

Stepan Melnyk and Victor Reutskyy

TECHNOLOGICAL ASPECTS OF DICARBOXYLIC ACIDS ESTERIFICATION IN THE PRESENCE OF APROTIC CATALYSTS

*Lviv Polytechnic National Univeristy**12, S. Bandery str., 7013 Lviv, Ukraine; st_melnyk@yahoo.com**Received: March 23, 2013 / Revised: June 27, 2013 / Accepted: November 12, 2013*

© Melnyk S., Reutskyy V., 2014

Abstract. The investigation results of the regularities of diesters of aliphatic dicarboxylic acids obtained in the presence of aprotic catalysts – Lewis acids – have been generalized. The effect of catalysts (metal salts) nature and concentrations, reagents nature and ratio, water content in them, as well as the influence of reaction temperature on the technological characteristics of esterification process have been determined. The technological aspects of the process have been examined in the presence of aprotic acids. The investigated catalysts may be reused in the technological process.

Keywords: esterification, catalyst, Lewis acids, dicarboxylic acids, alcohols C₄–C₈.

1. Introduction

The esters of aliphatic dicarboxylic acids are obtained in the industry *via* their interaction with alcohols in the presence of mineral and organic acids and titanium organic compounds [1]. Over the last years the number of investigations aimed at the search of new catalytic systems, improvement of technology, and reduction of the esterification energy intensity has considerably increased. Besides the titanium organic compounds the following organic and inorganic substances are proposed to be used as aprotic catalysts of the esterification process: aluminium, cuprum(II), zinc, magnesium, potassium-aluminium, sodium and nickel sulfates, lanthane(I) nitrate, aluminium and stanum(IV) chlorides [2], stanum(IV) and hafnium(IV) bis(perfluorineoctanesulphonyl)amide complexes [3], palladium chloride [4], zirconyl chloride [5], metal salts of trifluorinemethasulphoacid [6], *etc.*

The aim of our investigations was to establish and generalize the regularities and technological aspects of aprotic catalysts usage in the esterification process of aliphatic dicarboxylic acids C₄–C₆ by alcohols.

2. Experimental

2.1. Materials

The Lewis acids – metal salts – perfluorine(4-methyl-3,6-dioxaoctane)sulfonates (pfos[−]), *n*-toluenesulfates (TsO[−]), pentadecylsulfates (C₁₅H₃₁SO₃[−]), chlorides (Cl[−]), sulfates (SO₄^{2−}), acetates (OAc[−]), and stearates (St[−]) were used as the catalysts of esterification of adipic acid (AA), succinic acid (SA), and their mixture with glutaric acid (LDCA) by butan-1-ol (BA), 2-methylpropan-1-ol (iBA), 3-methylbutan-1-ol (iAA), pentan-1-ol (PA) and 2-ethylhexan-1-ol (EHA). The following Bronsted-Louri acids were used for comparison: sulfuric, chloric, perfluorine(4-methyl-3,6-dioxaoctanesulfuric), and *n*-toluenesulfuric acids.

2.2. Experiments and Analyses Methods

The esterification process was studied in the open system where the formed water was distilled off and accumulated in Dean-Stark trap. The alcohol: dicarboxylic acid (DCA) molar ratio was (2.1–3.0) : 1. The catalysts concentration was ranged from 2·10^{−5} to 7.5·10^{−3} mol/dm³.

During the experiments the heat carrier temperature (to ensure the conditions of equal heating) and the reaction temperature were measured.

The reaction products were analyzed by means of titration (acid number) and gas-liquid chromatography (diester content). The column with the length of 1 m and diameter of 3 mm was filled by stationary phase 5 % Silicone SE30 over Chromaton N-AW. The column temperature was 443 K and gas-carrier consumption was 3 dm³/h. The heat-transfer detector was used.

The results of titration analysis were used to calculate the conversion of carboxy groups C_{CG} of DCA and its monoester.

The amount of DCA (*n*_{DCA}, mol) and its monoester (*n*_{ME}, mol) in the reaction products were calculated using

determined acid number (AN , mg KOH/g), diester amount (n_{DE} , mol), DCA amount taken for the reaction ($n_{DCA,0}$, mol), and mass of the reaction products (m , g) from the system of equations:

$$\begin{cases} n_{DCA,0} = n_{DCA} + n_{ME} + n_{DE}; \\ AN = (2n_{DCA} + n_{ME})56000 / m. \end{cases}$$

According to the determined values of n_{DE} , $n_{DCA} = AN \cdot m / 56000 - n_{DCA,0} - n_{DE}$ and $n_{ME} = n_{DCA,0} - n_{DCA} - n_{DE}$ the composition of the reaction mixture, DCA conversion, and yields of mono- and diester were calculated. The error did not exceed $\pm 6.0\%$.

