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OPTIMIZATION OF 2,3-DIMETHYLBUTA-1,3-DIENE AND 2-HYDROXYETHYL METHACRYLATE CYCLIZATION REACTION CONDITIONS

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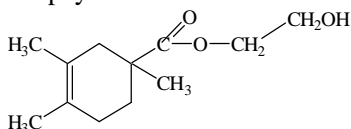
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Abstract. Based on the experimental studies and mathematical modeling method, we have chosen the optimal conditions of the 2,3-dimethylbuta-1,3-diene and 2-hydroxyethyl methacrylate cyclization reaction with obtaining of 2-hydroxyethyl-1,3,4-trimethylcyclohex-3-en carboxylate.

Keywords: optimization, 2,3-dimethylbuta-1,3-diene, 2-hydroxyethyl methacrylate, 2-hydroxyethyl-1,3,4-trimethylcyclohex-3-en carboxylate, full factorial experiment.

1. Introduction

Alkylcyclohexene substances are used as monomers in order to receive new polymeric materials and polyfunctional polymers of different structure with predefined set of physical and chemical characteristics [1].



Optically active liquid crystals, which are used as components of liquid-crystal compositions in electro-optical devices, are synthesized on their basis [2]. Also, alkylcyclohexene substances can be used for the synthesis of the secondary and tertiary hydroaromatic hydrocarbons [3].

The method of full factor experiment (FFE) is widely used to determine the optimal conditions for technological process stages in different industries, which allows to significantly decrease both the research duration and financial expenses on its implementation. The FFE method was applied, for example, for the process optimization of trans-esterification of sunflower-seed oil

with sodium methoxide [4], modeling of anthracite coal oxidizing desulfurization process [5], and also for investigating of the technological factors influence on durability of the weld-fabricated microsubstances [6]. Optimization of α -ethylacrolein cyclization process with ethyl ester α -ethylacrylic acid in Diels-Alder reaction was conducted by us in [7] using the FFE method. In this work according to the FFE method, the conditions of 2,3-dimethylbuta-1,3-diene and 2-hydroxyethyl methacrylate cyclization reaction were optimized.

2. Experimental

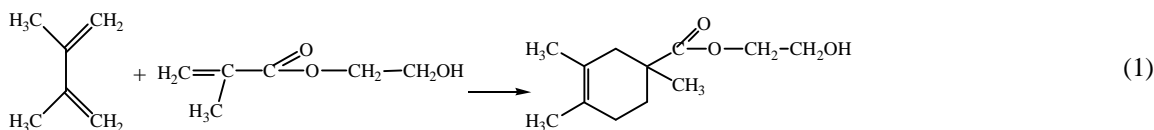
2.1. Materials

2-Hydroxyethyl methacrylate is a commercially available product of P.A. purity. The product purity was controlled by chromatograph using the SELMI Chrom-1 device. $T_{boil.} = 340$ K/3.5 mm Hg, $d_4^{25} = 1.073$, $n_D^{20} = 1.453$.

2,3-Dimethylbuta-1,3-diene was synthesized by catalytic dehydration of 2,3-dimethyl-2,3-butandiol according to a methodology [8]. Yield 98 %, $T_{boil.} = 343$ K, $d_4^{20} = 0.7147$, $n_D^{20} = 1.4290$, $MR_{found.} = 28.98$, $MR_{calcd.} = 29.14$.

2.2. Synthesis Procedure

2-Hydroxyethyl-1,3,4-trimethylcyclohex-3-en carboxylate was received *via* the cyclization of 2,3-dimethylbuta-1,3-diene with 2-hydroxyethyl methacrylate in accordance with the Diels-Alder reaction (see Section 1):



The synthesis was carried out in glass vacuum-sealed ampoules, according to the method [9]. Depending on the ratio, either 0.7–1.2 ml (0.01–0.0175 mol) of 2,3-dimethylbuta-1,3-diene or 1.2 ml (0.01 mol) of 2-hydroxyethyl methacrylate were put into an ampoule, with adding 0.0025 g of hydroquinone into it. The temperature interval of the reaction research was in the range of 403–433 K, and duration was 3.5–6.5 h. Depending on the conditions of the reaction, the product yield was 41–86 %, determined by the chromatogram. Separation of 2-hydroxy-1,3,4-trimethylcyclohex-3-en carboxylate was conducted by vacuum factious distillation with deflegmator of 20 cm length.

