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EVALUATION OF AVAILABLE ADSORBENTS FOR THE DRY WASHING OF THE WASTED FRYING OIL BASED CRUDE ETHYL ESTERS

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Russia's invasion of Ukraine strongly actualized the issue of liquid biofuels production. Ethyl esters biodiesel may be produced from widely available domestic Ukrainian oils and locally produced bioethanol. Dry washing with adsorbents is an advanced biodiesel purification technique. There is still a lack of information on the dry washing of alkaline ethanolysis products, especially concerning the removal of heavy contaminants, originating from partially polymerized waste oils. Current work deals with the investigation of available materials as adsorbents for the purification of crude ethyl esters (88% esters, 1.61% monoacylglycerols, 0.73% diacylglycerols, 0.19% tryacylglyceroles, 1.04% soaps, 0.12% fatty acids, 1.07% glycerol, and 0.17% ethanol). Esters were prepared via alkaline-catalyzed transesterification of wasted frying sunflower oil (2.46 mg KOH/g, 7.1% palmitic, 3.5% stearic, 27.7% oleic, and 59.3% linoleic acids). Activated anthracite, synthetic carbon Chemviron, colloidal silica, meta-kaolin, talc, and bentonite were evaluated as adsorbents. All samples provided the removal of the majority of soaps and glycerol, decreased the ethanol concentration, and, in most cases, acid value. Dry washing had almost no impact on the acylglycerols content. Activated carbons, characterized by a combination of developed micro- and mesoporosity, produced the greatest results, including a minor amount of monoacylglycerols removal. However, none of the adsorbents provided the removal of heavy oligomer contaminants, which is indirectly indicated by no higher than 90% esters content in treated samples. Improvement of these characteristics may be achieved by vacuum distillation.

Keywords: biodiesel, ethyl esters, dry washing, adsorbents, glycerol, soaps, acylglyceroles, oligomeric esters.

Introduction

Ongoing Russia's war in Ukraine is close to triggering the tectonic shifts in the global energy sector. Obvious Russia's use of its extensive hydrocarbons export potential as a geopolitical weapon has once again proved the urgent necessity of the fastest possible abandonment the fossil fuels as a primary energy source with transfer towards the tomorrow day carbon-free renewable-based world energetic. Apart from the global tendencies, the rapid development of the production and utilization of traditional liquid biofuels, such as bioethanol and biodiesel (BD), may partially cover the deficit of transport fuels during the continuing war of attrition in Ukraine. In such conditions, both possibilities for the import of petroleum products and for agricultural export are limited (mainly due to sea blockage). The large stocks of the harvest of cereals and oilseeds is difficult to be sold abroad. The most rational answer to such challenges is to produce biofuels from this available feedstock here and now. BD production from wasted frying oils (WFO) is also very topical, but the availability of such kind of feedstock is limited, especially in martial law. Bioethanol may be produced using the facilities of numerous Ukrainian alcohol plants. However, domestic biodiesel production facilities should yet to be created.

BD is the widespread alternative fuel for diesel engines, composed of monoalkyl (usually methyl) esters of long-chain fatty acids [1,2]. It is mainly produced via the catalytic transesterification of fresh or wasted vegetable oils or fats with monohydric alcohol over soluble base catalysts (sodium or potassium hydroxides or alkoxides). Using the locally produced ethyl alcohol as a transesterification reagent instead of imported methanol looks like the most rational and obvious option. However, there are additional obstacles to carrying out the conventional alkaline transesterification with alcohols other than methanol due to their lower acidity and polarity [3]. This may cause more intense soap formation, especially in the presence of even small amounts of water in the reaction media. As a results, the yield of esters decreases, while formed soaps may stabilize the mixture of the reaction products, preventing phase separation. Self-separation of most of the glycerol together with alkaline catalyst and soaps into a separate phase (glycerol layer, GL) is very desirable for easier purification of the biodiesel obtained. It is generally known that production of ethyl esters, regardless of initial feedstock via alkaline transesterification, is more complex compared to methyl esters due to formation of strong, stable emulsions of reaction products [4].

