

ALKALI SYNTHESIS OF FATTY ACID BUTYL AND ETHYL ESTERS AND COMPARATIVE BENCH MOTOR TESTING OF BLENDED FUELS ON THEIR BASIS

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Abstract. Alkaline transesterification of sunflower oil by *n*-butanol and ethanol on alkoxide-containing dried solutions of potassium hydroxide has been carried out. Complex character of spontaneous dividing of butanolysis products, accompanying with formation of three different species of glycerol layers, was observed. One of the later was found to be high-alkaline pure glycerol. Bench motor testing of biodiesel/diesel blends demonstrated slightly better power performance of butyl esters comparing with ethyl esters and regular decrease of harmful emissions (CO₂, CO, NO_x, CH) while increasing biodiesel fraction in mixture.

Keywords: biodiesel, alkaline transesterification, fatty acid ethyl esters, fatty acid butyl esters, glycerin, motor testing.

1. Introduction

Nowadays, the presence of biomass derived motor fuels in energy balance of every single country becomes more and more topical issue in the context of its energy security. This aspect is especially crucial for countries, which are traditional importers of oil and oil products. Furthermore, alternative motor fuels, based on biological raw materials, have apparent environmental benefits as compared with those obtained from mineral sources. Therefore, partial replacement of the later with biofuels in consumption pattern is able to mitigate the ecological load on the environment.

Biodiesel fuel, or briefly biodiesel (BD), is the only biomass derived fuel for compression-ignition engines, which can be utilized without any engine modification.

BD is a mixture of fatty acid alkyl esters (FAAE), produced by transesterification (TE) of triglycerides (TG) by low molecular alcohols. A wide variety of natural stock containing triglycerides, such as a number of fresh and wasted vegetable oils or animal fats, can be used to obtain biodiesel fuel [1-4]. World production of the later keeps upward trend even after sufficient decreasing of oil prices in 2014-2015. Namely, in 2017 near 25 million tonnes of oil equivalent of BD (approximately 30 million tonnes in absolute terms) were produced – the 4% increase compared to 2016 [5].

When saying biodiesel, almost always fatty acid methyl esters (FAME) are implied. Moreover, the terms biodiesel fuel and FAME are traditionally equated [1, 2, 4]. Extensive use of methanol as transesterification agent is due to its relatively abundance and lowest price among short-chain alcohols [6, 7], as well as due to ease and processability of its use for BD production. However, methyl alcohol in this role has disadvantages associated with its high toxicity and ecological harmfulness. In addition, since methanol is usually produced from fossil raw materials (notably natural gas), BD on its basis cannot be considered as fully biorenewable fuel. In spite of sufficient progress in the development of heterogeneous catalytic TE processes [9-13], methanolysis of vegetable oils using soluble alkali catalysts, such as sodium and potassium hydroxides or methoxides, remains the predominant industrial way of biodiesel production [1-4, 14, 15].

Far less hazardous bioalcohols, produced by biotechnological fermentation of sugar-containing natural raw stuff, are regarded as attractive substitute of methanol in the role of TE reagent in biodiesel production. Besides ethanol, *n*-butanol (biobutanol) is also looking very promising in this context. Biotechnological process of biobutanol synthesis, based on the use of numerous bacteria strains of *Clostridiaceae* family, becomes object of rising interest both of industry and scientists [16, 17].

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In spite of a huge list of published works concerning fatty acid ethyl esters (FAEE) production and properties (fullest information can be found in reviews [18-20]), there is no reliable data about ethanol-based biodiesel industrial production. Fatty acid butyl esters (FABE) are regarded as only promising in the role of alternative fuel for diesel engines. FABE and other fatty acid esters of low-molecular alcohols also look promising as raw materials for obtaining of another valuable chemical product, for example multifunctional additives for lubricants [21].

