Optimization of the Process Catalytic Cycloalkylation of Phenol with Methyl Ether of 4-Methylcyclohexenecarboxylic Acid

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Abstract— The study explored the catalytic cycloalkylation reaction of phenol with methylcyclohexenes in the presence of zeolite-Y impregnated with orthophosphoric acid. The primary objective was to optimize the reaction conditions to achieve the maximum yield of the target product. To achieve this, the influence of several input variables was examined: reaction temperature, duration, molar ratio of reactants, and the amount of catalyst. Mathematical processing of the experimental data led to the formulation of second-order equations that describe the partial dependencies of the output parameter on each input factor. A generalized equation was also developed, capturing the simultaneous dependence of the output optimization parameter on all input variables.

Keywords—Phenol, methyl ether of 4-methylcyclohexene carboxylic acid, catalyst, cycloalkylation, alkylphenol, optimization

I. INTRODUCTION

Alkylphenol chemical additives are one of the most common types of additives, due to their high spectral performance properties, relative availability of raw materials, and fairly simple production technology [1-5].

The purpose of this work is to study the reaction of obtaining methyl ether of 4(4'-hydroxyphenyl)-4 methylcyclohexanecarboxylic acid in the presence of a zeolite-containing catalyst KN-30, and to develop a regression mathematical model of the process parameters [6-9].

II. EXPERIMENTAL PART

The starting products for the alkylation reaction were phenol and the methyl ether of 4-methylcyclohexene carboxylic acid (MEMCHCC). MEMCHCC was obtained by the reaction of isoprene with the methyl ether of acrylic acid via the Diels–Alder reaction: Tk.=197-198°C; n_D^{20}=1,4620; ρ_4^{20}=0,9.

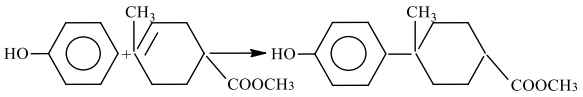
Zeolite-containing KN-30 (TU 2177-011-0752227-2008) was used as a catalyst.

The cycloalkylation of phenol with ME MCHCC was carried out in a laboratory batch reactor. The calculated amount of phenol and catalyst was added to a three-necked flask. When the temperature reached 45°C, ether was added dropwise into the flask. After stopping the addition of ether, the reaction temperature is raised to 80–140°C and the mixture is stirred at this temperature for 2–6 hours.

At the end of the work, the catalyst is separated from the alkylate; then the reaction mixture is distilled. During rectification, the ether and phenol that did not participate in the reaction were first distilled off at atmospheric pressure (up to 200°C), and then the target product of the process was isolated under vacuum (665.5 Pa).

The structure of the obtained product was determined by IR and H NMR spectroscopy. The IR spectra of the samples were recorded on an ALPHA IR Fourier spectrometer (BRUKER, Germany) in the wavenumber range of 600–4000 cm^{-1}. The ^1H NMR spectra were recorded on a BRUKER TOPSPİN instrument (^1H 300.18 MHz) at room temperature in $CDCl_3$ solutions. Tetramethylsilane was used as a standard.

Alkylation of phenol by ME MCHCC was carried out according to the following scheme:



To find optimal conditions that provide maximum yield, the influence of temperature, time, molar ratio of the starting components and the amount of catalyst on the yield and selectivity was studied.

Temperature solutions are taken in the range of 80–140°C; time 2-6 hours, milk ratio of phenol to ether 5:0.5÷2, amount of catalyst –5-15% per phenol taken.

To establish quantitative ratios reflecting the influence of key technological factors on the output parameters, experiments were conducted, the results of which are presented in Table 1.

Table 1. Dependence of the yield and selectivity of cycloalkyl substituted phenol on the reaction conditions

№	Molar ratio Phenol: ether	Temperature, °C	Time, h	Quantity of cat., %	Output, %	Selectivity, %
1	1:0,5	120	5	10	75,3	88,5
2	1:1	120	5	10	73,6	90,3
3	1:2	120	5	10	51,4	81,6
4	1:1	80	5	10	38,7	94,0
5	1:1	100	5	10	53,1	92,9
6	1:1	120	5	10	72,6	92,3
7	1:1	140	5	10	58,3	84,1
8	1:1	120	5	10	40,7	95,6
9	1:1	120	3	10	55,3	93,2
10	1:1	120	5	10	71,6	92,5
11	1:1	120	6	10	67,4	86,8
12	1:1	120	5	5	54,7	96,5
13	1:1	120	5	7,5	65,3	94,2
14	1:1	120	5	10	74,0	92,3
15	1:1	120	5	15	77,2	83,7

To develop a regression model of a process, it is necessary to identify the functional connection between process parameters and use it for further process prediction.

