Information-analytical system of chemical technology processes modeling by the use of parallel calculations

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Abstract. An information-analytical system for modelling of chemical technology processes by the use of parallel computing has been developed. On the basis of this system a kinetic model for the synthesis of benzylidene benzylamine has been built. The optimal conditions to maximum yield of target product were found.

1. Introduction

In order to explore mechanisms for chemical technology processes, the kinetic models should be developed. The development of a kinetic model requires solving the inverse kinetic task. This stage the most laborious and time consuming [1-4]. The use of parallel computing is becoming increasingly instrumental method of mathematical processing of experimental data [5, 6].

Inverse chemical kinetics problems suppose a significant amount of computation. The use of high-performance computing systems has fundamentally changed the ability to analyze complex chemical processes. A detailed analysis of rather complex kinetic models with a large amount of experimental information became available. The time required to build kinetic models has been significantly reduced. The accuracy of solutions has been improved.

Authors of this work has developed and tested the information-analytical system for modeling chemical technology processes. On the basis of the technology of parallel calculations the actual method of search of kinetic parameters is offered.

The use of high-performance systems allows us to reduce the time of study and development of new chemical processes.

2. Information-analytical system for modelling chemical technology processes

The information-analytical system (IAS) is proposed to use for studying chemical technology processes. Its structure is given on the figure 1.

Input information flows include:

- Experimental conditions: reactor type, process flow mode, temperature, pressure, volume of reaction mixture.
- Chemical formula involved in the reaction.
- Concentrations at the initial time.
- Concentrations at some fixed points in time.

- Evaluation of kinetic parameters: ratios between constants, certainty intervals of some kinetic parameters.
- Proposed mechanisms of chemical reactions.

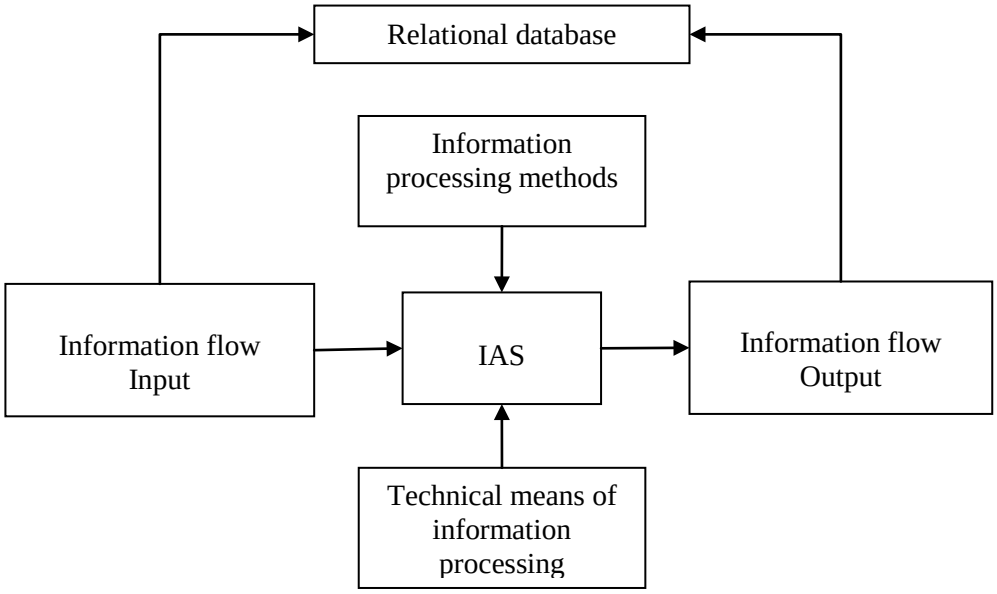


Figure 1. Information-analytical system structure for modeling chemical technology processes.

Information processing methods include:

- The algorithm for solving the direct kinetic problem.
- Parameters of computing control in solving the inverse kinetic problem.
- The algorithm for solving the inverse problem.
- Graph plotting for comparison the calculated and experimental concentrations of the reacting substances.
- The algorithm for determining the activation energies of the reaction stages.

Output information flows include:

- Calculated concentrations of all reacting substances.
- Calculated activation energies of all reaction stages.
- Graphs for comparison the calculated and experimental concentrations of the reacting substances.
- Graphs of change in reaction stage rate.

Technical means of information processing include:

- Experimental unit.
- Industrial reactor.
- Computing system: personal computer, multiprocessor computer system.

3. Application of parallel computing

The genetic algorithm for the parallel solution of the inverse problem of chemical kinetics is the most effective. This algorithm is borrowed from biology. It is based on the idea of selection, i.e. the predominant reproduction of the most adapted individuals [7]. The practical application of the genetic algorithm in all known cases has led to positive results [8, 9]. The genetic algorithm is a universal method for finding the optimum regardless of the complexity of the functions [9]. The basis of the genetic algorithm presents the following sequence of operations.

