Modeling of the catalytic of benzyland butyl alcohols etherification

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Abstract. On the basis of experimental data obtained at different temperatures and different initial components concentrations, mathematical model of catalytic reaction of benzylbutyl ether synthesis was developed.Value of kinetic parameters, such as the rate constants and activation energies of reaction stages are determined. Thus, the developed mathematical model within the limits of the permissible error allows to adequately describe the experimental data.

1. Introduction

Benzyl butyl ether is a valuable aromatic substance and is widely used for flavoring products in the perfumery, cosmetic and food industries. Benzyl butyl ether usage use as a food flavoring (ice cream, ice, beverages, desserts, baking, etc.) is permitted in many countries. Benzyl butyl ether is a large-tonnage industrial product [1, 2].

The synthesis of benzylbutyl ether was performed by reactionbetween benzyl alcohol and n-butanol. Copper bromide (II) ($CuBr_2$) was used as a catalyst [3-7] at temperature within 140-175°C at time range of 2-10 hours at different molar ratios of initial components([$CuBr_2$]:[BnOH]:[n-C_4H_9OH] = 1:100:100-300).

Mathematical model of the reaction of benzylbutyl ether synthesis based on reaction scheme [8] wasdeveloped.Chosen reaction mechanism is represented below in Table 1.

Table 1. Scheme of the reaction of benzylbutyl 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	$[Bu]^+[CuBr_2(OH)]^-\ (\mathbf{X_{10}}) + PhCH_2OH(\mathbf{X_1}) \rightarrow [PhCH_2OBu]H^+ [CuBr_2(OH)]^-(\mathbf{X_5})$

2. Kinetic model

2.1 Mathematic model

Using reactionscheme represented above (Table 1) mathematic model was established, based on system of differential equations:

$$\frac{dc_i}{dt} = \sum_{j=1}^{J} v_{ij} w_j(k_j, k_{0j}, E_j, T, c_i), \quad i = 1,...,I \qquad (1)$$

where W_j– rate of j-th elementary reaction, [mole*min], v_{ij} – stoichiometric coefficient of i-th substance in j-th reaction, j – number of elementary reactions in kinetic model ($j = \overline{1,9}$), k_j – constant of j-th elementary reaction rate, c_i – concentration of i-th substance, [mole/lit], i – number of substance, I – overall number of components in the system (I=12), k_j– constant of j-th elementary reaction rate, t – time, [min], k_{j0} – preexponential coefficient for j-th constant of elementary reaction rate, T – temperature, E_j– activation energy of j-th reaction [KJ/mole].

After obtaining k_j values at different temperatures k_{j0} and E_j were determined from Arrhenius equation. Condition of minimization of the functional (2) was used [9-15].

$$F = \sum_{i=1}^{N} \sum_{j=1}^{M} \left| x_{ij}^{e} - x_{ij}^{c} \right| \qquad (2)$$

where x_{pi}^{e} and x_{pi}^{r} are the experimental and calculated values of concentrations of the components.

2.2 Kinetic model

Using mathematical model (1), (2) and reaction scheme represented (Table 1) we solved inverse and direct kinetic tasks. In order to do this genetic algorithm and Runge-Kutta of 4th order method were used which were implemented in MATLAB software environment. Minimizing the functional (2) the kinetic parameters for different temperatures were obtained (Table 2).

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

N stage	k_i		
	T=140°C	T=160°C	T=175°C
1	0.0851	0.1134	0.2268
2	1.0280	3.0560	4.7289
3	0.1013	0.8000	1.0773
4	0.9612	2.2108	5.1905
5	0.2260	0.7000	0.8500
6	0.0003	0.0006	0.0009
7	1.1699	2.3399	4.6797
8	0.0001	0.0002	0.0004
9	0.0750	0.1500	0.3400

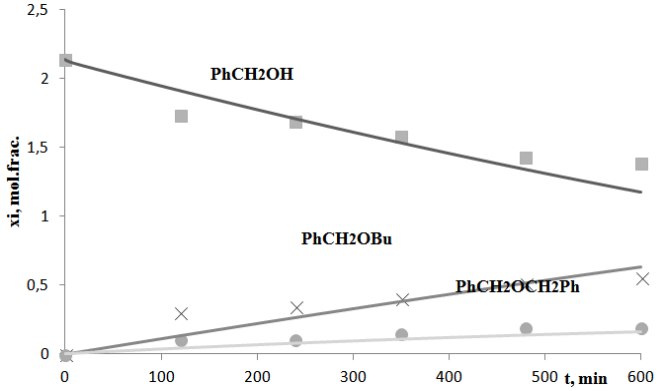

Figure 1. Graphs of correspondence of experimental data (points) and calculated values (lines) of changes in the concentration of the observed substrates at the ratio [$CuBr_2$]:[BnOH]:[n-C_4H_9OH] = 1:100:300, T = 140 °C.

