

Article

A New Approach for Synthesizing Fatty Acid Esters from Linoleic-Type Vegetable Oil

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Abstract: Countries around the world recognize the numerous social, economic and environmental advantages of promoting liquid biofuels. They invest in its development and introduce tax incentives for its manufacture and tariffs of production regulation. In most studies, the process of synthesizing fatty acid esters takes a long time from 1 to 8 h. In this work, the synthesis of fatty acid esters was carried out in the range of volumetric ratios of ethanol to linoleic type oil in order to increase the kinetics of the process. The main parameters of the synthesis were studied by use of magnetic stirred tank reactors in a parallel reactor system, H.E.L. The synthesis was carried out in the presence of a homogeneous alkaline catalyst. The volumetric ratio of ethanol to oil was maintained at 1:1, 2:1, 3:1, 4:1 and 5:1. The amount of catalyst added to the reaction mixture ranged from 0.25 to 2.5% by the weight of the reaction alcohol. The dryness of ethanol varied from 91 to 99%. Effective process conditions have been established to reduce the reaction time from 2.5 h to 5 min while maintaining a high degree of conversion. The results obtained during the study suggest the possibility of using a continuous reactor to produce fatty acid esters from linoleic raw materials containing up to 16% of free fatty acids. This also means the possibility of using second generation biofuel feedstock.

Keywords: biofuels; rapeseed oil; ethanol; homogeneous catalysis; transesterification; fatty acid esters



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1. Introduction

Due to the reduction in crude oil reserves and the harmful effects of the toxic emissions of conventional diesel fuel on the environment, biodiesel has become important over the past few years as an environmentally friendly, sustainable and renewable energy source [1–3]. According to the Energy Outlook Review forecast, it is expected that by the year 2030, a mixture of 30% biodiesel with petrodiesel (B30) will be promoted as an alternative to petrodiesel [4,5]. According to the estimates of the world community, biodiesel accounts for 70% of the transport fuel that will be in demand by 2040 [6,7].

Since biodiesel is made from natural ingredients, vegetable oil, animal fat or waste oil, it is biodegradable and renewable. Despite the fact that biodiesel has various advantages over conventional diesel fuel, it is still necessary to solve numerous technical and economic problems [8–11]. Among them are the lower cost of diesel fuel derived from oil, the choice of suitable catalysts and the development of technology for the economical and efficient synthesis of biodiesel.

Since 60–80% of the cost of biodiesel is due to its raw materials, the most difficult task is to choose inexpensive raw materials from a wide range of available sources [4,12,13]. Conditionally, three generations of biodiesel raw materials are distinguished. The raw materials of the first generation are oilseed crops. Initially, this raw material was seen as a promising option to reduce the extraction and use of traditional fuels. However, worries have arisen about the use of food crops as raw materials and their impact on arable land, biodiversity and global food needs [14–17].

Biofuels of the second generation are produced from non-food lignocellulose or wood biomass as well as agricultural waste. This raw material is grown on infertile lands or on arable lands, but is a by-product of the main crop and is not used directly in the production of food [18]. For example, straw, pulp, perennial herbs, yellow grease and solid household waste can act as raw materials for the second generation. The advantage of second-generation raw materials is an increase in waste-free production and the use of resources unclaimed in industry. Nevertheless, there are still some limitations related to economic efficiency since there are problems with expanding production to a commercial level [14].

The raw material of the third-generation biofuels is the biomass of micro- and macroalgae cultivated in ponds or reservoirs on land or in the sea. The advantages of this type of feedstock are high yields with minimal impacts on freshwater resources and the possibility of production in seawater or wastewater. On the other hand, their production requires a large amount of energy and fertilizers. Moreover, the resulting fuel has a shorter shelf life than other types of biofuels and is inferior in low-temperature properties [14].

Based on the advantages and disadvantages presented, the most practical application in the world is still found in first-generation raw materials. Among the EU countries and North and South America, soybeans and rapeseed have become the most popular oilseed crops. In Southeast Asia, it is the fruits and seeds of the oil palm. The main source of biodiesel production in the world is rapeseed oil (53% of all raw materials for biodiesel production) [19].

In the Russian Federation, rapeseed is one of the most promising oilseed crops for biodiesel production. According to the NeoAnalytics research of 2021, rapeseed oil production in Russia amounted to 701.4 thousand tons and increased by 11.8% over the year. At the same time, the volume of the domestic consumption of rapeseed oil in Russia remains small and accounts for only 1.34% of the total market (sunflower oil occupies more than 50%). Most of the rapeseed oil produced in Russia (more than 85%) is exported.

Based on this information, it can be concluded that the use of rapeseed oil as a raw material for biodiesel is more reasonable for the Russian market.

Depending on the choice of feedstock containing an excess of free fatty acids or their triglycerides, one of two reactions will be most effective for obtaining FAE—acid esterification for FFA and basic transesterification for triglycerides (Figures 1 and 2). The choice of reaction will determine the catalyst. Bronsted acid catalysts, such as H_2SO_4 , are more active in the esterification reaction due to their availability and high catalytic activity; the basic homogeneous catalysts in the transesterification reaction are potassium and sodium hydroxides [20–22].

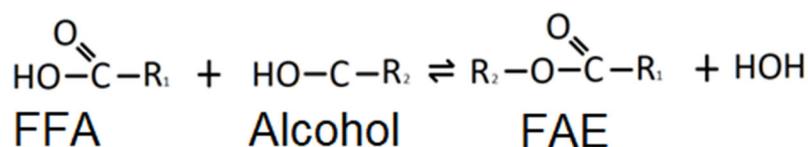


Figure 1. Free fatty acid esterification reaction.

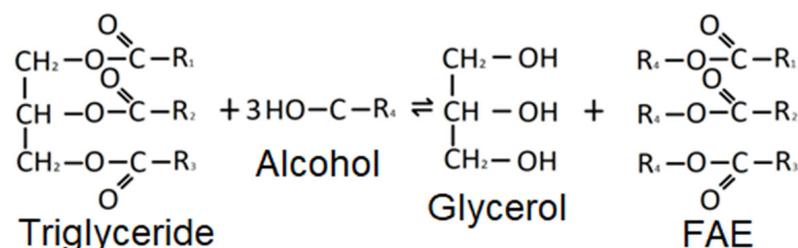


Figure 2. Transesterification reaction of vegetable oil.

Both reactions are reversible. Therefore, the addition of an excess of reaction alcohol is necessary in order to shift the equilibrium of the reaction towards the formation of products. In the esterification reaction, it is also required to remove a by-product—water—from the reaction system. In the case of vegetable oils, represented mainly by triglycerides, the transesterification reaction will be preferable.

The quality of the feedstock—the content of free fatty acids and impurities—affects the properties of the biodiesel. If the amount of free fatty acids in the raw material exceeds 1%, then the side saponification reaction reduces the yield and the rate of formation of FAE, which creates difficulties for the following technological processes [23,24]. For the same reason, water is an undesirable impurity in the feedstock since, in the presence of water, the FFAs quickly react with the catalyst, deactivating and reducing its concentration in the reaction mixtures.

The fatty acid composition of the starting oil affects some key properties of biodiesel, such as cetane number, pour point, flash point, oxidation resistance, etc. [4,25]. To improve the quality of the resulting biofuels, the refining of the raw materials (vegetable oils) is often carried out. However, this process requires complex technological operations, such as hydration, distillation refining and the use of solid activated adsorbents [26], which affects the increase in the cost of raw materials.

