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OPTIMIZATION PROCESS OF THE ALKYLATING OF PHENOL WITH HEXENE-1 ON THE SULFOKATIONITE KU-23.

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Abstract

In the article we reported of results of optimization process of phenol alkylating with hexene-1 in the presence of sulphocationite KU-23. By means of build regressive model have been the Box BenkinD program module. By calculation there were established, that maximum yield of derivatives of the alkylphenol: Y_1-20,116% wt., were obtained at the x_1=2:1, x_2=4h., x_3=2:1 mol, x_4=10%wt., that was in good correlation with the results of conducted experiments.

Key words: *phenol, catalysis alkylating, optimization, module Box BenkinD*

Introduction

As known [1-4], the additives based on the alkylphenols are widely used in lubricating oils and fuels, in order to improve their antioxidant and anticorrosion properties. Although, in that area there were conducted extensive researches, many questions, related to the optimization of process of synthesis the alkylphenols, which are intermediates in the production of additives, have not found their decision in proper way depend the further of investigations [5].

In this article we carried out our investigations of optimization of the process alkylating of phenol with hexene-1 in the presence of sulphocationite KU-23.

EXPERIMENTAL PART

Experiences of alkylation the phenol with hexene-1 conducted in the mixer reactors of batch with the volume 0,5l. As the initial reactors, phenol and hexene-1 were distilled under the vacuum and were synthesed by oligomerization of ethylene. As the catalyst there used the macro porous industrial sulphocationite KU-23 (moisture contain of less than 1%).

With the aim of provide an accurate fixind of time of the beginning of reaction and the process activation of catalyst, the loading of components was realized in the certain sequence. At the first the phenol, then the calculated amount of catalyst KU-23 (from 5 to 15% from the weight of phenol) were loaded in reactor.

We heated the mixture (60, 80, 100°C), after that we mixed it during an hour for activation of catalyst. Further we injected into the reaction mixture the hexene-1 in a certain molar ratio to the phenol (1:1, 1:2, 1:3) and conducted the reaction of alkylation during the certain time. After

1, 2, 3 and 4 h from the beginning of the reaction we take the samples for analysis. Taken samples were distilled under the vacuum, with the aim to separated unreacted initial reagents. The phenol distillation was carried at the vapor temperature (70-100˚C) and osmotic pressure (6 mm Hg), but the alkylating agent of hexene-1- at atmosphere pressure. By using high efficiency liquid chromatograph (HELC) we followed the course of the process. By the method of decantation the alkylate was isolated and distillated under the vacuum at the end of the process.

RESULTS AND DESCUSSIONS

Based on the experimental data there were conducted the mathematical calculation of detection of the dependencies indicators. The chosen levels of factors are expressed by the codes and comply with +1 and -1. The volume of the experiment and the efficiency of optimization depend of the number of levels of the experiment. Based on the conducted experiences were established, that the main various factors of the process are: temperature (˚C)-X_1, the reaction time (h)-X_2, the mole ratio phenol:hexene-1-X_3, the catalyst concentration (wt. %)-X_4, [6]. As indicators of yield-Y_1 (yield of alkyl derivers, %. These factors have been encoded by the linear coordinate conversion factor space and the choice of the scale of the axes in units various intervals. In this case the ratio used [7]:

$$X_i = \frac{c_i - c_{i0}}{\Delta c}$$

where C_i- performance indicators of operating parameters

C_{i0}- the average value of indicators

ΔC- the range of the existing indicators

In particular:

$$X_1 = (T - 80)/20$$
$$X_2 = (\tau - 3)/1.0$$
$$X_3 = (n_i - 2)/1.0$$
$$X_4 = (C_k - 10)/5.0$$

Where x_i is coded value factor. For the building the regression model there was used the module Box BenkinD. Location of experimental points in the factor space for the full factor experiment was showed at pic.1.