On the first step the algorithm randomly creates the initial population of N individuals. Then N points are formed in the space of kinetic parameters. Each point has m coordinates, i.e. values of the parameters.

At the stage of mutation, individuals of the population change in accordance with a predetermined operation. The coordinates/parabolic descent from the points of the space were taken as the operation of mutation.

At the stage of selection, a certain fraction of the entire population is selected. The chosen fraction will remain "alive" at this stage of evolution. The probability of survival of the individual depends on the value of the adaptiveness function for this individual. The function of adaptiveness is characterized by the residual function. The fraction of survivors (s) is a parameter of the genetic algorithm. According to the results of the selection from N individuals of the population the total population will comprise s×N individuals. In the considered case s=1/2. The crossing is used to form a new generation. It needs two parents to produce a descendant. To form a new point in the parameter space, one of the "survivors" and one of the "dying" points are selected as parents. The crossing is carried out by choosing m/2 coordinates from the first point and the remaining ones from the second. In this case, the descendant inherits features of both parents. To exclude the degradation of the population, the individuals for reproduction are selected from the entire population. This set of actions is repeated iteratively. By this way the "evolutionary process" is modeled and several life cycles (generations) continue. The algorithm stops when one of the following conditions is met:

- finding a global or suboptimal solution;
- exhaustion of the number of generations for evolution;
- exhaustion of time given for evolution.

Parallelization of the computational process takes place at the stage of initial filling. Pseudo-random points in the parameter space are uniformly distributed over the flows of a multi-core computing system. The mutation is carried out by each flow independently. Data exchange is carried out at the selection stage. The autonomous operation time of flows significantly exceeds the interaction time between flows. Therefore this algorithm is effective.

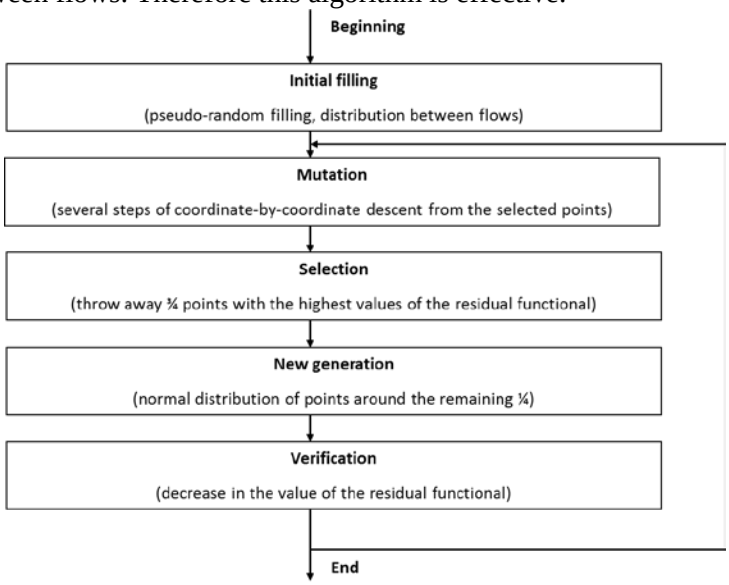
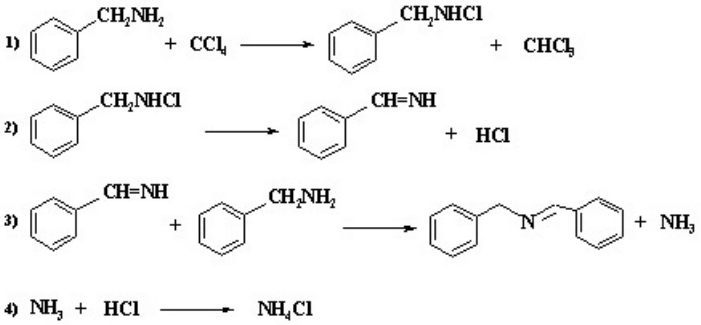


Figure 2. Genetic algorithm.

