

FATTY ACID ETHYL ESTERS AS BIODIESEL FUEL: PRODUCT QUALITY AND EFFICIENCY OF VARIOUS PURIFICATION TECHNIQUES

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Abstract. The efficiency of removal of glycerol, soaps, and unconverted acylglycerols by repeated washing with water, alcohol removal by distillation, distillation of esters, and using of sorbents, as well as a combination of these techniques, was evaluated. The use of a number of commercially available sorbents (Magnesol, talc, and coal) and ion exchange resins (KU-2-8, Purolite CT275) was investigated. Glycerol and soap were found to be effectively removed with all tested materials except talc, while Magnesol and Purolite also effectively removed monoacylglycerols. However, none of the materials tested was able to withdraw diacylglycerols. A three-stage purification of esters was proposed. The latter includes the alcohol removal by distillation, which contributes to the additional settling of pollutants, vacuum distillation, and final use of sorbents (Purolite). The utilization of the indicated stages allows obtaining a product that meets the quality indicators of EN 14214. The proposed approaches will be valuable in the engineering of industrial technology for obtaining fuel-grade ethyl esters.

Keywords: fatty acid ethyl ester, purification, sorbent, distillation and ion exchange resin.

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Introduction

The production of fatty acid methyl esters, commonly known as biodiesel fuel, is continuously increasing worldwide, despite its unprofitability due to the high price of oils and alcohol. Thus, after some decline related to the Covid-19 pandemic, it returned to its previous level in 2021. At the same time, big efforts are being made to attract low-grade substitute feedstock for biodiesel synthesis, which helps maintain price stability and process sustainability [1-4]. According to forecasts until 2035, the prospects of biodiesel fuel are high, in spite of the spread of electric transport and the production of so-called renewable diesel [5-9]. Fatty acid ethyl esters, the production of which is completely based on renewable raw materials, can compete with methyl esters as biofuel. Moreover, they have big potential as a new, green and renewable solvent.

An essential part of the technology, which largely determines the competitiveness of biodiesel production, is an effective purification procedure. At the same time, the higher the content of superfluous impurities in "crude" biodiesel, the

more difficult its purification is. This work examines the problems of the purification of ethyl esters obtained by homogeneous catalytic technology using soluble alkaline catalysts, which was and remains the only large-scale method of biodiesel fuel (methyl esters) production.

The vast majority of research is devoted to the features of methanol biodiesel purification, while for ethyl esters, there is practically no information. The production of ethyl esters by alkaline ethanolysis, regardless of the type of raw material, is much more complicated compared to methanolysis due to the formation of stable emulsions, which stand in the way of the easy separation of the reaction products [9]. Furthermore, it is known that transesterification with ethanol produces three times more soaps than methanolysis [6]. Therefore, the separation and purification of ethyl esters are decisive for the production of ethanol biodiesel [11]. Achieving a sufficiently complete conversion is more problematic, as it requires the reaction to be carried out under technological conditions that make it difficult to separate the products.

Both Ukrainian and foreign standards strictly regulate fuel quality requirements. According to European EN 14214 (methyl esters) and Ukrainian DSTU EN 14214:2019 and DSTU 7178:2010 (methyl and ethyl esters, respectively), the concentration of esters in biodiesel must be at least 96.5%. "Crude" biodiesel, obtained immediately after transesterification and primary separation, certainly contains a number of impurities-raw materials, semi-products, and by-products of the reaction. Among them, the most important are mono-, di-, and triacylglycerols (MAG, DAG, and TAG); the content of the former is limited to 0.7–0.8% by weight and the content of the second and third is limited to 0.2% by weight. In addition, biodiesel should not contain glycerol (<0.02% by weight) and soluble potassium/sodium compounds (mainly soap). The content of soap is not directly limited; however, the content of sodium and potassium is limited to 5 mg/kg, which corresponds to 0.004% by weight of soap. The acid number (AN) of biodiesel (≤ 0.50 mg KOH/g) is also an important indicator. Removal of alcohol is necessary both to meet regulatory requirements ($\leq 0.2\%$) and for economic reasons to return it to the production process.

Washing with water is a widely used and effective industrial method of purification of fatty acid methyl esters from soaps, glycerol, catalyst residues, and alcohol. There is a wide variety of approaches to its implementation using neutral or acidic water with strong acids [12-15]. Its disadvantages include the formation of large volumes of contaminated effluents, significant product losses, and difficulties in separating the emulsions formed [13,14]. There are also known methods of so-called "dry" washing using adsorbents and ion exchange resins, as well as membrane purification, which are devoid of the mentioned disadvantages [12-16]. Another potentially promising method of purification is crystallization using solvents (1-butanol, 2-methyltetrahydrofuran) [17,18].

In general, "dry" washing of biodiesel is reduced to the removal of the same pollutants as traditional washing, predominantly soaps and free glycerol. However, getting rid of the problems of the latter, the use of "dry" washing raises a number of other issues related to the effectiveness of adsorbents and their limited resources, which lead to the necessity of their regeneration or utilization.

Nowadays, Magnesol, consisting of magnesium silicate and anhydrous sodium sulphate, is considered commercially available

and effective for the purification of methyl esters [12,19]. Leading global manufacturers also offer a number of specialized brands of ion exchange resins: Dowex DR-G8 (Dow Chemical), Lewatit S7968 (LANXESS), Amberlite BD10 Dry (Rohm and Haas), PD206 (Purolite), and DW-R10 (Duda Energy LLC) [12,13,20-22]. When using the latter, the removal of soaps (potassium or sodium salts of fatty acids) occurs not as a result of their adsorption but as a result of ion exchange with the formation of the corresponding acids. Therefore, with a significant content of soaps, an increase in the AN of biodiesel samples can be observed. The possibilities of using adsorbents based on silica gels, zeolites, clay minerals, silica, talc, carbon materials, cellulosic and lignocellulosic substrates, starch, etc. are also widely investigated [13,16,20-23].

