

SEARCH OF THE OPTIMAL CONDITIONS AND CONSTRUCTION OF KINETIC MODEL OF THE REACTION ESTERIFICATION OF ALLYL ALCOHOL WITH NATURAL OIL IN PRESENCE OF ION-LIGUID CATALYST.

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Abstract-The regression model of the process have been developed. The quantities correlation, reflecting influence of the base factors on parameters of the process have been determined. The optimal values of inlet variables, allowing to determine the maximal value of the yield of aim product have been determined. The kinetic model of reaction in form of differential equations systems, describing change of initial substances concentration and also reaction products in time have been developed. The kinetic parameters (rate constant and reaction order, activation energy and preexponential multipliers) of separate stages are determined. The developed kinetic model is equivalently describe the esterification reaction.

Key words: esterification, allyl alcohol, oil acid, cinetic model, regressive model.

1.INTRODUCTION

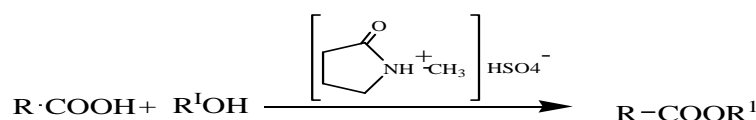
The research of the last time shown, that development of improved process synthesis of esters on accounte of selection of new catalysts by observance of optimal norms of economy and ecological standards will allow to widen a fields use of specified products [1-3].The presented research indude in include one self two stages of the first stage on base of statistical working of laboratory data making of regressive model with following determination of the optimal values of regime parameters, on the second stage - study of kinetic regularities of esterification reaction, determination of its probable mechanism and making of kinetic model. The aim of given work is development of mathematical model in form of regressive equation of allyl alcohol esterification with natural oil acid, separated from Baku oils and solution on base of model the task of optimization and also research in wide interval change of inlet variables.

1.1 Synthesis of allyl ethers of natural oil acids 1

Interaction of propen – 2 ol with oil acid have been realized by the following method [4, 5]. At the three neck flask, supplied by mechanical mixer, thermometer and water-separator of Dine-Stark with opposite cooler the

distillated natural oil acid, allyl alcohol and ion-liquid catalyst – N- methylpyrrolidone hydrosulphate have been put. This mixture was heated up to given temperature by intensive mixing of solution until stopping separation of reaction of reaction water and decrease of acid number up to 0,1-1 mg KOH/g, on what about 2,5-3 hours was required. By reaction completion, the mixture was cooled up to room temperature and was separated from catalyst by filtration. After solvent distillation the raw-ester have been subjected to vacuum distillation and then was analyzed. Reaction esterification of allyl alcohol with natural oil acid proceeds by the following scheme 1.

Scheme 1.



Where R = naphthen radical, $R^1 = \text{CH}_2\text{CH=CH}_2$

Synthesis of allyl ester of oil acid was realized by the following method. The mixture, consisting from 205 g (1mole) of oil acid, 75 g (1,3 mole) of allyl alcohol, 6,15g (0,03 mole) of ion liquid catalyst and 87 g (1,1 mole) of benzene was boiling until separation of reaction water (18 g) on what 3 hours was required. After corresponding processing the aim product - allyl ester of the natural oil acid have been received, possessing by the following indices: n_D^{20} 1.4589; d_4^{20} 0,9223; boiling point 100/4-180/2; $J_2/100r$ 36,5; $\eta_{40}^{20} = 2,75$; freezing temperature – low than (-60°C) . Yield 90% mas.

The identification of chemical structure of the esters was conducted on device I R- Furrye spectrometer ALPHA (firm BRUKER Germany) within range of wave frequency 600-4000 cm^{-1} on crystal sezn and spectrum of NMRH and ^{13}C were registries on device Bruker WP – 300 (300 MHz), solvent - CD_3COCD_3 , the chemical displacements were shown – relatively TMC. In IR-spectrum of allyl ester of natural oil acid (NOA) the following band of absorption were registries = 2924, 1455 cm^{-1} -is characteristic for C-H bond of CH_2 groups; 2862, 1375 cm^{-1} -for C-H bond of CH_3 groups; 988, 926 cm^{-1} for C=C bond (in α position); 3086,1648 cm^{-1} for CH_2 groups by C=C bond; 1239, 1162 cm^{-1} for C-O bond; 1736 cm^{-1} for C=O bond of ester.