Existing studies and technologies for the production of biofuels by the method of alkaline transesterification make a bias towards the use of methanol as an alkylating component due to its high reactivity [27,28]. However, methanol has a high toxicity. Its maximum permissible concentration (MPC) in the air of the working area is 5 mg/m³ (Table 1).

Table 1. Monohydric alcohols MPC.

Alcohol	Molecular Formula	MPC of the Working Area, mg/m ³
Methanol	CH ₃ OH	5
Ethanol	C ₂ H ₅ OH	1000–2000
Propanol	C ₃ H ₇ OH	10
Butanol	C ₄ H ₉ OH	10

A complete or partial alternative to methanol in the synthesis of fatty acid esters can be its homologues—ethyl, propyl, butyl alcohols, etc. [29–31]. Studies show that the use of alcohols with a longer and branched carbon chain increases the calorific value of esters obtained from them and improves the value of the pour point [32]. However, it is worth considering the influence of the spatial volume of the molecule—the steric effect. Thus, an increase in the carbon chain of an alcohol atom can slow down the reaction transesterification or make it impossible; therefore, methyl or ethyl alcohols are most often used.

In this list, ethyl alcohol has a number of advantages that determine the choice of this monatomic alcohol in the synthesis of liquid biofuels. Firstly, ethyl alcohol occupies the position closest to methanol in the homologous series of monatomic alcohols. Therefore, its reactivity will be greater than that of other similar alkylating agents—*isopropanol* and *isobutanol*. Secondly, the MPC of ethyl alcohol is many times higher than the MPC of other alcohols (Table 1). Thirdly, unlike others homologues obtained during the processing of petroleum products, there is a technology for obtaining *bioethanol* from vegetable raw materials [33–35].

The disadvantage of ethanol is the formation of an azeotropic mixture with water (4–6%) with a boiling point of 78.5 °C. Therefore, the use of ethanol in the process of transesterification requires a deeper drying of the alcohol, which increases the complexity of the technological scheme. Nevertheless, due to the advantages of ethyl alcohol as an alternative to methanol, research is currently underway in parallel with the study of the triglyceride methanolysis transesterification of vegetable oils in the presence of ethanol [36–39].

Most studies devoted to the basic transesterification of vegetable oils recognize the work in the optimal range of the initial components' molar ratios. This is 6–10 moles of

alcohol per 1 mole of oil. However, the use of such a molar ratio has an impact on the kinetics of the reaction, since during the entire process the reaction mixture will remain in a heterogeneous state. Initially, there will be oil and alcohol phases, and at the exit from the process—an essential and a glycerin. In turn, this will affect the productivity and cost of commercial products.

For example, in research papers, the basic synthesis of FAE in the range of the molar ratios of ethanol:oil, equal to 6 ÷ 14:1, is taken from 1 to 6 h [36,37,40].

Reducing the reaction time can be achieved by reducing the volume of the reaction mixture. In this option, the FAE synthesis can be implemented in plug-flow microreactors (PRE) [39,41]. However, the use of reactors with small cross sections reduces the plant productivity.

On the other hand, the issue can be solved by homogenizing the reaction mixture during synthesis. As is known, the ethyl esters of fatty acids contribute to the homogenization of the reaction mixture [42]. However, in this case, part of the desired reaction product will be involved in the recycling of the technological scheme.

In this article, we suggest combining the above decisions and increasing the ratio of components towards a volumetric excess of ethanol. Therefore, the reaction mixture will be homogenized during the process. As a consequence, it will increase the rate of the transesterification reaction and make it possible to use a bigger cross section for the plug-flow reactor.

2. Experimental Section

2.1. Materials and Reagents

As objects of the study, two types of vegetable oil were used—refined sunflower (RSO) and unrefined rapeseed (URO). The acid number and acidity of the oils were determined according to ISO 660-83 “Animal and vegetable fats and oils. Determination of acid value and acidity” by the titrimetric method.

The fatty acid composition of vegetable oil was determined according to GOST 30418-96 “Vegetable oils. Method for determination of fatty acid content”.

Moisture content in oils was determined according to ISO 662-2019 “Animal and vegetable fats and oils. Determination of moisture and volatile matter content”.

The results of the analysis of RSO and URO oils are presented below. (Table 2, Figure 3).

Table 2. Acidity and acid value of feedstock.

Oil Type	Acid Value, mg KOH/g Oil	% Acid	Moisture, %Mass
Refined Sunflower Oil	3.49	1.76	0.076
Unrefined Rapeseed Oil	32.36	16.27	0.063

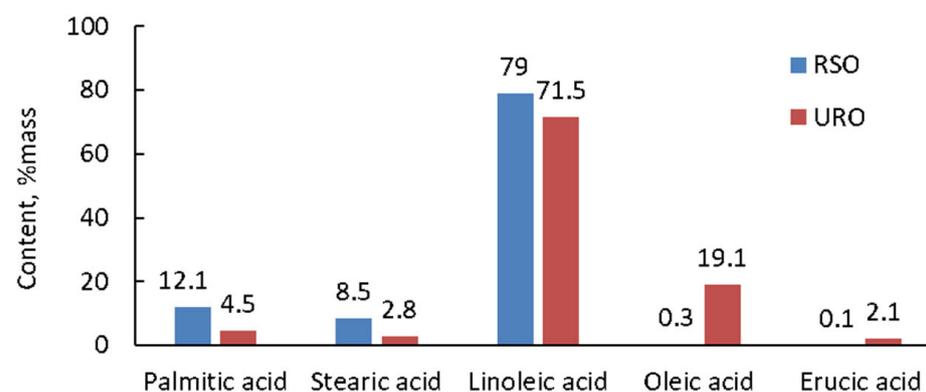


Figure 3. Fatty acid composition of sunflower (RSO) and rapeseed (URO) oil.

To prepare biodiesel by basic catalyzed transesterification, potassium and sodium hydroxides were used. Technical ethyl alcohol containing 5% water was used as the reaction alcohol.

2.2. Alcohol Drying

Absolute ethanol was obtained using GOST 30418-96 “Vegetable oils. Method for determination of fatty acid content”. The principle method consists of boiling ethanol in the presence of CaO for 6–8 h, followed by distillation of absolute alcohol from the mixture (Figure 4). The required amount of calcium oxide was calculated from the lime slaking reaction:

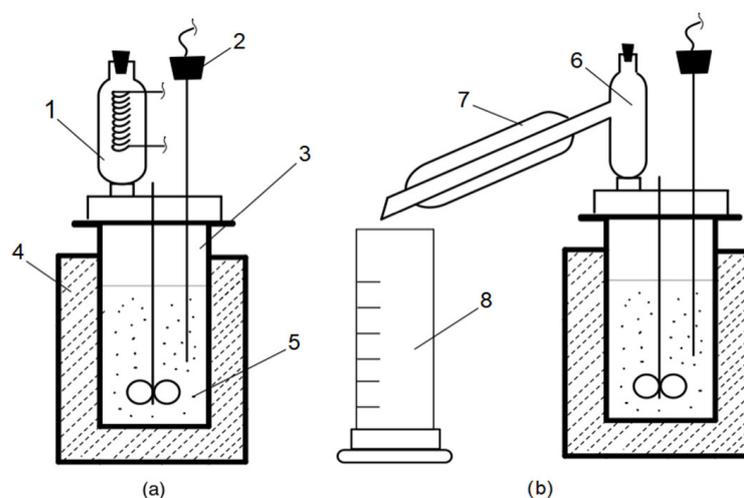
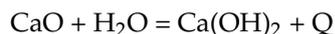


Figure 4. Schematic illustration of a laboratory unit for drying alcohol: (a) suspension mixing step; (b) absolute alcohol distillation step; 1—reflux condenser; 2—temperature probe; 3—glass reactor with magnetic bar stirrer; 4—mantle heater; 5—ethanol–CaO suspension; 6—Wurtz’s nozzle; 7—condenser; 8—distillation receiver.