It should be noted that distillation separation methods, common for oil refining processes, are practically ignored in the field of biodiesel research. Episodic references to the use of vacuum distillation as a method of purification of methyl esters occur only in a few rather old works [24-26]. In some cases, molecular distillation has been used for the purification of ethyl esters [27].

In the event of ethyl esters, special attention should be paid to unconverted acylglycerols, which do not create additional problems in the case of methanolysis since their low content is achieved by ensuring high oil conversion on the transesterification stage of the process.

From the point of view of the considered features, the purpose of the work was to compare the efficiency of such methods of purification of "crude" ethanol biodiesel as repeated washing with water, alcohol removal by distillation, distillation of esters, and using of sorbents, as well as a combination of these techniques to obtain fuel-quality esters as well as to establish the most rational and sustainable sequence of purification stages.

Experimental

Materials

Unrefined frozen sunflower oil "for frying" DSTU 4492:2017 ("Sadky", Poltava region, Ukraine) and technical rectified ethanol (ethanol GC area assay 99.11%, Ukraine) were the raw materials for the synthesis of ethyl esters. Ethanol was previously dried on KA zeolite to a residual moisture content of $\leq 0.2\%$. The AN of the oil was 1.18 mg KOH/g, and the content of water and phospholipids was 0.05 and 0.06%, respectively. The fatty acid profile was typical for the local

Ukrainian sunflower oil and included oleic (38%) and linoleic (50%) acids, as well as a limited fraction of saturated fatty acids (6% palmitic and 2% stearic acids).

Among the investigated sorbents, ion exchange resins in H-forms KU-2-8 (GOST 20297-74, Reakhim, Cherkasy, Ukraine) and Purolite CT275 (Purolite®, USA) as well as technical ground talc (JS “Novokhim”, Ukraine), activated anthracite (steam activation, Ukraine), and Magnesol (KFC filter Aid, USA) were used.

Synthesis of fatty acid ethyl esters

Preparation and purification

Having considerable experience in obtaining fatty acid ethyl esters from oils of different nature [28–30], the synthesis was carried out by alkaline transesterification of oil with ethanol using an ethoxide-containing solution of an alkaline catalyst obtained according to the method described in a Ukrainian patent [31].

Transesterification was performed in a conical flask. To begin with, the calculated amounts of oil and dehydrated ethanol were put in, then a catalytic solution of potassium ethylate was added, and, finally, stirring was started. The molar ratio of oil (TAG) to ethanol and potassium

ethylate was 1:5.5:0.2. The synthesis was carried out for one hour at room temperature (20°C). When the reaction was complete, the mixture was moved to a separatory funnel, where the product was divided into two layers as a result of gravity separation. The top one is the ester layer, and the bottom is the glycerol one.

Figure 1 shows a block scheme of the preparation and purification of ethyl esters. The simplest purification option (method I) consists in the distillation of ethanol under vacuum (20–30 mm Hg, 90°C) followed by additional phase separation. According to another method (method IIa), the ester layer was washed 13 times with hot (60–80°C) tap water, using 50% of the volume of the ester phase at each stage. The washed sample was dried with anhydrous sodium sulphate (10% by weight). The IIb purification method consists in vacuum distillation (7–8 mmHg) of washed and dried esters. The fraction of esters was condensed in the temperature range of 145–170°C.

“Dry” washing (method III) was performed for the product after the removal of ethanol (method I). For this, the fuel sample was mixed with 10% by weight of sorbent for 30 min at 50°C.

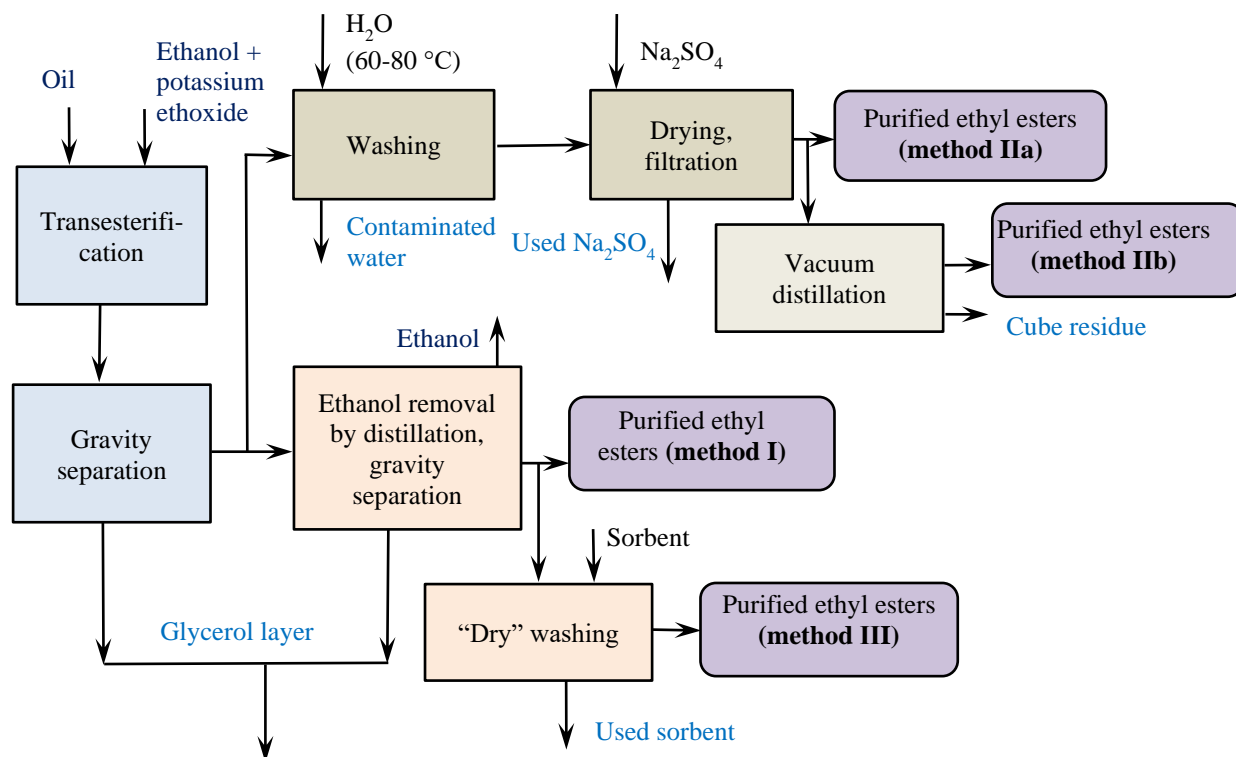


Figure 1. Block-scheme of synthesis and purification of ethyl esters.