2-Hydroxy-1,3,4-trimethylcyclohex-3-en carboxylate is a transparent colourless liquid. $T_{boil.} = 652 \text{ K/4 gPa}$, $d_4^{20} = 0.971$, $n_D^{20} = 1.479$, $MR_{found.} = 58.71$, $MR_{calcd.} = 59.09$.

The structure of 2-hydroxy-1,3,4-trimethylcyclohex-3-en carboxylate was confirmed by ^1H NMR spectrum. ^1H NMR spectrum was observed by the spectrometer Bruker AM-300 (300 MHz) in CDCl_3 taking TMS as the internal standard. ^1H NMR spectrum completely confirms 2-hydroxy-1,3,4-trimethylcyclohex-3-en carboxylate structure. The spectrum has signals at 1.38, 1.82, 1.82, 1.84, 1.91, 2.01, 2.09, 2.15, 2.40, 3.55, 4.27, and 4.90 ppm. Six protons of cyclohexene fragment cause four doublet signals at 1.84, 1.91, 2.01, 2.09, 2.15, and 2.40 ppm. Methyl groups of a cycle in 3,4 position resonate as two singlets at 1.82 and 1.82 ppm, and methyl group in 1 position resonates as singlet at 1.38 ppm. Hydroxyethyl fragment protons are recorded as two triplets at 3.55 and 4.27 ppm and as a singlet at 4.90 ppm.

2.3. Method of Analysis

The products of cycloaddition reactions were analyzed using chromatograph of SELMI CHROM-1 under such conditions: a detector by heat transfer is DHC, Polysorb-1 chromatogram column with 1 m length and 3 mm diameter, detector current – 37 mA, column temperature – 393 K, detector temperature – 423 K, vaporizer temperature – 423 K, gas-transmitter – hydrogen with the consumption of 20–22 ml/min, amount of test – 1 μl . Under the current temperature conditions we have received completely full splitting of matters in the isothermal mode [9]. Chromatograms were registered by computer, determinations of peaks area were conducted in the Mathcad environment, and quantitative analysis was conducted with the method of internal normalization taking into account the coefficients of detector sensitiveness for each of matters independently.

2.4. Method of Optimization

The terms and conditions of experiment realization are described in [9]. We chose the regression equation (2)

in order to get the mathematical description of the process using the method of full factor experiment [10, 11] with three factors

$$Y_i = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 \quad (2)$$

where Y is a response function (the process efficiency parameter) which depends on the individual technological parameters; X are the independent coded variables (the process parameters).

Based on the previous investigations [3] of reactivity of the 2,3-dimethylbuta-1,3-diene cyclization with 2-hydroxyethyl methacrylate, we chose three factors as the technological parameters: the temperature in the range of 403–433°K, the reaction time in the range of 3.5–6.5 h, and the molar ratio of the starting materials 1:1 to 1:1.5. The response functions were: the productivity of the process relative to 2-hydroxyethyl-1,3,4-trimethylcyclohex-3-en carboxylate, and the yield of the product.

The productivity (G_p , Y_1) at the reaction stage was calculated as the specific productivity for the batch-type reactor [12] ignoring the unproductive time expenses, dividing the concentration of product [g/l], which was chromatographically got for the period of the reaction proceeding.