4. Kinetic model of the reaction for the synthesis of benzylidene benzylamine

The developed information-analytical system was tested when modeling of a kinetic model for the synthesis of benzylidene benzylamine. In the series of Schiff bases, N-benzylidene benzylamine has an important place and has wide application in practice. In particular, N-benzylidene benzylamine is known as an indicator for the quantitative determination of lithium-organic compounds by titrimetric method [10-12]. N-benzylidene benzylamine is used as an initial compound for the synthesis of a number of heterocycles. It has a wide range of physiological activity: analgesic, anticonvulsive, anticonvulsant [13]. Based on the analysis of the experimental data and the results of their

mathematical treatment [14-15] the following sequence of chemical transformations in reactions of benzylideneaniline synthesis is proposed:



The sequence of reaction transformations and their corresponding kinetic equations are represented by equations:

1. $C_1 + C_2 \rightarrow C_3 + C_4$ $W_1=k_1C_1C_2$
2. $C_3 \rightarrow C_5 + C_6$ $W_2=k_2C_3$
3. $C_5 + C_1 \rightarrow C_7 + C_8$ $W_3=k_3C_5C_1$
4. $C_8 + C_6 \rightarrow C_9$ $W_4=k_4C_8C_6$

where C_i – concentration of components, mol/L: $C_1=C_7H_9N$ – benzylamine, $C_2=CCl_4$ – carbon tetrachloride, $C_3=C_7H_8NCl$ – chlorbenzylamine, $C_4=CHCl_3$ – chloroform, $C_5=C_7H_7N$ – 1-phenylmethanimine, $C_6=HCl$ – hydrogen chloride, $C_7=C_{14}H_{13}N$ – benzylidene benzylamine, $C_8=NH_3$ – ammonia, $C_9=NH_4Cl$ – ammonium chloride; W_j – rate of the j-th reaction, mol/(L×h); k_j – kinetic rate constant of the j-th reaction, $l\times mol^{-1}\times h^{-1}$ (j=1, 3, 4), h^{-1}.

The kinetic equations of the transformation sequence are analyzed within the law of acting masses [16]. The correct description of a laboratory reactor with a stirrer is the ideal mixing model:

$$\frac{d\overline{N}}{dt} = F_N,\ F_N = \frac{1}{V_o}\sum_{j=1}^{J}\delta_j\omega_j,\ \delta_j = \sum_{i=1}^{I}\nu_{ij}$$

$$\frac{dX_i}{dt} = \frac{F_i - X_i F_N}{\overline{N}}$$

with the initial conditions: at $t = 0, X_i = X_i^o,\ \overline{N} = 1,$ где $\overline{N}$ = C/C_o – the relative change in the number of moles of the reaction mixture; C and C_o – molar density and its initial value, mol/L; $X_i=C_i/C$ – concentration of components, mole fractions; V_o – volume of reaction space, L; $\omega_j=W_j/C_o$ – adjucted reaction rates, h^{-1}; j – number of stages of chemical transformation; i – number of components.

The right-hand sides of the system of nonlinear differential equations have the following form:

$F_1 = -\omega_1 - \omega_3$; $F_2 = -\omega_1$; $F_3 = \omega_1 - \omega_2$; $F_4 = \omega_1$; $F_5 = \omega_2 - \omega_3$; $F_6 = \omega_2 - \omega_4$; $F_7 = \omega_1$; $F_8 = \omega_3 - \omega_4$; $F_9 = \omega_4$; $F_n = \omega_2 - \omega_4$.

To solve a system of ordinary nonlinear differential equations with initial conditions at t=0 – $X_i = X_i^o,\ \overline{N} = 1$ the modified fifth-order Kutta-Merson method was chosen [17].

Algorithm for solving a system of differential equations $\frac{dx}{dt} = f(x)$ requires a fivefold calculation of the right-hand sides f(x):

$F_1=f(x_k)\cdot h,$
$F_2=f(x_k+F_1/3)\cdot h,$
$F_3=f(x_k+(F_1+F_2)/6)\cdot h,$
$F_4=f(x_k+(F_1+3\cdot F_2)/8)\cdot h$
$x_{k+1}=x_k+(F_1-3\cdot F_2+4\cdot F_4)/2$
$F_5=f(x_{k+1})\cdot h$
$x^*_{k+1}=x_k+(F_1+4F_4+F_5)$

where h – the step of integration over the space or time coordinate, x_k – values of variables at the beginning of the integration interval. At the end of the integration interval, two solutions are obtained: x_{k+1} – by the Runge-Kutta method with accuracy $O(h^4)$ and x^*_{k+1} – by the Kutta-Merson method with accuracy $O(h^5)$.

Based on the developed information-analytical system, the stage rate constants and activation energies are found. The values are given in Table 1.

Table 1. Kinetic parameters for the synthesis of benzylidene benzylamine at temperature of 23° C.

	Kinetic constants, h^{-1}	Activation energy, kcal/mol
k_1	1.5×10^{-2}	10.6
k_2	4.7	7.7
k_3	13.4	1.6
k_4	0.6	0.4

For this reaction, the adjusted and true constants are related by the following equations: $K_i=k_i \cdot C_o$ (i=1, 2, 3, 4), k_i ($L\times mol^{-1}\times h^{-1}$); $k_5=K_5$ (h^{-1}).