On Figure1 – Figure 6 below are represented calculated and experimental concentrations profiles for X1, X2, X9at different temperatures and molar ratios of initial compounds.

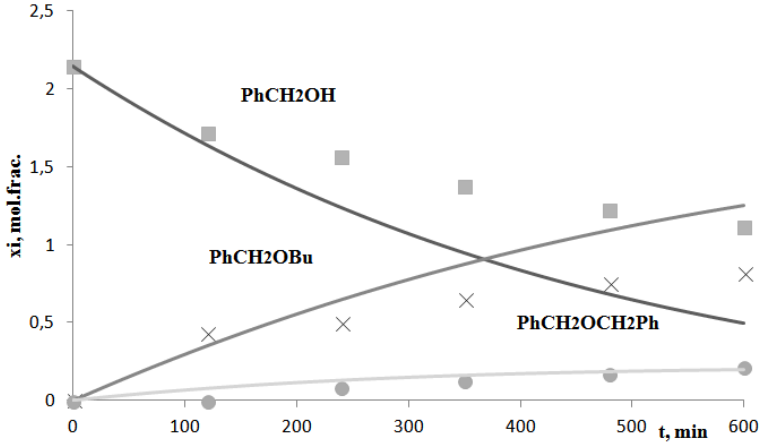

Figure 2. Graphs of correspondence of experimental data (points) and calculated values (lines) of changes in the concentration of the observed substrates at the ratio [$CuBr_2$]:[BnOH]:[n-C_4H_9OH] = 1:100:300, T = 160°C.

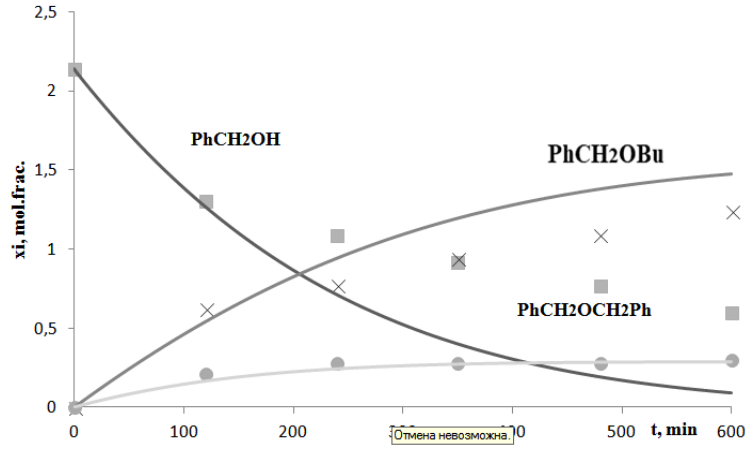

Figure 3. Graphs of correspondence of experimental data (points) and calculated values (lines) of changes in the concentration of the observed substrates at the ratio [$CuBr_2$]:[BnOH]:[n-C_4H_9OH] = 1:100:300, T = 175 °C.

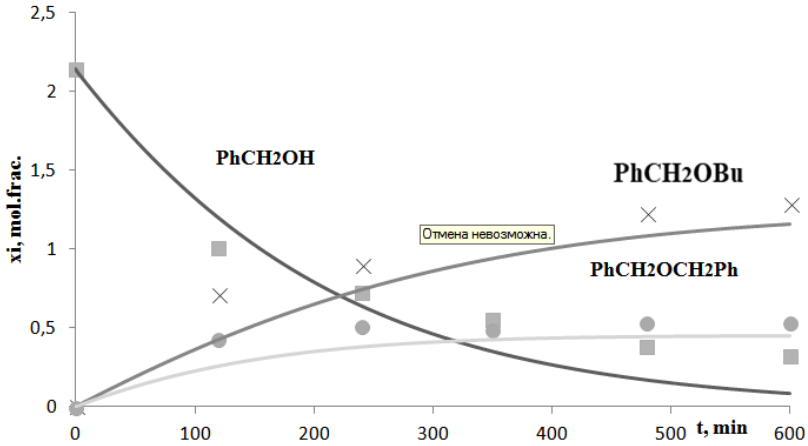

Figure 4. Graphs of correspondence of experimental data (points) and calculated values (lines) of changes in the concentration of the observed substrates at the ratio [$CuBr_2$]:[BnOH]:[n-C_4H_9OH] = 1:100:150, T = 175 °C.