$$G_p = \frac{C_p}{t} \cdot M_p = Y_1 \quad (3)$$

The yield of product (Y_2) at the reaction stage was calculated according to the results of chromatographic analysis, as the ratio of molar concentration of product (P) to the initial concentration of 2-hydroxyethyl methacrylate – reagent (A) which was taken in smaller amount relative to stoichiometry, by the formula:

$$Y_2 = \frac{C_p}{C_A^0} \cdot 100\% \quad (4)$$

Verification of experiments reproducibility was conducted on the basis of two parallel experiments ($k = 2$) for each combination of technological parameters of the chosen local area of factor space and for each series from two parallel experiments estimation of reproducibility dispersion was calculated (s_y^2). The assessment of reproducibility dispersion (s_y^2) was received by dispersions averaging in all eight experiments. In addition dispersion assessment of average value (s_y^2) has been calculated. Dispersion s_b was calculated for error estimate at determination of coefficients of regression b_i . Significance of the received coefficients of regression was estimated by Student's criterion ($t_{tabl} = 2.31$ for the number of degrees of freedom ($f = N(k-1) = 8 \cdot (2-1) = 8$) according to the correlation (5).

$$|b_i| > S_b \cdot t_{\text{tabl}} \quad (5)$$

Adequacy of the received equations, which were suggested for the process description, was estimated using Fisher's criterion (F_c)

$$F_c \leq F_{\text{tabl}} \quad (6)$$

where F_{tabl} is tabular value of Fisher's criterion, F_c – calculated Fisher's criterion. Dispersion of adequacy s_{ad}^2 was calculated by the formula (7)

$$s_{ad}^2 = \frac{1}{N-B} \sum_{j=1}^N (Y_j^e - Y_j^p) \quad (7)$$

where B is a number of regression coefficients in equation, including the free term; Y_j^e , Y_j^p – experimental and calculated by regression equation values of response function in j^{th} investigation, respectively; $N = 8$ is an amount of investigations in a full factor experiment. The coefficients of regression equation (4) for parameters in the encoded variables were got based on the results of PFE according to [10, 11].

3. Results and Discussion

Preliminary research of the influence of the initial reagents ratio on the yield of 2-hydroxyethyl-1,3,4-trimethylcyclohex-3-en carboxylate was conducted at 433 K and with the molar ratio 2,3-dimethylbuta-1,3-diene : 2-hydroxyethyl methacrylate 1:1; 1.25:1; 1.5:1; 1.75:1 (Fig. 1).

As we can see from Fig. 1, the increase of excess more than 1.5:1 does not significantly influence the changes of 2-hydroxyethyl-1,3,4-trimethylcyclohex-3-en carboxylate yield. Moreover, due to the decrease in the reaction product concentration and increase of surplus component recirculation volume, reduction of the process productivity takes place.

Thus, at the temperature of 433 K, the reaction time of 3.5 h and at the growth of 2,3-dimethylbuta-1,3-diene from stoichiometric value (1:1) to its excess (1.5) the product yield increases from 45.9 to 48.2 %, and at 1.75 excess – only to 49.2 %. At the increase of the reaction time to 6.5 h and the ratio of 1.5 the product yield increases approximately by 5 % (from 81.7 to 86 %), and at further increase of excess to 1.75 – only by 1 %. At the same time the productivity of the process at both reaction times of 3.5 and 6.5 h is identical (Fig. 1). Table 1 shows the results of the reproducibility in eight experiments for the given response functions.

The coefficients b in the regression (1) were calculated using the values of coded variables X associated with the physical quantities (temperature, duration, and reagents ratio) according to Eq. (8).

