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Optimization of the Process of the Allyl 1,3,4-Trimethylcyclohex-3-en-1-carboxylate Production by the Full Factorial Experiment

I. S. Polevaya, I. P. Polyuzhin, N. M. Karpyak, O. I. Marshalok, and Ya. M. Zakharko

National University "Lviv Polytechnic," ul. Bandery 12, Lviv, 79013 Ukraine
e-mail: Polyova.ira@gmail.com

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Abstract—Based on experimental studies and mathematical modeling method, the effectiveness of technological process for the production of allyl 1,3,4-trimethylcyclohex-3-en-1-carboxylate was forecasted. The optimal conditions of the process were revealed.

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The allyl 1,3,4-trimethylcyclohex-3-en-1-carboxylate was synthesized by the cyclization of 2,3-dimethylbuta-1,3-diene (dimethylbutadiene) with allyl methacrylate in the Diels–Alder reaction. To optimize the experimental studies and to determine the optimum process conditions, we applied a method of full factorial experiment. For the mathematical description of the process by this method [1, 2] with three factors we choose the regression equation (1).

$$Y_i = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3, \quad (1)$$

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

Based on previous studies [3] of reactivity in the 2,3-dimethylbuta-1,3-diene cyclization with allyl methacrylate, we chose three factors as the technological parameters: the temperature in the range of 120–170°C, the reaction duration in the range of 2–5 h, and the molar ratio of the starting materials, 1:1 to 1:2. The response functions were: the productivity of the process with respect to allyl trimethylcyclohexanoate, and the yield of the product.

The experiment reproducibility was checked by carrying out two parallel experiments ($k = 2$) for each combination of the process parameters in this local region of the factor space. Table 1 shows the results of the reproducibility checking in eight experiments for the given response functions. For each series of parallel experiments the estimate for the variance was calculated by Eq. (2).

$$S_j^2 = 1/(k-1)\sum_{i=1}^{k}(y_{ji} - \bar{y}_j)^2,\ k = 2. \quad (2)$$

Estimates of the uniform variance in the several series of parallel experiments were averaged, and the estimates of the reproducibility variance were found by Eq. (3).

$$S_y^2 = 1/N\sum_{j=1}^{N} S_j^2,\ N = 8. \quad (3)$$

The estimate of the mean variance, which like the estimate of the variance of reproducibility is related to the number of the degrees of freedom $f = N(k–1)$ was calculated by the formula (4).

$$S_{\bar{y}}^2 = S_y^2/k. \quad (4)$$

Table 2 shows the planned experimental conditions and the average values of the corresponding 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. (5).

$$X = (x - x_0)/(\Delta x), \quad (5)$$

where the values of x_0 for each factor were taken, respectively, 140°C, 3.5 h and 1.5:1 molar ratio of allyl methacrylate to dimethylbutadiene, and the steps Δx

Table 1. The variance of reproducibility estimates and their average values

Exp. no.	Allyl trimethylcyclohexanoate productivity, g l^{-1} h^{-1}		Product yield, %	
	Y_1	Y_2	Y_1	Y_2
1	86.5	87.5	20.4	21.4
2	153.0	154.8	36.2	37.8
3	74.1	76.5	44.1	46.3
4	112.4	114.2	67.2	68.8
5	56.4	58.0	20.5	21.9
6	103.8	106.2	37.8	39.9
7	49.4	51.4	45.6	47.6
8	73.9	76.3	68.4	70.6
S^2_y (3)	1.958		1.663	
$S^2_{\bar{y}}$ (4)	0.979		0.831	

20°C, 1.5 h and 0.5, respectively. The planning matrix of the three-factor full factorial experiment was prepared according to [4] using the coded variables for the regression Eq. (1). Table 3 shows the coefficients of the regression Eq. (3) calculated for the parameters represented in the coded variables on the basis of the results of the fully crossed design along formulas (6)–(8):

$$b_0 = 1/N \sum_{j=1}^{N} y_j, \quad (6)$$

$$b_i = 1/N \sum_{j=1}^{N} X_{ji} y_j, \quad (7)$$

$$b_{1m} = 1/N \sum_{j=1}^{N} X_{jl} X_{jm} y_j \text{ (where } l \neq m). \quad (8)$$

Here $N = 8$ is the total number of the experiments in the full factorial experiment; j is the number of an experiment, i, l, m are the numbers of the factors.