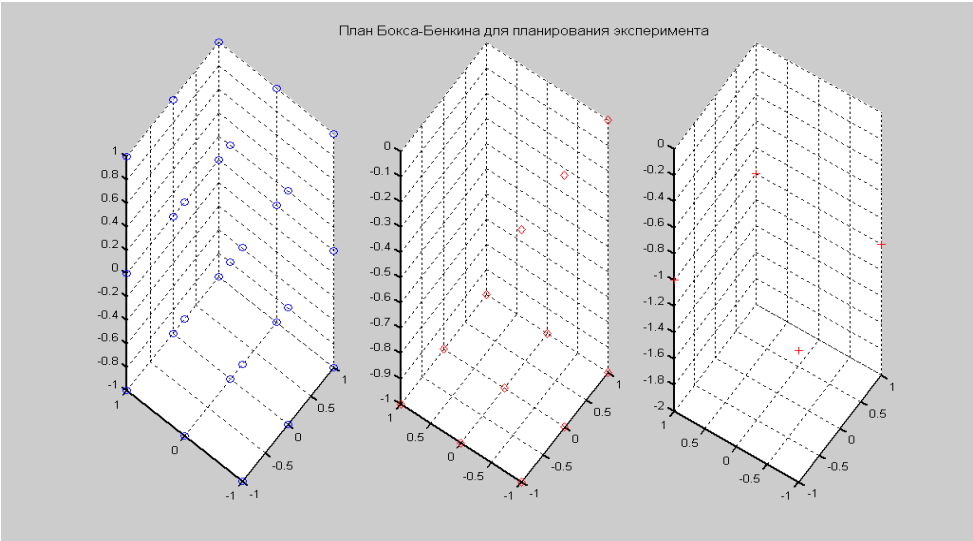


Fig.1. the plan of the Box BankinD experiment

This program allows to build the calculation matrix and realize the calculation of coefficients of the four-factor model, and conduct regression analysis to test the adequacy of the model (by Fisher's criterion), as well as to calculate the error between the payment data and experimental data [8].

During the optimization process, the alkylation of phenol hexene-1 were determined the directive factors of the reaction which allow to group the experiments so as to minimize the effect of changes of external conditions on the values of the estimated parameters (Table 1).

Table 1. The center of the experiment and intervals of the varying factors process of alkylation of

phenol with hexene-1 in the presence of CS-23 catalyst.

	Temperarure ^{0}C	Reaction time,h	Ration of phenol:hexene – 1, mol	Catalyst concentration, % wt.
Lower level	60	2	1:1	5
Top level	100	4	3:1	15
The base level	80	3	2:1	10
Interval of varying	20	1	1:1	5

By using the full factors analysis the number of required experiments was determined by the following formula:

$$N = n^k$$

where N - number of experiments; n is the number of levels, ie in the particular case of the maximum and minimum boundaries point to k - the number of factors influencing the process.

n our case, n = 2; k = 4. Then the number of variants of the experiment $N = 2^4$, ie, 16.

Modern computer tools are of great ability to process data and select the type of regression equations by experimental method. [10]

$$Y_j = a_0 + \sum_{i=1}^{4} a_{ij} x_j, \quad j = 1,2,3,4$$

$$a_{ij} = \frac{\sum_{i=1}^{n} X_{ij} Y_i}{\sum_{i=1}^{n} X_i^2}$$

The dispersion assessment of the experiment was conducted according to the formula:

$$S^2 = \frac{\sum (Y_i - \overline{Y^2})}{N - P - 1}$$

The value of S is the standard error of regression. Than the lower S, the regression equation better describes the independent variable Y. S-plus professional has been used for the determination of the coefficients of the program [11]. This program is developed by Mathworks to automate Rowan-mathematical processing of the experimental data obtained, ie, for statistical data analysis, calculation of the regression coefficients and coefficients of pair correlation for these attempts. Taking into account the respective experimental results output products Y^{eks}, the plan of experiment for the study is shown in Table 2.

Table 2. Matrix experiment with full factors of the process the alkylating phenol with hexene - 1 KU - 23.