$$X = \frac{x - x_0}{\Delta x} \quad (8)$$

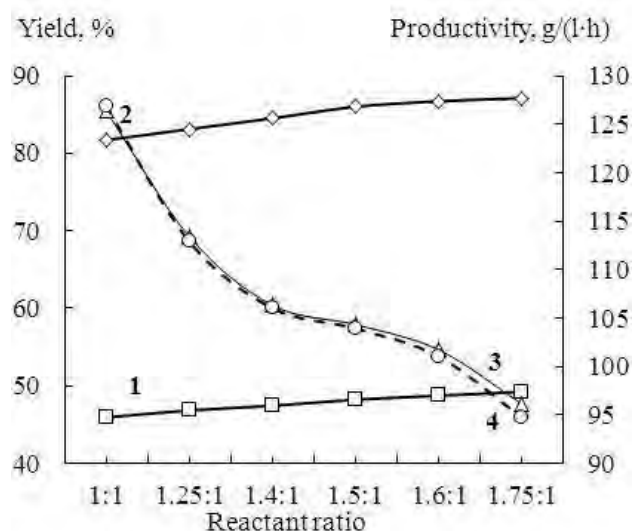


Fig. 1. Dependence of the process productivity and the product yield on the molar ratio of reactants at the temperature of 403 K: 2-hydroxyethyl-1,3,4- trimethylcyclohex-3-en carboxylate yield after 3.5 h (1); 2-hydroxyethyl-1,3,4- trimethylcyclohex-3-en carboxylate yield after 6.5 h (2); the process productivity toward 2-hydroxyethyl-1,3,4- trimethylcyclohex-3-en carboxylate after 3.5 h (3) and the process productivity toward 2-hydroxyethyl-1,3,4- trimethylcyclohex-3-en carboxylate after 6.5 h (4)

where for each factor the values of x_0 are equal to 418 K, 3.5 h and 1.25:1 molar ratio of 2-hydroxyethyl acrylate to 2,3-dimethylbutadiene; $\Delta x = 288$ K, 1.5 h and 0.25, respectively. The planning matrix of the full three-factor experiment was prepared according to [11] using the coded variables for the regression Eq. (2). Table 3 shows the coefficients of the regression for the parameters represented in the coded variables. The values of dispersion (S_b) used to assess an error during the determination of regression coefficients b_i are shown in Table 3.

Table 2 shows the experimental conditions and the average values of the corresponding response functions.

According to the assessment, all coefficients in the equation of the response function Y_1 (the process performance) are significant, while the coefficients b_3 , b_{12} , b_{13} , and b_{23} in the equation of the response function Y_2 (yield) are insignificant.

Table 4 shows the variances and the calculated values of Fisher's criterion confirming adequacy of the process description according to the selected mathematical model.

Thus, the correlation of the initial components should be fixed at the level of 1.5:1, as an optimum value, for which the encoded variable size is $X_3 = (1.5 - 1.25) / 0.25 = 1$. While molar correlation of the parameter value of 2,3-dimethylbuta-1,3-diene : 2-hydroxyethyl methacrylate is fixed, Eq. (2) turns into Eq. (9) with two variables – temperature and time of the experiment.

Table 1

The variance of experiments reproducibility

Exp.	Process productivity (Y_1), g/l·h		Product yield (Y_2), %	
	Exp. 1	Exp. 2	Exp. 1	Exp. 2
1	104.88	106.08	40.62	41.42
2	125.97	126.77	45.4	46.4
3	110.26	111.46	74.25	74.95
4	126.49	127.29	81.2	82.2
5	90.77	91.37	41.7	42.5
6	103.67	104.87	47.85	48.55
7	91.99	92.59	76	76.8
8	103.19	104.59	85.7	86.3
s_y^2 (4)	0.518		0.329	
s_y^2 (5)	0.259		0.164	

Table 2

Conditions of experiments and response functions average values

Temperature, K (X_1)	Reaction time, h (X_2)	2,3-Dimethylbuta-1,3-diene : 2-hydroxyethyl methacrylate molar ratio (X_3)	Process productivity, g/l·h (Y_1)	Product yield, % (Y_2)
403	3.5	1 : 1	105.48	41.02
433	3.5	1 : 1	126.37	45.90
403	6.5	1 : 1	110.86	74.60
433	6.5	1 : 1	126.89	81.70
403	3.5	1.5 : 1	91.07	42.10
433	3.5	1.5 : 1	104.27	48.20
403	6.5	1.5 : 1	92.29	76.40
433	6.5	1.5 : 1	103.89	86.0

Table 3

Regression coefficients of the response functions

Regression coefficients	Response functions	
	Process productivity (Y_1), g/(l·h)	Product yield (Y_2), %
b_0	107.64	61.99
b_1	7.715	3.46
b_2	0.843	17.685
b_3	-9.76	1.185
b_{12}	-0.808	0.715
b_{13}	-1.515	0.465
b_{23}	-0.632	0.34
$S_b(10)$	0.180	0.143
$S_b \cdot t_{table}$	0.415	0.331

