Mathematical modeling of the synthesis reaction benzyl butyl ether

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Abstract. On the basis of experimental data obtained at different temperatures, a mathematical model of synthesis of benzylbutyl ether by intermolecular dehydration of benzyl and n-butyl alcohols under the influence of the catalyst CuBr₂ is proposed. Optimization of the kinetic parameters of the catalytic synthesis of benzylbutyl ether is solved by genetic algorithm using the island model of parallelizing the computational process. As a result of the simulation, the values of the rate constants and activation energies of the stages are determined at different temperatures of the reaction. Thus, the developed mathematical model within the limits of the permissible error allows adequately describing the experimental data.

1. Introduction
Benzyl butyl ether having fruity and floral aromas is a valuable aromatic substance and is widely used for flavoring products of the perfumery, cosmetic and food industries. Benzyl butyl ether is permitted in many countries for use as a food flavoring (ice cream, ice, beverages, desserts, baking, etc.). Benzyl butyl ether is a large-tonnage industrial product [1-4].

In this paper, mathematical model of the reaction for obtaining benzylbutyl ether by intermolecular dehydration of benzyl and n-butyl alcohols under the influence of the catalyst CuBr₂ is developed. The synthesis of benzylbutyl ether is performed by interaction of benzyl alcohol with n-butanol. CuBr₂ is used as a catalyst at temperature within 140-175°C range for 2-10 hours at a molar ratio [CuBr₂]:[BnOH]:[n-C₄H₉OH] = 1-5:100:100-400. Conversion of benzyl alcohol is 99%, and the yield of benzylbutyl ether is 91% under optimal conditions (175°C, 10 h, [CuBr₂]:[BnOH]: [n-C₄H₉OH] = 1:100: 400). Dibutyl ether is not formed under this reaction conditions. Reaction does not proceed without a catalyst [8].

![Chemical reaction diagram](image-url)
The advantages of this method are:
- Availability and low cost of the catalyst CuBr₂.
- Lack of by-products.
- Selectivity of the process and high yield of the target product: when converting benzyl alcohol to 99%, the total yield of benzyl butyl ether is 91%.

We use experimental data at various temperatures in order to determine the parameters of the kinetic model and probable mechanism of reaction of formation of benzyl butyl ether.

2. Mathematical model

Heterogeneous chemical reactions in closed systems are described by a mathematical model, based on the law of mass action [3-5]. For each reagent differential equations are defined (1)

\[
\frac{dx_i}{dt} = \sum_{j=1}^{J} v_{ij} w_j (k_j, k_j^0, E_j, T, x_j), \quad i = 1, \ldots, I
\]

with initial conditions: at \( t=0 \), \( x_i(0) = x_i^0 \); where \( t \) is time, min; \( v_{ij} \) is the stoichiometric coefficient; \( J \) is the number of stages; \( x_i \) is the concentration of substance, involved in the reaction, mol/l; \( I \) is the number of substances; \( w_j \) is the speed of the \( j \)-th stage, 1/min; \( k_j \) is the rate constant for the stages, 1/min; \( E_j \) is the activation energy of the stages, kcal/mol; \( T \) is temperature, K; \( k_j^0 \) is pre-exponential factor, 1/min.

The determined kinetic parameters of the system of differential equations (1) are \( k_j^0, E_j \) and \( k_j \) accordingly to the Arrhenius equation. Unknown parameters are determined from the condition of minimization of the functional (2) [5-7, 9, 10].

The functional residuals are selected depending on the conditions of the experiment. All methods have their advantages and disadvantages.

\[
F = \sum_{i=1}^{N} \sum_{j=1}^{M} (x_{ij}^e - x_{ij}^c)^2
\]

where \( x_{pi}^e \) and \( x_{pi}^c \) are the experimental and calculated values of concentrations of the components, \( \gamma_i \) is the weight coefficient, \( I \) is number of substances, \( P \) is the number of measurement points in time for the observed substances during the reaction.

The disadvantage of the least squares method (2) is the excessive sensitivity of the estimates to the sharp emissions found in the initial data.

\[
F = \sum_{i=1}^{N} \sum_{j=1}^{M} |x_{ij}^e - x_{ij}^c|
\]

The main advantage of the criterion (3) is the stability of the obtained estimates to sharp emissions in the initial data.

\[
F = \sum_{i=1}^{N} \sum_{j=1}^{M} \psi_{ij} (x_{ij}^e - x_{ij}^c)^2
\]

where \( \psi_{ij} \) is the reagent weight coefficient.

Functional (4) is used when it is necessary to take into account the significance and accuracy of individual observations.

For the task in question, the functional (4) will be used, in view of the need to take into account the concentrations of target and side products of the reaction.

