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MULTI-CRITERIAL OPTIMIZATION OF A HETEROGENEOUS CATALYTIC REACTION

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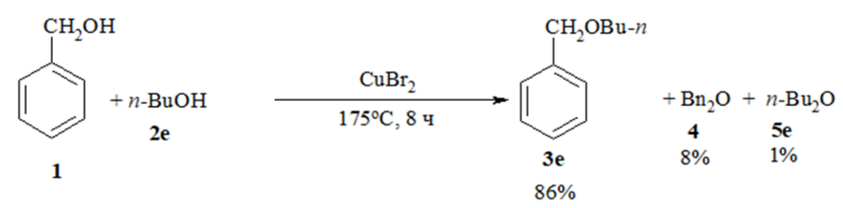
Introduction

The aim of laboratory catalytic reactions modeling is to find optimal reaction conditions for its further introduction to the industrial manufacturing. It is necessary to elaborate a kinetic model that describes experimental data. The main optimality criterion for new catalytic reactions is high yield of target products and absence or low yield of co-products. It is also necessary to define the conditions that provide for achieving the extreme points of all the criteria, which determines the task of multicriteria optimization.

The subject of this paper is benzyl butyl ether catalytic synthesis reaction carried out through the dehydration of benzyl alcohol with butanol-1. Based on the kinetic experimental data obtained at different temperatures, a few possible mechanisms of the studied process were proposed which allowed us to elaborate an adequate combined kinetic model.



[Cu]: [BnOH]:[*n*-BuOH] = 1:100:400

Experimental section

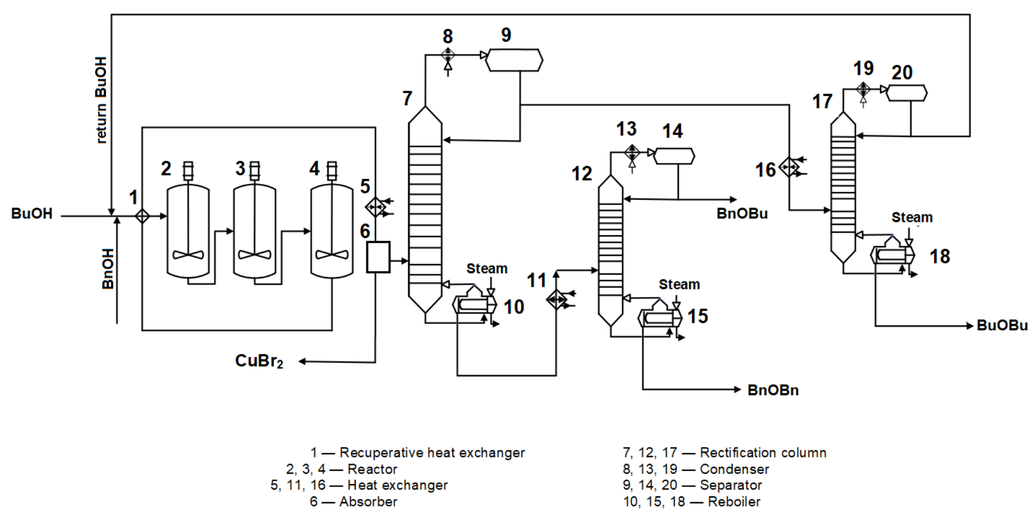


Fig. 1. Schematic technological diagram of benzyl butyl ether production by intermolecular dehydration of benzyl alcohol with n-butyl alcohol in the presence of a CuBr2 catalyst ([CuBr2]:[BnOH]:[BuOH]=1:100:150÷400, temperature 140-175°C)

The direct and inverse problems of chemical kinetics

$$\begin{cases} \dot{y}_1(t) = \varphi_1(y_1, y_2, \ldots y_n, k_1, k_2, \ldots, k_m) \\ \dot{y}_2(t) = \varphi_2(y_1, y_2, \ldots y_n, k_1, k_2, \ldots, k_m) \\ \ldots \\ \dot{y}_n(t) = \varphi_n(y_1, y_2, \ldots y_n, k_1, k_2, \ldots, k_m) \end{cases}$$

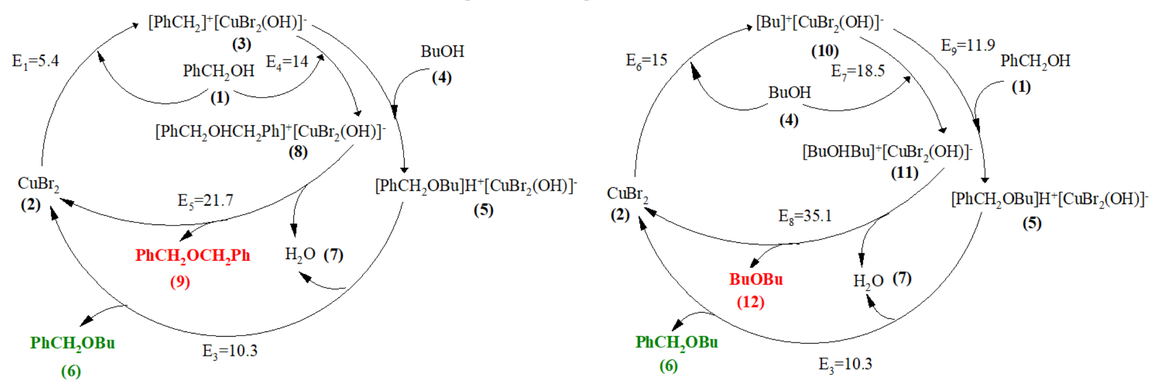
$$\sum_{i=1}^{n}\sum_{p=1}^{P}\frac{\left|y_{ip}^{\exp} - y_{ip}^{calc}\right|}{y_{ip}^{e}} \to \min$$