The variance for estimating the error in determining the regression coefficients b_i was calculated with formula (9). The values of S_b obtained are given in Table 3.

$$S_b = \sqrt{S^2_{\bar{y}}/N}. \quad (9)$$

Testing significance of the regression coefficients was performed with the Student's test $t_{table} = 2.31$ by Eq. (10).

$$|b_i| > S_b t_{tabl}. \quad (10)$$

According to the evaluation, all coefficients for the equation of the response function Y_1 (the process performance) are significant, while the coefficients b_3, b_{12}, b_{13}, b_{23} in the equation of the response function Y_2 (yield) are insignificant and were excluded from the equation. After exclusion of insignificant coefficients, the regression Eq. (1) for the response function Y_2 is transformed into Eq. (11). Table 4 shows the coefficients in Eq. (11).

$$Y_i = a_0 + a_1X_1 + a_2X_2 + a_{12}X_1X_2. \quad (11)$$

The adequacy of the equations proposed to describe the process was confirmed by the consistency of the calculated and tabulated Fisher criterion, $F_{calc} \leq F_{table}$, where F_{table} is the tabulated value, while F_{calc} is the Fisher's criterion calculated by the formula (12). The adequacy variance S^2_{ad} was calculated by the formula (13).

$$F_{calc} = \frac{\max(S^2_{ad}, S^2_y)}{\min(S^2_{ad}, S^2_y)} \quad (12)$$

$$S^2_{ad} = 1/(N - B) \sum_{j=1}^{N} (y_j^{exp} - y_j^{calc}), \quad (13)$$

where B is the total number of regression coefficients in the equation, including the constant term; y_j^{exp} and y_j^{calc} are experimental response and the value of the response function calculated by the regression formula for the jth experment, $N = 8$ is the total number of experiments in the full factorial design.

Table 5 shows the variances and the calculated

Table 2. Conditions of experiments and measured values

Temerature, °C (X_1)	Reaction duration, h (X_2)	Dimethylbutadiene : allyl methacrylate molar ratio (X_3)	Process productivity, g l^{-1} h^{-1} (Y_1)	Product yield, % (Y_2)
120	2	1:1	87.0	20.9
160	2	1:1	153.9	37.0
120	5	1:1	75.3	45.2
160	5	1:1	113.3	68.0
120	2	1:2	57.2	21.2
160	2	1:2	105.0	38.9
120	5	1:2	50.4	46.6
160	5	1:2	75.1	69.5

values of the Fisher criterion confirming adequacy of the selected mathematical model to the process.

A preliminary study of the influence of the ratio of initial reagents on the yield and productivity of allyl trimethylcyclohexanecarboxylate (Fig. 1) showed that an increase in the allyl methacrylate excess did not increase substantially the product yield, while the process productivity fell significantly due to the decrease in the reaction product concentration and the increase in the recycling of excess component. The coefficient of the coded variable related to the ratio of the formed reagents in the regression equation for the response function Y_2 (yield) was also proved to be insignificant and was excluded from the Eq. (11). Thus, the ratio of initial components was fixed at the optimal value of 1:1, for which the value of coded variable $X_3 = (1–1.5)/0.5 = –1$.

At the fixed value of the dimethylbutadiene : allyl methacrylate molar ratio the Eq. (1) is transformed into Eq. (11) with two variables: the process temperature and duration. Table 5 lists the coefficients of Eq. (11).

Calculation of the productivity and yield of the target product was performed with Eq. (13) using a step 0.1 of the respective coded variables, which corresponds to the change in temperature 2°C and the reaction duration 9 min. The response surfaces are shown in Figs. 2 and 3.