The purification of the crude esters after transesterification is an essential part of the BD production technologies, as the existing normative standards set severe requirements for fuel quality. According to the European normative standard EN 14214 (methyl esters), Ukrainian counterparts DSTU 6081 (methyl esters) and DSTU 7178 (ethyl esters) the content of esters is not lower than 96.5%. Monoacylglyceroles (MG), diacylglyceroles (DG), and triacylglyceroles (TG) have respective upper limits of 0.7% (or 0.8% under Ukrainian standards), 0.2% and 0.2%. BD also should not contain more than 0.2% of residual alcohol and 0.02% of free glycerol. The soap content is not regulated directly, but there is a 5 ppm upper limit for Na and K (only about 0.005% in terms of soaps). However, the composition of transesterification products may not be limited by the listed components, especially in the case of WFO processing. Since the fatty acid acyl chains of oils TG contain highly-reactive olefinic bounds, vegetable oils undergo significant chemical alteration during frying. As a result, TG polymers and dimers, oxidized TG, as well as DG and fatty acids (FA) form [5]. All these compounds are characterized by higher polarity compared with TG and are usually referred to as polar compounds. The latter's content is the most universal characteristic of the vegetable oils depth of degradation [6,7]. Their presence causes the lower esters yield after WFO samples transesterification, as well as the lower content of esters in biodiesel obtained. Polar compounds content and composition may broadly vary depending on the oil nature, conditions of frying, and utilization time. A number of WFO samples, which were investigated in work [6], contained 15−50% of the polar fraction. The concentration of FA was in the range of 0.4−1.7% and did not correlate with the latter's content. Methanolysis products from WFO samples contained 5.5−23% of polar fraction, which included methyl esters, oligomers, dimers, and oxidized monomers. It was discovered a strong relationship between the polar compound content of the initial waste oil and the transesterification products. It should be mentioned that low-volatile oligomeric esters are not detected in standard gas chromatographic methods of BD analysis. The presence of such admixtures frequently prevents reaching the target of 96.5% esters in BD obtained from WFO. For example, among 24 samples of wasted sunflower and rice bran oils, studied in work [7], only one sample was suitable to obtain BD with a high enough methyl esters content after methanolysis (either one- and two-stage alkaline or two-stage acid-alkaline) followed by water washing. The content of methyl esters in all other obtained products ranged from 85 to 96%.

Washing with water is a traditional and widely used industrial method of biodiesel purification. It has been shown to be effective in the removal of glycerol, soaps, residual catalysts, and alcohol. The disadvantages of the method are also well known. It includes the generation of extensive volumes of contaminated wastewater, a considerable loss of the product, and possible difficulties with emulsion formation [2]. Additionally, washed BD requires drying. In the case of alkaline ethanolysis, emulsification may be the more serious problem compared with methanolysis [4]. Advanced BD purification techniques via dry washing (treatment with adsorbents or ion-exchanged resins) are free of the mentioned disadvantages. In recent years, the issue of BD dry cleaning has been still under investigation. However, it has also been used in industrial plants for a long time [2].

Magnesol® is a commercially available biodiesel adsorbent composed of magnesium silicate and anhydrous sodium sulfate. It can be used to remove water, soap, free glycerol, and acylglycerols from biodiesel [2,8]. Ionic exchange resins, designed for BD dry washing applications (Amberlite®, Purolite®), effectively remove water, soaps, glycerol, and residual

catalyst [8]. In addition, a number of abandonment materials may be used for crude BD purification from the listed contaminants. Their list includes various clay minerals, silica, talc, bleaching earths, activated carbons, the number of biomass- and waste-derived adsorbents [2,8−11]. Experimental studies show very limited efficiency of dry washing for acylglycerols (mainly only MG) removal [8−10]. This fact is true both for investigated samples and for commercial adsorbents. Let us emphasize that relevant literature sources lack of information about the efficiency of BD treatment with adsorbents for the removal of heavy contaminants, which may originate from the partially polymerized triglycerides in WFO composition. Also, literature sources dealing with the peculiarities of the dry washing applying for the actually alkaline ethanolysis products are still short.

The aim of the present study was to evaluate the efficiency of some widespread porous and fine powder materials for the purification of the WFO-derived crude ethyl esters from various types of contaminants and to elucidate whether dry washing treatment is able to provide the fuel quality ethanol-based BD obtaining.

Experimental
Chemicals

A sample of wasted sunflower oil, used in deep frying, was kindly provided by a local catering establishment. The acid number of the oil was 2.46 mg KOH/g; water content was 0.065% (Karl-Fisher titration). The main components of the sample fatty acid composition were palmitic (7.1%), stearic (3.5%), oleic (27.7%), and linoleic (59.3%) acids; other fatty acids accounted for the rest 1.2%. By the moment of current study wasted oil sample has been storing during about 1.5 years in sealed plastic vessel at ambient temperature (varying in range of 15−30⁰C during year).