Figure 2 shows the main chemical processes that occur during transesterification using soluble alkaline catalysts and indicates the components that have to be removed during purification (as an example of transesterification of TAG with ethanol using potassium ethoxide). The transesterification of TAG takes place in three successive equilibrium stages with the formation of DAG, MAG, and, ultimately, glycerol. The target products, the ethyl esters, are formed in each of the three stages. In addition to the main process of transesterification, when alkaline catalysts are used, the formation of soaps as a result of alkaline hydrolysis of the ester bonds of all the above components (TAG, DAG, MAG, or ethyl esters) can undergo.

The mass yield of the obtained product relative to oil Y_{prod} (%) was calculated according to Eq.(1).

$$Y_{\text{prod}} = \frac{m_{\text{prod}}}{m_{\text{oil}}} \cdot 100\%, \quad (1)$$

where, m_{oil} and m_{prod} are masses (g) of oil and appropriate product.

The mass yield of esters relative to the oil in the obtained product was also calculated Y_{est} (%) using Eq.(2).

$$Y_{\text{est}} = \frac{m_{\text{prod}} \cdot C_{\text{est}}}{m_{\text{oil}}}, \quad (2)$$

where, C_{est} is measured value of ethyl esters concentration.

It should be emphasized that the values of the yields of the corresponding products and esters in their composition were calculated regardless of whether they could be considered biodiesel according to the results of the analyses.

Characterization of sorbents and products

Based on isotherms of low-temperature adsorption/desorption of nitrogen (Quantachrome Autosorb NOVA 1200e®), the specific surface areas of sorbents were calculated according to the BET theory and the distribution of pores by size using density functional theory.

The content of ethyl esters, unconverted MAG and DAG, as well as glycerol, was investigated using gas chromatography (Agilent 7890A, equipped with a J&W HP-5 capillary column and a flame ionization detector). When determining the concentration of esters, the recommendations of EN 14103 were followed; however, the more affordable methyl palmitate was used instead of methyl heptadecanoate as an internal standard. Determination of the concentration of MAG and DAG, as well as glycerol, involved the derivatization of hydroxyl groups by trimethylsilylation using *N*-methyl-*N*-trimethylsilyl trifluoroacetamide according to ASTM D 6584. Tricaprin (tridecanoylglycerol) was used as an internal standard in both cases. The sensitivity ratio of the detector to the standard and to the corresponding components was pre-calibrated using a series of standard solutions of monoolein, diolein, and glycerol in pyridine as described in [32].

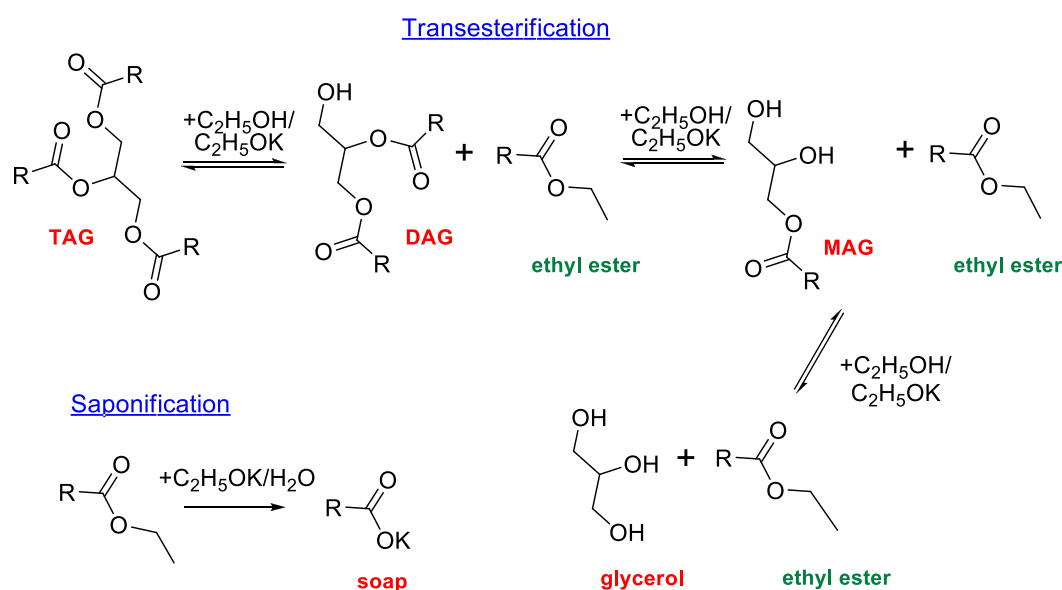


Figure 2. Reaction scheme of ethyl esters alkaline synthesis (R – alkyl chains of fatty acids acyl moieties).

The acid number of oil and purified esters was determined by the titrimetric method according to the technique described in detail in [33]. To determine the content of alkaline catalysts and soaps, a sample of esters dissolved in *i*-propanol was titrated with HCl solution in the presence of phenolphthalein and bromophenol blue, respectively. At the same time, “crude” esters were titrated with 0.01 N HCl, while in the analysis of purified ones, 0.001 N acid solution was used.

Results and discussion

Analysis of the ester layer after the initial separation of the glycerol layer showed that there were no catalyst residues in it, and only soap was detected. The concentration of the latter indicates that less than one-third of the potassium (about 28%), which was loaded in the composition of the alkaline catalyst, remained in the ester layer as soaps. After removal of the alcohol excess by distillation (~7–8% by weight), a small amount of additional glycerol layer was separated and the bulk of the soaps transferred into its composition. Their residual amount in obtained “crude” esters corresponded to less than 1% of the initial amount of alkaline catalyst.