NMR/H spectrum of allyl ester of NOA ($\delta, \text{m.d.}, \text{CD}_3\text{COCD}_3$)- protons of naphthen cycles are displayed in field from 0,897 kp to 2,804 md, signals of groups (OCH_2) are displayed by 4,57 m.d, signals of protons of = CH_2 groups have a form of two duplets with chemical displacement in field $\delta = 5.181\text{-}5.343$ m.d. signal of metine proton (CH) group are observed in form of multiplied in field with chemical displacements $\delta = 5.958$ m.d.

2. Optimal conditions of the reaction esterification

For determination of quantitative correlation of inlet variables (temperature of experiment – X_1 °C; amount of catalyst – X_2 mas.%; correlation of acid to allyl alcohol) – X_3 , duration of experiment – X_4 hour; yield of ester Y_1

% and value of acid number – Y_2 my of KOH/g the method of active planning of experiment by type 2^4 with following mathematical – statistical processing of experimental data [6] have been used.

In the table 1 the matrix of planning and results of experiments are shown. In it symbols «+», «-», «0» - are the encoded values of high, low and base levels.

As a preliminary the limits changes of inlet variables have been chosen.

$$80^{\circ}\text{C} \leq X_1 \leq 90^{\circ}\text{C}; \quad 1 \text{ mas.}\% \leq X_2 \leq 4\text{mas.}\%$$

$$1:1 \leq X_3 \leq 1:1,4 \quad 1 \text{ hour} \leq X_4 \leq 3 \text{ hour.}$$

The mathematical expression of dependence of optimization parameter from inlet independent variables is presented in form of regressive equation:

$$Y_k = a_0 + \sum_{i=1}^n a_i X_i + \sum_{\substack{i=1 \\ i \neq j}}^n a_{ij} X_i X_j \quad (1)$$

Y_k – value of optimization parameter $X_i X_j$ – encoded designation of model factors; n-amount of factors; a_0 – value of free member in regression equation ; a_i, a_{ij} –coefficients of linear affect and pair interaction of factors.

Table-1: Matrix, lining and result of experiments

Variables N ^o of experiment	X ₁	X ₂	X ₃	X ₄	Inlet parameters	
					Y ₁ % yield of esters, %	Y ₂ acid number mg KOH/g
1	+	+	+	+	74,6	56
2	+	+	+	-	53,7	89
3	+	+	-	+	58,1	91,5
4	+	+	-	-	37,2	124,5
5	+	-	+	+	71,2	58,6
6	+	-	+	-	50,4	92
7	+	-	-	+	54,75	93
8	+	-	-	-	33,85	126
9	-	+	+	+	75,7	66
10	-	+	+	-	54,9	99
11	-	+	-	+	71,1	80
12	-	+	-	-	50,3	113
13	-	-	+	+	67,7	65,8
14	-	-	+	-	46,9	99,02
15	-	-	-	+	63,1	80,5
16	-	-	-	-	42,3	113,2
17	0	0	0	0	77	17,4
18	0	0	0	0	76	16,50
19	0	0	0	0	75	17,0

On base of experimental data the values of regression coefficients (1) which characterize the outlet parameters have been determined:

$$Y_1 = 59,63 + 2,396 \cdot X_1 + 2,834 \cdot X_2 + 5,27 \cdot X_3 + 10,44 \cdot X_4 - 2,096 \cdot X_1 \cdot X_2 - 0,48 \cdot X_1 \cdot X_3 - 1,03 \cdot X_1 \cdot X_4 + 0,59 \cdot X_2 \cdot X_3 - 1,163 \cdot X_2 \cdot X_4 + 2,97 \cdot X_3 \cdot X_4; \quad (2)$$

$$Y_2 = 80,259 - 0,979 \cdot X_1 - 0,415 \cdot X_2 - 12,22 \cdot X_3 - 16,56 \cdot X_4 + 1,9 \cdot X_1 \cdot X_2 + 5,26 \cdot X_1 \cdot X_3 + 3,969 \cdot X_1 \cdot X_4 - 0,77 \cdot X_2 \cdot X_3 - 0,538 \cdot X_2 \cdot X_4 - 5,153 \cdot X_3 \cdot X_4; \dots\dots \quad (3)$$

Valuation of significance of regression coefficients was determined by help of student criterion «+». The calculation shown that for equation (2) the coefficients a_{13} , a_{23} turned out to be insignificant and for equation (3) the coefficients: b_2 , b_{23} and b_{24} by X_2 , $X_2 \cdot X_3$; $X_2 \cdot X_4$ are insignificant.

