

ACIDIC SYNTHESIS OF THE ESTERS OF FATTY ACIDS  
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**Abstract.** Present research aimed to develop a method for synthesizing long-chain alcohol esters of fatty acids in high product yields and low excess of alcohol using available components and a catalyst. All samples were obtained under similar conditions: the molar ratio of the fatty acid and the corresponding alcohol was 1/1.1 mol/mol using *p*-toluenesulfonic acid as a catalyst. The cyclohexane was used to remove water. The esterification of oleic and stearic acids with linear alcohols C<sub>5</sub>-C<sub>22</sub> and non-linear (isomeric and cyclic structure) alcohols C<sub>5</sub>-C<sub>8</sub> was carried out in conversions above 99.5%. The alcohols did not line up in a chain length-dependent manner.

**Keywords:** esterification, alcohols C<sub>5</sub>-C<sub>22</sub>, acid catalyst, reactive distillation

## 1. Introduction

Fatty acid esters of C<sub>1</sub>-C<sub>4</sub> alcohols are usually used as diesel fuel components (C<sub>1</sub> and C<sub>2</sub> are widely used, C<sub>3</sub> and C<sub>4</sub> are prospective components) and are mainly considered in this role.<sup>1-14</sup> Fatty acid esters of C<sub>5</sub>-C<sub>26</sub> alcohols are found in pharmaceuticals and cosmetics as components of creams and lotions, and they are also considered renewable components of lubricants.<sup>15</sup>

Fatty alcohols are produced in two basic ways: hydrolysis of olefins from petrol and catalytic hydrogenation of fatty acids or fatty acid methyl esters.<sup>16</sup>

The literature does not provide suitable methods for obtaining those compounds. However, it shows some techniques for obtaining those products as esters of alcohols.

Special attention was concentrated on fatty acid esters of ethyl hexanol (a product of butyraldehyde aldol condensation, dehydration, and hydrogenation) as more desirable lubrication materials because they have a low pour point and, therefore, a high viscosity index.<sup>17</sup> Those

characteristics are essential for the exploitation of lubrication fluids.

Obtaining esters by acid esterification has some advantages because obtaining high-quality fatty acids is not difficult nowadays. However, transesterification processes for triglycerides or low-molecular-weight esters do not allow high-yield product production without excess alcohol. This allows for increasing complications with high-molecular-weight alcohol separation from the product mixture.

The production of fatty acid esters from high molecular weight alcohols is being studied intensively. Many studies consider the output of the corresponding esters on enzyme catalysts based on the environmental friendliness of biocatalysts. The products obtained on catalysts of this type are used for esterification with 3-methyl-1-butanol,<sup>18-23</sup> *n*-octanol,<sup>24-29</sup> and 2-ethyl-1-hexanol.<sup>20-33</sup> However, this type of catalyst currently can't provide a product mixture that can be purified.

Examples of the synthesis of fatty acid esters of C<sub>5</sub>-C<sub>18</sub> alcohols on acid catalysts are given in Table 1. In studies,<sup>34-36</sup> sulfuric acid with high conversion of fatty acids was used as an esterification catalyst. The catalyst with 12% Nb<sub>2</sub>O<sub>5</sub> resulted in products with no more than 80% conversion.<sup>37</sup> Using sulfonated activated carbon as a catalyst allowed the conversion of fatty acids to a high degree (91-99%) with very mild selectivity for esterification.<sup>38</sup> Carrying out the process at a relatively high temperature (473 K), with the addition of molecular sieves to completely remove moisture from the reaction medium and additional condensation of the distillate in a Dean-Stark trap, allows for an acid conversion of about 100% in 24 hours.<sup>39</sup> The use of sulfocationites, depending on the amount, types, and properties, leads to high conversions (96-99%), mild (72-80%), and poor (28%).<sup>40-42</sup> *p*-Toluenesulfonic acid provides high acid conversion (98-99%) and final product yield (97%).<sup>43-47</sup> This is evidence of the high selectivity of this catalyst.