As can be seen from the data in Table 1, as a result of purification according to method I, the content of glycerol decreased by about an order of magnitude, and the content of potassium soap decreased by more than 20 times. However, both characteristics exceeded the requirements of the standards by more than an order of magnitude. The content of MAG decreased slightly, while that of DAG even slightly increased. Despite a

significant increase in the ester content from 83.8% to 95.8%, it is still below the minimum allowable. There is no such problem in the case of methanolysis, when the yield of esters is practically quantitative [12-14].

Figures 3 and 4 display the chromatograms of the purified samples of ethyl esters from Table 1. Besides ethyl esters of palmitic (C16:0), stearic (C18:0), oleic (C18:1), and linoleic (C18:2) acids, only peaks of internal standard (methyl palmitate) and solvent can be observed on the chromatograms, recorded in accordance with the EN14103 method (Figure 3). Minor admixtures are not detectable at chromatographic conditions applied. The example of the Original table report from ChemStation Rev.B.03 software can be found in the Supplementary Materials section. A precise determination of glycerol, MAG, and DAG content was carried out in accordance with ASTM D 6584. The peaks of the derivatized forms of these components are marked on the corresponding chromatograms (Figure 4). One can observe the clear difference in these signals for different purification methods applied.

During purification by washing the ester layer with water and drying with Na₂SO₄ (method IIa), virtually complete removal of glycerol was observed. However, as already mentioned, 13 consecutive washing steps were carried out to obtain pure wash water. As a result, the content of soaps decreased at least to the limit of sensitivity of the method used for analysis. The content of esters also improved, up to 96.7%, but the removal of acylglycerols with water is inefficient.

Table 1
Purification of “crude” ethyl esters by means of ethanol distillation (I) and washing (IIa) with vacuum distillation (IIb).

Characteristic	Raw material (“crude” esters)	Method of purification			EN 14214
		I Vacuum distillation of ethanol and gravity separation	IIa Washing with hot water and drying with Na ₂ SO ₄	IIb Vacuum distillation of washed and dried esters	
Ethyl esters content, % by weight	83.8	95.8	96.7	97.6	96.5
Y _{prod} , %	116	95.9	98.0	94.2	-
Y _{est} , %	97.2	91.9	94.8	90.9	-
Potassium soap content, % by weight	1.66	0.069	≤0.03*	0	≤0.004**
Glycerol content, %	1.56	0.145	0.001	0.008	≤0.02
MAG content, %	1.22	0.91	0.87	0.25	≤0.70
DAG content, %	0.15	0.29	0.17	0.01	≤0.20
AN, mg KOH/g	-	0.24	0.24	0.14	≤0.50

*on the limit of sensitivity of the titrimetric method of analysis;

**it is not directly regulated.

The proper content of MAG and DAG could be achieved only after vacuum distillation of the washed esters. It should be noted that glycerol and esters are distilled in the same temperature range, so the absence of glycerol in the distillate is solely due to the preliminary washing. It is obvious that the multi-stage washing of the ester layer with large volumes of water leads to the accumulation of a significant amount of effluents, which require purification as well. This approach also eliminates surplus alcohol, which might be recycled during the transesterification process. Therefore, this method has critical disadvantages from the point of view of biodiesel production sustainability. "Crude" methyl esters, normally, contain less MAG and DAG, so their content meets the requirements of the standards [22].

The AN of the products was not an issue in any of the three considered purification procedures. It should be noted that, unlike methyl esters, ethyl esters should not be neutralized with acids when purified. This approach often improves purification; nevertheless, it causes a large increase in the acid number of biodiesel, particularly when there is a high soap component in the ester product.

Table 2 summarizes the "dry" washing performance parameters. The values of the specific surface area of the sorbents according to BET, calculated from nitrogen low-temperature adsorption-desorption isotherms (Figure 5(a,b)), were 6, 25, 400, 110, and 640 m²/g for samples KU-2-8, Purolite CT275, Magnesol, talc, and activated carbon, respectively. Despite a significant number of scientific publications devoted to "dry" washing, unfortunately, the data

presented in them do not allow for a systematic view of the practice, effectivity, and limits of the used methods. Therefore, the utilization of sorbents in this work had several features. Firstly, in order to approach production realities, a significant amount of them was used (10% by weight), while in laboratory studies, as a rule, "dry" washing is investigated using batch reactors with a small loading of adsorbent (~1–2% by weight) [21-23]. This approach is too far from the realities of industrial production, where adsorption purification is carried out in flow devices with stationary loading. Secondly, due to the lack of special brands of ion exchange resins for purification of biodiesel on the domestic market, available samples of strong acid cationites (Purolite CT275 and KU-2-8), which are chemically identical polymers of styrene cross-linked with divinylbenzene and functionalized with -SO₃H groups, were used. However, the first of them is a macro-mesoporous cationite for a catalytic purpose, and the second is a traditional water purification cationite with a gel non-porous structure of a polymer matrix. The specified features are clearly reflected by isotherms (Figure 5(a)). Unlike Purolite, whose isotherm is typical for mesoporous materials, KU-2-8 has a linear isotherm, which is typical for non-porous samples. Thirdly, "dry" washing was performed after removing ethanol and additional phase separation. Considering the issue of energy consumption, as a rule, "dry" washing is carried out at a temperature close to the esterification step temperature which is higher than the ambient [16,21,22].

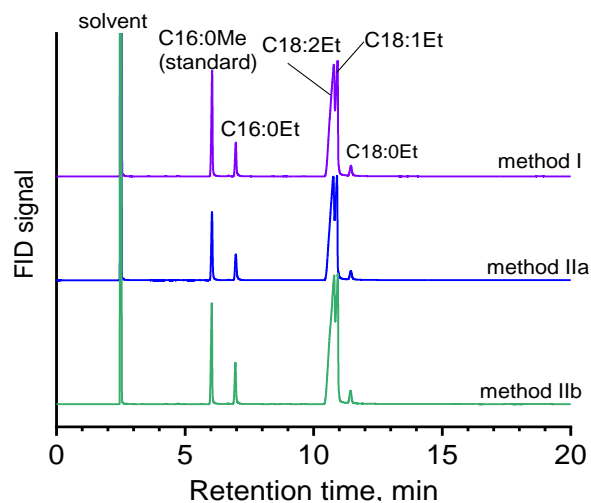


Figure 3. Chromatograms of purified ethyl esters (EN 14103).