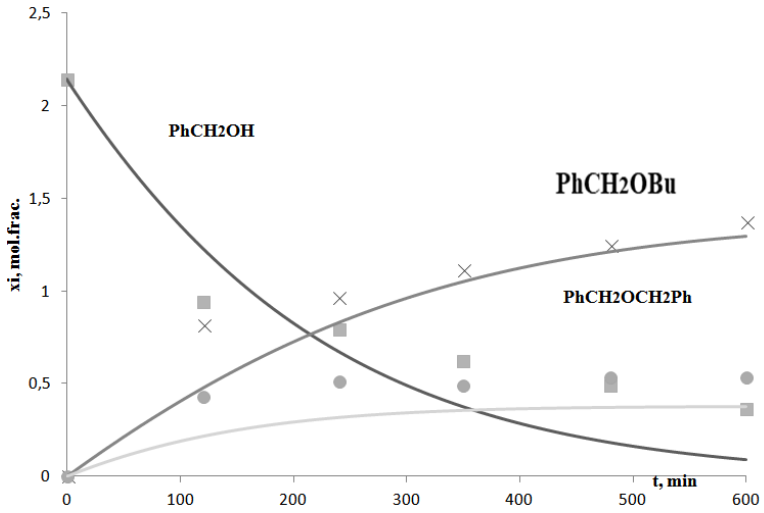

Figure 5. Graphs of correspondence of experimental data (points) and calculated values (lines) of changes in the concentration of the observed substrates at the ratio $[CuBr_2]$:[BnOH]:[n-C_4H_9OH] = 1:100:200, T = 175 °C.

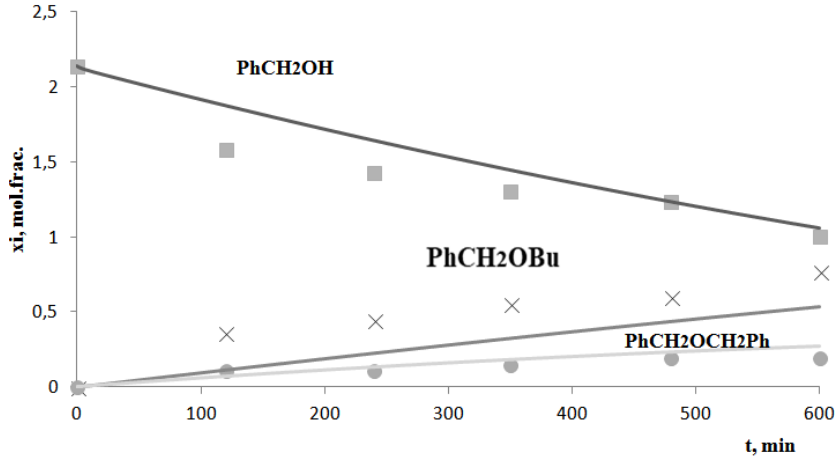

Figure 6. Graphs of correspondence of experimental data (points) and calculated values (lines) of changes in the concentration of the observed substrates at the ratio $[CuBr_2]$:[BnOH]:[n-C_4H_9OH] = 1:100:150, T = 140 °C.

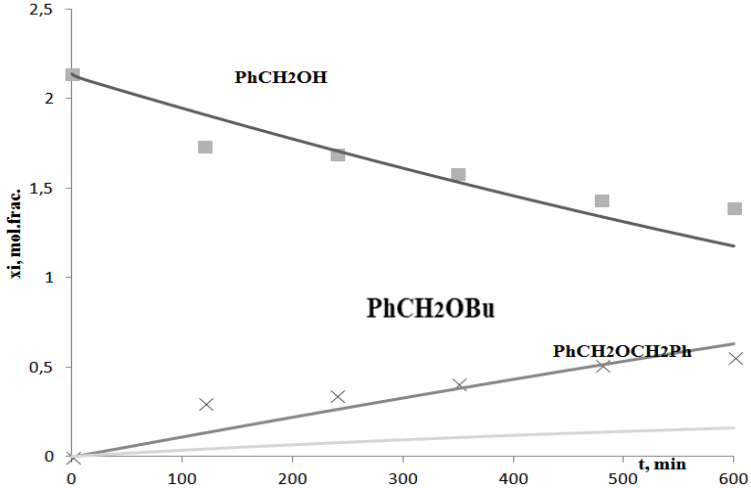

Figure 7. Graphs of correspondence of experimental data (points) and calculated values (lines) of changes in the concentration of the observed substrates at the ratio $[CuBr_2]$:[BnOH]:[n-C_4H_9OH] = 1:100:200, T = 140 °C.