**Table 1.** Synthesis of fatty alcohol fatty acid esters

Alcohol	Catalyst (amount to acid)	Acid	Molar ratio alc./acid	Reaction conditions	Conv., %	Lit.
1	2	3	4	5	6	7
2-Ethyl-1-hexanol (C <sub>8</sub> )	H <sub>2</sub> SO <sub>4</sub> (0.15 mole)	Fatty acid dimers	10/1	72 h, 393 K	-	<b>34</b>
2-Ethyl-1-hexanol (C <sub>8</sub> )	H <sub>2</sub> SO <sub>4</sub> (~0.3 mole)	Isooleic acid	1.1/1	Toluene, Dean-Stark trap, 48 h, 413 K	Yield* (96.4)	<b>35</b>
2-Ethyl-1-hexanol (C <sub>8</sub> )	H <sub>2</sub> SO <sub>4</sub> (~0.07 mole)	Jatropha oil fatty acids epoxides, acylated by Jatropha oil fatty acids Soybean oil fatty acids epoxides, acylated by Soybean oil fatty acids	1/1 2/1 2.5/1 3/1  1/1 2/1 2.5/1 3/1	2 h, 403 K	86.2 94.4 96.7 91.7  87.7 94.1 97.8 90.9	<b>36</b>
2-Ethyl-1-hexanol (C <sub>8</sub> )	12% <sub>wt.</sub> Nb <sub>2</sub> O <sub>5</sub> over porous silicagel SBA-15 (10% <sub>wt.</sub> )	Castor oil fatty acids	2/1	8h, 373 K 8h, 393 K 8h, 413 K	25 80 75	<b>37</b>
<i>n</i> -Octanol (C <sub>8</sub> ) 2-Ethyl-1-hexanol (C <sub>8</sub> )	Sulfonated activated carbon (three samples) (4% <sub>wt.</sub> )	Oleic acid	4/1	6h, 363 K	93-99 Sel. (65-78) 91-99 Sel. (83-93)	<b>38</b>
<i>n</i> -Hexanol (C <sub>6</sub> ) <i>n</i> -Octanol (C <sub>8</sub> ) 2-Ethyl-1-hexanol (C <sub>8</sub> )	Noncatalytic, used molecular sieves 3A for in situ drying moisture (15% <sub>wt.</sub> )	Fatty acid dimers	4.5/1	Dean-Stark trap, 24h, 473 K	~100 99.6 98.8	<b>39</b>
<i>n</i> -Octanol (C <sub>8</sub> )	Sulfocationite Amberlyst-15 (10% <sub>wt.</sub> )	Oleic acid	4/1	6h, 363 K	Yield* (97)	<b>40</b>
2-Ethyl-1-hexanol (C <sub>8</sub> )	Sulfocationite Purolite PD206 (5% <sub>wt.</sub> ) Purolite CT269DR (5% <sub>wt.</sub> ) Purolite CT275DR (5% <sub>wt.</sub> )	Castor oil fatty acids	2/1	4h, 393 K	72 96 96	<b>41</b>
2-Ethyl-1-hexanol (C <sub>8</sub> )	Sulfocationite Dowex 50W 8X (10% <sub>wt.</sub> ) Amberlyst-15 (10% <sub>wt.</sub> ) Purolite CT275DR (10% <sub>wt.</sub> )	Castor oil fatty acids	2/1	4h, 373 K	28 ~99 80	<b>42</b>
Oleyl alcohol (C <sub>18</sub> )	<i>p</i> -Toluenesulfonic acid (-)	Karanja oil fatty acids	-	Toluene, Reflux, 6-7h	-	<b>43</b>
2-Ethyl-1-hexanol (C <sub>8</sub> )	<i>p</i> -Toluenesulfonic acid (1% <sub>wt.</sub> )	Rubber oil fatty acids	1.5/1	Xylene, Dean-Stark trap, until theoretical reactive water is collected, 408-413 K	Wt. yield (96.5)	<b>44</b>

Continuation of Table 1.