For example, for 100 mL of 95% ethanol, the following mass of calcium oxide will be required:

$$m_{\text{CaO}} = 0.28 \text{ mol} * 56 \text{ g/mol} = 15.7 \text{ g}$$

It is understood that increased water content in alcohol leads to the need to add a large amount of CaO to the alcohol; consequently, a suspension would be generated. The suspension can be overheated during the alcohol dehydration, which makes the reaction system unstable and results in the loss of absolute ethanol. Therefore, in order to optimize the drying process, the temperature in the reactor was lowered to 65–75 °C (depending on the density of the suspension). Uniform mix was achieved with magnetic bar stirrer.

The purity of the alcohol was checked with a refractometer using the graphic dependence of the optical density on the composition of the ethanol–water mixture (Figure 5). Reactive alcohol with water content in the range of 2–9% was obtained by mixing absolute ethanol with distilled water in a certain ratio.

2.3. Synthesis of Fatty Acid Esters (FAEs)

The synthesis of fatty acid ethyl esters was carried out at ethanol excess in a stirred tank reactor in Auto-MATE system H.E.L (Figure 6) with a reflux condenser and a magnetic stirrer [43–45]. The volumetric ratio of ethanol to oil was maintained at 1:1, 2:1, 3:1, 4:1 and 5:1. The amount of catalyst added to the reaction mixture ranged from 0.25 to 2.5% by weight of the reaction alcohol. The dryness of ethanol varied from 91 to 99%.

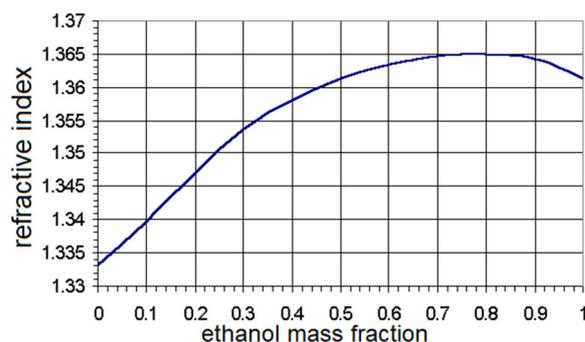


Figure 5. The refractive index dependence of the solution on the mass fraction of ethanol in water at 20 °C.



Figure 6. The ideal mixing reactor used for synthesis (Auto-MATE Reactor System H.E.L.).

The transesterifications were carried out at 70 °C and 200–250 rpm for 2–4 h. Upon completion of the synthesis, the upper ether phase was separated from the glycerol phase by using a separation funnel.

In cases where a homogeneous phase was formed as a result of transesterification, it was filtered. The ethereal phase was purified from excess alcohol by distillation, then the glycerol phase was separated using a separating funnel.

The pilot study was divided into two blocks. Based on the theory of the transesterification reaction, it can be said that refined oil is a higher quality type of upstream material. That is why, in the first block basic process, conditions were determined by the example of refined sunflower oil. Then—in the second block of the study—unrefined rapeseed oil was used as a feedstock. In this block, the influence of unrefined oil on the parameters of the transesterification process was investigated.

Moreover, in another series of experiments, the synthesis of FAEs from sunflower and rapeseed oils was carried out using mixtures of absolute ethyl alcohol with water in the range of 91–99%.

2.3.1. Refined Sunflower Oil (RSO) Transesterification—Classical Method

An amount of 10 mL of refined sunflower oil and KOH catalyst in an amount of 0.5 to 2.5% by ethanol weight were placed in a 250 mL steel reactor. Then, 10 to 40 mL of ethanol was added to the reaction mixture and the stirring process was started. Ethyl alcohol was not subjected to pretreatment. The water content in it was 4–5%.

The reaction mixture was heated to 70 °C with constant stirring at 200–250 rpm. The mixing time was 2.5 h (Table 3). The process was stopped after the specified time. The reactor was unloaded after complete cooling. The ether phase was analyzed for the content of fatty acid esters by chromato-mass spectrometry.

Table 3. FAE-RSO synthesis conditions.

No. Test Series	1		2		3	4
Temperature, °C	70		70		70	70
Stirring speed, rpm	200 ÷ 250		200 ÷ 250		200 ÷ 250	200 ÷ 250
Catalyst	KOH	NaOH	KOH	NaOH	KOH	KOH
Catalyst quantity, mass% (by weight of alcohol)	1		1		0.5 ÷ 2.5	1
Ethanol drying degree, %vol.	95		95		95	91 ÷ 99
Synthesis time, hour	2.5		0 ÷ 2.5		2.5	2.5
V _{al} /V _{oil}	1 ÷ 5		3		3	3

2.3.2. Crude Rapeseed Oil (URO) Transesterification—Improved Method

In the first series of tests, the FAEs of unrefined rapeseed oil were obtained by the same method as the FAEs of refined sunflower oil. However, after observations about the kinetics of the process, the synthesis method was subject to change in order to measure the degree of conversion of raw materials for small periods of time.

An amount of 10 mL of unrefined rapeseed oil and KOH catalyst in an amount of 0.25 to 2.0% by ethanol weight were placed in a 250 mL steel reactor. The feedstock with the catalyst was heated in the reactor to 80 °C with constant stirring at 200–250 rpm. Then, without stopping the process, 10 to 50 mL of ethanol was added to the reaction mixture (Table 3). The temperature of 70 °C was reached in the reactor in 30 s by reducing the mantle heating.

The reaction mixture was stirred at constant temperature for 0.25–95 min. Then, the synthesis process was stopped by rapid cooling of the reactor. The ether phase was analyzed for the content of fatty acid esters by chromato-mass spectrometry.

The choice of starting point in the study of transesterification of rapeseed oil was based on a priori knowledge about the effect of FFA in the composition of vegetable oils on the process of alkaline transesterification. This is why a zero experiment was carried out with rapeseed oil (Tables 3 and 4).

Table 4. FAE-URO synthesis conditions.

No. Test Series	0	1	2	3	4
Temperature, °C	70	70	70	70	70
Stirring speed, rpm	200 ÷ 250	200 ÷ 250	200 ÷ 250	200 ÷ 250	200 ÷ 250
Catalyst	KOH	KOH	KOH	KOH	KOH
Catalyst quantity, mass% (by weight of alcohol)	1	1	0.25 ÷ 2	0.5	1
Ethanol drying degree, % vol.	93	91 ÷ 99	95	99	99
Synthesis time, hour	2.5	2.5	2.5	2.5	0 ÷ 2.5
V _{al} /V _{oil}	3	3	3	1 ÷ 5	3

2.4. Analysis of FAEs Composition

Fatty acid ethyl esters (FAEs) were determined using gas chromato-mass spectrometry equipped with an RTX HP-5MS (30 m × 0.25 mm) column equipped with flame ionization detector (FID). Helium was the carrier gas. The sample was injected at a flow rate of 0.5 mL/min. The injector temperature was 280 °C, and the detector temperature was 260 °C. The initial temperature of the oven was 120 °C for 2 min, increased at 5 °C/min to 250 °C, held for 10 min [46,47].

The internal standard method was used to determine the yield of the target product. A 10 µL sample of the ether fraction was introduced into 1 mL of a solvent containing

a known amount of an internal standard. Dodecane was used as an internal standard ($C_{12}H_{26}$). The concentration of the target product was calculated by the (1):

$$C_{FAE} = \frac{S_{FAE}}{S_{st}} \cdot C_{st} \quad (1)$$

where C_{FAE} and C_{st} —the ether and internal standard concentrations; $\frac{S_{FAE}}{S_{st}}$ —the ratio of ether peak area to internal standard peak area.