The hypothesis about adequacy of models (2), (3) have been examined by criterion of Fisher F. By comparison of determined values of F with tabular by choose confident probability equal 95% and number degree of freedom $f_1=7$ and $f_2=2$ it is evident that calculation values of $F_c = 2,4$ are less that tabular $F_T = 19,6$. It is testify about that these regression equations (4), (5) equivalently describe the surface of response.

By using of the formulas transition from fixed variables X_i to natural Z_i by way of transformation the equations have been received in the following form:

$$Y_1 = 19,5 + 0,185 \cdot Z_1 + 11,8 \cdot Z_2 - 3,15 \cdot Z_3 - 0,42 \cdot Z_4 - 0,06 \cdot Z_1 \cdot Z_2 - 0,045 \cdot Z_1 \cdot Z_4 - 0,65 \cdot Z_2 \cdot Z_4 + 17,25 \cdot Z_3 \cdot Z_4; \quad (4)$$

$$Y_2 = 321,45 - 2,586 \cdot Z_1 - 2,985 \cdot Z_2 - 136,5984 \cdot Z_3 - 4,961 \cdot Z_4 + 0,0633 \cdot Z_1 \cdot Z_2 + 1,315 \cdot Z_1 \cdot Z_3 + 0,1985 \cdot Z_1 \cdot Z_4 - 2,956 \cdot Z_2 \cdot Z_3 - 0,858 \cdot Z_2 \cdot Z_4 - 26,755 \cdot Z_3 \cdot Z_4; \quad (5)$$

2. 1 Construction of kinetic model of kinetic model of the reactions esterification

On base of developed mathematical model (4) – (5) on personal computer the calculation by determination of the optimal values of inlet variables, giving the maximum yield of esters by minimum value of acid number have been made.

The calculation shown that by temperature 90°C, amount of catalyst 3 mas.%, correlation of alcohol to alcohol 1:1,3 and duration of reaction 3 hours yield of ester makes up 91% and its acid number equal 0,5 mg KOH/g.

By these optimum values of inlet variables the control experiment of reaction esterification of allyl alcohol by natural oil acid, separated from Baku oils in presence of ionic liquid catalyst – N-methylpyrrolidonehydrogensulphate, which shown that maximum yield of ester equal 91,6% that testify the acceptability of developed regressive model.

The aim of research is determination of the most probable mechanism of its proceeding and construction on its base of equivalent kinetic model. The last is necessary condition for modeling, optimization

and scaling of chemical process, allowing in short period to transfer laboratory conditions to it industrial integration [7]. The kinetic regularities of reaction have been investigated within variation of temperatures from 80°C up to 90°C by amount of catalyst 3mas.% and correlation of acid to alcohol equal 1:1,3.

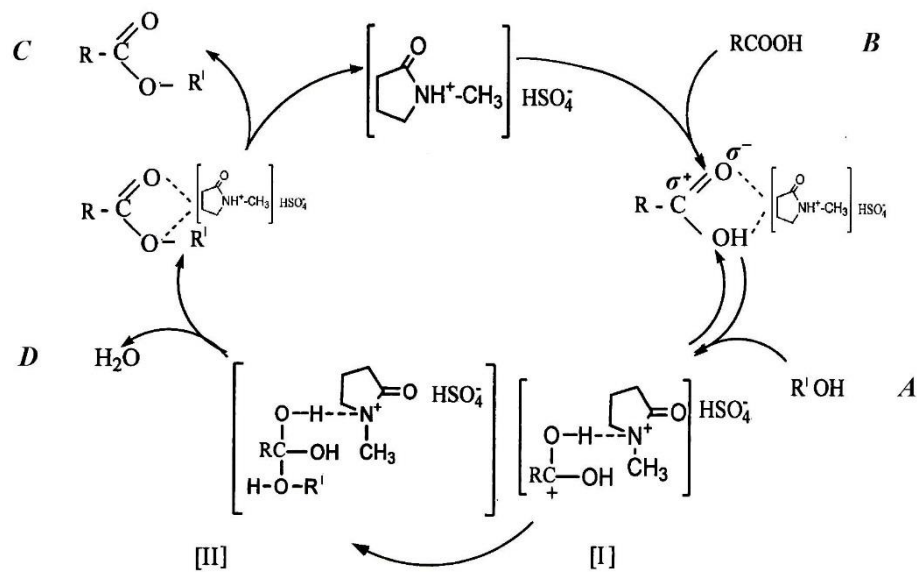
RESULTS AND IT DISCUSSION

In the table 2 the experimental values of component concentrations C_i of reaction mixture are presented.