Technical grade bioethanol, purchased as an alternative component of automobile gasoline («KMPA», TU U 24.6-30219014-009:2007), was used as a transesterification reagent. Its water content was not higher than 0.2% (manufacturer specification), and the concentration of denaturing organic admixtures was 0.8% (GC area assay). Before transesterification bioethanol was additionally dehydrated over synthetic zeolite KA-Y/3A (Russian Federation, dynamic water vapor capacitance of 150 mg/cm^3) molecular sieves up to moisture content <0.1%. The same zeolite KA-Y/3A was also used for water removal in the preparation of ethoxide catalytic solution from potassium hydroxide (China, 89.7% KOH according to the titration of freshly-

opened reagent) solution in ethanol. Sodium butoxide solution, prepared from reagent grade sodium hydroxide and *n*-butanol as described in ref. [12], 0.1 N HCl water solution (prepared from fixanales), as well as indicators bromothymol blue, bromophenol blue and phenolphthalein, were used in the acid-base titration. *N,N*-dimethylformamide (DMFA, 99.9%), reagent grade *n*-hexane, and reagent-grade *iso*-propyl alcohol were used as solvents for the analytic purposes.

In gas chromatographic analyses, methylpalmitate (reagent grade, GC area assay 98.65%), pharmaceutical grade glycerol, analytic grade ethyl alcohol, *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA), pyridine solution of tricaprin, 1,2,4-butanetriol, glycerol, 1-monoolein, 1,3-diolein and triolein, as well as high-pure helium and hydrogen gases, were used.

The nitrogen of high purity (99.99%) was used in adsorption measurements.

Adsorbents, utilized for the dry washing of crude ethyl esters, include commercial synthetic activated carbon Chemviron, activated anthracite (AA), colloidal silica (Aeorosil), meta-kaolin (*m*-Kaolin), technical talc powder (Talc) and bentonite clay (Bentonite). *m*-Kaolin was obtained by calcination (750⁰C, 4 h) of natural kaolin powder (Prosyana deposit, Ukraine). AA sample was obtained by means of successive steam and alkaline activation of anthracite. Chemviron, Aerosil, Talc, and Bentonite were used as received.

Synthetic and purification methods

The ethanolysis reaction was carried out using a soluble base catalyst, which was potassium ethoxide dissolved in ethyl alcohol. It was obtained according to the method pending by patent [13] from KOH solution in ethanol by selective water removal from condensed ethanol-water azeotrope over zeolite KA-Y/3A, placed in a Soxhlet-like apparatus. In more detail, the method of ethoxide preparation is described in ref. [3].

Transesterification of wasted oil sample was carried out in a 0.5 l conic flask, the weight of loaded oil being 300 g. One and a half time excess of ethanol over stoichiometry (alcohol-to-oil molar ratio of 4.5:1) was used. The amount of loaded alkaline catalyst, calculated as initial KOH, was 1.25% relative to the mass of oil, including about 0.25% for neutralization of fatty acids. The reaction mixture was stirred by magnetic stirrer (500 rpm) for 45 min. Maintaining the lower-ambient reaction temperature (18⁰C) was provided by a water bath, filled with chilled water. The mixture after reaction was immediately transferred into a separation funnel,

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where phase separation of the reaction products by gravity occurred. Then the upper ester-enriched phase was placed into a round-bottom flask and residual ethanol was removed by distillation under a mild vacuum (waterjet pump, 3−4 kPa) and continuous stirring (500 rpm) at 80^{0}C. The obtained crude ethyl esters were treated by adsorbents in round-bottom flask for 30 min under stirring (500 rpm, magnetic stirrer) at 50^{0}C. A load of adsorbents was 5% relative to the weight of esters. Only in case of Aerosil, having a very low bulk density, its load was 2%. Prior to use in dry washing, Bentonite, Aerosil, AA, and Chemviron samples were dried to constant weight at 110−120^{0}C. Talc sample was calcined at 400^{0}C for 4 h, while *m*-kaolin was used as prepared (stored in a dry exicator). Samples of esters after dry washing and settling overnight were separated from the adsorbent by decantation, filtration through a paper filter, and centrifugation if needed.

Analytical methods

Structural-adsorption characteristics of adsorbents samples were calculated from low-temperature (−196^{0}C) nitrogen adsorption/desorption isotherms recorded by Nova 1200e (Quantochrome) high-speed surface area and pore size analyzer. The calculations were carried out using NovaWin v11.04 software. The specific surface area (S^{BET}) has been calculated according to the standard Brunauer-Emmett-Teller (BET) method; the areas of the outer surface and mesopores S^t and micropores volumes V^t_{micro} have been estimated using the t-plot method; micropores surface area S^t_{micro} has been calculated as the difference between S^{BET} and S^t; total pore volume (V_Σ) has been calculated from known amounts of adsorbed N_2; average pore size R was calculated according to the $R=2V_\Sigma/S^{BET}$ formula; pore size distribution estimation is based on the density functional theory (DFT).