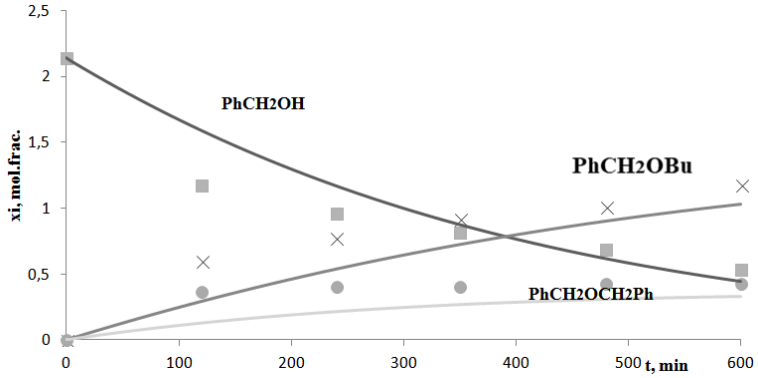

Figure 8. Graphs of correspondence of experimental data (points) and calculated values (lines) of changes in the concentration of the observed substrates at the ratio [$CuBr_2$]:[BnOH]:[n-C_4H_9OH] = 1:100:150, T = 160 °C.

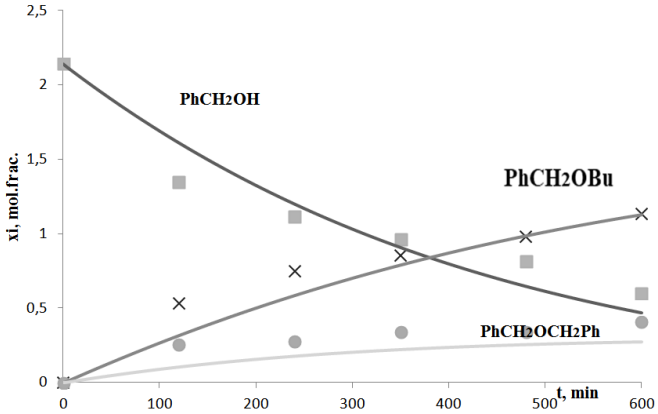

Figure 9. Graphs of correspondence of experimental data (points) and calculated values (lines) of changes in the concentration of the observed substrates at the ratio [$CuBr_2$]:[BnOH]:[n-C_4H_9OH] = 1:100:200, T = 160 °C.

In Table 3 below values of activation energies represented along with values of preexponential coefficients. There also represented values of activation energies which we obtained in earlier research [7].

Table 3. Activation energies and preexponential coefficient values[8].

N stage	E_j, kcal/mol	K_{0j}	E_j, kcal/mol
1	9.93	14200.04	5.36
2	16.27	438995622.7	12.18
3	25.68	4.70666E+12	10.31
4	17.51	1676543382	13.96
5	14.35	9722953.614	21.69
6	11.60	435.72	15.03
7	14.40	47204510.15	18.46
8	14.40	3952.09	35.10
9	11.60	435.72	11.94

3. Conclusion

In this paper kinetic parameters for represented reaction scheme of benzyl butyl ether synthesis were determined.Calculationswerebasedonexperimentaldatawhichwasobtainedfromexperimentsconductedat different temperatures and molar ratios of initial components. Kinetic parameters were compared with previous results [8]. It was established that developed kinetic model gives more accurate results at lower temperatures (140-160^{o}C) and at molar ratio of initial compounds: [$CuBr_2$]:[BnOH]:[n-

C_4H_9OH] = 1:100:150-200. In order to get more accurate results at higher temperatures it is suggested to include mass exchange factors in model and make additional research in order to establish are any of elementary reactions (Table 1) of equilibrium type.

4. Acknowledgments
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5. References

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