The FAEs yield was calculated as the ratio of the number of synthesized product moles to the theoretical amount of product received at full product conversion:

$$\gamma_{FAE} = \frac{\vartheta_{exp}}{\vartheta_{teor}} \cdot 100\% \quad (2)$$

where γ_{FAE} —the product yield; ϑ_{exp} —the number of synthesized product moles; ϑ_{teor} —the product moles received at full product conversion.

The ϑ_{teor} was calculated from the amount of raw material:

$$\vartheta_{teor} = \frac{\vartheta_{oil}}{3} \quad (3)$$

2.5. FTIR Analysis of FAEs

The Fourier Transform Infrared (FTIR) spectra of FAEs were determined by using the FTIR spectrophotometer Nicolet 6700 (Thermo Scientific, USA). The ZnSe cell was used for this purpose. The FTIR spectrum was measured within a range of $400\text{--}4000\text{ cm}^{-1}$ with 4 cm^{-1} resolution.

3. Results and Discussions

3.1. Influence of the Water Content

As a result of the synthesis of rapeseed oil esters under zero experiment conditions, the yield of the product was lower than in the transesterification of sunflower oil. The FAE-URO yield did not exceed 24%.

The change in the yield of fatty acid esters (FAEs) could be affected by two factors: the acidity of the vegetable oil and the drying degree of the ethanol. The use of the refined oil with a low FFA content made it possible to eliminate the side reaction of saponification and use ethyl alcohol with a drying degree of 95–97%, while in the zero experiment with unrefined raw materials the ethanol of lower quality was used (93%). This conclusion confirms the dependence of the FAE yield on the drying degree of the ethanol (Figure 7).

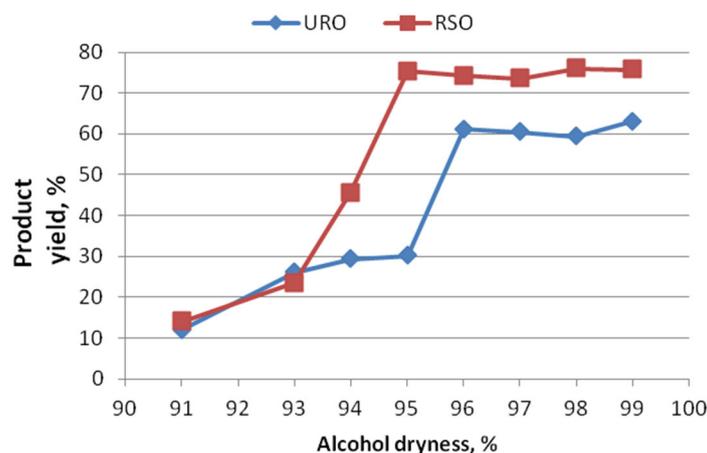


Figure 7. The FAEs' yield dependence of alcohol drying degree.

The yield of the target product remains low at concentration of water in alcohol $>4\%$. At a water concentration of $<4\%$, a jump in values is observed in the graph and a “plateau” is reached. The maximum yield of FAEs is achieved by using absolute ethanol (99%). When refined sunflower oil is used as a raw material, the jump in the yield of the target product shifts to the left. A high yield of the target product is achieved with a content of up to 5% water in ethanol for this type of raw material.

3.2. Influence of the Oil: Alcohol Ratio

Figure 8 shows the results of the first and third test series with refined sunflower oil and unrefined rapeseed oil, respectively.

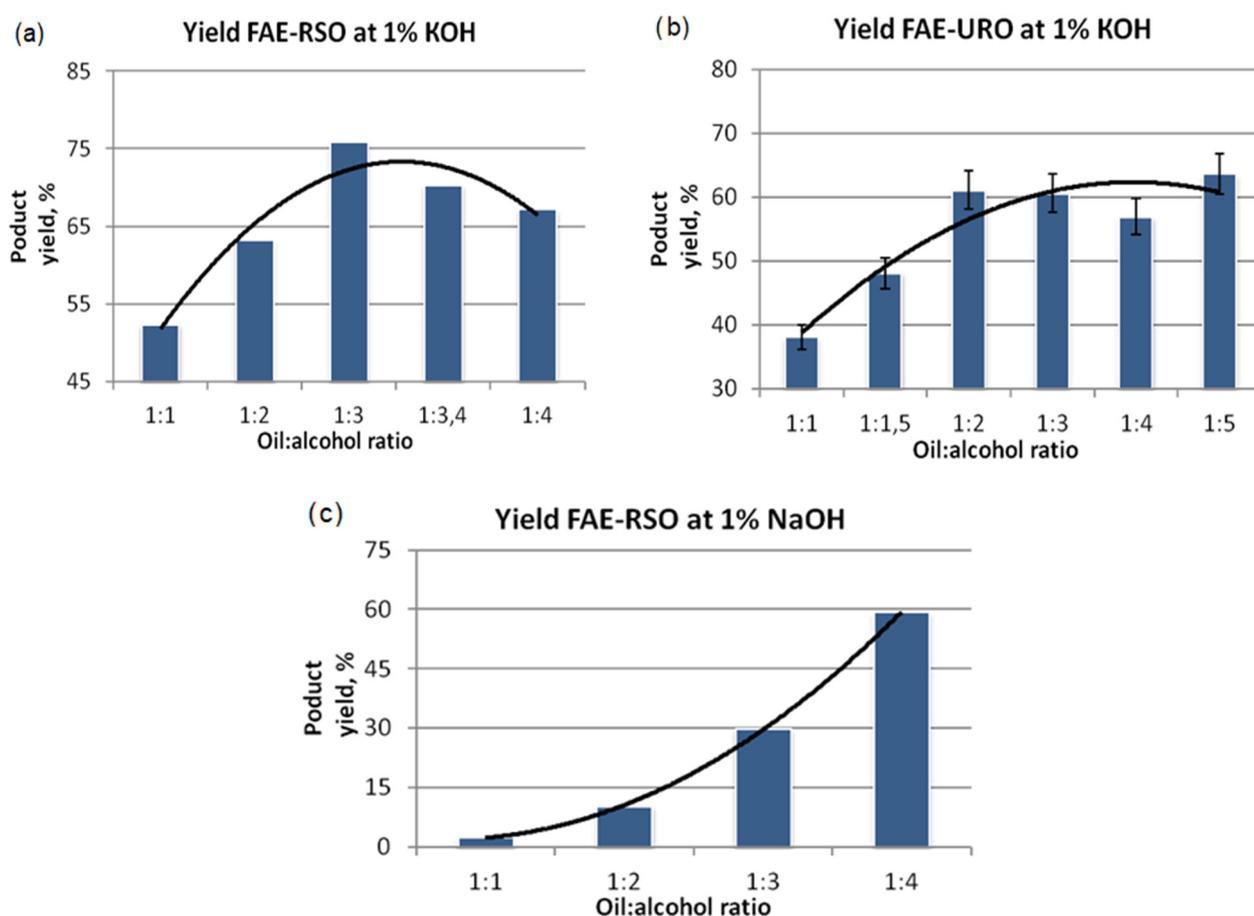


Figure 8. Effect of the proportions of oil:ethanol components on the yield of FAE-RSO and FAE-URO catalyzed by 1% KOH (a,b) and 1% NaOH (c).

We observe a linear increase in the concentration of the target product with an increase in the oil–alcohol ratio in the reaction catalyzed by potassium hydroxide (Figure 7). This corresponds to increases in the oil conversion degree and the yield of the target product, respectively.