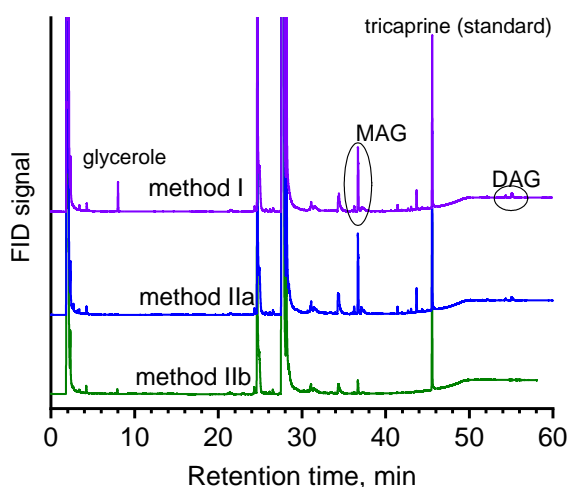


Figure 4. Chromatograms of purified ethyl esters (ASTMD 6584).

As shown in Table 2, ethyl esters after alcohol distillation contained residual soaps, glycerol, MAG, and DAG. All sorbents, with the exception of talc, removed soaps with excellent efficiency, ensuring compliance with the potassium content standard. In addition, all adsorbents were obviously effective in glycerol removal. The latter molecule has a kinetic diameter of 0.63 nm, so there are no problems with its adsorption in porous sorbents. On the other hand, in the case of non-porous KU-2-8, removal is

possible even in the absence of pores as such by the penetration of molecules deep into the polymer structure due to the well-known ability of ion exchange resins to swell, *i.e.*, actually absorb glycerol [34]. Other non-porous material, talc (Figure 5(b) and (d)), which has a significant specific surface area (110 m²/g) due to a high degree of dispersion, also removes glycerol quite effectively. However, in addition to being ineffective in removing soaps, it yields a product with an ester concentration less than 96.5%.

Table 2

Influence of "dry" washing (method III) on the quality indicators of biodiesel fuel.							
Characteristic	"Crude" esters without ethanol	KU-2-8	Talc	Coal	Purolite CT275	Magnesol	EN 14214
Colour	yellow	yellow	yellow	light-yellow	light-yellow	yellow	-
Ethyl esters content, % by weight	95.8	97.1	96.3	98.3	97.4	98.4	≥96.5
Glycerol content, %	0.145	0.001	0.008	0.000	0.000	0.007	≤0.02
MAG content, %	0.91	0.91	0.85	0.72	0.19	0.40	≤0.70
DAG content, %	0.29	0.29	0.30	0.33	0.30	0.34	≤0.20
AN, mg KOH/g	0.24	0.12	0.04	0.16	0.36	0.03	≤0.50
Potassium content, mg/kg	84	1.7	7.0	1.7	0.00	<1.0	≤0.0005 (K+Na)

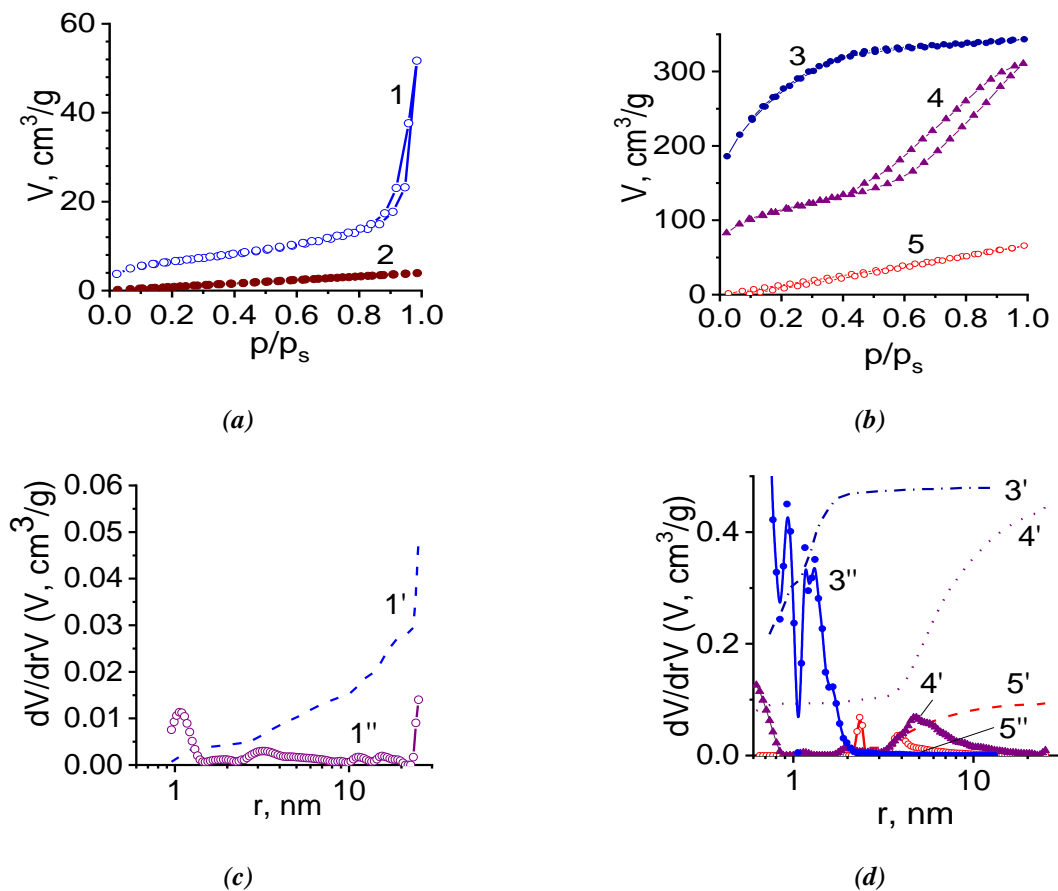


Figure 5. Isotherms of low temperature nitrogen adsorption/desorption (a, b), integral (with one dash) and differential (with two dashes) pore size distributions (c, d) for Purolite CT275 (1, 1', 1''), KU-2-8 (2, 2', 2''), activated carbon (3, 3', 3''), Magnesol (4, 4', 4'') and talc (5, 5', 5'').