1	2	3	4	5	6	7
2-Ethyl-1-hexanol (C <sub>8</sub> )	<i>p</i> -Toluenesulfonic acid (1% <sub>wt.</sub> )	Sal fat oil fatty acids	1.5/1	Xylene, Dean-Stark trap, 3h, 408-413 K	98.4, Wt. yield (97)	<b>45</b>
2-Ethyl-1-hexanol (C <sub>8</sub> )	<i>p</i> -Toluenesulfonic acid (1% <sub>wt.</sub> )	Estolides of castor oil fatty acids and dicarbon acids (C <sub>6</sub> , C <sub>8</sub> , C <sub>10</sub> )	2.5/1	Xylene, 8h, 378 K	-	<b>46</b>
3-methyl-1-butanol (C <sub>5</sub> ) 2-Ethyl-1-hexanol (C <sub>8</sub> )	<i>p</i> -Toluenesulfonic acid (10% <sub>wt.</sub> )	Babassu oil fatty acids	2/1	4.5h, 263 K	99.1 99.1	<b>47</b>

Alc. – alcohol, Conv. – conversion of fatty acids, Sel. – selectivity by main products, Lit. – literature, \*Yield – authors named the amount of aim products in the final purified product as yield, Wt. yield – the mass yield of products after the purification process compared to the theoretical mass of the product.

To shift the equilibrium towards the products of the reaction and improve the reaction flow, the molar ratio of alcohol/fatty acid is usually more than 1/1. Many researchers oppose the equimolar ratio in the esterification process. A study notes that the use of equimolar amounts of acid and alcohol for esterification takes longer or requires special conditions, such as elevated temperatures and the use of special catalysts.<sup>48</sup> However, excessive amounts of alcohol reduced the efficiency of the esterification process. A study using sulfuric acid as a catalyst for ethylhexyl esters of fatty acids noted that when the molar ratio of alcohol/fatty acid is exceeded, the acid conversion decreases significantly.<sup>36</sup> The authors explained this decrease by a decrease in the reaction rate due to dilution with alcohol. Still, they did not exclude possible cross-reactions involving alcohol (formation of an ether or alkene).

The following way to shift the equilibrium is to remove one of the reaction products (mainly water). In study,<sup>49</sup> the authors proposed reactive extraction as an effective method for preparing long-chain alcohol esters. In this method, the reaction water is extracted with the components of the reaction mixture, and after the process is completed, it is dried in a vacuum. Another method of water removal is evaporation of water (reactive distillation). It is also noted that reactive distillation is generally not applicable to forming long-chain esters due to the presence of high-boiling components and complex azeotropes.<sup>49</sup> However, only a few studies have used the property of the substance to form a heterogeneous azeotrope. In this case, *n*-hexanol, *n*-octanol, and 2-ethyl-1-hexanol,<sup>39</sup> toluene,<sup>35</sup> and xylene were used.<sup>44,45</sup>

In industry, xylene is most commonly used for reactive distillation due to its high boiling point (compared to benzene and toluene) and relative availability and cheapness. Aromatic compounds are proven carcinogens, so the modern civilized world is trying to build production around them.

Technologists and researchers should not avoid using cyclohexane. This reagent is gaining popularity because it is a hydrogenation product of currently undesirable benzene and has a relatively low price. Like benzene, it can form a heterogeneous azeotrope with water, but it has much lower toxicity.

At the same time, cyclohexane is successfully used in the formation of the ternary azeotrope cyclohexane-isopropanol-water, which is used, for example, in reactive distillation to produce isopropyl esters of fatty acids.<sup>50</sup> It is also widely used in the absolutization of isopropanol and ethanol.