The inverse task refers to incorrectly posed tasks and does not have a unique solution. Therefore, when choosing numerical calculation methods, it is necessary to combine methods for global search and search for a local extremum. The fastest methods, that is, methods in less time lead to the required residual functionality – global search and multistart; Hook-Jeeves method (pattern search); genetic algorithm; simulated annealing and others.

1) Global search and multistart
They use methods based on the calculation of the gradient. The calculation starts with finding of local solutions (in OptimizationToolbox) from several initial points and storing of local and global solutions found during the search.

2) Hook-Jeeves method (pattern search)

Uses direct search algorithms. Performs optimization problems with non-linear, linear and variable constraints and does not require differentiability or continuity of the function.

3) Genetic algorithm

Solves optimization tasks, imitating the principles of biological evolution, repeatedly changing the population of individual points using the rules on the pattern of combinations of genes in biological reproduction. Due to its random nature, the genetic algorithm increases the chances of finding a global solution. It allows to solve problems without restrictions, with restrictions on variables, and general optimization tasks. The solver does not require differentiability or continuity of the objective function.

4) Simulate annealing

Solves optimization tasks using a probabilistic search algorithm that simulates the physical annealing process, in which the material heats up and then the temperature slowly drops to reduce defects, thus minimizing the energy of the system. By analogy, each iteration of the simulated annealing algorithm tends to improve the current minimum, slowly reducing the search volume.

The obtained task of optimization of kinetic parameters was solved by a genetic algorithm in the MatLab software using the computational process from the island model [11-17].

This parallelization model implies the creation of a multi-population consisting of a number of subpopulations (islands) equal to the number of processors used (S is a multi-population, S is a sub-population) islands, |P| is the number of used processors) (figure 1). Each island is processed by its own processor. During a given period, subpopulations are developed independently, and then an additional process is used to synchronize the islands, which carries out data exchange [18-20].

![Figure 1. The island model of parallelization of the computational process.](image)

3. Results

For the process under consideration, a scheme of chemical reactions is proposed (Table 1).

It is established that the intermolecular dehydration of benzyl alcohol X1 with n-butyl alcohol X4 with the formation of ethers is catalyzed by copper compounds. The best for this reaction is CuBr2. Benzyl butyl ether X6 is the target product of the reaction. Experimental study of the reaction is carried out at temperatures 140°C, 160°C, 175°C. The reaction time is 8-10 hours.

Minimizing the functional (2), the kinetic parameters are calculated – the rate constants of the stages and the activation energy of the stages – table 2.
Table 1. Scheme of the reaction of benzylbutyl ether synthesis.

| №  | Scheme                                                                 |
|----|------------------------------------------------------------------------|
| 1  | PhCH₂OH(X₁) + CuBr₂(X₂) → [PhCH₂][CuBr₂(OH)]⁻(X₃)                      |
| 2  | [PhCH₂][CuBr₂(OH)](X₃) + BuOH(X₄) → [PhCH₂OBu][H][CuBr₂(OH)]⁻(X₅)     |
| 3  | [PhCH₂OBu][H][CuBr₂(OH)]⁻(X₅) → PhCH₂OBu(X₆) + H₂O(X₇) + CuBr₂(X₈)   |
| 4  | [PhCH₂][CuBr₂(OH)]⁻(X₅) + PhCH₂OH(X₈) → [PhCH₂OHCH₂Ph][CuBr₂(OH)]⁻(X₇) |
| 5  | [PhCH₂OHCH₂Ph][CuBr₂(OH)]⁻(X₇) → PhCH₂OCH₂Ph(X₉) + H₂O(X₇) + CuBr₂(X₈) |
| 6  | BuOH(X₈) + CuBr₂(X₂) → [Bu][CuBr₂(OH)]⁻(X₁₀)                           |
| 7  | [Bu][CuBr₂(OH)]⁻(X₁₀) + BuOH(X₄) → [BuOHBu][CuBr₂(OH)]⁻(X₁₁)          |
| 8  | [BuOHBu][CuBr₂(OH)]⁻(X₁₁) → BuOBu(X₁₂) + H₂O(X₇) + CuBr₂(X₂)          |
| 9  | BuOH(X₈) + CuBr₂(OH)⁻(X₅) + PhCH₂OH(X₈) → [PhCH₂OBu][H][CuBr₂(OH)]⁻(X₇) |

Table 2. The values of the kinetic parameters of the reaction of the synthesis of benzylbutyl ether.