Anyway, the presence of a significant number of strong acid sites facilitates the efficient removal of soaps by cationite samples, ensuring potassium removal *via* ion exchange. Due to this, Purolite slightly increased the AN of the product, which nevertheless remained within the normal range. Magnesol and talc utilization, as inorganic bases ($H_0 = +4.0 \div +3.3$) [35], resulted in greatly lower acidity of the purified samples. Coal and Purolite, simultaneously with glycerol removal, additionally sorbed natural dyes, brightening the colour of samples. Magnesol performed the best for glycerol, soaps (potassium), and acid number, which is consistent with the results of [22], however, other sorbents, except talc, offered satisfactory purification for these parameters. Despite the fact that inorganic sorbents are often more efficient than ion exchange resins due to their more rigid structure [22], the obtained results show that mesoporous Purolite is relatively close to Magnesol in terms of purifying efficiency.

The drop in MAG content while utilizing some sorbents is particularly significant. Purolite, Magnesol, and activated carbon were the most successful in this aspect (in descending order). Purolite performance is clearly attributed to its porous character (Figure 5(a) and (c)). Thus, its structure contains mesopores with a diameter of up to 20 nm, as well as macropores, the contribution of which is not reflected in the given distribution curves. Magnesol and activated carbon have a total volume of pores of 0.40–0.43 cm³/g based on their radius distribution (Figure 5(d)). Coal, on the other hand, is mostly a microporous sorbent, whereas Magnesol is predominantly composed of mesopores. Purolite and Magnesol pore sizes are

orders of magnitude larger than MAG kinetic diameters, which can be approximated at 1.4 nm as the sum of the kinetic diameters of glycerol (0.63 nm) and linoleic acid (0.8 nm). Accordingly, it leads to their accumulation in the pores of these sorbents. DAG molecules are not only larger but also more spatially branched, which obviously might impair their diffusion in the pores. The absence of DAG adsorption can also be associated with its lower polarity compared to MAG. As a result, none of the investigated adsorbents reduced the content of DAG to the level of regulatory requirements, and, therefore, the ester product requires following vacuum distillation. The low efficiency of MAG and DAG removal by using of a number of sorbents was also stated in previous work [16] on low-grade wasted frying oil esters.

Taking this into account, a batch of ethyl esters was additionally synthesized from the same raw material according to method I and divided into two parts. One of them was purified by vacuum distillation and subsequent dry washing, and the second by dry washing and subsequent distillation. The corresponding results are summarized in Table 3. “Crude” esters-2 sample, unlike the first “crude” esters (Tables 1 and 2), consist more potassium soap (Table 3). The latter can be connected with some deviations from the regime during alcohol distillation. As can be seen, vacuum distillation under the conditions used does not provide purification from glycerol, while dry washing, accordingly, does not purify from diacylglycerols. Their combination in any sequence makes it possible to obtain a product that meets the requirements of EN 14214.

Table 3

Purification of ethyl ester layer by means of both vacuum distillation and “dry” washing.

Characteristic	“Crude” esters-2	“Crude” esters-2 without ethanol	“Dry” washing with Purolite CT275 and vacuum distillation purification			
			distillation	distillation + “dry” washing	“dry” washing	“dry” washing + distillation
Colour	yellow, clear	dark-yellow, muddy	colourless, muddy	colourless, clear	yellow, clear	colourless, clear
Ethyl esters content, % by weight	83.7	96.4	99.4	99.6	96.7	99.0
Glycerol content, %	2.23	0.139	0.083	0.004	0.001	0.006
MAG content, %	1.13	0.96	0.05	0.02	0.30	0.05
DAG content, %	0.16	0.24	0.06	0.05	0.51	0.06
AN, mg KOH/g	-	0.04	0.04	0.24	0.40	0.36
Potassium soap content, % by weight	1.61	0.15	-	-	0.00	-
Potassium content, mg/kg	1959	181	-	-	0	-

It should be emphasized that in the case of the purification of ethyl esters, the situation is similar to the purification of methyl esters synthesized from low-grade feedstock [24-27]. In both cases, the distillation stage cannot be omitted for the production of good-quality products. At the same time, the acidity of the sample is also lower, at 0.24 versus 0.36 mg of KOH/g. This sequence is also justified from the point of view of the longer operation of the cationite due to the slower filling of its sorption capacity exclusively with glycerol and not with soaps. Moreover, in this case, cationite can be regenerated much easier since there is no need to restore its exchange capacity via treatment with strong mineral acid.

Conclusions

Thus, it was found that, in contrast to the purification of “crude” fatty acid ethyl esters by washing with water, the use of sorbents and ion exchange resins can be effective in removing not only glycerol and soaps but also unconverted MAG. Among the studied sorbents, commercially available Magnesol and Purolite CT275 proved to be the most effective. However, at the same time, the task of achieving the appropriate degree of purification of ethyl esters of the alkaline homogeneous-catalytic method of synthesis cannot be realized in one step. The efficiency of the use of sorbents for the “dry” purification of ethyl esters of fatty acids as a component of biodiesel fuel was compared, and it was shown to be successful when combined with distillation. The most rational and sustainable “crude” ester layer purification procedure includes first ethanol removal by distillation followed by secondary separation, then vacuum distillation, and, finally, adsorption product polishing from glycerol. This sequence of stages allows recycling of surplus ethanol, the removal of impurities of glycerol and soaps, as well as unconverted MAG and DAG. The application of the specified technological stages results in ethyl esters that meet the EN 14214 quality indicators and may be utilized as a biocomponent in biodiesel fuel.