The most widely available acid catalyst is organosoluble toluenesulfonic acid, regardless of sulfuric acid. Toluenesulfonic acid, unlike sulfuric acid, does not cause tar formation and does not lead to loss of raw materials. It can also be called a truly homogeneous catalyst, since for the homogenization of sulfuric acid, the sulfuric acid must form a sulfonated compound with the feedstock, or the reaction proceeds in a pseudo-homogeneous state in the presence of two mutually insoluble liquid phases.

Therefore, this work aimed to develop and test a suitable method for synthesizing fatty acid esters of long-chain alcohols in high yields and with minimal loss of excess alcohol using available components and catalysts on the alcohol line.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Chemicals

Raw material included commercial non-refined high oleic sunflower oil (Ukraine; acid value 2.60 mg KOH/g and marked oleic acid content about 82%; as raw material for oleic acid preparation). Another chemicals, used in current study, were the following: technical grade NaOH (China, 99% NaOH); chemical grade H<sub>2</sub>SO<sub>4</sub> (Ukraine, 44.5% solution in water); chemical grade *p*-toluenesulfonic acid (PTSA) (China, monohydrate); analytic grade cyclohexane (Netherlands); chemical grade stearic acid (Indonesia); technical grade *n*-butanol (Turkey, 99.6%); reagent-grade *n*-pentanol (distilled); reagent-grade 3-methyl-1-butanol (Class A); reagent-grade *n*-hexanol (distilled); analytic grade cyclohexanol (Germany); reagent-grade *n*-heptanol (distilled); analytic grade benzyl alcohol (China); reagent-grade *n*-octanol (distilled at vacuum); reagent-grade 2-ethyl-1-hexanol (Sweden); reagent-grade *n*-decanol; reagent-grade *n*-undecanol; reagent-grade *n*-dodecanol; reagent-grade *n*-hexadecanol; reagent-grade *n*-octodecanol (USA); technical grade oleyl alcohol (Germany, 80-85% oleyl alcohol, Iodine Value 112.2 g I<sub>2</sub>/100g); reagent-grade *n*-docosanol (Japan); potassium *n*-butoxide (self-prepared by developed method,<sup>51</sup> 1% solution in *n*-butanol); indicator bromothymol blue.

#### 2.1.2. Oleic acid preparation

Oleic acid was prepared in a 2000 cm<sup>3</sup> conical flask with mechanical mixing using a water bath and a bath temperature of 363-366 K, according to the described method<sup>44</sup> with a few modifications. 500 g of high oleic sunflower oil was put in a reaction flask. In another flask, 95 g of NaOH was dissolved in 1100 cm<sup>3</sup> of water. After the alkali had dissolved, the solution was put into the reaction flask and mixed with oil. The reaction flask was fixed in a previously heated water bath, and then the agitation of the mixture was started. The reaction mixture was agitated at the required temperature for 4 h. Due to the

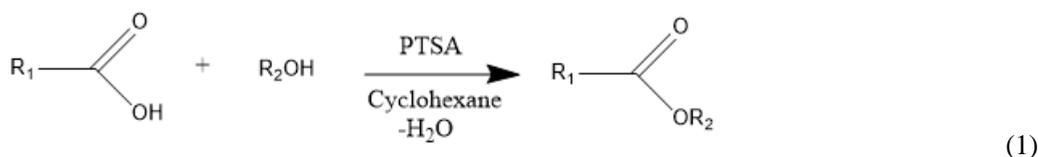
formation of soap, the viscosity of the mixture increases. After 4 h of stirring, 250 cm<sup>3</sup> of 44.5% sulfuric acid water solution was added without stopping the mixture. The acid should be added in small portions because the exothermic reaction of soap neutralization in the soap medium forms the bubbles, leading to the mixture's ejection. After that, the reaction mixture was stirred at the required temperature for 1 h. The final product was poured into a 2000 cm<sup>3</sup> settling funnel. The lower layer was poured out, and the upper layer was washed with hot water (water/layer 1/3) 10 times. The obtained hot fatty acids were dried under vacuum by bubbling with N<sub>2</sub>. The dried fatty acid was distilled under vacuum with N<sub>2</sub> bubbling. The resulting oleic acid was a colorless liquid with an acid value of 198 mg KOH/g and an iodine value of 97 g I<sub>2</sub>/100g.