3. Results and Discussion

The catalyst concentration and nature, reagents nature, their ratio, presence of azeotrope forming agent (hydrocarbon added to the reagents which allows to extract water from the system due to the formation of azeotropic mixture), and the presence of water in the reagents affect proceeding of dicarboxylic acids esterification by lower aliphatic alcohols. All the mentioned indexes influence the process temperature, time, and parameters.

One can see from Fig. 1a that the consecutive increase of the catalyst (zinc perfluorine(4-methyl-3,6-dioxaoctane)sulfonate) concentration in the reaction of

AA esterification by butan-1-ol proportionally increases the intensity of carboxy groups conversion by 2–5 times till the catalyst concentration of $1.1 \cdot 10^{-3}$ mol/dm³. Then the reaction intensity slightly changes and the maximal conversion is achieved for the same time at catalyst concentrations of $1.1 \cdot 10^{-3}$ and $2.2 \cdot 10^{-3}$ mol/dm³. The accordance between the reaction temperature, carboxy groups concentration, and catalyst concentration is observed (Fig. 1b): the higher the catalyst concentration the more intensive the esterification and the sharper increase in the temperature of the reaction mass. The same change in the process rate is observed while esterification of SA by 3-methylbutan-1-ol in the presence of stanum perfluorine(4-methyl-3,6-dioxaoctane)sulfonate (Fig. 2, curve 1).

Since the esterification of dicarboxylic acids by aliphatic alcohols under non-stationary conditions takes place when boiling the reaction mixture it combines two processes: chemical conversion and mass transfer (distillation of volatile components out of the reaction medium). Correspondingly, the esterification rate depends on the ratio between the rates of water formation and removal. Hence, the increase in the catalyst concentration leads at first to the equalization of these rates and then the rate of water formation gets higher, which retards the whole process. At high catalyst concentration the rate of water distillation limits the technological process due to its accumulation in the reaction system and acceleration of