Acknowledgments

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Supplementary information

Supplementary data are available free of charge at <http://cjm.ichem.md> as PDF file.

References

1. Ngomade, S.B.L.; Fotsop, C.G.; Bhonsle, A.K.; Rawat, N.; Gupta, P.; Singh, R.; Tchummegne, I.K.; Singh, R.K.; Atray, N. Pilot-scale optimization of enhanced biodiesel production from high FFA *Podocarpus falcatus* oil via simultaneous esterification and transesterification assisted by zirconia-supported ZSM-5. *Chemical Engineering Research and Design*, 2024, 209, pp. 52–66. DOI: <https://doi.org/10.1016/j.cherd.2024.07.031>
2. Ngomade, S.B.L.; Rawat, N.; Ngueteu, M.L.T.; Anensong, C.S.D.; Bopda, A.; Nche, G.N.-A.; Anagho, S.G.; Atray, N. Optimization of the oil extraction process by response surface methodology from *Podocarpus falcatus* seed as a low-grade substitute feedstock for biodiesel applications. *Biomass Conversion and Biorefinery*, 2023. DOI: <https://doi.org/10.1007/s13399-023-05122-8>
3. Ngomade, S.B.L.; Bhonsle, A.K.; Rawat, N.; Kuete, H.-I.T.; Nana, A.; Nche, G.N.-A.; Anagho, S.G.; Atray, N. Biodiesel production from high-free fatty acids *Podocarpus falcatus* oil and identification of fatty acid methyl esters by FT-IR, NMR (¹H and ¹³C) and GC/MS studies. *Iranian Journal of Science*, 2024, 48, pp. 865–878. DOI: <https://doi.org/10.1007/s40995-024-01649-1>
4. Shaah, M.A.H.; Hossain, M.S.; Allafi, F.A.S.; Alsaedi, A.; Ismail, N.; Ab Kadir, M.O.; Ahmad, M.I. A review on non-edible oil as a potential feedstock for biodiesel: physicochemical properties and production technologies. *RSC Advances*, 2021, 11(40), pp. 25018–25037. DOI: <https://doi.org/10.1039/D1RA04311K>
5. Joo, H.; Kumar, A. Eds. *World Biodiesel Policies and Production*. CRC Press: Boca Raton, USA, 2019, 238 p. DOI: <https://doi.org/10.1201/9780429282881>
6. Mizik, T.; Gyarmati, G. Economic and sustainability of biodiesel production—a systematic literature review. *Clean Technologies*, 2021, 3(1), pp. 19–36. DOI: <https://doi.org/10.3390/cleantech3010002>
7. Energy Institute. *Statistical Review of World Energy*. 2024, 76 p. <https://www.energyinst.org/statistical-review>
8. Flach, B.; Lieberz, S.; Bolla, S.; Geller L. *Biofuels Annual Report: European Union 2023*. USDA foreign agricultural service, 2023, 45 p. <https://fas.usda.gov/data/european-union-biofuels-annual-3>