### 2.2. Methods

#### 2.2.1. Esterification of fatty acids

All samples were prepared under close conditions and with molar ratios of the components by esterification of fatty acid by alcohol (Equation 1). The molar ratio of fatty acids (FA) and corresponding alcohol was 1/1.1 mol/mol, with a slight excess of alcohol. *p*-Toluenesulfonic acid (PTSA) was used as a catalyst in a ratio of 1% wt. to FA (PTSA/FA 0.015/1 mol/mol). Cyclohexane was used to remove water because of its ability to form a heterogeneous azeotrope.

Ceramic pieces were placed in a 250 cm<sup>3</sup> round-bottom flask to provide stable boiling, then all reaction components were loaded, without allowing them to melt or dissolve. The amount of FA was 30-50 g, depending on the length of the alcohol chain, to provide a close amount of the resulting mixture, and the amount of cyclohexane was 25 g in all syntheses. The syntheses were carried out under reflux conditions with condensation in a Dean-Stark trap. The reaction time was calculated from the beginning of condensation in the trap until a stable amount of water appeared, at least 0.5 h. The reaction flask was heated using an oil bath with a hot plate. The mixture's temperature was increased during the reaction and ranged from 388 to 433 K, depending on the alcohol used and the reaction conditions.



R<sub>1</sub>COOH – oleic or stearic acid, R<sub>2</sub>OH – alcohols C<sub>5</sub>-C<sub>22</sub> normal or branched (also cyclic or unsaturated)

#### 2.2.2. Titration of the reaction products

The acid value of the alkyl ester samples was measured by titration with a solution of potassium butoxide

in *n*-butanol. Approximately 2-5 g of the sample was weighed in a titration flask and dissolved in 10-15 g of *n*-butanol. Then, the solution was titrated with potassium butoxide in *n*-butanol solution (~1 %<sub>eq</sub> KOBu) with a

bromothymol blue indicator until the color changed from orange to blue, according to the described method.<sup>52</sup>

### 2.2.3. Determination of FA conversion

The conversion of the corresponding FA was calculated by reducing the acid value to the following scheme. A weighed mixture of the products was sampled and titrated with potassium butoxide in butanol solution. The acid value of the mixture was then calculated and converted to the corresponding FA used in the experiment using Eq. (2).

$$FA \text{ conversion} = \left(1 - \frac{m(FA)_t - m(cat)}{m(FA)_l}\right) \times 100 \% \quad (2)$$

where  $m(FA)_t$  is the titrated results converted to corresponding FA;  $m(cat)$  is an amount of acidic catalyst, converted to corresponding fatty acid (converting coefficient was measured by titration of pure catalyst solution in butanol);  $m(FA)_l$  is a mass of loaded FA.

## 3. Results and Discussions

As shown in Table 2, the esterification of oleic and stearic acids with linear alcohols C<sub>5</sub>-C<sub>22</sub> proceeds with

more than 99.5% conversions in 1-4.3 h, depending on the alcohol. But they did not line up depending on the length of the chain. This can be explained by cyclohexane forming a heterogeneous azeotrope with the produced water. Produced water is not soluble in a non-polar reactive mixture and can be easily removed. It also promotes an increase in ester yield, significantly speeding up the esterification reaction. In this case, the alcohol is a hydroxyl group donor and is practically not involved in the water removal process, because alcohols C<sub>5</sub> and higher do not form a triple water-cyclohexane-alcohol azeotrope. The amount of the bottom layer in the trap after the reaction was the calculated amount of reaction water from esterification, which may show complete reactive water removal.

