Mathematical modeling of the synthesis reaction benzyl butyl ether

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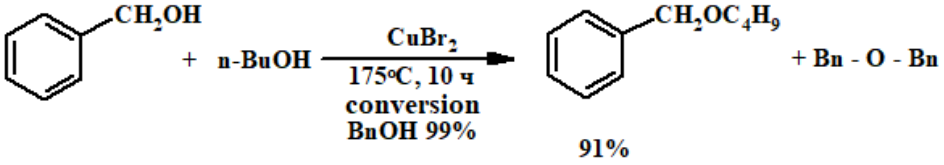
Abstract. On the basis of experimental data, the mathematical model for the synthesis of benzyl butyl ether by intermolecular dehydration of benzyl and n-butyl alcohols under the influence of the catalyst $CuBr_2$ is proposed. The values of the rate constants and activation energies of the stages are determined.

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].

In this paper, a mathematical model of the reaction for obtaining benzyl butyl ether by intermolecular dehydration of benzyl and n-butyl alcohols under the influence of the catalyst $CuBr_2$ is developed.

The synthesis of benzyl butyl ether was performed by interaction of benzyl alcohol with n-butanol and $CuBr_2$ used as catalyst at temperature within 140-175°C range for 2-10 hours at a molar ratio [$CuBr_2$]: [BnOH]: [n-C_4H_9OH] = 1-5:100:100-400. Conversion of benzyl alcohol is 99%, and the yield of benzyl butyl ether is 91% under optimal conditions (175°C, 10 h, [$CuBr_2$]:[BnOH]: [n-C_4H_9OH] = 1:100: 400). Dibutyl ether is not formed under this reaction conditions. Reaction does not proceed without a catalyst [2].



[$CuBr_2$]:[BnOH]:[n-C_4H_9OH]= 1:100:400

The advantages of this method are:

1. Availability and low cost of the catalyst $CuBr_2$.
2. Lack of by-products.
3. The selectivity of the process and the high yield of the target product: when converting benzyl alcohol to 99%, the total yield of benzyl butyl ether is 91%

In order to establish the kinetic parameters and the probable mechanism of reaction of formation of benzyl butyl ether on the basis of experimental data obtained at different temperatures mathematical modeling of this reaction was carried out.

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)

$$\frac{dx_i}{dt} = \sum_{j=1}^{J} v_{ij} w_j(k_j, k_j^{\,0}, E_j, T, x_i), \quad i = 1,...,I \tag{1}$$

Initial conditions: at $t=0$, $x_i(0)=x_i^0$; where t – time, min; v_{ij} – stoichiometric coefficients; J – number of stages; x_i – concentrations of substances involved in the reaction, mol/l; I – the number of substances; w_j – speed of the j-th stage, 1/min; k_j – the rate constants for the stages, 1/min; E_j, – the activation energy of the stages, kcal/mol; T – temperature, K; k_j^0 – pre-exponential factors, 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) [6, 7].

$$\sum_{p=1}^{P}\sum_{i=1}^{I} \gamma_i (x_{pi}^e - x_{pi}^r) \to \min, \tag{2}$$

where x_{pi}^e and x_{pi}^r – experimental and calculated values of the concentrations of the components, γ_i – the weight coefficient, I – the number of substances, P – the number of measurement points in time for the observed substances during the reaction.

The obtained problem of optimization of kinetic parameters was solved by a genetic algorithm in the MatLab computing environment using the computational process from the island model [8, 9].

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_i is a sub-population (islands), |P| is the number of processors used) (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 [10-12].

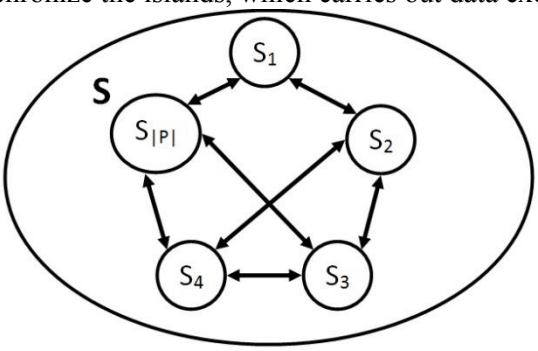


Figure 1. The island model of parallelization of the computational process.

3. Results

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

Table 1. Scheme of the reaction of benzyl butyl ether synthesis.