. № Experience	Factors of natural coordinates				Factors of coordinates without limits				Yield of alkylphenol derivatives
	T	τ	n_i	C_k	X_1	X_2	X_3	X_4	$Y^{эксп}$
1	60	2.0	1:1	5.0	-1	-1	-1	-1	31,32

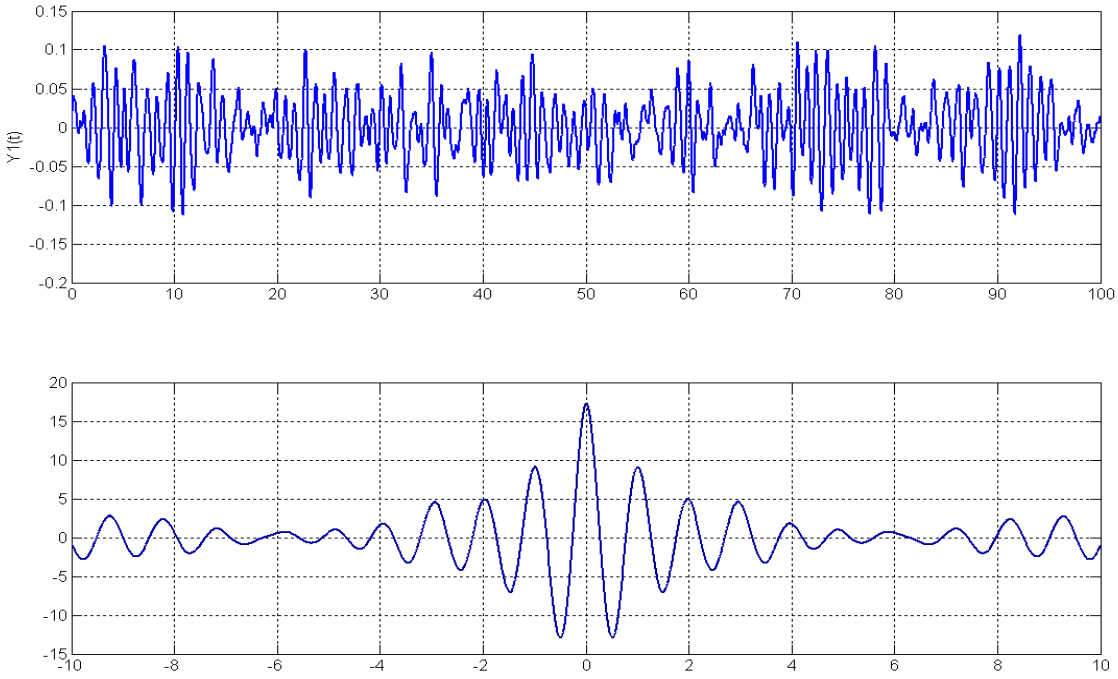
2	100	2.0	1:1	5.0	+1	-1	-1	-1	46,45
3	60	4.0	1:1	5.0	-1	+1	-1	-1	43,63
4	100	4.0	1:1	5.0	+1	+1	-1	-1	47,76
5	60	2.0	3:1	5.0	-1	-1	+1	-1	36,84
6	60	2.0	1:1	15.0	-1	-1	-1	+1	39,35
7	60	2.0	3:1	15.0	-1	-1	+1	+1	45,63
8	100	4.0	3:1	5.0	+1	+1	+1	-1	54,84
9	100	4.0	1:1	15.0	+1	+1	-1	+1	44,05
10	100	2.0	3:1	15.0	+1	-1	+1	+1	62,83
11	60	4.0	3:1	15.0	-1	+1	+1	+1	61,68
12	60	4.0	3:1	5.0	-1	+1	+1	-1	59,91
13	100	2.0	1:1	15.0	+1	-1	+1	-1	46,45
14	100	2.0	3:1	5.0	+1	-1	-1	+1	61,77
15	60	4.0	3:1	15.0	-1	-1	-1	+1	64,68
16	100	4.0	3:1	15.0	+1	+1	+1	+1	67,89