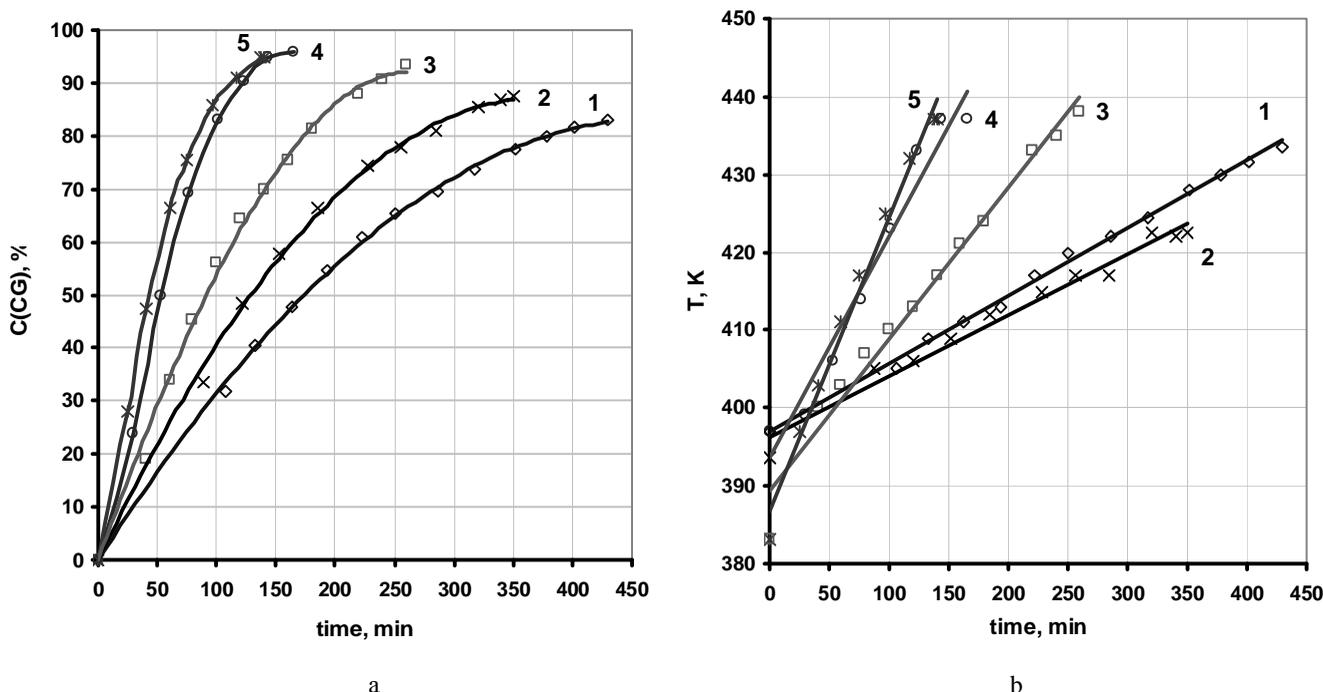


Fig. 1. Change of carboxy groups conversion (a) and reaction temperature (b) during esterification of adipic acid by butan-1-ol at different concentrations of the catalyst $Zn(pfos)_2$, mmol/dm³: 0.02 (1); 0.1 (2); 0.4 (3); 1.1 (4) and 2.2 (5). Molar ratio BA:AA = 2.5:1

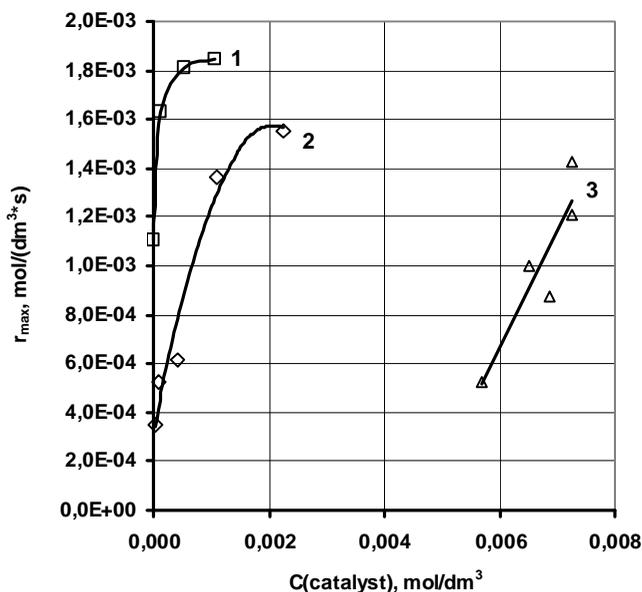


Fig. 2. Maximal rate of esterification reaction vs catalyst concentration: $\text{Sn}(\text{pfos})_2$, iAA-BA (1); $\text{Zn}(\text{pfos})_2$, BA-AA (2) and $\text{Sn}(\text{pfos})_2$, iBA-AA (3). Molar ratio alcohol : DCA = 2.5:1

ester hydrolysis reverse reaction. Thus, exceeding of the catalyst concentration optimum value does not affect the esterification rate and, as a consequence, brings no effect. Moreover, the increase of aprotic catalyst amount increases the prime cost of the target product due to the increase of Lewis acid losses at its regeneration stage. When mineral or organic acid is used as protone catalyst, the consumption of alkaline or soda necessary for the catalyst excess neutralization increases.

At the same time during interaction between AA and 2-methylbutan-1-ol the increase in stanum perfluorine(4-methyl-3,6-dioxaoctane)sulfonate does not retard the process rate. The reason is the low intensity of the process chemical component: under the reaction conditions water is removed faster than it is formed (Fig. 2, curve 3).

With the increase of catalyst concentration the composition of esterification products changes in a similar way independently of alcohol or metal cation nature. For the same reaction time the diester concentration in the reaction mixture is higher, and monoester and DCA concentrations are lower. The increase in catalyst concentration considerably decreases the DCA concentration (to 1 wt %) and monoester concentration remains within 2–4 wt %. Such relatively high concentration of monoester is needed to be neutralized and causes additional costs at the stage of target product extraction.