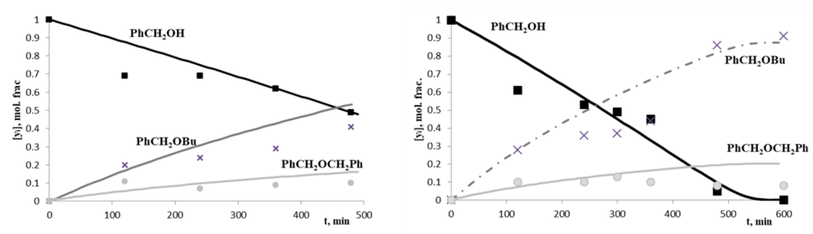
$$t \in [0; t^*]; y_i(0) = y_i^0, i = 1,2,\ldots n$$

$$k_j = k_j(k_j^0, E_j, T),\ j = 1,2,\ldots m$$

$Y(t) = (y_1(t), y_2(t), \ldots, y_n(t))$ – vector of phase variables, mol/l;
$Y_0 = (y_1^0, y_2^0, \ldots, y_n^0)$ — vector of initial concentrations of compounds, mol/l;
φ_i — functions of the right parts of stage speeds; t^* – reaction time, min;
T – temperature, K; t – time, min;
$K = (k_1, k_2, \ldots, k_m)$ – vector of stage speed constants, 1/min or l/(mol*min);
k_j^0 – pre-exponential factors, 1/min or l/(mol*min); E_j – activation energy of reactions, kcal/mol;

Kinetic model of the catalytic synthesis reaction of benzyl alkyl ethers





Multicriteria optimization of the conditions of benzyl alkyl ethers catalytic synthesis reaction

The variable parameters

$x_1 = T \in [140;180]$
$x_2 = N \in [1;4]$
$x_3 = t^* \in [200;800]$

N - mole ratio of butyl alcohol reagents to benzyl alcohol;

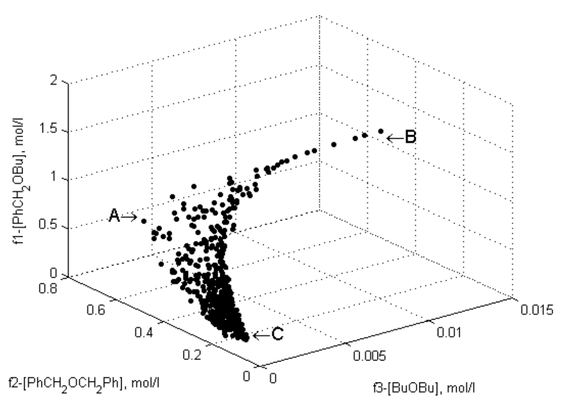
Optimality criteria

$f_1(X) = y_{PhCH_2OBu(Y_6)}(t^*, T, N) \to \max$
$f_2(X) = y_{PhCH_2OCH_2Ph(Y_9)}(t^*, T, N) \to \min$
$f_3(X) = y_{BuOBu(Y_{12})}(t^*, T, N) \to \min$

- Vector of variable parameters $X=(x_1, x_2, x_3)$, where x_1 – reaction temperature, T; x_2 – mole ratio of butyl alcohol reagents to benzyl alcohol $N=[Y_4]:[Y_1]$; x_3 – reaction duration time, t^*.
- Vector function of optimality criteria $F(X)=(f_1(X), f_2(X), f_3(X))$.
- $F(X)$ with the values $\{F\}=R^{(F)}=R^3$ in the objective space is defined in the region D_X $\{X\}=R^{|X|}=R^3$: $T \in [T_{\min}; T_{\max}]$, $y_{ct} \in [y_{ct\,\min}; y_{t\,\max}]$, $t^* \in [t^*_{\min}; t^*_{\max}]$.
- Then we need to maximize the optimality criteria in the area D_X according to (3).

$$\max_{X \in D_X} F(X) = F(X^*) = F^* \qquad (3)$$

The multicriteria optimization task was resolved by application of the Pareto-approximation algorithm NSGA-II*



N	Temperature T, °C	Reaction duration time, min	Reagents mole ratio N=[Y4]:[Y1]	Concentration of $PhCH_2OBu$ (Y_6), mol/l	Concentration of $PhCH_2OCH_2Ph$(Y_9), mol/l	Concentration of BuOBu (Y_{12}), mmol/l
A	144	656	1,15	0,64	0,41	0.043
B	168	766	3,95	1,66	0,24	1,1
C	145	389	3,40	0,43	0,12	0.047

Conclusion

A kinetic model for the catalytic reaction of synthesis benzyl butyl ether has been developed. In the reaction, several catalytic cycles are realized, leading to the formation of the target and by-products. From the values of stages activation energies of catalytic cycles follows that the formation of benzyl butyl ether is more probable by the attack n-butanol with a benzyl cation (complex $[PhCH_2]^+[CuBr_2(OH)]^-$), which is generated from benzyl alcohol by the action $CuBr_2$. Based on the elaborated kinetic model, we performed three-criteria optimization.

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