In order to identify the obtained mathematical model, the MATLAB program was used. This program allows to obtain the correlation function x_{corr}, which can be used in calculations. According to the formula [11]:

$$x_{corr} = \frac{n\sum_{i=1}^{n} x_i y_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{\sqrt{[n\sum_{i=1}^{n} x_i^2 - (\sum_{i=1}^{n} x_i)^2][n\sum_{i=1}^{n} y_i^2 - (\sum_{i=1}^{n} y_i)^2]}}$$

You can define the qualitative and quantitative characterization of closeness of the connection between the input and output factors (Table 2). The results of calculation showed that the correlation coefficients found are within 0.3-0.5 Cheddoka scale, i.e. closeness of the relationship is weak.

Fig. 2 shows the plots of the calculated correlation input function and cross-correlation function between input and output. This shows that the correlation functions satisfy the requirements of stationary processes and tend over time to zero.



Pic. 2. Assessment of the correlation function of the input (a) and the cross-correlation function between input and output (b).

The resulting regression mathematical model of the process is as follows:

$$Y_{pac} = 25.86 + 0.000012 * X_1 + 0.000019 * X_2 - 4.41 * X_3 + 0.0002 * X_4 - 0.19994 * X_1X_2 + 0.06 * X_1X_3$$
$$- 0.0068 * X_1X_4 + 1.44 * X_2X_3 - 0.1007 * X_2X_4 + 0.138 * X_3X_4 + 0.0047 * X_1^2 + 2.869 * X_2^2 + 0.0537 * X_4^2$$

To test the adequacy of the resulting model was used Fisher criterion [12]:

$$F = \frac{S_{ad}^2}{S_t^2},$$

where, respectively, the dispersion of the adequacy and reproducibility. On the basis of calculations

$$F_p = \frac{5.46 \cdot 10^{-9}}{0.11875 \cdot 10^{-7}} = 0.4598$$

at a significance level of 5% of the payment value is $F_t = 4{,}49$. As the static model adequately describes the monitoring process and can be applied to determine the optimal regime parameters of the process (Fig.3).