The maximum conversion of the oil is achieved with an oil:ethanol ratio of 1:3. A further increase in proportions leads to a decrease in this value. On the one hand, this negative effect can be attributed to a decrease in the oil concentration in the system. On the other hand, increasing the volume of the reaction mixture requires more energy and time to completely heat and blend the components. Another reason can be an increase in water concentration in the system, leading to the deactivation of the catalyst.

An exponential increase in the yield of FAEs is observed in the transesterification reaction catalyzed by 1% wt. sodium hydroxide (Figure 8b). However, the maximum oil

conversion is beyond the selected ratio range. In this case, to achieve maximum efficiency, more reactive alcohol is required and, consequently, the volume of the reaction mixture in the reactor increases.

This can be explained by the lower activity of Na compared with K. Since K is in the fourth row of the alkali metal group of the periodic table it has one more energy level than Na in the third row.

Thus, it can be concluded that potassium hydroxide is more effective as a catalyst in comparison with sodium hydroxide in the example of the transesterification of refined sunflower oil.

In the case of unrefined rapeseed oil, it can be seen that the maximum FAE yield is achieved at a ratio of 1:2. After this point, the indicators level off (Figure 8b). In the synthesis of FAE-URO, 99% ethanol has been used. This explains why the concentration of the target product was not reduced by an increase in the oil–ethanol ratio, as was observed in the synthesis of FAE-RSO. Therefore, it can be concluded that the moisture content of ethanol has a predominant effect on the result obtained in the FAE-RSO synthesis (Figure 8a).

3.3. Influence Catalyst Concentration

We can see that the concentration of potassium hydroxide below 1% is not sufficient to initiate the transesterification process of refined sunflower oil (Figure 9). The FAE yield at a KOH catalyst concentration of 0.5% did not exceed 50%. There is an extreme concentration of the target product in the reaction mixture after the synthesis of FAE-RSO in the presence of 1% wt. KOH. A further increase in concentration results in a gradual decrease in the FAEs' yield. This decrease is correlated with a power function (Figure 8). This effect can be explained by the fact that an increase in catalyst content in the system above 1% leads to the esters' hydrolysis in the presence of water. Potassium salts of fatty acids are the products of this hydrolysis. The formation of potassium salts as a product of hydrolysis has been proven to make the reaction mixture more viscous, and therefore reduce the conversion rate [48–50].

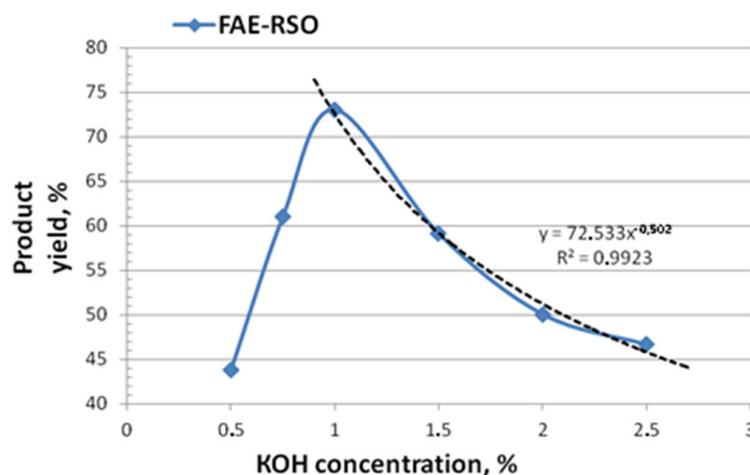


Figure 9. FAE-RSO yield dependence on different KOH catalyst content.

In the case of an increase in the content of FFA in the oil, the quality of alcohol has more influence on the transesterification process. Therefore, the optimal concentration of the potassium hydroxide would change (Figure 10). For instance, the peak of the FAEs' yield on the graph had shifted towards a decrease in the catalyst content due to the use of absolute ethanol. For this reason, a 0.25% KOH point was added to bring the optimum point into the limits of the curve's extreme values (Figure 10a). In the previous section, we determined the effect of the oil–alcohol ratio on the FAE yield at 1% KOH catalyst. To confirm the optimal catalyst concentration, we have built an additional curve at 0.5% KOH

(Figure 10b). It can be seen that, for a concentration of KOH at 0.5%, the optimal ratio is 1:3. For a concentration of 1% KOH, it is 1:2.

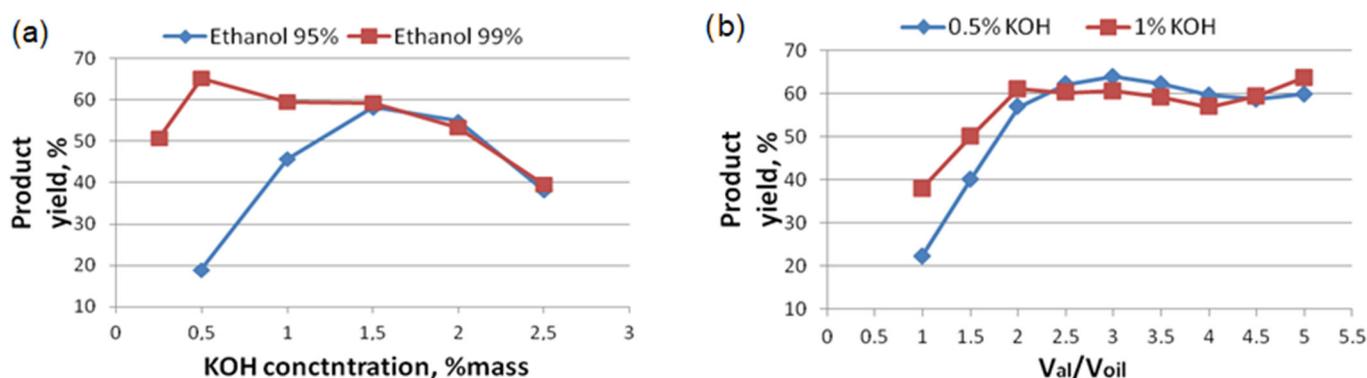


Figure 10. FAE-URO yield dependence on: (a) catalyst content; (b) oil-ethanol ratio.

It took more catalyst to use ethanol without pre-drying. Moreover, the optimum point is located below (Figure 10a). These results also confirm the negative effect of the water content not only on the reaction balance, but on the catalyst efficiency due to its deactivation by side saponification processes [23,24]. Therefore, less quality ethanol will require more KOH. Increasing the KOH content beyond the optimum point leads to the yield decrease the same way as in the sunflower oil experiment.

3.4. Process Kinetics

Since the FAEs synthesis takes place in the system of excess ethanol, this reaction can be attributed to the pseudo-first order reaction [51]. Graphs (Figure 11a,b) show the kinetic curves constructed for the first and second order reactions. The correlation coefficient of the first order curve is greater than the correlation coefficient of the second order curve. Therefore, it can be concluded about the first order of the transesterification reaction.

The KOH kinetic curve passes above the NaOH kinetic curve (Figure 11). This confirms the fact that potassium hydroxide is a more efficient catalyst than sodium hydroxide.

The results of the FAE-URO synthesis, according to the method applied to refined oil, are presented in Figure 12. The kinetic curve of rapeseed oil transesterification with absolute ethanol is shown below in Figure 13.

It can be seen from the graph that the presence of water in the system strongly affects the rate of the reaction. Thus, in the process of studying the kinetics of the zero experiment, the FAE-URO yield remained low (Figure 12).