№	Scheme
1	$PhCH_2OH(\mathbf{X_1}) + CuBr_2(\mathbf{X_2}) \rightarrow [PhCH_2]^+[CuBr_2(OH)]^-(\mathbf{X_3})$
2	$[PhCH_2]^+[CuBr_2(OH)]^-(\mathbf{X_3}) + BuOH(\mathbf{X_4}) \rightarrow [PhCH_2OBu]H^+\ [CuBr_2(OH)]^-(\mathbf{X_5})$
3	$[PhCH_2OBu]H^+\ [CuBr_2(OH)]^-(\mathbf{X_5}) \rightarrow PhCH_2OBu(\mathbf{X_6}) + H_2O(\mathbf{X_7}) + CuBr_2(\mathbf{X_2})$
4	$[PhCH_2]^+[CuBr_2(OH)]^-(\mathbf{X_3}) + PhCH_2OH(\mathbf{X_1}) \rightarrow [PhCH_2OHCH_2Ph]^+\ [CuBr_2(OH)]^-(\mathbf{X_8})$
5	$[PhCH_2OHCH_2Ph]^+\ [CuBr_2(OH)]^-(\mathbf{X_8}) \rightarrow PhCH_2OCH_2Ph\ (\mathbf{X_9}) + H_2O(\mathbf{X_7}) + CuBr_2(\mathbf{X_2})$
6	$BuOH(\mathbf{X_4}) + CuBr_2(\mathbf{X_2}) \rightarrow [Bu]^+[CuBr_2(OH)]^-\ (\mathbf{X_{10}})$
7	$[Bu]^+[CuBr_2(OH)]^-\ (\mathbf{X_{10}}) + BuOH(\mathbf{X_4}) \rightarrow [BuOHBu]^+[CuBr_2(OH)]^-\ (\mathbf{X_{11}})$
8	$[BuOHBu]^+[CuBr_2(OH)]^-\ (\mathbf{X_{11}}) \rightarrow BuOBu(\mathbf{X_{12}}) + H_2O(\mathbf{X_7}) + CuBr_2(\mathbf{X_2})$
9	$[Bu]^+[CuBr_2(OH)]^-\ (\mathbf{X_{10}}) + PhCH_2OH(\mathbf{X_1}) \rightarrow [PhCH_2OBu]H^+\ [CuBr_2(OH)]^-(\mathbf{X_5})$

It has been established that the intermolecular dehydration of benzyl alcohol X_1 with n-butyl alcohol X_4 with the formation of ethers is catalyzed by copper compounds, the best for this reaction is $CuBr_2$. Benzyl butyl ether X_6 is the target product of the reaction.
Experimental study of the reaction was carried out at temperatures 140°C, 160°C, 175°C. The reaction time was 8-10 hours.
Minimizing the functional (2), the kinetic parameters were calculated – the rate constants of the stages and the activation energy of the stages – table 2.

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

N stage	k_j			E_j, kcal/mol
	T=140°C	T=160°C	T=175°C	
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 the calculated for the measured substrates of the reaction of the synthesis of benzyl butyl ether at T = 175°C. The observed substrates are initial substance (benzyl alcohol [$PhCH_2OH$]), the target substance (benzyl butyl ether $PhCH_2OBu$]) and the dibenzyl ether [$PhCH_2OCH_2Ph$]. 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%).

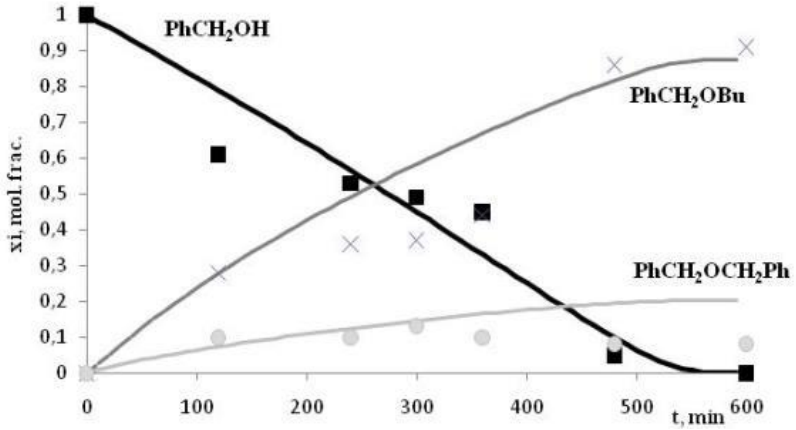


Figure 2. Graphs of correspondence between experimental data (points) and calculated values (lines) of changes in the concentration of the observed substrates at T = 175°C.

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 speeds of stages 2, 3 is observed – a decrease after 450 minutes, 6,7,8,9 – an increase after 450 minutes, which corresponds to a change in the concentrations of substances X_3, X_5, which decrease drastically, and X_2, X_{10}, X_{11} - increase dramatically. At lower temperatures, there is a gradual increase in X_3, X_5 and a decrease in X_2, X_{10}, X_{11}. At T = 175°C, a drastic change in the rates of consumption or formation of substances X_4, X_6, X_7, X_{11}, X_{12} 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.

Thus, the developed mathematical model within the limits of the permissible error allows to adequately describe the experimental data. In the work, the values of the rate constants and the activation energy of the stages of the reaction of the synthesis of benzyl butyl ether are determined.

4. References

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Acknowledgments

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