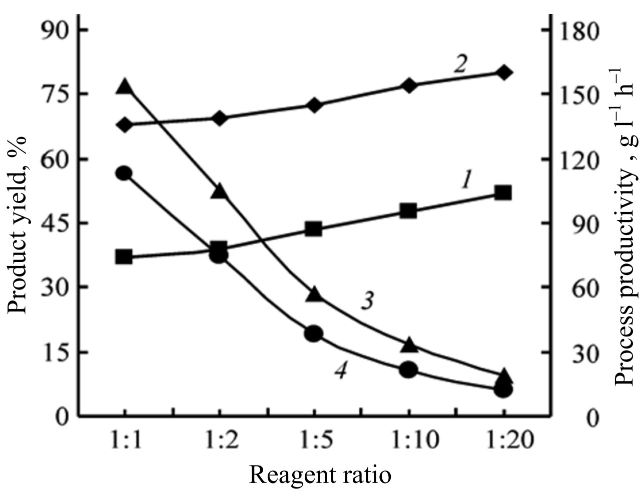

Fig. 1. Dependence of the process productivity and the product yield on the molar ratio of reactants: (*1*) the product (allyl trimethylcyclohexanoate) yield in 2 h, (*2*) the product yield in 5 h, (*3*) the process productivity toward allyl trimethylcyclohexanecarboxylate at the 2 h duration, (*4*) the process productivity toward allyl trimethylcyclohexanecarboxylate at the 5 h duration.

Table 3. Regression coefficients of the response functions

Regression coefficients	Response functions	
	process productivity, g l^{-1} h^{-1}	product yield, %
b_0	89.649	43.383
b_1	22.181	9.928
b_2	–11.154	13.915
b_3	–17.714	0.633
b_{12}	–6.501	1.490
b_{13}	–4.051	0.207
b_{23}	1.959	0.090
S_b	0.350	0.322

Table 4. The coefficients of regression equations on the temperature and duration of the process

Response function (Y_i)	a_0	a_1	a_2	a_{12}
Process productivity, g l^{-1} h^{-1}	107.363	26.232	–13.113	–6.501
Product yield, %	43.383	9.928	13.915	1.49

Table 5. Calculated values of variance adequacy and Fisher criterion

Response function (Y)	S^2_{ad}	S^2_y	F_{calc}	F_{tabl}
Process productivity, g l^{-1} h^{-1}	2.139	0.979	2.19	4.46
Product yield, %	0.076	0.831	10.93	19.25

A condition of the process feasibility is the high enough productivity of the target product, which should not be less than at least 100 g in 1 h at the highest selectivity and the product yield. The area of the productivity values greater than 100 g per 1 h (Fig. 2) corresponds to the triangular sector with the vertex coordinates corresponding to the following values of temperature and duration A (160°C, 2 h) 153.2 g l^{-1} h^{-1}), B (120°C, 2 h) 100.8 g l^{-1} h^{-1}, C (160°C, 6 h) 100.3 g l^{-1} h^{-1}. The maximum yield of the target product, 68%, is achieved at 160°C and reaction duration 5 h (Fig. 3). Since the maximum productivity and yield of allyl trimethylcyclohexanoate were obtained at 160°C, it is necessary to find the minimum duration that corresponds to the productivity at which is desirable to implement the process. The productivity of the target product no less than 100 g l^{-1} h^{-1} at 160°C is reached for the coded duration parameter X_2 = 1, which corresponds to the duration value 5 h.

Thus, we can predict that the optimal technological conditions of the cyclization process are as follows:

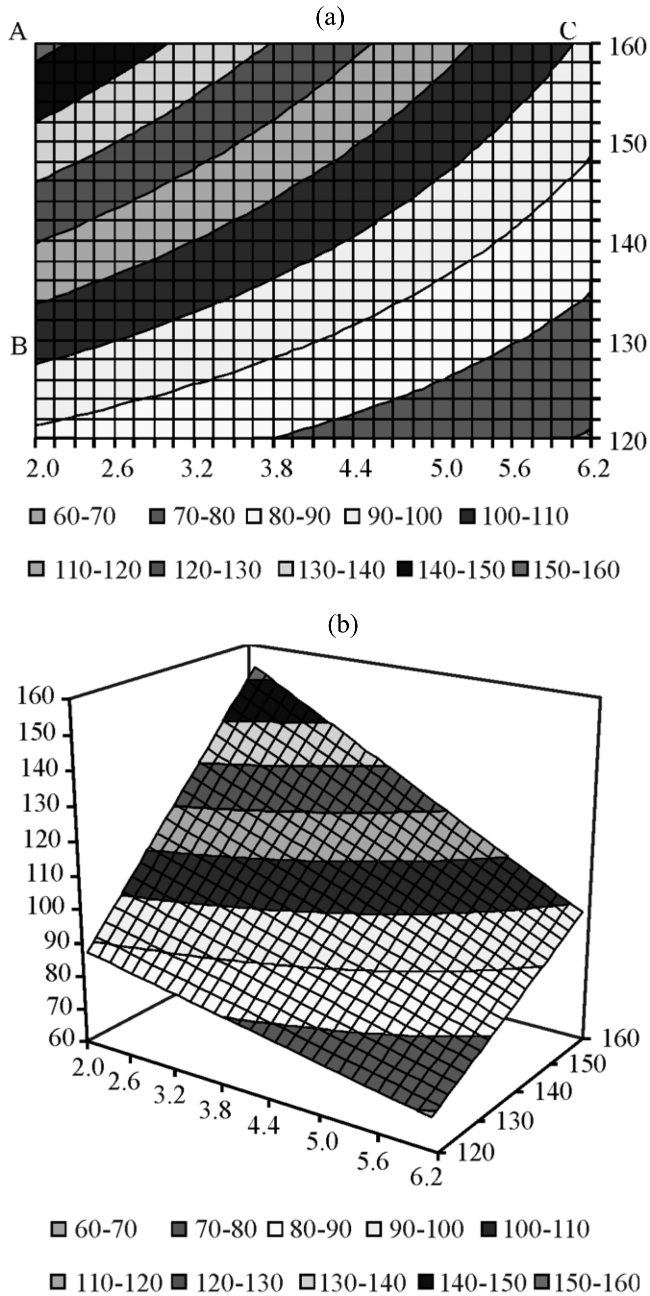

Fig. 2. (a) Surface and (b) the projection of the response function of the process productivity.

temperature 160°C, duration 5 h, the molar ratio dimethylbutadiene : allyl methacrylate = 1:1, therewith the yield reaches 68.72%. On the basis of the carried

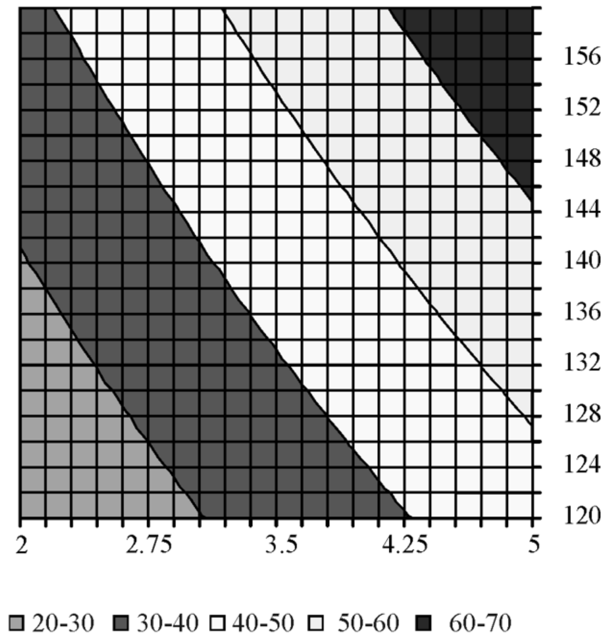

Fig. 3. Surface of the response function of the target product yield.

out balance syntheses it was found that under these conditions the yield reached 68%. Thus, the results obtained coincide satisfactorily with the data of mathematical modeling.

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