There are relatively few publications dedicated to the issues of FABE synthesis and properties. Acid-catalyzed TE on strong mineral acids is regarded as efficient way of synthesis of butyl esters [6, 22], but alkali-catalyzed process is far more suitable in practice. It is generally known that efficient alkali synthesis of FABE is possible on alkali metal alkoxides as catalysts [23-25].

When fueled with biodiesel or its blends with conventional diesel slight reducing of engine performance occurs due to the presence of 10–12 % of oxygen in FAEE molecules [26-30]. On the other hand, using biodiesel allows to substantially decrease such harmful emissions as unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter [31]. Available information about emissions of nitrogen oxides (NO_x) is quite controversial. It was reported that engines powered by BD produce higher amount of NO_x as compared with conventional diesel fuel [26-28, 32, 33]. Increasing of NO_x emissions varies from up to 8 % for pure FAEE and 10.5 % for pure FAME [33] to 17 % in case of 50 % of FAME in fuel mixture [32]. However, it was also reported [26] that diesel engine fueled by pure methyl and ethyl esters of rapeseed oil produces 2-3 times higher amounts of NO_x per power unit as compared to petroleum diesel fuel; level of emissions in case of FAME is notably higher. To the contrary, approximately 10 % drop of NO_x emission was shown [34] when diesel engine was working on ethyl and methyl esters of rapeseed oil. The level of emissions was slightly lower in case of ethyl esters.

Unlike for methyl or ethyl esters, authors have not ever met any publications dealing with power and environmental performances of diesel engine fueled with FABE or their blends with conventional diesel fuel. Therefore, the aim of the current work was to obtain investigation batches of both fatty acid butyl and ethyl esters by means of alkali homogeneous transesterification of vegetable oil and to compare the power-ecological characteristics of diesel engine working on a range of fuel blends on their basis as well as on pure mineral diesel fuel.

2. Experimental

2.1. Materials

As raw stuff for obtaining of FAEE investigating batches unrefined unfrozen first grade sunflower oil (Ukrainian state standard DSTU 4492:2005), produced by JSC “Nizhynsky zhyrcombinat” (Nizhyn, Ukraine), was used. Acid value of oil, determined by titrimetric method according ISO 660:2009, was 1.2 mg KOH/g, which corresponds to approximately 0.6 % of free fatty acids (FFA). Fatty acid composition of the oil was the following (in % relative to the sum mass of all fatty acids): palmitic acid (C16:0) – 6.7 %, stearic acid (C18:0) – 2.7 %, oleic acid (C18:1) – 34.1 %, linoleic (C18:2) – 53.2 %, linolenic acid (C18:3) – 1.2 %, other fatty acid with number of carbon atoms more than 18 – 2.1 %. Refined frozen sunflower oil purchased from local market (acid number 0.08 mg KOH/g; C16:0 – 6.7 %, C18:0 – 2.8 %, C18:1 – 33.0 %, C18:2 – 54.6 %, C18:3 – 1.1 %, >C18 – 1.8 %) was also used in preliminary synthesis.

Technical-grade *n*-butanol (Turkey, 99.8%, 0.147 % of H_2O) and technical grade rectified ethyl alcohol (Ukraine, 95.6 vol %) were purchased from Ltd company “Chimlaborreactiv” (Brovary, Ukraine). *n*-Butanol was used as received, and ethanol was selectively dehydrated up to ≥ 99.5 % using molecular sieves KA-Y/3A (Russian Federation, dynamic water vapor capacitance 150 mg/cm³). For the preparation of alcohol solutions of alkali catalysts analytical grade potassium hydroxide (Czech Republic) was used. Its total alkalinity, calculated as KOH according to results of acid-base titration with phenolphthalein as indicator, was 85.5 %. The major impurity of reactive is believed to be water due to high hygroscopicity of KOH.

Methyl heptadecanoate for gas chromatography (Sweden, >95%), purchased from Sigma-Aldrich, was used as an internal standard for chromatographic analysis of FAEE. As solvent for samples preparation we used reagent grade *n*-hexane (Germany, 98.5%).