The composition of ethyl esters samples prior to and after purification was determined by gas chromatography using an Agilent 7890A chromatograph, equipped with a split-splitless inlet, flame-ionization detector, and a proper capillary column. Ethyl esters content was determined using a J&W HP-5 capillary column and the modified method of methyl esters analysis described in EN 14103. Methyl palmitate instead of methyl heptadecanoat was used as an internal standard. Samples were dissolved in *n*-hexane. The chromatographic conditions were as follows: injection volume of 1 ml, inlet temperature of 250^{0}C, inlet excess pressure of 83 kPa (constant pressure mode), split ratio of 38:1, and detector temperature of 250^{0}C; the column temperature program −210^{0}C/15 min−

5^{0}C/min up to 280^{0}C−280^{0}C/10 min. The concentration of ethanol was measured by the calibration curve method using the same column. The samples were dissolved in DMFA, and the column temperature program was 35^{0}C/9 min−10^{0}C/min up to 80^{0}C−80^{0}C/1 min−5^{0}C/min up to 380^{0}C−380^{0}C/7.5 min. Obtained chromatogram also enables us to evaluate (calibration curve methods) the concentration of glycerol higher than 0.5% in products after synthesis. Glycerol, monoacylglyceroles, diacylglyceroles, and triacylglyceroles concentrations were determined by means of derivatization with MSTFA followed by chromatographic analyses (DB-5HT capillary column) as described in ASTMD 6584. In more detail, chromatographic techniques are described elsewhere [3].

The acid value of the initial oil and samples of alkyl esters was measured by means of titration by sodium butoxide solution in n-butanol with the indicator bromothymol blue as described in ref. [14]. In order to determine the residual alkaline catalyst and soap content in the samples of ethyl esters, a two-step acid-base titration method was applied [15]. Alkali concentration was determined in a first titration step, using HCl 0.1 N solution as reactant, *iso*-propanol as solvent, and phenolphthalein as an indicator. In a second titration step, the soap content was determined by titration with HCl 0.1 N, using bromophenol blue as an indicator.

Results and discussions

Structural-adsorption characteristics of adsorbents samples

The characteristics of adsorbents samples porous structure, calculated from low-temperature nitrogen adsorption/desorption isotherms, are given in Table. As can be seen from the given data, the porous structure of activated anthracite sample AA is mainly formed by micropores, accounting for about 90% of total surface (S^{BET}) and about 75 % of the total pore volume (V_Σ). The rest of the surface and volume correspond to mesopores. Pore size distribution by volume, calculated by the DFT method, contains two maximums. One of them corresponds to micropores with a radius of 0.7−0.8 nm and another corresponds to mesopores with a radius of about 1.4 nm. S^{BET} of another activated carbon sample (Chemviron) is almost twice higher than S^{BET} of the AA sample, while the fraction of the micropores from S^{BET} is almost the same. At the same time, micropores occupy a lower fraction of total volume due to the larger size of mesopores. DFT method shows besides the main maximum for micropores with a radius of about 0.9 mm also the presence of

Structural-adsorption characteristics of adsorbents samples

Sample	S^{BET}, m^2/g	S^t, m^2/g	S^t_{micro}, m^2/g	V^t_{micro}, cm^3/g	V_Σ, cm^3/g	R, nm
AA	628	74	554	0.39	0.51	1.64
Chemviron	1180	134	1046	0.72	0.95	1.62
Bentonite	73	27	46	0.02	0.07	2.03
m-Kaolin	8.4	2.6	5.7	0.02	0.04	8.5
Talc	103	63	40	0.02	0.10	1.98
Aerosil	259	187	72	0.03	0.46	3.56

mesopores in radius range of 1.2−3 nm.

Both S^{BET} and V_Σ for the Bentonite sample are about an order of magnitude less than in the case of activated carbons samples. Micropores account for about two-thirds of the total surface area, but less than one-third of the total pore volume of the sample. This fact is due to the presence of relatively wide mesopores. Pore size distribution by volume, calculated by the DFT method, includes the maximum for micropores with a radius of 0.9−1.0 nm and no apparent maximum for mesopores. The latter's radius is in the relatively wide range of about 1−4 nm, with the prevalence of mesopores in the radius range of 1−2 nm.

The total surface of *m*-Kaolin sample was extremely low compared to the other adsorbents samples. About two-thirds of the S^{BET} and about one-third of the total pore volume correspond to micropores. The DFT pore size distribution by volume indicates the maximum for micropores with a radius of about 0.9−1.0 nm. The mesopores radius varies between 3−40 nm, with 3−20 nm being the most common. It should be mentioned that the S^{BET} of initial kaolin clay was around 300 m^2/g. Milder calcination conditions are more likely to produce a sample with a larger surface area.