Consequently, in spite of maximal removal of formed water at the catalyst high concentration, during the esterification in the open system the equilibrium

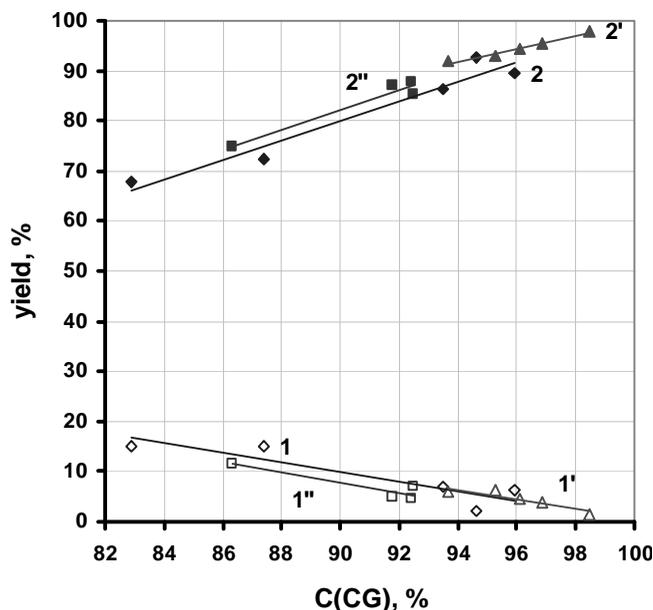


Fig. 3. Dependence between mono- (1, 1', 1'') and diester (2, 2', 2'') yields and carboxy groups conversion during esterification: BA-AA, $\text{Zn}(\text{pfos})_2$ (1, 2); iBA-AA, $\text{Sn}(\text{pfos})_2$ (1'', 2''). Molar ratio alcohol : DCA = 2.5:1

concentration of the reagents and reaction products, as well as maximal equilibrium conversion of the carboxy groups are established, determined by the process parameters and conditions.

Fig. 3 shows a linear dependence between mono- and diester yields and carboxy groups conversion regardless of the nature of alcohol, acid or catalyst. The same correlation was determined for esterification of AA by butan-1-ol in the presence of different catalyst including Bronsted-Louri acids (Fig. 4). This fact indicates the similarity of the esterification process mechanisms in the presence of different catalysts.

The nature of the catalyst-salt ligand does not influence the process mechanism, because the dependence between the reaction products yield and carboxy groups conversion is a linear one (Fig. 5). Combination of the salt's high solubility and high electron-acceptor properties of perfluorineoxasulfate-anions ensures high activity of the catalyst $\text{Co}(\text{pfos})_2$ during esters obtaining. Using salts with such electron-acceptor ligands as Cl^- , SO_4^{2-} is less effective due to the restricted solubility of chlorides and sulfates in the organic medium. At the same time, despite the high solubility of cobalt stearate, the low electron-acceptor effect of ligand also influences the catalyst activity.

Thus, the effect of ligand nature on the esterification process appears in the increase in catalyst activity due to the improved solubility and high active concentration of Lewis acid in the reaction medium, as well as due to electron density reduction over catalyst cation.

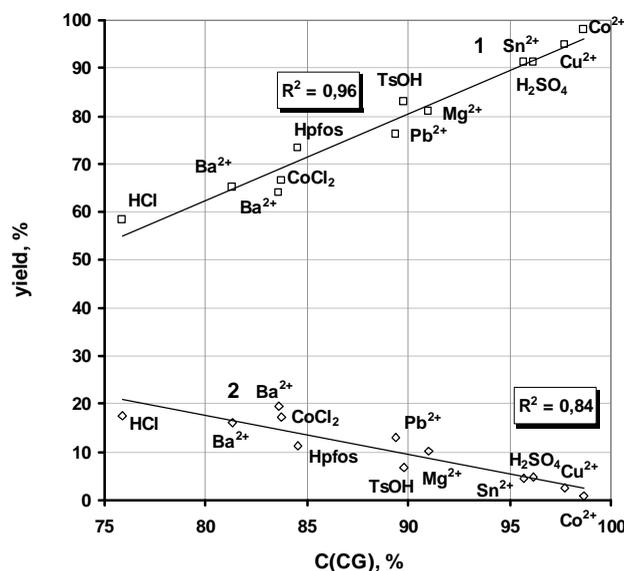


Fig. 4. Ratio between the yields of mono- (1) and dibutyladipic (2) esters and carboxy groups conversion during esterification of adipic acid by butan-1-ol in the presence of different catalysts (cation corresponds to the perfluorine(4-methyl-3,6-dioxaoctane)sulfuric acid salt. Molar ratio AA : BA = 2.5:1; $C_{cat} = 1.1 \cdot 10^{-3} \text{ mol/dm}^3$

The obtained experimental results allow to assert that the effect of temperature (intensity of heat supply) and catalyst concentration on the esterification process should be considered holistically. The increase in the catalyst concentration or heating intensity accelerates the esterification. Due to this fact the composition of the reaction medium is changed. The part of low-boiling components decreases and the part of high-boiling ones increases resulting in the further increase of the reaction temperature and rate.