At the same time, the use of absolute alcohol (99%) made it possible to reach a plateau of oscillations relative to the equilibrium line. This indicates that the concentration of the target product has already reached its maximum in less than 15 min (Figure 13a,b).

Figure 13 shows the results of the synthesis of FAE-URO in excess of absolute ethanol according to the optimized method. The maximum degree of the FAE-URO conversion is already reached in the second minute of the process. Then, a plateau of values takes place. These values fluctuate relative to the conditional equilibrium line (Figure 13a).

This result can be justified by the homogenization of the reaction mixture during synthesis in a volumetric excess of ethanol and by the small total volume of the mixture in the reactor (<50 mL). The improved synthesis method together with the optimal process conditions allows us to make an assumption about the possibility of a transition from the ideal mixing reactor model of the ideal displacement reactor.

Thus, in the paper [52], the authors compare two reactor models—oscillatory flow reactor (OFR) and stirred tank reactor (STR). The synthesis time of the stirred tank reactor in their work was 60 min. It is worth noting that, in paper [52], the synthesis in the stirred tank reactor was carried out at a molar ratio of waste cooking oil to methanol of 1:6. Furthermore, there was a large volume of reactor loading (5 L).

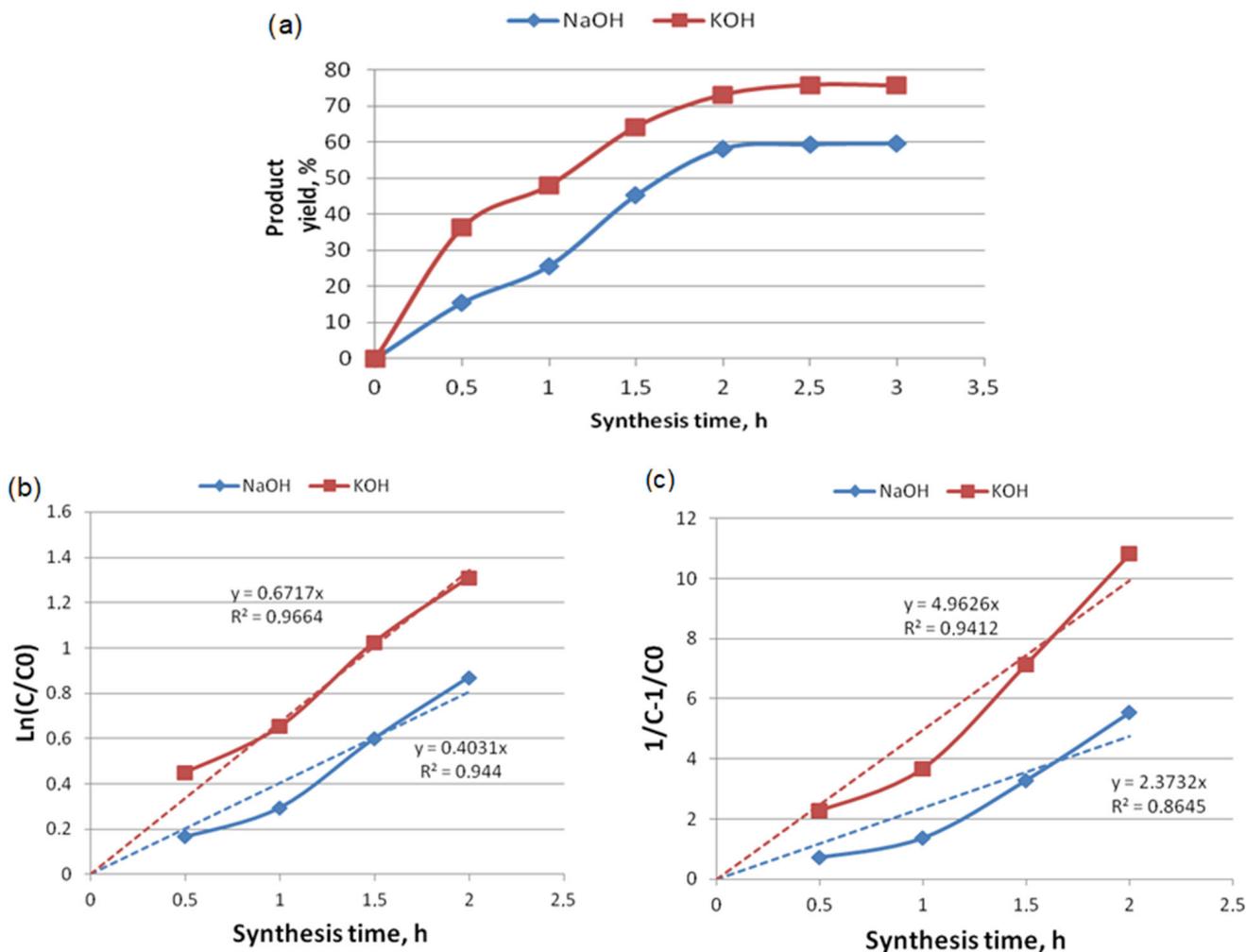


Figure 11. FAE-RSO synthesis kinetics: (a) the product yield change with time; (b) first order reaction kinetic curve; (c) second order reaction kinetic curve.

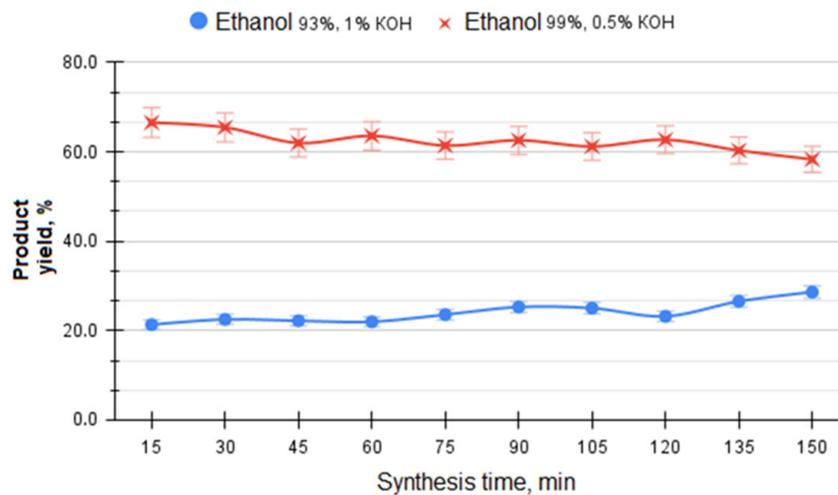


Figure 12. The FAE-URO synthesis kinetics in the period from 15 min to 2.5 h.