Talc, being crystalline hydrous magnesium silicate, has an isotherm, which is typical for fine non-porous powder with relatively high S^{BET}. The latter is formed mainly by the particles outer surface and by the mesopores surface (S^t). Mesopores occupy the major part of the total pore volume, while the micropores volume is very low. The DFT pore size distribution indicates that prevail mesopores have a radius of 2−3 nm. Aerosil, being a colloidal dispersion of silicon oxide, also has the typical non-porous powder sample isotherm. Its S^{BET}, mainly formed by the outer surface of the particles, is about two and a half times higher than in the case of Talc. At the same time, the total pore volume of Aerosil (predominantly mesopores) is almost five-times higher than in the case of the talc sample. The prevailing mesopores radiuses, according to the DFT method, are in the range of 2−4 nm.

Purification of crude ethyl esters

Transesterification of the WFO sample by ethanol over an ethoxide catalyst resulted in an effective yield of ethyl esters of about 80%. By «effective yield», we mean the molar yield when taking into account only esters in the composition of reaction products upper phase. The initial oil sample is considered as only TG (less fatty acids content, determined from acid value) for the calculations. The value of a 100% effective yield is unachievable in practice. At first, some decrease in the yield is inevitable due to the partial saponification of acylglyceroles or formed ethyl esters. Second, some ethyl esters always transfer into the composition of the bottom glycerol layer. Third, as was discussed earlier, wasted frying oils contain oligomerized triacylglyceroles, which cannot be fully converted into monoalkylesters. As for the phase separation, it appeared to be enough total. The bulk of the glycerol by-product was transferred into the glycerol layer, which amount was 24% relative to the mass of the oil sample. The ester layer contained only 1.2% of glycerol, 83% of ethyl esters, and 4.7% of ethanol. Acid-base titration revealed the absence of the alkaline catalyst, while the concentration of the soaps was about 0.8%. This is roughly equal to one tenth of the potassium loaded in the composition of the alkaline catalyst. Thus, the vast majority of the alkali or soaps are also transferred into the composition of the glycerol layer.

Removing the ethanol by distillation under vacuum did not provide the additional phase separation. Thus, all impurities remained in the composition of crude ethyl esters. It should be noted that typically, removing ethanol from esters layers results in additional phase separation and the transfer of the majority of soaps and glycerol to the bottom layer. For example, such an observation was made in the earlier study of our group [3] during both fresh and wasted oil samples processing (including the less aged wasted oil sample, used in current work). The lack of the discussed phase separation may significantly complicate the purification of biodiesel. However, in the current study, it provided a useful