The alcohol nature, the same as the catalyst concentration, defines the temperature range of DCA esterification. Alcohol forms azeotrope with water and thus eases its removal from the reaction medium at lower boiling temperature. The reduction of alcohol part in the mixture and decrease of water formation intensity result in the temperature increase to alcohol boiling point and higher temperatures. In particular, under the same conditions the intensity of AA esterification by C₄–C₅ alcohols in the presence of ammonium pentadecylsulfate raises, as alcohol boiling point increases. Therefore, the technological characteristics of the process are improved (Table 1).

The increase of alcohol excess or use of azeotrope forming agent (benzene, toluene) decrease both average temperature of the reaction and its intensity due to the increase of part of the low-boiling components.

The presence of small amount of water in the reagents increases active concentration of Lewis acid due

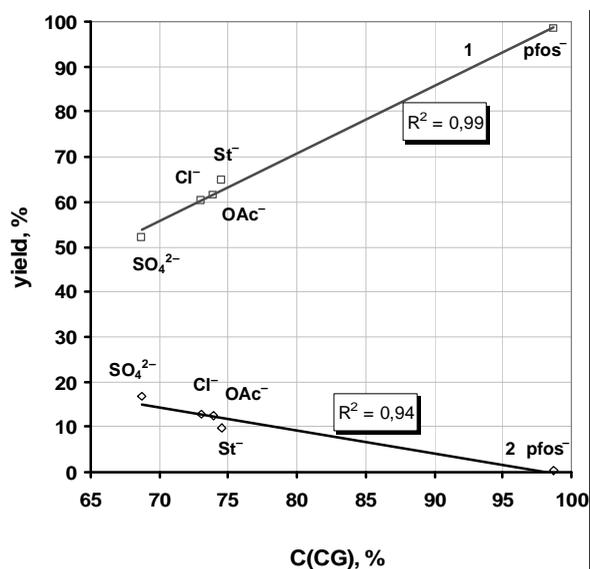


Fig. 5. Correlation between mono- (2) and dibutyladipic (1) esters yields and carboxy groups conversion for the cobalt salts with the ligands of different nature. Molar ratio AA:BA = 2.5:1

to its better solubility, which accelerates the esterification process (Table 2).

Table 1

Effect of alcohol nature on the technological characteristics of AA esterification by butan-1-ol

Alcohol	Time, min	$r_{max} \cdot 10^3, \text{ mol}/(\text{dm}^3 \cdot \text{s})$	$C_{CG}, \%$	AN, mg KOH/g
PA	150	2.1	95.3	14.4
BA	175	1.6	95.9	13.8
iAA	190	1.5	94.5	16.5
iBA	230	1.1	92.8	24.5

Note: $C(\text{C}_{15}\text{H}_{31}\text{SO}_3)_3\text{Al} = 5.1 \cdot 10^{-3} \text{ mol/dm}^3$; molar ratio BA:AA = 2.5:1

Table 2

Effect of water on the technological characteristics of the esterification process

w(H ₂ O), wt %	Time, min	AN, mg KOH/g	$C_{CG}, \%$
$C(\text{Al}(\text{TsO})_3) = 2.1 \cdot 10^{-3} \text{ mol/dm}^3$; BA:AA = 2.1:1 (mol)			
0	165	36,1	90,2
1.8	110	32,6	91,1
5.6	90	59,6	83,3
$C(\text{Al}(\text{TsO})_3) = 5.2 \cdot 10^{-3} \text{ mol/dm}^3$; EHA:LDCA = 2.5:1 (mol); w(C ₆ H ₆) = 14 wt %			
0	140	3,4	98,4
1.2	100	1,5	99,3