A similar phenomenon can be observed (Table 3) during the esterification of acids with non-linear (isomeric and cyclic) C<sub>5</sub>-C<sub>8</sub> and unsaturated (C<sub>18</sub>) alcohols. The conversion of fatty acids above 99.8% was achieved in 1.2-2.8 h. The only exception was the action of cyclohexanol. It took 4.5 h to synthesize its corresponding esters. However, the conversion of oleic acid was only about 99.3% in 4.6 h of reaction. These differences can be explained by the fact that only cyclohexanol, among the other alcohols mentioned above, has a secondary structure. Due to the secondary structure, alcohols have lower reactivity.

**Table 2.** Esterification of stearic and oleic acids with linear alcohols

Chain length of alcohol	Alcohol name	Stearic acid			Oleic acid		
		$\tau$ , h	$t^{\circ}_{\text{react}}$ , K	Acid conversion, %	$\tau$ , h	$t^{\circ}_{\text{react}}$ , K	Acid conversion, %
C <sub>5</sub>	<i>n</i> -Pentanol	2.5	389-410	99.6	1.7	401-422	99.7
C <sub>6</sub>	Hexanol	1.8	393-411	99.9	2.8	402-417	99.9
C <sub>7</sub>	Heptanol	2.6	396-420	99.5	3.1	394-422	99.8
C <sub>8</sub>	Octanol	4.3	399-423	~100	2.7	417-432	99.8
C <sub>10</sub>	Decanol	3.0	407-428	~100	1.7	421-427	99.8
C <sub>11</sub>	Undecanol	1.7	413-422	~100	2.3	410-425	99.8
C <sub>12</sub>	Dodecanol	1.8	402-429	99.5	3.3	401-432	~100
C <sub>16</sub>	Hexadecanol	2.3	395-423	~100	1.8	403-422	99.7
C <sub>18</sub>	Octodecanol	1.4	403-418	~100	1.7	420-422	99.9
C <sub>22</sub>	Docosanol	1.0	421-432	~100	2.1	398-418	99.7

\* $\tau$  – reaction time,  $t^{\circ}_{\text{react}}$  – temperature of oil bath

**Table 3.** Esterification of stearic and oleic acids with nonlinear and unsaturated alcohols

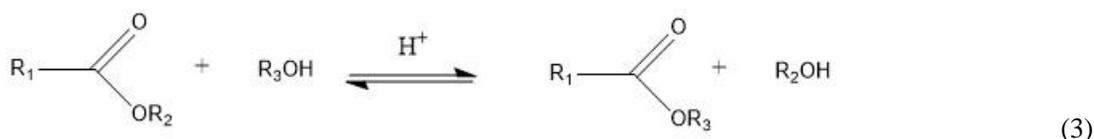
Chain length of alcohol	Alcohol name	Stearic acid			Oleic acid		
		$\tau$ , h	$t^{\circ}_{\text{react}}$ , K	Acid conversion, %	$\tau$ , h	$t^{\circ}_{\text{react}}$ , K	Acid conversion, %
C <sub>5</sub>	3-methyl-1-butanol	2.2	390-415	99.9	1.2	399-412	99.8
C <sub>6</sub>	Cyclohexanol	4.5	394-431	~100	4.6	417-422	99.3
C <sub>7</sub>	Benzyl alcohol	1.8	398-417	99.9	2.8	399-420	99.9
C <sub>8</sub>	2-Ethyl-1-hexanol	2.7	400-426	99.9	2.3	411-419	99.8
C <sub>18</sub>	Oleyl alcohol	2.4	403-420	~100	2.1	401-425	99.8

\* $\tau$  – reaction time,  $t^{\circ}_{\text{react}}$  – temperature of oil bath

The process is carried out by refluxing cyclohexane with a Dean-Stark trap in the state of aqueous-cyclohexane azeotrope or anhydrous cyclohexane. After all, the formation of triple azeotropes of the composition water-cyclohexane-alcohol for alcohols C<sub>5</sub> and higher is not known from the literature. Evaporation of the liquid is highly energy-intensive and can indicate the progress of a reaction. The proposed alcohol/fatty acids system is a molecules with long hydrocarbon chains. Based on this, it can be assumed that the forces of intermolecular interaction between cyclohexane molecules and molecules of raw compounds and the force of interaction between cyclohexane and reaction products are close. That is, almost the same energy is consumed for the evaporation of cyclohexane at the initial and final stages of the process. In the reaction flow, it is necessary to increase the temperature to keep the condensation of cyclohexane at the same rate. This may indicate that during the esterification reaction, the process needs an increase in energy in the system.