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test sample of crude esters, containing a significant amount of various impurities, for the comprehensive evaluation of the efficiency of various adsorbents in their removal.
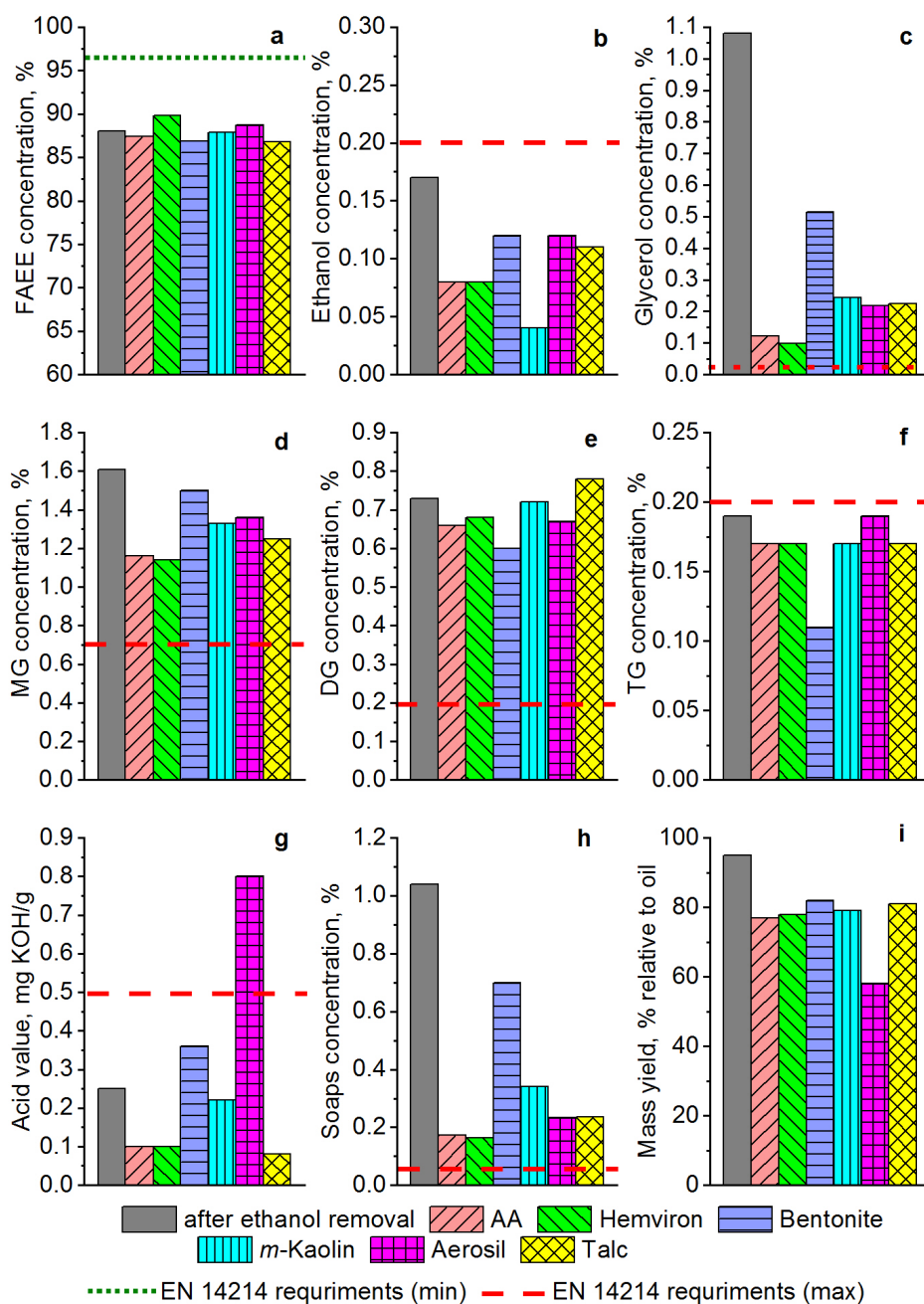
The composition of the ethyl esters samples prior to and after purification via dry washing over corresponding adsorbents is given in Figure. The sample of crude esters was out of the BD requirements range for FAEE, MG, DG, glycerol, and soap content. All adsorbents, besides the Bentonite sample, appeared to be able to remove the vast majority of glycerol (Fig.,c) and soaps (Fig.,h). However, even in the case of the most efficient activated carbon samples (AA and Chemviron), the residual concentration of the discussed components exceeded the allowed level many times. Also, dry washing over these samples provided a significant decrease in acid value (Fig.,g) and ethanol content (Fig.,b). As for the unconverted acylglycerols, we observed no meaningful impact of the dry washing on their concentration. DG and TG content remained almost unchanged, and MG content decreased insignificantly. Both AA and Chemviron utilization provided the removal of roughly one-fourth of MG, which was the best performance among studied samples. However, the resulting MG content was still far out of the BD requirement range. It is interesting, that only Bentonite provided some notable decrease in TG concentration, while its efficiency in other impurities removal was the lowest among studied samples. The most likely reason for the highest efficiency of activated carbon adsorbents is the combination of both developed micro- and mesoporosity in their structure (Table). Both microspores surface area and volume in the structure of AA and Chemviron samples are many times higher than in the structure of all other samples. At the same time, the mesopores surface area and volume are also significant. The composition of ethyl esters after dry washing over m-Kaolin, Talc, and Aerosil was similar. All samples were roughly two times less effective in glycerol removal (Fig.,c) and 1.5−2 times less effective in soap removal (Fig.,h) than activated carbon adsorbents. Three discussed samples had almost no impact on MG, DG, and TG content (Fig.,d,e,f). *m*-Kaolin utilization provided the lowest residual ethanol concentration in the series. At the same time, the resulting acidity of purified esters varied over a quite wide range. The talc sample decreased the acid value to an even lower level than the activated carbons (AA and Chemviron).

However, in the case of Aerosil, the acid value increased more than three times and significantly exceeded the allowed level for biodiesel. This indicates the chemical alterations, proceeding with the adsorbent participation in the course of treatment. Following mixture settling, a significant amount of a separate non-fluent jelly-like adsorbent-containing bottom phase was observed. The low yield of the purified sample indicates the partial transfer of ethyl esters into its composition. Finally, it should be emphasized that impurities removal in the course of dry washing is not necessary due to only the adsorption process. More likely, partial removal of glycerol and soaps may disturb the phase stability of the purified mixture. As a result, the phase, which is enriched in impurities, may form and separate together with the adsorbent in the course of settling and filtration.