Considering that the numbers of experiments and output variables are m=15 and n=3, respectively, the functional relationship can be represented as a nonlinear polynomial:

$$Y_k = a_0 + \sum_{i=1}^{n} a_i z_i + \sum_{j \neq i}^{n} a_{ij} \times z_i z_j + \sum_{i=1}^{n} a_{ii} \times z_i^2 \quad (1)$$

where Y_k are output parameters Zi , Z_j are input variables; a_0, a_{ii}, a_{ij} are the coefficients of the regression model; i=1, 2, 3, 4.

To determine the coefficients of equation (1), the S-plus 2000 Professional program [4] was used, which models and coefficients of pair correlation. The results of the coefficient calculations allow for the automated calculation of statistical analysis data, the regression coefficients are presented in Table 2.

Table 2. Coefficients of regression model

Y_k	a_0	a_1	a_2	a_3	a_{11}	a_{22}	a_{33}
Y_1	-205.9	0	1.93	37.83	-0.15	0.01	-0.21
Y_2	214.02	0	-1.03	-23.11	0.161	-0.08	0.18

To check the significance of the regression equation coefficients, we use the Student's test:

$$t = \frac{|a_i|}{\sqrt{S_a^2}} \quad (2)$$

where S_{ai}^2 is the variance of the regression coefficient error, determined by the formula:

$$S_{ai} = \sqrt{\frac{S_{irep}^2}{N}} \quad (3)$$

Substituting the numerical values S_{1rep}^2 =42,6 and S_{2rep}^2=26,3 into formula (3), we find the values S_{ai} = 0,35 and S_{bi} = 0,53.

Knowing the numerical values of S_{ai} and S_{bi} i and substituting them into formula (2), we calculate the calculated values of the Student's t test for each coefficient.

Calculations showed that all coefficients are significant. In this case, equation (1) takes the following form:

$$Y_1 = -205.96 + 1.93X_2 - 37.83X_3 - 0.16X_1X_2 + \\ +0.01X_1X_3 - 0.21X_2X_3 \quad (4)$$

$$Y_2 = 214.02 - 1.03X_2 - 23.11X_3 + 0.161X_1X_2 - \\ -0.08X_1X_3 + 0.18X_2X_3 \quad (5)$$

The hypothesis about the adequacy of models (4), (5) was tested using Fisher's criterion [5]:

$$F = \frac{S_{res}^2}{S_{rep}^2} \leq F_{tabl.} \quad (6)$$

where S_{res}^2 is the residual variance, determined by the formula:

$$S_{res}^2 = \sum_1^N \frac{(y_i^p - y_i^e)^2}{N-1} \quad (7)$$

where S_{res}^2 и S_{1rep}^2 are the coefficients of residual variance and variance of reproducibility of the experiment, respectively. The $S_{1\text{воспр}}^2$ indicator was determined by the formula

$$s_{res}^2 = \frac{1}{m-1} \sum_1^m (Y_0^{av} - Y_0^c)^2 \quad (8)$$

where m is the number of experiments at zero values; where Y_0^{av}, Y_0^c are the average and current values at zero values. Substituting the numerical values into formula (8), we obtained the values: S_{1rep}^2=2,5; S_{2rep}^2=0,36.

Substituting the values of S_{iad}^2 и S_{irep}^2 into formula (6), we obtained the Fisher values: F_1=6; F_2=3.

Comparing the found values of the criterion with the tabular ones at the selected confidence probability of 95% and the numbers of degrees of freedom $f_1 = 3$, $f_2 = 2$ we see that the calculated values of F_c are less than the tabular $F_T = 19.3$. This indicates that the regression equations (7) and (8) adequately describe the response surface. Consequently, they can serve as a statistical model of the regularity of the process parameter changes and can be used in solving the optimization problem, as well as in studying the response in a wide range of output variable changes.

Using the formulas for the transition from normalized variables X_i to natural Z_i, by transformation we obtained equations in the following form:

$$y_1 = -280.3 + 0.0083Z_1 + 1.94Z_2 + 108.9Z_3 - \\ -0.0035Z_1Z_2 + 0.009Z_1Z_3 - 0.4Z_2Z_3 \quad (9)$$

$$y_2 = 259.6 - 0.0041Z_1 - 1.312Z_2 - 66.1Z_3 + \\ +0.0035Z_1Z_2 - 0.0076Z_1Z_3 + 0.342Z_2Z_3 \quad (10)$$

Using the developed regression model on a PC, calculations were performed to study the influence of each factor on the output parameters.

III. Conclusion

Based on experimental data, a regression mathematical model of the process of catalytic cycloalkylation of phenol MCP has been developed, reflecting the influence of key technological factors on the yield of the target product. The optimization problem was solved, namely, the optimal values of the input variables were found (temperature 120°C, reaction duration 6 h, amount of catalyst 10%), at which the yield of the target product was 79%, and the selectivity was 92%.

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