Euro-4 grade summer diesel fuel with zero fatty acid esters content (Ukrainian state standard DSTU 7688:2015), used as mineral component for fuel mixtures preparation, was purchased from local petrol station network.

2.2. Measurements

FAEE and FABE content in transesterification product, as well as their fatty-acid composition, were determined by the adapted technique, based on the method of quantitative gas chromatography analysis of FAME in biodiesel according to European standard EN14013. Analyses were performed by the gas chromatograph

Agilent 7890A Series, equipped with split/splitless inlet, flame-ionization detector and Agilent J&W HP-5 capillary column ((5% phenyl)-methyl polysiloxane, 30 m length, 0.32 mm internal diameter, 0.25 μm film thickness); high-purity helium was used as carrier gas. Samples for analysis were prepared in form of solution in *n*-hexane. Methyl heptadecanoate was used as an internal standard. Conditions of analyses were the following: inlet temperature 523 K, inlet excess pressure 82.7 kPa, split ratio 38:1, chromatographic column oven temperature 483 K, detector temperature 523 K. Duration of the analysis was 60 min for FAEE and 80 min for FAE. Concentration of alkyl esters in samples analyzed was calculated from known masses of the sample and of the internal standard, purity of standard and ratio of the peak of standard area to total area of esters peaks, calculated from chromatogram.

The FTIR-spectra of transesterification products were recorded by Shimadzu IRAffinity-1S infrared spectrometer, equipped with ATR accessory Specac GS 1801-B, using attenuated total reflectance technique.

Alcohol content in FAEE was estimated as 24-hour total mass loss of the sample (initial mass near 10–15 g) after evaporation in Petri dish at ambient temperature (293–298 K).

Density of alkyl esters and mineral diesel fuel at 288 K was measured by means of areometers according to EN ISO 3675. Kinematic viscosity of FAEE was determined as described in EN ISO 3104 using glass capillary viscometer. Higher heating value of the BD samples and mineral diesel fuel has been determined by isoperibolic calorimetry according to procedure, described in ASTM D 240.

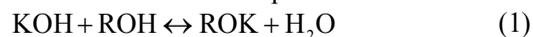
2.3. Synthesis of Fatty Acid Alkyl Esters

2.3.1. Preparation of alcohol solutions of alkaline catalyst

For the alkaline catalysis of triglycerides of sunflower oil potassium hydroxide in the form of solution in corresponding alcohol was used. Both ethanol and butanol solutions were prepared in two different ways – by conventional dissolving of KOH in alcohol and by its dissolving followed by special treatment to remove water from the solution.

To prepare the non-dried alkaline catalyst solutions potassium hydroxide pellets were put in conical flask together with alcohol and mixed by magnetic stirrer at 250–500 rpm during 10–30 min up to complete dissolving. The obtained solutions were clear and colorless. The quantity of solution of certain concentration required for one experiment was prepared immediately before synthesis of fatty acid alkyl esters. Solution prepared in such a way contains small amounts of water. It can be

present in initial alcohols and hydroxide, as well as to appear by reaction of formation of potassium alkoxides



where R is C_2H_5 or $n\text{-C}_4\text{H}_9$. Removing the water from the system provides the equilibrium shift of reaction (1) towards forming of products, which enables to obtain alkaline alcohol solutions with high content of alkoxides, using only KOH and corresponding alcohols as reactants.

Dried solutions of alkali catalyst were obtained in concentrated form. Dilution of the concentrate by necessary amount of corresponding alcohol was performed just before each synthesis. To obtain dried alkaline butanol concentrate firstly 7% solution of KOH in butyl alcohol was prepared. It was put into 0.5 l round-bottom flask and heated at oil bath (413–453 K) to provide reflux and condensation of water-butanol heterogenic azeotrope in Dean-Stark trap. The heavy water-enriched layer collected in the bottom of the trap and butanol-enriched mixture returned into the flask from the top of the trap. The process of azeotropic distillation was carried out until the amount of water layer stopped to grow. Knowing the mass of collected water layer and regarding all unspecified impurities in initial KOH as water, one can estimate the yield of potassium butoxide. It was about 78–82 % for all prepared solutions. Some peculiarities of potassium butoxide preparation in this way were discussed in more detail in paper [35].

