components of the reaction medium:

\[
\sum_{i=1}^{m} x_i = 1.
\]

The initial molar density of the reaction medium \( (C_o) \) is constant at all temperatures. Then, having divided (9) on \( C_o \), we will receive system of the differential equations

\[
\frac{dx_i}{dt} = \frac{F_i - x_i F_N}{N}, \quad F_i = \sum_{j=1}^{n} v_{ij} W_j,
\]

\[
\frac{dN}{dt} = F_N, \quad F_N = \sum_{j=1}^{n} \delta_j W_j,
\]

where \( N = C/C_o \) – relative variation in the reaction medium molecular weight, \( W_j = r_j/C_o \) - given chemical reaction rates, with initial conditions

\[
x_i(0) = x_i^0, \quad i = 1, m, \quad N(0) = 1.
\]

Thus, we obtain a kinetic model taking into account the change in the number of molecules of the reaction medium of the process in the form of equations (11)-(12).

The next stage of modeling is calculation of material and thermal balance of the process in the reactor.

2.1. Mathematical model of process in ideal mixing reactor

Ideal mixing reactors can be continuously or periodically operating. In the first case, reagents are continuously fed into the reactor and a mixture of reaction products and non-reactive reagents is removed. The intermittent reactor is simultaneously loaded with all types of initial substances or their mixture and after a certain time required to achieve a given degree of completeness of the process, the production mixture is unloaded. The process of functioning is a periodically recurring cycle. Periodical processes are used as an integral part of the chain of operations, as well as in such reactors,
as a rule, low-tonnage processes are conducted. In the created program the reactor of ideal mixture of periodic action (IMR) is considered.

In developing a mathematical model, it's accepted that:

- there is no gradient in the properties of the reaction medium in the entire volume of the reaction space at a given moment in time; the process is assumed to be carried out with a sufficiently energetic stirring (500-600 rpm);
- the total mass in the IMR is constant; other characteristics (composition, temperature) change only in time;
- the reaction is for the fresh catalyst, i.e. the process of deactivation of the catalyst is not taken into account;
- internal and external diffusion processes do not slow down the process. This is because a finely dispersed catalyst with a grain diameter of ~0.1 mm is used. The presence of the catalyst is taken into account in the values of kinetic constants of the reaction.

As the values of physical quantities are the same in the entire reaction volume, the material and heat balance equations can be written for the reactor as a whole [5].

As equations of material balance of IMR we use the kinetic model of reaction (11)-(12).

Thermal balance equation is

\[ C_p \frac{dT}{dt} = \sum_{j=1}^{n} Q_j W_j(x,T) + \frac{\alpha_x S_x}{C_0} (T_x - T) \]

\[ G_x C_x \frac{dT_x}{dt} = \alpha_x S_x (T - T_x), \]

with initial conditions

\[ T(0) = T_0, \quad T_x(0) = T_{x0}. \]

where \( T \) and \( T_x \) - reaction and refrigerant temperatures; \( C_p \) - molar reaction mixture heat capacity; \( Q_j \) - heat effects of reactions; \( \alpha_x \) - heat transfer coefficient; \( S_x \) - specific heat dissipation; \( C_x \) - molar refrigerant capacity; \( G_x \) - molar refrigerant flow.

2.2. Mathematical model of process in the reactor of ideal displacement.

When developing a mathematical description of the process in a tube reactor, the following assumptions were made:

- diffusion does not have a significant effect on the process flow;
- evenly distributed reaction flow over the reactor cross-section;
- the reactor ensures perfect contact of raw materials with the catalyst;
- changes in catalyst properties over time are not considered.

The material balance equations on the basis of the kinetic model (11)-(12) are as follows [6]

\[ \frac{1}{S} \frac{dx_i}{dl} = \frac{F_i - x_i F_N}{N}, \quad F_i = \frac{1}{\theta C_0} \sum_{j=1}^{n} v_{ij} r_j, \quad i = 1, m, \]

\[ \frac{1}{S} \frac{dN}{dl} = F_N, \quad F_N = \frac{1}{\theta C_0} \sum_{j=1}^{n} \delta_j f_j, \]

where \( S \) - cross-sectional area; \( x_i = N_i / N \), \( N = \sum N_i \) - total reaction mixture molar flow \( (N(0)=N_0) \); \( N_i = \theta \cdot C_i \) - molar i-flow; \( \theta \) - volumetric flow speed; \( l \) - reactor length; \( \overline{N} = N / N_0 \) - relative flow rate of reaction.