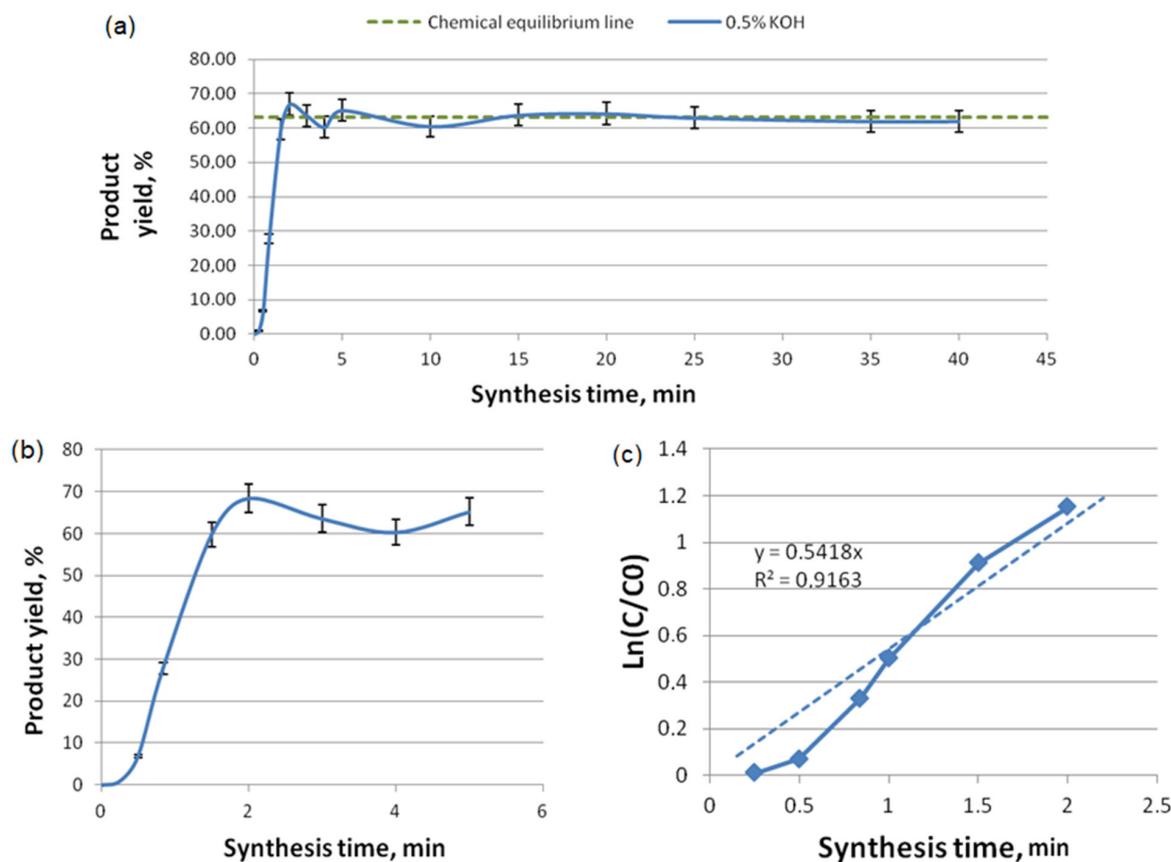


Figure 13. The FAE-URO synthesis kinetics: (a) whole period up to 2.5 h; (b) in the period less than 15 min; (c) kinetic curve of the first order reaction.

3.5. FAEs' Composition

The IR spectra show characteristic peaks confirming the qualitative composition similarity of the product with a mixture of fatty acid esters (Figure 14a,b). First of all, this is a peak of stretching vibrations of the carbonyl group C=O bond, the shift of which coincides with a narrow range for the esters of long chain fatty acids ($1736\text{--}1744\text{ cm}^{-1}$) [53]. For sunflower and rapeseed oil, this peak has a wave number of 1743 cm^{-1} , which corresponds to the fluctuation range characteristic of triglycerides ($1744\text{--}1748\text{ cm}^{-1}$).

Moreover, characteristic of FAEs is a pair of peaks of the stretching vibrations of the C-O bond. This most intense peak is around 1170 cm^{-1} (1178 cm^{-1} on the graph) with a less strong band around 1245 cm^{-1} (1243 cm^{-1} peak on the graph). In contrast to the FAEs' IR spectrum, the characteristic peaks of the stretching vibrations of the C-O bond in triglycerides are shifted and are located at about 1236 , 1164 (more intense) and 1100 cm^{-1} . For sunflower oil, these peaks are 1236 , 1159 and 1098 cm^{-1} . For rapeseed oil, these peaks are 1237 , 1160 and 1096 cm^{-1} (Figure 14a).

In the FAEs' IR spectrum, there is a small wide band of -O-H bond vibrations corresponding to the carboxylic acid group ($3500\text{--}2500\text{ cm}^{-1}$). There is also a small peak around 1560 cm^{-1} . This peak is characteristic of vibrations of the carbonyl group in the structures of the potassium and sodium salts of fatty acids [54]. This can indicate the presence of water, catalyst, and soap residues in the FAEs. These impurities can be removed from the product by washing with weak solutions of sulfuric or phosphoric acid and water [55].

GC-MS analysis made it possible to determine the qualitative composition of the resulting FAEs mixture (Figure 15a,b). Since the initial raw material was linoleic type oil, the ethyl ester of linoleic acid predominates in the composition (Figure 15c). FAE-RSO contains no ethyl esters of oleic and erucic fatty acids because of the sunflower oil composition.

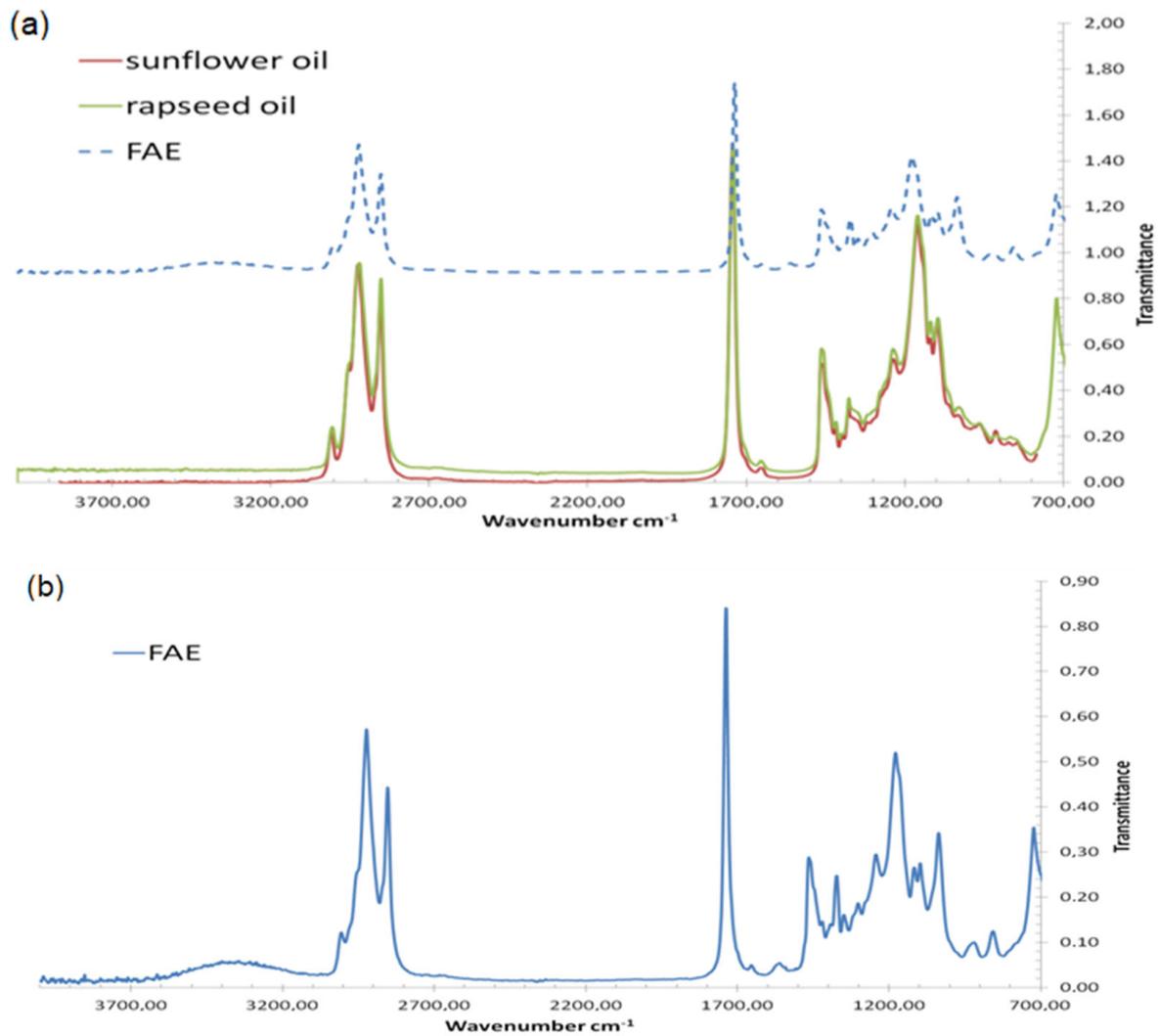


Figure 14. IR spectra of the FAEs and feedstock.