Components	C, mol/mol (by t, min)					
	0	30	60	90	120	150
T=80°C (353K)						
Allyl alcohol	0,387	0,372	0,350	0,320	0,280	0,230
Oil acid	0,297	0,286	0,272	0,258	0,228	0,184
Allyl ester of oil acid	0	0,022	0,050	0,082	0,116	0,157
Water	0	0,018	0,040	0,063	0,087	0,113
T=85°C (358K)						
Allyl alcohol	0,387	0,354	0,310	0,220	0,190	0,140
Oil acid	0,297	0,270	0,240	0,200	0,150	0,090
Allyl ester of oil acid	0	0,030	0,070	0,120	0,180	0,247
Water	0	0,020	0,050	0,090	0,140	0,207
T=90°C (363K)						
Allyl alcohol	0,387	0,320	0,210	0,140	0,090	0,020
Oil acid	0,297	0,257	0,200	0,160	0,090	0,010
Allyl ester of oil acid	0	0,050	0,120	0,190	0,265	0,367
Water	0	0,030	0,060	0,100	0,180	0,287

Analysis of experimental data allow to suppose that the all totality of reactions, proceeding by esterification of allyl alcohol by oil acid may be presented in total form by the scheme 2.

It is known, that reaction formation of ester of unsaturated alcohols is balanced, state of which is determined by individual peculiarities of acids and alcohols. For achievement of high conversion the alcohol is given in molar excess by relation to acid. Esterification is to a great extent accelerated in presence of acid catalysts, by that its rate is proportional to concentration of hydrogen ions. In molecules of carbon acids p-electrons of oxygen atoms of hydroxyl group interact with electrons of π -bond of carbonyl group, in result of which the polarity of O-H bend increase, bond in carbonyl group is consolidated, the partial charge (δ^+) on carbon atom is decreased and the partial charge (δ^+) on hydrogen atom is increased. The last contribute to formation of the stable hydrogen acid bonds between molecules of carbon acids.



According to scheme, offered for explanation of esterification with ion liquid (I L) in acid medium oxygen of carboxyl group engross the proton of N-MPHS (II) forming the onium cation (2) which further react with alcohol R₁-OH forming the complicate complex (3). Cation of ester (3), splitting I L and water form the molecule of ester (4) ly scheme 2.

For creation of kinetic model of reaction in total case it is necessary to describe the character change of every component, participating in reaction. The total change of concentration of any substance in reacting system take into consideration participation of this substance in all reactions.

Therefore for every substance the following equation may be written:

$$\frac{dC_i}{dt} = \sum \gamma_{ik} \omega_k$$

Where C_i – concentration of initial substances and products of reactions; ω_k – rate of k-reaction, which is taken with sign minus for reaction, in which the given substance is initial substance and with sign plus, when substance present itself the product of reaction; γ_{ik} – stoichiometric coefficient of i – substance of k – reaction.

On base of high mentioned scheme of reaction mechanism the system of differential equations, describing the changes of initial substances concentrations and also reaction products in time have been made:

$$\frac{dC_A}{dt} = -k_1^I \cdot C_A^{n_1} C_B^{n_2} \quad (6)$$

$$\frac{dC_B}{dt} = -k_1^{II} \cdot C_A^{n_1} C_B^{n_2} \quad (7)$$

$$\frac{dC_I}{dt} = -k_1^{III} \cdot C_A^{n_1} C_B^{n_2} - K_2 \cdot C_I \quad (8)$$

$$\frac{dC_{II}}{dt} = -k_2 \cdot C_I - K_3 \cdot C_{II} \quad (9)$$

$$\frac{dC_C}{dt} = -k_3^I \cdot C_{II} \quad (10)$$

$$\frac{dC_D}{dt} = -k_3^{II} \cdot C_{II} \quad (11)$$

Where $C_A, C_B, C_C, C_D, C_{II}, C_{III}$ – concentration of allyl alcohol, oil acid, allyl ester of oil acid, water, intermediate complex, onion catione (I), complicate complex (II), $k_1^I, k_1^{II}, k_1^{III}, k_2, k_3^I, k_3^{II}, k_3$ - constants of reaction rates; n_1, n_2 – order of reaction, t- time of reaction.