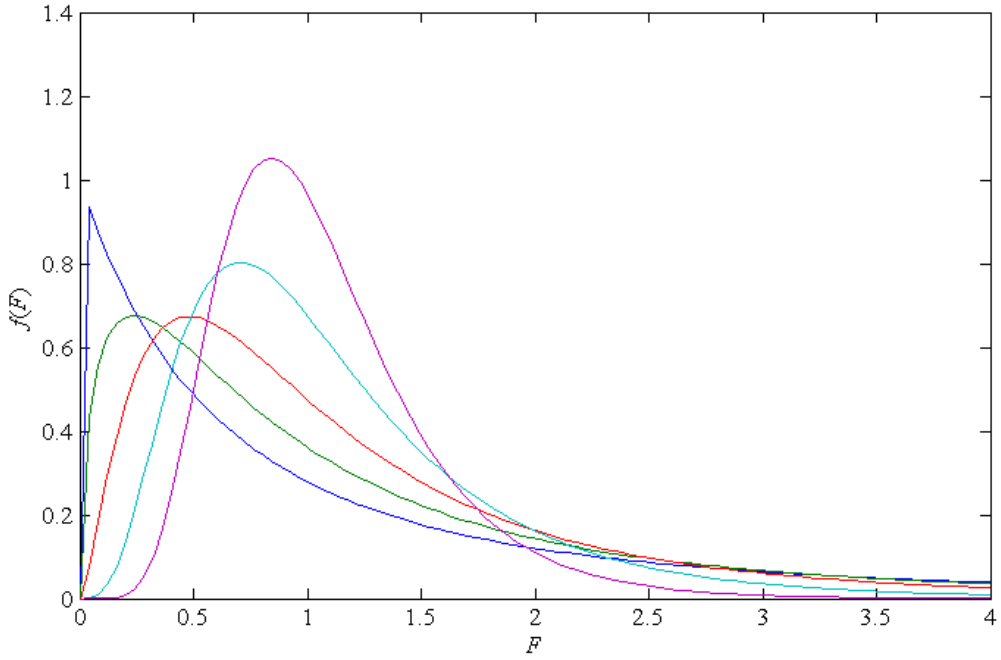


Fig.3. The diagram of density (OF) distribution of Phisher

Table 4. Results of experimental and computed value

$У_{расч.}$	$У_{эксп.}$	$\lvert Y_{расч.} - Y_{эксп.} \rvert$
31,41	31,32	0,09
46,33	46,45	0,12
43,04	43,63	0,59
48,42	47,76	0,66
36,53	36,84	0,31
40,25	39,35	0,90
45,21	45,63	0,42
54,41	54,84	0,43
42,62	44,05	1,43
62,81	62,83	0,02
61,24	61,68	0,44
59,23	59,91	0,68
46,35	46,45	0,10
61,61	61,77	0,16
65,42	64,68	0,74
68,22	67,89	0,33

As can be seen, from table 4, statistical model provides a high accuracy of the calculation and adequately describes the monitoring process.

Interpretation of results of the investigation revealed influence of selected factors to the yield of products of reaction. Temperature is the basic important factor into the regression equation. By the transition of the factor X_1 from the lower level ($X_1^- = 60^0C$) to the top level ($X_1^+ = 100^0C$) at a fixed value of other factors, effect of changing of response is $\Delta \overline{Y}_1 = |\overline{Y}_1 - \overline{Y}_1^{'}| = |46,$ 45-31, 32| = 15.13 % wt., i.e. mass yield of alkylating derivatives increase to 15.13 % wt.

The second important factor is the factor X_2 – reaction time. By the transition of the factor X_2 from the lower level ($X_{2-} = 2$ h) to the top level ($X_2^+ = 4$ h) at a fixed value of other factors, effect of changing of response is $\Delta \overline{Y}_1 = |\overline{Y}_1 - \overline{Y}_1^{'}| = |42, 03 -31, 32| = 11, 71$ % wt., i.e. mass yield of alkylating derivatives increase to 11, 71 % wt.

The third important factor in the equation is the factor X_3 – phenol:hexene-1 mol/mol. By the transition of the factor X_3 from the lower level ($X_{3-} = 1:1$) to the top level ($X_2^+ = 3:1$) at a fixed value of other factors, effect of changing of response is $\Delta \overline{Y}_1 = |\overline{Y}_1 - \overline{Y}_1^{'}| = |36,83 -31,32| =$ 5,51 % wt., i.e. mass yield of alkylating derivatives increase to 5,51 % wt.

The fourth important factor is the factor X_4 – catalyst concentration % wt. By the transition of the factor X_4 from the lower level ($X_{4-} = 5$) to the top level ($X_2^+ = 15$) at a fixed value of other factors, effect of changing of response is $\Delta \overline{Y}_1 = |\overline{Y}_1 - \overline{Y}_1^{'}| = |36,34 -31,32| = 5,01$ % wt., i.e. mass yield of alkylating derivatives increase to 5,01 % wt.

The equations of regression allow not only predicting the values of the response function for the given experimental conditions, but also give the necessary information to choose optimal mode of technical process [9].

To solve the problem of optimization there were used the Matlab-6 program, which include modern algorithms of solution the linear programming problem.

As the criteria of the optimization was taken the maximum of the functional

$$Fmax = f(x_1,x_2,x_3,x_4)$$

to the next restrictions to the indicators of the process:

$$60.0 \le X_1 \le 100;\quad 2 \le X_2 \le 4;\quad 1 \le X_3 \le 3;\ 5 \le X_4 \le 15;$$

For the learning of configuration of the response surface the equation transited to the canonically form.