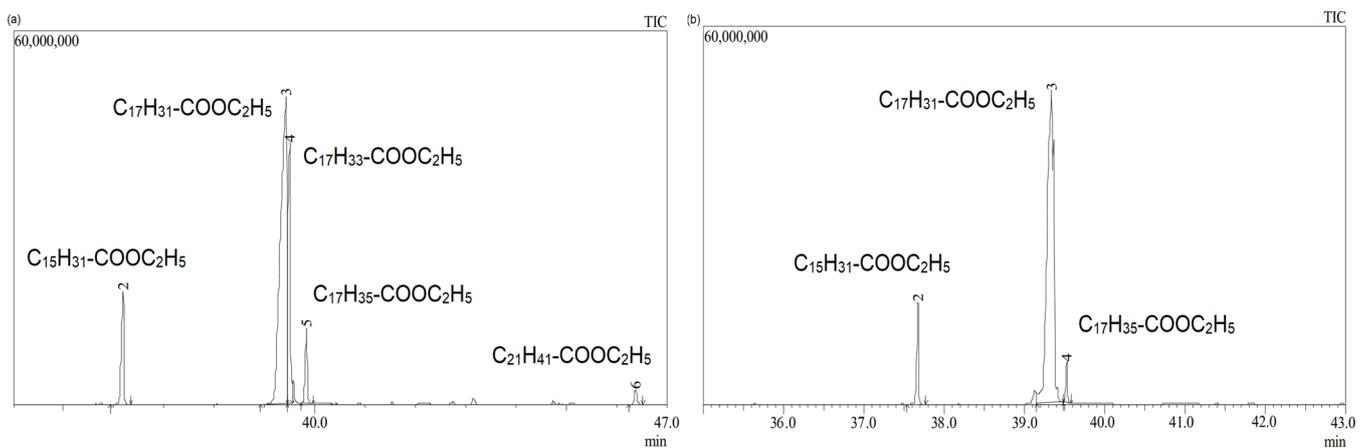


Figure 15. Cont.

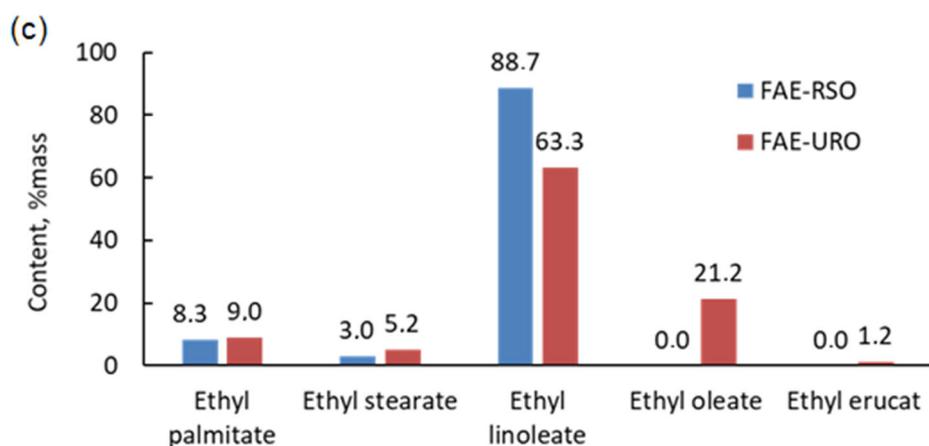


Figure 15. FAE Total Ion Chromatogram: (a) FAE-URO; (b) FAE-RSO; (c) FAE's composition.

4. Conclusions

The production of ethyl ester from refined sunflower and unrefined rapeseed linoleic type oil through the classical and optimized method of alkali-catalyzed transesterification in volumetric excess of ethanol was investigated. In both methods, the ideal mixing reactor model was used.

The results most significant for this study were obtained by changing the oil:ethanol ratio. The use of volumetric ratios and absolute ethanol made it possible to reduce the reaction time from 2.5 h to 5 min while maintaining a high degree of conversion. This allowed us to consider the technological scheme with the use of a linear flow reactor or perfect displacement reactor. The improved synthesis method also made it possible to fix the conversion rate at different points of the kinetic curve by inhibiting the reaction by abruptly cooling the reactor. With this method, it becomes possible to plot the kinetic curve of processes occurring over short time intervals.

The materials presented serve to augment the study of the vegetable oils transesterification process. In the case of refined oil, despite the water content of the reaction alcohol in the amount of 5% and the replacement of methanol with ethyl alcohol, alkaline catalysis made it possible to achieve a high yield of the target product—75%. The optimal synthesis conditions for refined sunflower oil were a KOH catalyst in a content equal to a 1% mass of the ethanol, a volume ratio oil:alcohol equal to 1:3, a stirring time of 2.5 h, and a temperature of 70 °C.

In homogeneous alkaline catalysis, the quality of the raw materials and the reaction alcohol has a strong influence on the balance of the reaction and, as a consequence, on the yield of the target product. For instance, the change in the acid value of the oil due to the change to the unrefined raw material led to a decrease in the target product yield and higher requirements for the quality of the reactive alcohol. This conclusion was confirmed by experimental evidence. Thus, while the sunflower oil esters yield was 75.8% for 95% ethanol, it was only 30.1% for unrefined rapeseed oil under the same synthesis conditions.

It is optimal to use absolute ethanol for unrefined rapeseed oil. However, due to the complexity of obtaining this alcohol drying degree, a range of concentrations of 96–99% can be considered. In this case, more time will be needed for the synthesis process.

The use of watered alcohol also affects the amount of catalyst used in the process. The optimum point on the graphical yield curve is shifted towards an increase in the KOH content. These values were 0.5 and 1.5%, respectively, for the absolute and 95% ethanol.

The analysis of the component ratio effect on the target product yield confirmed the earlier conclusion about the optimal value. The largest yield of the FAEs was obtained at 0.5% of KOH and the oil:ethanol ratio of 1:3. Therefore, the optimal synthesis conditions for unrefined rapeseed oil were: the use of absolute ethanol (99%), oil:ethanol volume ratio of 1:3 and the KOH catalyst content equal to 0.5% mass of ethanol.

Further research on this topic will be devoted to the implementation of a displacement reactor model for the optimal conditions for the synthesis of the fatty acid esters defined in this work.

It should be noted that the question of the further purification of fatty acid esters from excess ethanol, the glycerin phase, and the homogeneous catalyst remains relevant in this study. It will be considered in the following works.

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Abbreviations

TFA	Triglycerides of Fatty Acids
FFA	Free Fatty Acids
FAE/FAEs	Fatty Acid Esters
RSO	Refined Sunflower Oil
URO	Unrefined Rapeseed Oil
FAE-RSO	Fatty Acid Esters of Refined Sunflower Oil
FAE-URO	Fatty Acid Esters of Unrefined Rapeseed Oil

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