| N stage | k_j | T=140°C | T=160°C | T=175°C | E_j, kcal/mol |
|---------|-----|---------|---------|---------|--------------|
| 1       | 1.70| 2.47    | 2.8     | 5.36    |
| 2       | 2.06| 3.91    | 6.54    | 12.18   |
| 3       | 0.05| 0.08    | 0.14    | 10.31   |
| 4       | 1.92| 5.10    | 7.02    | 13.96   |
| 5       | 0.11| 0.49    | 0.85    | 21.69   |
| 6       | 0.00063| 0.00088| 0.00278| 15.029  |
| 7       | 0.117| 0.60    | 0.62    | 18.46   |
| 8       | 0.0002| 0.0025  | 0.005   | 35.10   |
| 9       | 0.15 | 0.16    | 0.5     | 11.94   |

In figure 2 is shown the correspondence of the experimental data with calculated for the measured substrates of reaction of the synthesis of benzylbutyl ether at T = 175°C. The observed substrates are initial substance (benzyl alcohol [PhCH₂OH]), the target substance (benzylbutyl ether PhCH₂OBu) and the dibenzyl ether [PhCH₂OCH₂Ph]. The graphs show the ratios of substances concentrations to the sum of all concentrations of the observed substances (mol. fractions). From figure 2 it can be concluded that the description of the experimental data is generally satisfactory (the relative error does not exceed 15%).

Based on the data given in table 2 and figure 2 we can make the following conclusions. At T = 175°C, a drastic change in the rates of consumption or formation of substances X₄, X₆, X₇, X₁₁, X₁₂ is

Figure 2. Graphs of correspondence between experimental data (points) and calculated values (lines) of changes in concentration of observed substrates at T = 175°C.

At lower temperatures, there is a gradual increase in X₃, X₅ and a decrease in X₂, X₁₀, X₁₁. At T = 175°C, a drastic change in the rates of consumption or formation of substances X₄, X₆, X₇, X₁₁, X₁₂ is
observed after 450 minutes. At other temperatures, a smooth increase or decrease of speed is observed. The lowest speed is observed for stage 8 at all temperatures. The greatest – at stage 1.

**Figure 3.** Graphs of correspondence between experimental data (points) and calculated values (lines) of changes in the concentration of the observed substrates at the ratio [CuBr2]:[BnOH]:[n-C4H9OH] = 1:100:200, T = 140 °C.

In figures 3-5 the correspondence of the experimental data with the calculated for the measured substrates the reactions of the synthesis of benzylbutyl ether with the following ratio of [CuBr2]:[BnOH]:[n-C4H9OH] = 1:100:200 is shown.

**Figure 4.** Graphs of correspondence between experimental data (points) and calculated values (lines) of changes in the concentration of the observed substrates at the ratio [CuBr2]:[BnOH]:[n-C4H9OH] = 1:100:200, T = 160 °C.

**Figure 5.** Graphs of correspondence of experimental data (points) and calculated values (lines) of changes in the concentration of the observed substrates at the ratio [CuBr2]:[BnOH]:[n-C4H9OH] = 1:100:200, T = 175 °C.
System of differential equations, based on (1) and (2) is solved in MATLAB software. Runge-Kutta method of 4th order is used to solve direct kinetic task. Genetic algorithm is used to solve inverse kinetic task. Target functional for inverse kinetic task is found in accordance to (2). For reliability criteria we choose difference between finale calculated and final experimental conversion no more then 15% for each substance (X1, X6, X9).

In figures 3-5 we notice the following: with increasing temperature, a relative sharp increase in conversion of X1 occurs. If at 140 °C the conversion is about 50%, then at 160 and 175 °C the conversion reaches values of more than 70% and 90%, respectively. Also, with increasing temperature, the nature of the curve of X1 concentration profile changes. If at 140 °C the X1 concentration changes over time smoothly, evenly throughout the experiment, then at 175 °C it can be noticed that there is a sharp drop in concentration. In the time interval from the beginning of the experiment to 300-400 min, is a gradual change in concentration. The nature of the change in the concentration of X6 over time also acquires a more abrupt and non-linear character with increasing of temperature. Separately, it should be noted the nature of the change in formation of X9. If at 140 °C the nature of formation of X9 is linear, then at 160 °C and 175 °C the concentration of X9 reaches a certain maximum value, and then practically does not change. At 175 °C, this value is higher and is achieved faster than at 160 °C. This is due to the fact that the rate of formation of X6 competes in the reaction model with the rate of reactions of formation of X9. The rate of formation of X6 is greater than X9 and more sensitive to an increase in temperature, which simultaneously leads to a significant increase in consumption of X1 in the elementary stage (1).

4. Conclusion
Based on the presented reaction scheme, a kinetic model that describes the process of obtaining benzylbutyl ether is developed. The developed mathematical model within the limits of the permissible error allows to describe adequately the experimental data. In the work, the values of the rate constants and the activation energy of the stages of reaction of synthesis of benzylbutyl ether are determined.

In further research the optimal reaction conditions will be determined based on the kinetic model.

5. References
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