Table 4

Calculated values of variance adequacy and Fisher's criterion

Response function (Y)	S_{ad}^2	S_y^2	F_p	F_{table}
Process productivity (Y_1), g/(l·h)	1.328	0.259	5.134	5.3
Product yield, %	0.205	0.164	1.246	5.3

Table 5

The coefficients of regression equations depending on temperature and process time

Response function (Y_i)	$a_0 = b_0 - b_3$	$a_1 = b_1 - b_{13}$	$a_2 = b_2 - b_{23}$	$a_{12} = b_{12}$
Process productivity, (Y_2), g/(l·h)	97.88	6.2	0.211	-0.808
Product yield, %	63.175	3.925	18.025	0.715

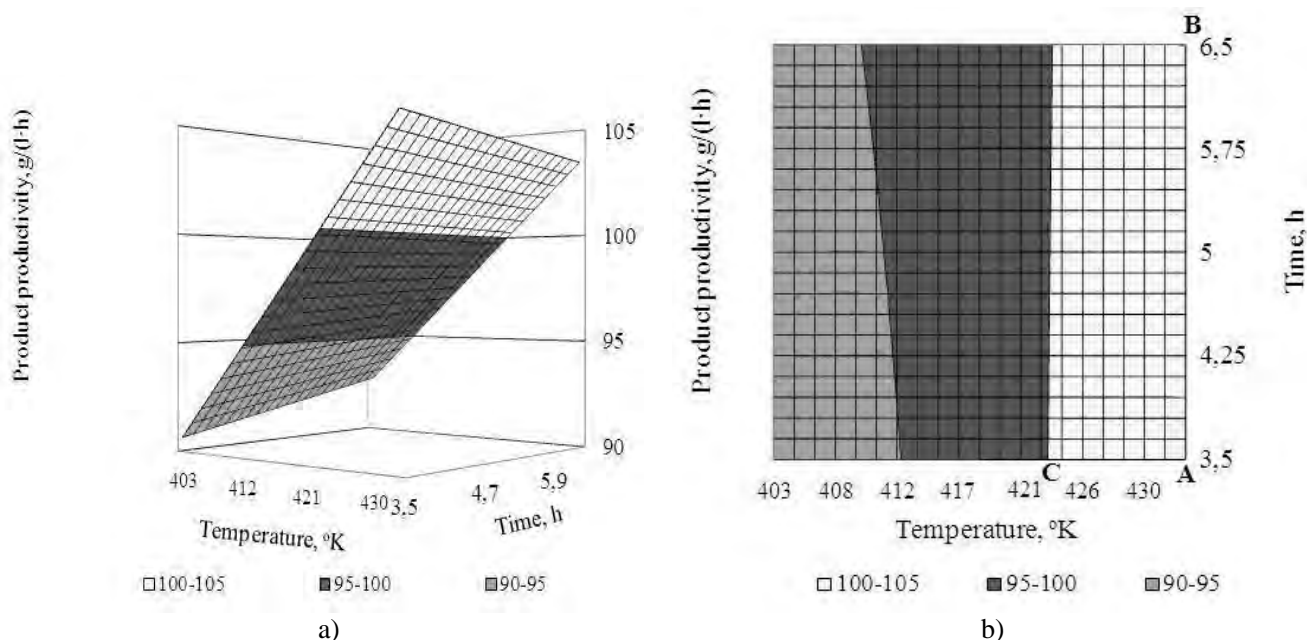


Fig. 2. Calculated response surface (a) and its projection for the process productivity function (b)

The coefficients of Eq. (9) are determined by the coefficients b_i according to the correlations shown in Table 5.

$$Y_i = a_0 + a_1 X_1 + a_2 X_2 + a_{12} X_1 X_2 \quad (9)$$

The calculation of the process productivity and output of a target product was carried out using Eq. (14) with a step in the encoded variables 0.1, that corresponds to the temperature change of 274.5 K and reaction time of 9 min. Visual assessment and search of optimum areas for reaction temperature and time can be performed by the calculated response surfaces and their projections, which are shown in Figs. 2 and 3.