An increase in the molar ratio of alcohol to acid reduces the reaction rate due to dilution of the acid and catalyst with alcohol, because the rate is directly proportional to the concentration of the starting reactants. Increasing the conversion rate to quantitative values (above 99%) leads to significant complications in the process. Firstly, the conditions of the reaction in the final stage are high dilution of the starting compounds by the reaction products. If the removal of water by an azeotropic mixture allows to reject the factor of influence of the reverse

reaction (Eq. 1), then the factor of reducing the probability of meeting reagent molecules due to dilution remains. Secondly, it should be remembered that the esterification reaction is an endothermic reaction that requires more and more energy to achieve higher conversions. Why is this happening? It is likely that in a system with high ester yields, the main impurities, which amount to more than 80%, are fatty acid esters. Since the energy incoming into the system is distributed among all the molecules in the reaction medium, it is also transferred to the fatty acid esters. Which, in turn, are characterized by the transesterification reaction that takes place on the same acid catalyst. In addition, the esterification reaction requires significantly more energy, and the yield can be fixed at a certain value (equilibrium conversion) while keeping the reaction temperature constant. The transesterification reaction is not usually considered as a competitive reaction to the esterification process. This is primarily due to the fact that both the starting materials and the reaction products are the same substance. That is, the ester is transferred with another alcohol molecule of the same type as the ester ("oscillating transesterification reaction") (Eq. 3). In fact, we can observe the effect of energy absorption without obtaining an increase in product concentration. To prove this, during the reaction, the need to raise the temperature, *i.e.*, increase the energy supplied to the system, is noted. This energy already exceeds the energy required for transesterification and enables the more energy-intensive esterification reaction to take place.



R<sub>1</sub>COO – acyl group of ester, R<sub>2</sub>OH and R<sub>3</sub>OH – different molecules of alcohol same type

The reactivity of oleic and stearic acids is practically the same, and the results obtained with the same alcohol can be compared with each other. As can be seen (Table 2), an increase in the final temperature leads to a decrease in the reaction time, which is observed for *n*-pentanol, octanol, and docosanol. Also, an increase in the average temperature leads to the same result, which is observed for hexanol, decanol (Table 2), and 3-methyl-1-butanol (Table 3). This may explain the incomplete conversion of oleic acid by cyclohexanol (Table 3). In this case, compared to the synthesis of stearic acid, the reaction temperature was 10 K lower, which is highly critical for the secondary alcohol. However, it is impossible to build dependence on a single sample of secondary alcohol. This topic should be investigated systematically with several samples of secondary alcohols. As can be seen from the results shown above, all samples obtained quantitative conversion at a temperature of 432 K. Therefore, it can be recommended to

carry out the esterification process at temperatures up to 432 K.

Thus, the following conditions for the esterification process with C<sub>5</sub>-C<sub>22</sub> alcohols can be recommended: reaction temperature from the beginning of boiling of the azeotrope agent rising to 432 K, reaction time for primary alcohols 3 h, for secondary alcohols 5 h.

A mixture of reaction products has a color from colorless to dark brown (Table 4). At the same time, no specific color dependence on the alcohol used was found. The saturated stearic acid products were almost colorless. The more intense coloration of esterified oleic acid indicates that acid catalyst PTSA causes a reaction with double bonds of contaminant molecules with two or more double bonds in the structure, which are always present in natural sunflower oil. Most stearic acid-based products crystallize at room temperature (289 K). However, the

products' purification and properties are not considered in this paper and will be described later.