The utilization of Talc as the adsorbent for dry washing deserves additional discussion. Powder talk (crystalline hydrated magnesium silicate) is a widely available, inexpensive material, having innumerous industrial applications. In the current study, Talk was used as the possible locally available substitute for the adsorbent for the BD treatment Magnesol®. The latter is not presented in the Ukrainian market due to the absence of local BD production, and it is also not purchased as a lab-scale material. Talk demonstrated relatively high efficiency (but lower than activated carbon samples AA and Chemviron) in removing such main impurities as glycerol and soaps, and in the acid value decreasing. Therefore, it can be useful for the dry washing of BD, containing a limited number of contaminants.

Probably, the most significant observation in the current study applies not the peculiarities of the BD purification from the various admixtures, but almost zero impact of dry washing on the content of the actual ethyl esters (Fig.,a). None of the studied samples did not meet the BD normative requirements for this characteristic (no less than 96.5%). Some very insignificant increase of ethyl esters was noted only for Chemviron sample, which demonstrated the best performance compared with other adsorbents. Nevertheless, even in this case, at least 8% of the sample is composed of some contaminants, which are not MG, DG, TG, FA, soaps, alkali, or glycerol. Since high-reactive diunsaturated linoleic acid accounts for 59% of the fatty acid composition of the WFO sample, there is no doubt of the quite high degree of oil polymerization during frying and prolonged storage. Most likely, the unidentified heavy admixtures in dry washed samples are composed of ethyl esters dimers or larger oligomers, formed via transesterification of partially polymerized TG. Regardless of the chemical nature of such admixtures, dry washing is not a suitable purification method for

The composition of the ethyl esters samples before and after dry washing: a − esters concentration; b − ethanol concentration; c − glycerol concentration; d − MG concentration; e − DG concentration; f − TG concentration; g − acid value; h − soaps concentration; and i − mass yield

their removal. It is worth emphasizing, that water washing is also totally useless for removing such kinds of contaminants [3,7].

Discussed results rise up the question about the reasonable purification technique, which will be able to ensure biodiesel-grade ethyl esters obtained from the partially polymerized wasted frying oils with high content of unsaturated fatty acids. Let us

mention, that sunflower oil with typically 50−60% linoleic and 25−35% oleic acid content is almost exclusively used for food frying in Ukraine. Hence, the processing of the locally available WFO feedstock will usually face similar problems. In the earlier study [3], it was demonstrated the efficiency of batch vacuum distillation as the purification method, enabling to obtaining of fuel-grade ethanol-based

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BD from the wasted sunflower oil samples (including less aged WFO sample from the current paper). Distillation may be effectively applied to the crude ester upper phase after ethanol removal by distillation, as well as even directly to the ester layer. Ethyl esters distillates contained 97−99% FAEE, no soaps or catalysts, no higher than 0.1% MG and 0.15% FA, and almost no DG, and no TG. However, since glycerol is distilled in the same temperature range as esters, its content in distillates may significantly exceed the allowed level (0.02%). At this stage, adsorption may be used to purify ethyl esters from glycerol residues and other polar admixtures, which probably form at elevated temperatures during distillation. Distillation and dry washing of distillate may be coupled in one technological unit with ester fraction condensation over the stationary bed of adsorbent. For such purposes, micro-mesoporous activated carbon adsorbents, such as those used in this study, activated anthracite or Chemviron, or other low-cost, widely available activated carbons, preferably originated from biomass and wastes.

Conclusions

Dry washing with a variety of widely available adsorbents was shown to be an efficient purification technique, removing the vast majority of contaminants such as soaps and glycerol from the crude ethyl esters, which were synthesized from wasted frying sunflower oil via one-stage alkaline-catalyzed transesterification. Dry washing reduced the acid value and residual ethanol content of most adsorbents but had no effect on the concentration of unconverted mono-, di-, and triacylglyceroles. Only in the case of the activated carbon samples, an insignificant decrease of monoacylglyceroles was achieved. Activated carbons also demonstrated the highest efficiency in the removal of other analyzed contaminants, which is more likely due to the combination of both developed micro- and mesoporosity in their structure.

At the same time, it was found that adsorbent treatment is not able to significantly increase the actual ethyl ester content, as it does not remove the high molecular weight components originating from partially polymerized triglycerides. The findings of this study indicate the impossibility of the dry washing purification method (alongside the traditional water washing one) to provide fuel-grade biodiesel in the case of the processing of wasted frying oils with a significant content of polyunsaturated acid residues, which are highly prone to polymerization reactions in frying conditions. Vacuum distillation may be recommended as a purification method in fuel-grade ethyl esters production from such feedstock. Dry washing with activated carbon may be useful for the final purification of distilled esters in order to remove the residual glycerol or other light polar compounds formed under elevated temperatures during distillation.