Table 1 shows the constants at reference temperature T_{ref}=23°C [73]. Recalculation of constants for any temperature is performed based on the selected reference temperature by expressions:

$$K_i(T) = K_i(T_{ref}) \cdot exp\left[\frac{E_i}{RT_{ref}}\left(1-\frac{T_{ref}}{T}\right)\right]; \quad K_i(T_{ref}) = K_i^o \cdot exp\left(-\frac{E_i}{RT_{ref}}\right)$$

To verify the adequacy of the constructed kinetic model, the calculated and experimental data are compared (Fig. 3, Fig. 4).

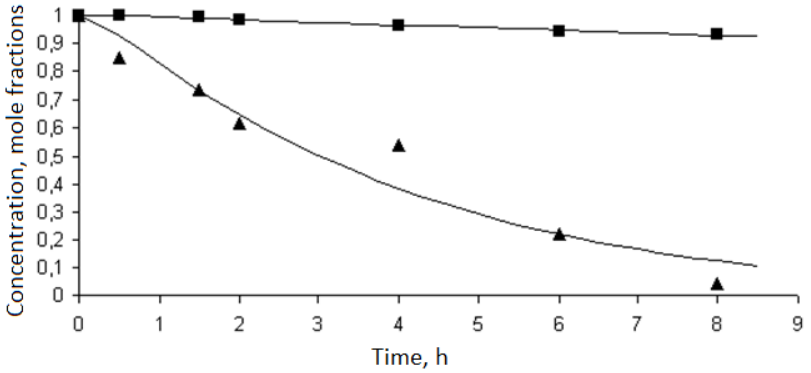


Figure 3. Calculated and experimental data on benzylamine consumption at temperatures: 1 (■) – 23° C; 2 (▲) – 85° C.

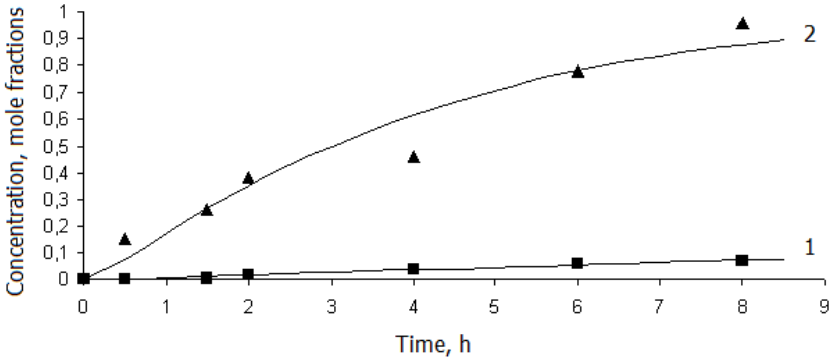


Figure 4. Calculated and experimental data on the formation of benzylidene benzylamine at temperatures: 1 (■) – 23° C; 2 (▲) – 85° C.

The developed kinetic model adequately describes the experimental observations. The divergence between the calculated data and the experimental changes in concentrations over time does not exceed the error in the quantitative analysis.

5. Optimal reaction conditions

Based on the developed kinetic model for the synthesis of benzylidene benzylamine, computational experiments were made. The molar ratio of the initial substances: benzylamine (X_1) and carbon tetrachloride (X_2) was chosen as the optimization criterion. The results of computational experiments on change in yield of the target product depending on the ratio X_1:X_2 at two temperatures are given in Table 2 and Table 3.

Table 2. Dependence of the target product yield on the initial substances molar ratio at 23º C.

Benzylamine (X_1), molar fraction	Carbon tetrachloride (X_2), molar fraction	Benzylidene benzylamine yield (X_7), %mol.
0.45	0.55	6.3
0.40	0.60	6.9
0.37	0.63	7.2
0.35	0.65	7.4
0.30	0.70	8.0
0.25	0.75	8.5
0.10	**0.90**	**9.7**
0.05	0.95	6.3

Table 3. Dependence of the target product yield on the initial substances molar ratio at 85º C.

Benzylamine (X_1), molar fraction	Carbon tetrachloride (X_2), molar fraction	Benzylidene benzylamine yield (X_7), %mol.
0.45	0.55	80.6
0.40	0.60	85.5
0.37	0.63	87.9
0.35	0.65	89.0
0.30	0.70	92.3
0.25	0.75	94.5
0.10	**0.90**	**97.6**
0.05	0.95	97.1

It was found that to reach the maximum product yield, the optimal molar ratio of initial substances is X_1:X_2=1:9.

6. Conclusions

The information-analytical system for modeling chemical technology processes has been developed. The parallel genetic algorithm for solving inverse kinetic problems is implemented. On the basis of information-analytical system the kinetic model for the synthesis of benzylidene benzylamine has been built. The adequacy of the built kinetic model has been established. In accordance with developed model the optimal molar ratio of the initial substances has been found as benzylamine: carbon tetrachloride = 1:9.

7. References

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