Coordinates of point S- center of the surface, which founded by the decision of systems of equation:

$$\frac{\partial y_1}{\partial x_1} = 0{,}00001+0{,}1994*X_2 +0.06*X_3 -0{,}0068*X_4 +0{,}0094*X_4 = 0$$

$$\frac{\partial y_1}{\partial x_2} = 0{,}00001+0{,}1994*X_1 +0.06*X_1 +1{,}44*X_3 -0{,}1007*X_4 +5{,}738*X_2 + 61.52*X_3 = 0$$

$$\frac{\partial y_1}{\partial x_3} = -4{,}41+0{,}06*X_1+1.44*X_2+0.138*X_4 = 0$$

$$\frac{\partial y_1}{\partial x_4} = 0{,}00001+0{,}1994*X_1 +0.06*X_1 +1{,}44*X_3 -0{,}1007*X_4 +5{,}738*X_2 +61.52*X_3 = 0$$

which allowed to find the canonically form of the equation:

$$Y_s = 0.7576*X_1 - 91.86*X_2 - 48.74*X_3+5.6*X_4$$

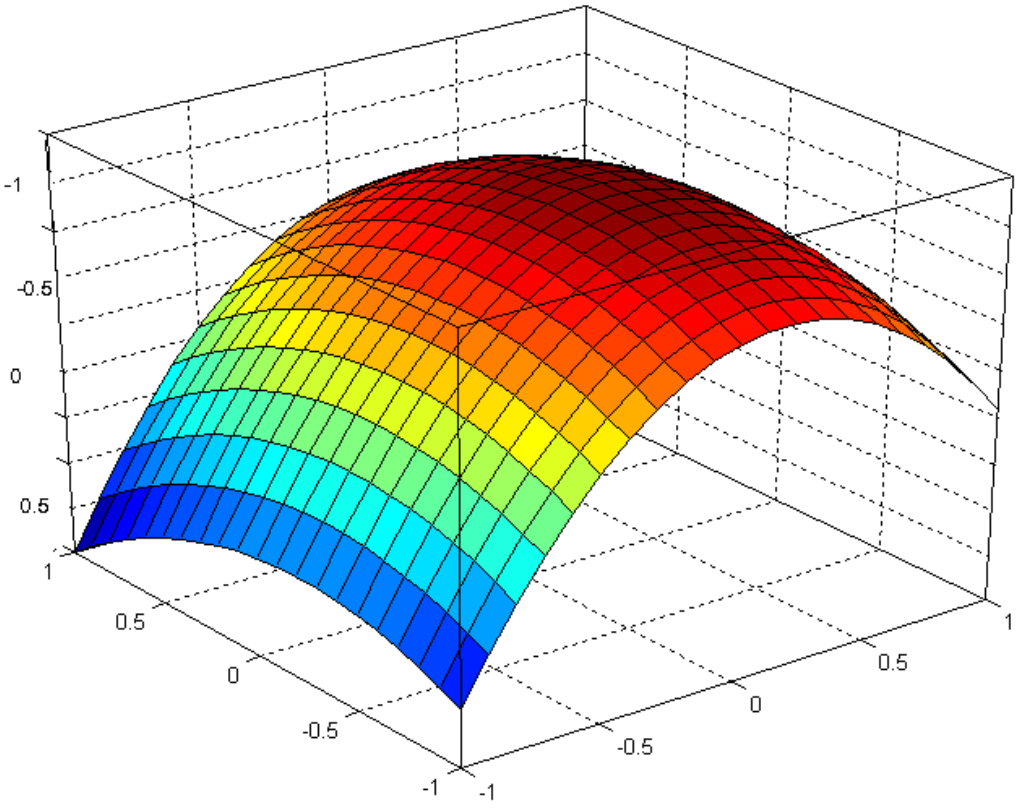


Fig.3. The optimal surface of responce

As can be seen from the equation, coefficients values have different signs, i.e., response surface is the hyperbolic parabolic "saddle". The surface of the center is the "Minimax" (Figure 3.).

In this way, the solution of optimization problem showed that the highest yield of alkylphenol derivatives Y1opt = 67.58 % by wt. can be obtained by X_1 = 1000˚C; X_2 =4 h; X_3 = 3,5: 1 mol / mol ; X_4 = 15% by wt. Carrying out the process under these conditions is in good consistent with the experimental data.

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