The intermediate complex compounds I-II are received and are consumed in proceeding of reaction and on entrance don't discovered. Therefore by equating to zero the rates formation and consumption of these complexes over the known substances A and B may be found.

$$\frac{dC_I}{dt} = -k_1^{III} \cdot C_A^{n_1} C_B^{n_2} - k_2 \cdot C_I = 0; \quad C_I = \frac{k_1^{III} \cdot C_A^{n_1} \cdot C_B^{n_2}}{K_2} \quad (12)$$

$$\frac{dC_{II}}{dt} = -k_2 \cdot C_I - k_3 \cdot C_{II} = 0; \quad C_{II} = \frac{k_2 \cdot C_I}{k_3} = \frac{k_1^{III} \cdot C_A^{n_1} \cdot C_B^{n_2}}{k_3} \quad (13)$$

$$\frac{dC_C}{dt} = k_3^I \cdot \frac{k_1^{III} \cdot C_A^{n_1} \cdot C_B^{n_2}}{k_3} \quad (14)$$

$$\frac{dC_D}{dt} = k_3^{II} \cdot C_{II} = k_3^{II} \cdot \frac{k_1^{III} \cdot C_A^{n_1} \cdot C_B^{n_2}}{k_3} \quad (15)$$

By substitution of equation (12-13) in equation (6,7,10,11) the new system of differential equations is received:

$$\frac{dC_A}{dt} = -k_1^I \cdot C_A^{n_1} C_B^{n_2} \quad (16)$$

$$\frac{dC_B}{dt} = -k_1^{II} \cdot C_A^{n_1} C_B^{n_2} \quad (17)$$

$$\frac{dC_C}{dt} = k_3^I \cdot \frac{k_1^{III} \cdot C_A^{n_1} \cdot C_B^{n_2}}{k_3} \quad (18)$$

$$\frac{dC_D}{dt} = k_3^{II} \cdot \frac{k_1^{III} \cdot C_A^{n_1} \cdot C_B^{n_2}}{k_3} \quad (19)$$

Valuation of kinetic constant of differential equations (16)-(19) have been realized by modified method of accidental search with automatic choice of step. By this aim the developed stack of applied programs have been used [8]. The kinetic constants have been determined for every temperature. The results calculation of the constants rates are presented in the table 3.

Table 3.Kinetic parameters of reaction

Constant of rate, k_i $l \text{ mol}^{-1} \text{ min}^{-1}$	Temperature, K			Energy of activation, E kcal/mol	Preexponential multiplier k_i $l \text{ mol}^{-1} \text{ min}^{-1}$
	353	358	363		
k_1^I	0,000507	0,00169	0,00479	$0,54 \cdot 10^5$	$0,245 \cdot 10^{31}$
k_1^{II}	0,000659	0,00181	0,00469	$0,518 \cdot 10^5$	$0,547 \cdot 10^{29}$
k_1^{III}	0,247	0,469	0,861	$0,452 \cdot 10^5$	$0,352 \cdot 10^{26}$
k_3	0,1948	0,3087	0,477	$0,395 \cdot 10^5$	$0,317 \cdot 10^{23}$
k_3^I	0,1382	0,2529	0,448	$0,378 \cdot 10^5$	$0,353 \cdot 10^{22}$
k_3^{II}	0,332	0,6725	1,312	$0,372 \cdot 10^5$	$0,313 \cdot 10^{22}$

By replacement of dependence of constant rate reaction from temperature in state of Arrhenius equation [9].

$$k = K_0 \exp(-E / RT),$$

where k - constant of rate ($l \text{ mol}^{-1} \text{ min}^{-1}$), K_0 - preexponential multiplier ($l \text{ mol}^{-1} \text{ min}^{-1}$), E - energy of activation (kcal/mol), R - the universal gas constant ($\text{kal mol}^{-1} \text{ K}^{-1}$) T - temperature (K) the energy activation and preexponential multiplier are determined. The orders of reaction also have been determined $n_1=0.95$, $n_2 = 0.85$.

The received data are shown in table 3. The kinetic model, made on base of chosen scheme mechanism of reaction and by determined values of constants rates good describe the reaction. The adequacy of chosen model have been examined on personal computer by way of minimization of sum of square difference of experimental and calculated values by formula [10]:

$$F = \sum_{j=1}^N \sum_{i=1}^m \left[\frac{c_{ij}^{\text{a}} - c_{ij}^{\text{p}}}{c_{ij}^{\text{a}}} \right] \rightarrow \min$$

where, $j=1, \dots, N$ - the total number of experiment; $i=1, \dots, m$ amount of components.

2 CONCLUSIONS

The results of calculation on personal computer (PK) shown a good convergence of experimental and calculated data. The divergence by initial and final products don't exceed 5-10%/ it is give a base to consider, that developed kinetic model of esterification reaction adequately describe the experimental data.

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