Thermal balance of the reactor is described by equations [7-8]
\[
\frac{C_p \cdot N}{S} \frac{dT}{dl} = \sum_{j=1}^{n} \frac{Q_j}{\theta C_0} + \frac{\alpha_S}{\bar{C}_0} (T_s - T),
\]

\[
\frac{G_x}{S} \frac{dT_x}{dl} = \alpha_x S_x (T - T_x),
\]

(16)

where \( G_x \) - molar refrigerant feed speed.

The system of equations (15)-(16) is added to the initial conditions

\[ l = 0: \quad x_i = x_i^0, \quad i = 1, \bar{m}, \quad \bar{N} = N^0, \quad T = T^0, \quad T_x = T_x^0. \]

For the further investigation we will move on to dimensionless variables and introduce additional upper indexation by reactor sequence. Then the material balance of the system in the \( j \) reactor is presented as equations [9]

\[
\frac{dx_j^i}{d\xi_j^j} = f_j^i(x, T), \quad i = 1, \bar{m} + 1, \quad 0 \leq \xi_j^j \leq 1,
\]

\[
\frac{dT_j^j}{d\xi_j^j} = f_{m+2}^j(x, T, T_x),
\]

\[
\frac{dT_x^j}{d\xi_j^j} = f_{m+3}^j(x, T, T_x), \quad j = 1, \bar{R}.
\]

(18)

where the right side \( f^j \) depends on the type of reactor; \( x_j^i \) - molar fraction of the \( i \)-th reagent in the \( j \) reactor; \( x_{m+1}^j \) - relative variation in the reaction medium molecule count in the \( j \)-reactor; \( \xi^j \) - residence time in \( j \)-core for the perfect mixing reactor or length of \( j \)-core for the perfect displacing reactor (dimensionless); \( T_j^j, T_x^j \) - reaction mixture and refrigerant temperature in the \( j \)-reactor; \( \bar{R} \) - reactor cascade number.

The system (18) closes the boundary conditions

\[ x_j^1(0) = x_i^0, \quad T_j^1(0) = T^0, \]

\[ x_j^{i+1}(0) = x_j^i(1), \quad T_j^{i+1}(0) = T_j^i(1), \]

(19)

it shows that the output of one reactor is the input for the next reactor. Thus, the mathematical model of the process in the reactor cascade is presented as a system of equations (18)-(19).

3. Programme overview

On the bases of the presented mathematical models with the use of various explicit and implicit numerical methods for solving the Cauchy problem (for each reactor in the chain) a program complex in the language of Borland Delphi.

The scheme of the complex is shown in figure 1.

On the main form of the program (figure 2) it is necessary to specify the mechanism of the investigated chemical reaction. Then user sets all kinetic parameters on the basis of which kinetic model is automatically generated (by formulas (11)). The kinetic model can be viewed and edited by the user if necessary (figure 3). Then the data are translated into program code and form a dll-library file, which is an independent element and can be used in other applications.

On the second tab of the form, all parameters presented in the kinetic model are set. Next tab (figure 4) contains description of reactor or reactor cascade with indication of regime parameters.

At the next stage, the process is calculated by some numerical method (from the existing set of methods, organized with the possibility of adding new algorithms) [10].
Figure 1. Logical scheme of the program complex.

Figure 2. Start tab of the program complex.

Figure 3. Forms of input of reaction mechanism and speed editing of stages.
Solving the problem numerically, it is important to investigate the stability of the used numerical algorithm. There are problems for which the question of stability of the used method is the most acute and requires great differentiation, the so-called rigid systems. Such tasks arising in different applied fields have been the object of increased attention of specialists in computational mathematics for the last decades and serve as a means on which notions, formulations, methods, algorithms and programs are honed. The essence of the phenomenon of rigidity is that the solution to be calculated changes slowly but there are quickly fading perturbations. The presence of such perturbations makes it difficult to obtain a slowly changing numerical solution. Problems of chemical kinetics are often rigid, due to the different orders of kinetic constants. Practice has shown that it is more effective to use implicit methods for solving rigid systems. But the phenomenon of rigidity is connected with the interval of investigation (one and the same system on different areas of investigation can be both rigid and non-rigid), so the explicit methods of calculation are also of interest.

The program complex was tested on the catalytic dimerization process $\alpha$-methyl styrene in the presence of NaH-form catalyst Y. The results of computational experiments are presented in the paper [9].

The program complex is based on the modular construction principle: the program consists of several parts - computational blocks and equations of communication between them. Each computing block serves as a description of one element - reactor, calculation algorithm or optimization algorithm, and is designed so that it does not depend on where the input information comes from or how it is used in the future. In such an organization the main load is borne by the organizing part of the program, which must provide interconnected operation of the blocks. Independence of computing blocks and modular principle of construction will allow to expand the bases containing descriptions of processes and devices, and freely connect them at any stage of work.

4. References

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