9. Sanli, H.; Alptekin, E.; Canakci, M. Production of fuel quality ethyl ester biodiesel: 1. Laboratory-scale optimization of waste frying oil ethanolysis, 2. Pilot-scale production with the optimal reaction conditions. *Waste and Biomass Valorization*, 2019, 10(7), pp. 1889–1898. DOI: <https://doi.org/10.1007/s12649-018-0195-z>
10. Mendow, G.; Querini, C.A. High performance purification process of methyl and ethyl esters produced by transesterification. *Chemical Engineering Journal*, 2013, 228, pp. 93–101. DOI: <https://doi.org/10.1016/j.cej.2013.05.007>
11. Brunschwig, C.; Moussavou, W.; Blin, J. Use of bioethanol for biodiesel production. *Progress in Energy and Combustion Science*, 2012, 38(2), pp. 283–301. DOI: <https://doi.org/10.1016/j.pecs.2011.11.001>
12. Demir, V.G. Biodiesel production using wet and dry purification methods. *European Journal of Engineering and Natural Sciences*, 2017, 2(1), pp. 137–143. DOI: <https://dergipark.org.tr/en/pub/ejens/issue/27741/292498>
13. Bateni, H.; Saraeian, A.; Able, C.; Karimi, K. Biodiesel purification and upgrading technologies. Tabatabaei, M.; Aghbashlo, M. Eds. *Biodiesel. Biofuel and Biorefinery Technologies*. Springer: Cham, 2019, 8, pp. 54–100. DOI: https://doi.org/10.1007/978-3-030-00985-4_4
14. Fonseca, J.M.; Teleken, J.G.; Almeida, V.D.C.; da Silva, C. Biodiesel from waste frying oils: methods of production and purification. *Energy Conversion and Management*, 2019, 184, pp. 205–218. DOI: <https://doi.org/10.1016/j.enconman.2019.01.061>
15. Eryilmazi, T.; Şahin, S. Investigation of fuel properties of biodiesel produced from crude, refined and fried safflower oils. *Turkish Journal of Agricultural and Natural Sciences*, 2023, 10(4), pp. 1121–1128. DOI: <https://doi.org/10.30910/turkjans.1294598>
16. Konovalov, S.V.; Zubenko, S.O.; Patrylak, L.K.; Povazhnyi, V.A.; Davitadze, D.Z. Evaluation of available adsorbents for the dry washing of the wasted frying oil based crude ethyl esters. *Voprosy Khimii i Khimicheskoi Tekhnologii (Issues of Chemistry and Chemical Technology)*, 2023, 6, pp. 144–123. DOI: <http://doi.org/10.32434/0321-4095-2023-151-6-114-123>
17. Ahmad, M.A.; Samsuri, S. Biodiesel purification via ultrasonic-assisted solvent-aided crystallization. *Crystals*, 2021, 11(2), 212, pp. 1–12. DOI: <https://doi.org/10.3390/cryst11020212>
18. Wan Osman, W.N.A.; Badrol, N.A.I.; Samsuri, S. Biodiesel purification by solvent-aided crystallization using 2-methyltetrahydrofuran. *Molecules*, 2023, 28(3), 1512, pp. 1–14. DOI: <https://doi.org/10.3390/molecules28031512>
19. Munson, J.R.; Cooke, B.S.; Bertram, B.L. Biodiesel purification by a continuous regenerable adsorbent process. WO Patent, No. WO2009099655A1, 2009. <https://patents.google.com/patent/WO2009099655A1/zh-TW>
20. Johnson, B.J.; Melde, B.J.; Moore, M.H.; Malanoski, A.P.; Taft, J.R. Improving sorbents for glycerol capture in biodiesel refinement. *Materials*, 2017, 10(6), 682, pp. 1–15. DOI: <https://doi.org/10.3390/ma10060682>
21. Na-Ranong, D.; Laungthaleongpong, P.; Khambung, S. Removal of steryl glucosides in palm oil based biodiesel using magnesium silicate and bleaching earth. *Fuel*, 2015, 143, pp. 229–235. DOI: <https://doi.org/10.1016/j.fuel.2014.11.049>
22. Faccini, C.S.; da Cunha, M.E.; Moraes, M.S.A.; Krause, L.C.; Manique, M.C.; Rodrigues, M.R.A.; Benvenuti, E.V.; Caramão, E.B. Dry washing in biodiesel purification: a comparative study of adsorbents. *Journal of the Brazilian Chemical Society*, 2011, 22(3), pp. 558–563. DOI: <https://doi.org/10.1590/S0103-50532011000300021>
23. Arenas, E.; Villafan-Carceres, S.M.; Rodriguez-Mejia, Y.; García-Loyola, J.A.; Masera, O.; Sandoval, G. Biodiesel dry purification using unconventional bioadsorbents. *Processes*, 2021, 9(2), 194, pp. 1–12. DOI: <https://doi.org/10.3390/pr9020194>
24. Enweremadu, C.C.; Mbarawa, M.M. Technical aspects of production and analysis of biodiesel from used cooking oil—a review. *Renewable and Sustainable Energy Reviews*, 2009, 13(9), pp. 2205–2224. DOI: <https://doi.org/10.1016/j.rser.2009.06.007>
25. Zullaikah, S.; Lai, C.-C.; Vali, S.R.; Ju Y.-H. A two-step acid-catalyzed process for the production of biodiesel from rice bran oil. *Bioresource Technology*, 2005, 96(17), pp. 1889–1896. DOI: <https://doi.org/10.1016/j.biortech.2005.01.028>
26. Zhang, Y.; Dube, M.A.; McLean, D.D.; Kates, M. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresource Technology*, 2003, 89(1), pp. 1–16. DOI: [http://doi.org/10.1016/S0960-8524\(03\)00040-3](http://doi.org/10.1016/S0960-8524(03)00040-3)
27. Rodriguez, N.E.; Martinello, M.A. Molecular distillation applied to the purification of biodiesel from ethanol and soybean oil. *Fuel*, 2021, 296, pp. 120597. DOI: <https://doi.org/10.1016/j.fuel.2021.120597>
28. Patrylak, L.K.; Patrylak, K.I.; Okhrimenko, M.V.; Ivanenko, V.V.; Zubenko, S.O.; Levterov, A.M.; Marakhovskiy, V.P.; Savytskyi, V.D. Ethanol containing ethyl esters of fatty acids as perspective environment like fuel. *Fuel*, 2013, 113, pp. 650–653. DOI: <https://doi.org/10.1016/j.fuel.2013.06.020>
29. Patrylak, L.K.; Okhrimenko, M.V.; Levterov, A.M.; Konovalov, S.V.; Yakovenko, A.V.; Zubenko, S.O. Engine performance and emission of biodiesel fuel prepared from different Ukrainian natural oils. *Chemical Papers*, 2019, 73, pp. 1823–1832. DOI: <https://doi.org/10.1007/s11696-019-00755-4>

30. Konovalov, S.; Patrylak, L.; Zubenko, S.; Ohkrimenko, M.; Yakovenko, A.; Levterov, A.; Avramenko, A. Alkali synthesis of fatty acid butyl and ethyl esters and comparative bench motor testing of blended fuels on their basis. *Chemistry and Chemical Technology*, 2021, 15(1), pp. 105–117. DOI: <https://doi.org/10.23939/chcht15.01.105>
31. Zubenko, S.O.; Konovalov, S.V.; Patrylak, L.K. A method of preparing a catalyst for obtaining fatty acid esters. UA Patent, 07.04.2021, No. 123473. (in Ukrainian). <https://bpci.kiev.ua/ua/publications/patents/>
32. McCurry, J.D.; Wang, Ch.-X. Analysis of glycerin and glycerides in Biodiesel (B100) Using ASTM D6584 and EN14105. Agilent Technologies, 2007. <https://grupobiomaster.com/wp-content/uploads/2021/08/144.pdf>
33. Zubenko, S.O. The simple method of vegetable oils and oleochemical products acid value determination. *Catalysis and Petrochemistry (Kataliz ta Naftohimia)*, 2021, 31, pp. 69–74. DOI: <https://doi.org/10.15407/kataliz2021.31.069>
34. Vlasenko, N.V.; Kochkin, Yu.N.; Filippov, A.P.; Serebrii, T.G.; Strizhak, P.E. Adsorption–desorption of ethanol on sulfonated resin catalysts for ethyl-tert-butyl ether synthesis. *Adsorption Science and Technology*, 2017, 35(7–8), pp. 630–640. DOI: <https://doi.org/10.1177/0263617417703758>
35. Wu, D.Y.; Matsue, N.; Henmi, T.; Yoshinaga, N. Surface acidity of pyrophyllite and talc. *Clay Science*, 1992, 8(6), pp. 367–379. DOI: <https://doi.org/10.11362/jcssjclayscience1960.8.367>