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ОЦІНЮВАННЯ ДОСТУПНИХ АДСОРБЕНТІВ ДЛЯ СУХОГО ВІДМИВАННЯ СИРИХ ЕТИЛОВИХ ЕСТЕРІВ, ОДЕРЖАНИХ З ВИКОРИСТАНОЇ ХАРЧОВОЇ СОНЯШНИКОВОЇ ОЛІЇ

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Вторгнення Росії в Україні особливо актуалізувало проблему виробництва рідких біопалив. Етилові естери як біодизель можна виробляти з широко доступних українських олій та біоетанолу місцевого виробництва. Сухе відмивання адсорбентами є передовим методом очищення біодизелю. Досі накопичено недостатньо інформації щодо сухого відмивання продуктів лужного етанолізу, особливо, що стосується видалення важких забруднювачів, що походять з частково полімеризованих використаних олій. Дана робота присвячена дослідженню доступних матеріалів як адсорбентів для очищення сирих етилових естерів (88% естерів, 1,61% моноацилгліцеролів, 0,73% диацилгліцеролів, 0,19% триацилгліцеролів, 1,04% мил, 0,12% жирних кислот, 1,07% гліцерину і 0,17% етанолу). Естери одержано шляхом переестерифікації використаної у смаженні соняшникової олії (2,46 мг КОН/г, 7,1% пальмітинової, 3,5% стеаринової, 27,7% олеїнової та 59,3% лінолевої кислот) на лужному каталізаторі. Активований антрацит, синтетичне вугілля Хемвірон, колоїдний діоксид кремнію, мета-каолін, тальк та бентоніт було оцінено як адсорбенти. Всі зразки забезпечили видалення переважної більшості мил та гліцерину, знизили концентрацію етанолу та, у більшості випадків, кислотне число. Сухе відмивання не спричинило майже ніякого впливу на вміст ацилгліцеролів. Зразки активованого вугілля, що характеризувалися поєднанням розвиненої мікро- та мезопористості, забезпечили найкращий результат очищення, включаючи незначне зниження вмісту моноацилгліцеролів. Однак жоден з адсорбентів не забезпечив видалення важких олігомерних забруднювачів, на що непрямо вказує не вищий за 90% вміст естерів в

оброблених зразках. Покращення цього показника можливо досягти шляхом вакуумної дистиляції.

Ключові слова: біодизель, етилові естери, сухе відмивання, адсорбенти, гліцерин, мила, ацилгліцероли, олігомери естерів.

EVALUATION OF AVAILABLE ADSORBENTS FOR THE DRY WASHING OF THE WASTED FRYING OIL BASED CRUDE ETHYL ESTERS

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Russia's invasion of Ukraine strongly actualized the issue of liquid biofuels production. Ethyl esters biodiesel may be produced from widely available domestic Ukrainian oils and locally produced bioethanol. Dry washing with adsorbents is an advanced biodiesel purification technique. There is still a lack of information on the dry washing of alkaline ethanolysis products, especially concerning the removal of heavy contaminants, originating from partially polymerized waste oils. Current work deals with the investigation of available materials as adsorbents for the purification of crude ethyl esters (88% esters, 1.61% monoacylglycerols, 0.73% diacylglycerols, 0.19% tryacylglyceroles, 1.04% soaps, 0.12% fatty acids, 1.07% glycerol, and 0.17% ethanol). Esters were prepared via alkaline-catalyzed transesterification of wasted frying sunflower oil (2.46 mg KOH/g, 7.1% palmitic, 3.5% stearic, 27.7% oleic, and 59.3% linoleic acids). Activated anthracite, synthetic carbon Chemviron, colloidal silica, meta-kaolin, talc, and bentonite were evaluated as adsorbents. All samples provided the removal of the majority of soaps and glycerol, decreased the ethanol concentration, and, in most cases, acid value. Dry washing had almost no impact on the acylglycerols content. Activated carbons, characterized by a combination of developed micro- and mesoporosity, produced the greatest results, including a minor amount of monoacylglycerols removal. However, none of the adsorbents provided the removal of heavy oligomer contaminants, which is indirectly indicated by no higher than 90% esters content in treated samples. Improvement of these characteristics may be achieved by vacuum distillation.

Keywords: biodiesel; ethyl esters; dry washing; adsorbents; glycerol; soaps; acylglyceroles; oligomeric esters.

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