Table 3

Reuse of Zn(pfos)₂ catalyst

$C(\text{Zn}(\text{pfos})_2)$, mol/dm ³	Water for washing, % from esterizate mass	AN, mg KOH/g	C_{CG} , %
$1.1 \cdot 10^{-3}$	–	14.2	95.9
Zn(pfos) ₂ washed from the previous experiment	13.5	51.0	83.7
$4.0 \cdot 10^{-4}$	–	22.3	93.5
Zn(pfos) ₂ washed from the previous experiment	9.1	36.2	88.6

Note: molar ratio BA:AA = 2.5:1

At the finishing stage of esterification water also decreases equilibrium concentration of carboxy groups due to dilution in BA and returning with it from water separator to the reactor, which is the reason of high value of acid number. To escape this negative influence it is possible to use effective cooling of the distillate and medium in the water separator, which would decrease water solubility in alcohol and improve conditions for extraction of aqueous and alcohol layers. Another way is to use hydrocarbon – azeotrope forming agent insoluble in water.

While using alcohol with long chain (EHA), whose solubility in water is minimal (Table 2), the problem becomes less evident. In the reaction medium the water binding may occur due to the hydration of catalyst-salt molecules, formation of hydrogen bonds with another molecule of alcohol, acid or water. In such case the equilibrium concentration of carboxy groups may slightly increase.

All the investigated catalysts are metal salts. Their peculiarities are different solubility in the reaction medium determined by the nature of ligand surrounding of metal cation or cation itself. Comparatively low solubility of some catalysts in the reaction medium and high solubility in water allow to extract them from the reaction products by filtration and extraction with water. Moreover, they may be reused in the technological process of DCA esters obtaining. We established that zinc perfluorineoxasulfonate may be reused in the esterification process after its washing by water from esterizate (Table 3).

The similar results were obtained for a series of catalysts and reagents [7].

4. Conclusions

The intensity of technological process of aliphatic dicarboxylic acid esterification by C₄–C₈ alcohols in the presence of catalysts – metal salts – is determined first of all by its temperature under non-stationary conditions. The temperature depends on joint effect of catalyst nature and

concentration, alcohol nature, alcohol : DCA ratio, and the presence of azeotrope forming agent. The linear correlations between mono- and diester yields and conversion of DCA and its monoester carboxy groups were established for aprotic catalysts of different nature and various ligand surroundings of metal cation. These dependences show that at the same conversion the ratio between esterification products does not depend on the catalyst nature. The investigated catalysts may be reused in the technological process after their filtration or extraction by water from the reaction mixture.

References

- [1] Barshteyn R., Kirilovich V. and Nosovskiy Yu.: *Plastifikatory dlya Polimerov*. Khimiya, Moskva 1982.
- [2] Svirskiy K., Kunakova R., Zaynullin R. and Dokichev V.: *Bashk. Khim. Zh.*, 2010, **2**, 162.
- [3] Gang L. and Wenhui P.: *Kinetika i Kataliz*, 2010, **4**, 583.
- [4] Xiuhua H., Akihiro Y. and Joji N.: *Tetrahedron Lett.*, 2004, **4**, 781.
- [5] Mantri K., Kenichi K. and Sugi Y.: *Synthesis*, 2005, **12**, 1939.
- [6] Finmans P. *et. al*: *Pat. WO 2005/049556*, Publ. Jun. 02, 2005.
- [7] Melnyk S., Kachmar-Kos N., Melnyk Yu. and Reutskyy V.: *Pat. UA 58200*, Publ. Apr. 11, 2011.

ТЕХНОЛОГІЧНІ АСПЕКТИ ЕСТЕРИФІКАЦІЇ ДИКАРБОНОВИХ КИСЛОТ У ПРИСУТНОСТІ АПРОТОННИХ КАТАЛІЗАТОРІВ

Анотація. Узагальнено результати досліджень закономірностей одержання діестерів аліфатичних дикарбонних кислот у присутності апротонних каталізаторів – кислот Льюїса. Визначено вплив природи каталізаторів – солей металів, їх концентрації, природи і співвідношення реагентів, вмісту в них води, а також температури реакції на технологічні показники процесу естерифікації. Розглянуто технологічні аспекти процесу естерифікації в присутності апротонних кислот. Визначено можливість повторного застосування досліджених каталізаторів у технологічному процесі.

Ключові слова: естерифікація, каталізатор, кислоти Льюїса, дикарбонні кислоти, спирти C₄–C₈.