One of the conditions of the process realization expediency is high productivity by the target product, which should not be less than 100 g/(l·h) at the highest selectivity or the product yield. The area of the great values of productivity (100 g/(l·h), Fig. 2) corresponds to the triangular sector with the vertex coordinates corresponding to the following values of temperature and time A (433 K, 3.5 h) 104.68 g/(l·h), B (433 K, 6.5 h) 103.43 g/(l·h), C (424 K, 3.5 h) 100.47 g/(l·h). The maximum yield of the target product 85.84 %, and productivity of 100.36 g/(l·h) is achieved at the temperature of 433 K and the reaction time of 6.5 h.

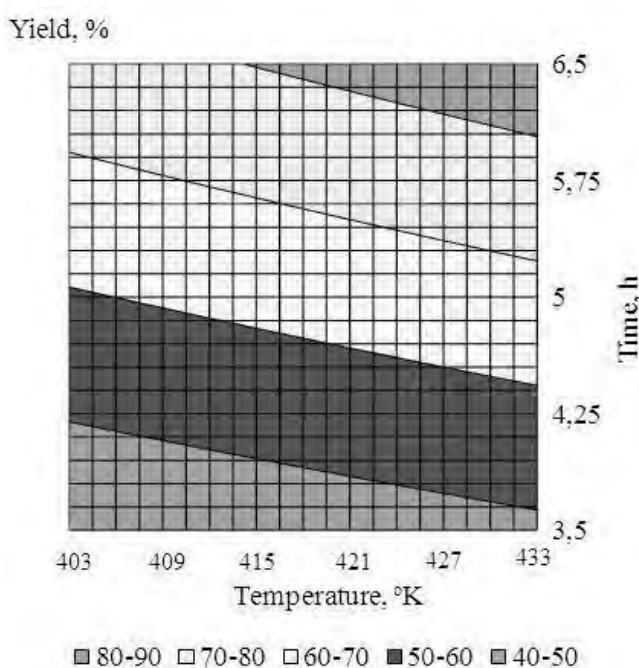


Fig. 3. Surface of the response function of the target product yield

Since maximum productivity and yield of 2-hydroxyethyl-1,3,4-cyclohex-3-en carboxylate can be achieved at 433 K it is necessary to set minimum time, which would correspond to the productivity at which realization of technological process is expedient. Productivity more than 100 g/(l·h) at 433 K appeared for the time of 6.5 h, which corresponds to $X_2 = 1$ of the encoded parameter of time. According to Eq. (14) the yield 85.84 % and the productivity 100.36 g/(l·h) for the reactionary stage of the process of obtaining 2-hydroxyethyl-1,3,4-cyclohex-3-en carboxylate at $X_1 = 1$ (433 K) and $X_2 = 1$ (6.5 h) have been calculated. Under experimental conditions the yield was found to be 86 % (Fig. 3).

4. Conclusions

Thus, the received results satisfactorily coincide with the data received from mathematical modeling of the process. Consequently, it is possible to predict that optimal conditions for realization of technological process of cyclization, under which the product yield is 86 %. They are following: temperature – 433 K, time – 6.5 h and molar ratio of 2,3-dimethylbuta-1,3-diene: 2-hydroxyethyl methacrylate = 1.5:1.

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ОПТИМІЗАЦІЯ УМОВ РЕАКЦІЇ ЦИКЛІЗАЦІЇ 2,3-ДИМЕТИЛБУТА-1,3-ДІЄНУ ТА 2-ГІДРОКСИЕТИЛМЕТАКРИЛАТУ

Анотація: На основі експериментальних досліджень методом математичного моделювання вибрано оптимальні умови реакції циклізації 2,3-диметилбута-1,3-дієну та 2-гідроксиетилметакрилату з отриманням 2-гідроксиетил-1,3,4-триметилциклогекс-3-енкарбоксилату.

Ключові слова: оптимізація, 2,3-диметилбута-1,3-дієн, 2-гідроксиетилметакрилат, 2-гідроксиетил-1,3,4-триметилциклогекс-3-енкарбоксилат, повний факторний експеримент.