## 4. Conclusions

Using the principles of reactive distillation, it was shown that it is possible to carry out the esterification of fatty acids with C<sub>5</sub>-C<sub>22</sub> alcohols without significant excess alcohols. Almost quantitative conversions were obtained using an alcohol/fatty acid molar ratio of 1.1/1 mol/mol.

The results obtained indicate that the esterification process with water removal by cyclohexane facilitates it

and allows obtaining products with a conversion of 99.3-100% without significant changes in the reaction temperature at 1-4.6 h of reaction.

Moreover, the length of the alcohol chain does not significantly impact the process. However, the branched structure of cyclohexanol, which is considered a secondary alcohol, makes the process slower. In any case, it allows for obtaining products with high conversion.

The condensed lower layer was also identical to the calculated theoretical amount of reaction water. This indicates that the reaction alcohol (considered in this paper) is not lost in the lower water layer.

**Table 4.** Visual properties of products mixture of stearic and oleic acids with linear, nonlinear, and unsaturated alcohols

Chain length of alcohol	Alcohol name	Stearic acid		Oleic acid	
		Color	Aggregate state	Color	Aggregate state
C <sub>5</sub>	<i>n</i> -Pentanol	slightly yellow	crystals 4/5	colorless	liquid
C <sub>6</sub>	Hexanol	slightly yellow	crystals 1/4	colorless	liquid
C <sub>7</sub>	Heptanol	colorless	crystals	dark brown	liquid
C <sub>8</sub>	Octanol	slightly yellow	crystals 4/5	brown	liquid
C <sub>10</sub>	Decanol	lemon yellow	crystals 4/5	brown	liquid
C <sub>11</sub>	Undecanol	yellow	crystals	slightly yellow	liquid
C <sub>12</sub>	Dodecanol	colorless	solid	brown	liquid
C <sub>16</sub>	Hexadecanol	slightly brown	solid	brown	crystals 4/5
C <sub>18</sub>	Octadecanol	colorless	solid	colorless	crystals 4/5
C <sub>22</sub>	Docosanol	colorless	solid	yellow	solid
C <sub>5</sub>	3-methyl-1-butanol	slightly yellow	liquid	slightly brown	liquid
C <sub>6</sub>	Cyclohexanol	colorless	solid	brown	liquid
C <sub>7</sub>	Benzyl alcohol	slightly brown	solid	colorless	liquid
C <sub>8</sub>	2-Ethyl-1-hexanol	colorless	liquid	brown	liquid
C <sub>18</sub>	Oleyl alcohol	slightly brown	solid	yellow	liquid

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## КИСЛОТНИЙ СИНТЕЗ ЕСТЕРІВ ЖИРНИХ КИСЛОТ ЗІ СПИРТАМИ З ДОВГИМИ ЛАНЦЮГАМИ

**Анотація.** Метою цього дослідження було вдосконалення методу синтезу естерів жирних кислот зі спиртами з довгими ланцюгами з високими виходами продуктів і малим надлишком спирту із застосуванням доступних компонентів і каталізатора. Усі зразки були синтезовані за близьких умов: молярне співвідношення жирної кислоти до відповідного спирту було 1/1,1 моль/моль з використанням пара-толуолсульфокислоти в ролі каталізатора. Для відведення води з реакційної суміші було застосовано циклогексан. Естерифікація олеїнової та стеаринової кислот за допомогою лінійних спиртів C<sub>5</sub>-C<sub>22</sub> та нелінійних (ізомерів та циклічної будови) C<sub>5</sub>-C<sub>8</sub> спиртів проходила з конверсією понад 99,5%. Перебіг процесу не має пропорційної зміни від довжини вуглецевого ланцюга спирту.

**Ключові слова:** естерифікація, спирти C<sub>5</sub>-C<sub>22</sub>, кислотний каталізатор, реактивна дистиляція