Dried alkaline catalyst solution in ethyl alcohol was prepared by means of selective removal of water using previously thoroughly dehydrated (653 K, 3 h) molecular sieves KA-Y/3A. Firstly 13% solution of KOH in dried ethanol was prepared in round-bottom flask of 0.5 l volume. The resulting solution was boiled on oil bath (373–393 K) to provide reflux and condensation of water-ethanol homogenous azeotrope through molecular sieves placed into Soxhlet extractor. Dried ethyl alcohol was returned into the flask.

2.3.2. Fatty acid esters synthesis and fuel mixtures preparation

In order to study the peculiarities of sunflower oil transesterification and to choose the main technological parameters for further production of batch parties of alkyl esters, numerous syntheses of relatively small volume were carried out. 100 g of oil per each synthesis were used. Weighing of components was performed by technical electronic scales with the accuracy of ± 0.01 g. Calculated amount of previously prepared alcohol catalyst solution of certain concentration was placed into 0.5 l conic flask. When using alkoxide-containing alkaline concentrates, the necessary amount of ethanol or *n*-butanol was added to obtain given ratio of alcohol with respect to oil. After that, 100 g of oil was added, and flask

was immediately put on magnetic stirrer. Reaction mixture was stirred for a given period at 500 rpm. The reaction was carried out at ambient temperature without special temperature control. Mixture after stirring was transferred into separation funnel to allow glycerol layer to settle down on its own. Transesterification products were settled during 20–72 h at current ambient temperature.

Total percentage yield of FAAE was calculated as the ratio of their total mass in TE products to maximal mass of alkyl esters, which could be formed from oil taken for synthesis. Oil was regarded as pure TG having average molar mass, calculated from known oil fatty acid composition. Therefore, FAAE yield, calculated in such a way may be slightly underestimated due to the presence of free fatty acids and minor non-fat components in initial oil. After spontaneous dividing of TE products occurs after synthesis minor amounts of esters may transit in glycerol layer (GL). In this instance total FAAE yield should take into account content of esters both in ester layer (EL) and glycerol layer. When saying effective yield of esters, yield calculated only for FAAE in EL is implied.

Batch parties of fatty acid esters were prepared by means of the numerous sequential syntheses in 2 l round-bottom flask, followed by products transfer into 20 l bottles for settling. Duration of each separate synthesis was 30 min, reactants were mixed by magnetic stirrer at 500 rpm using oval anchor. Both synthesis and settling occurred at ambient temperature (293–296 K) without special temperature control. After spontaneous settling of glycerol layers, they were siphoned off from the bottom of the bottles using flexible tube. Thereafter ELs obtained were stripped to remove excess or unreacted alcohols and washed from residual alkali catalyst. Stripping of alcohols occurred by its spontaneous evaporation from EL, placed in wide open vessels, at ambient temperature. It had been continued until mass of EL remained constant, which took 3–5 days. Washing was performed three times by adding of small amounts of distilled water (1–1.5 %), followed by settling of water layer at the bottom of the bottle. In case of FAAE preparation washing preceded stripping of

alcohol. In case of FABE butanol, which forms stable emulsions with water, was removed firstly.

On the basis of obtained sunflower oil ethyl and butyl esters fuel mixtures for motor testing were prepared. Since density of mixtures of biodiesel and diesel fuel is additive by volume fractions of biological-derived and mineral components [36], the procedure of preparation of blended fuels consisted in conventional blending of specified volumes of mineral diesel fuel with corresponding biocomponent. For this purpose, propeller mechanical stirrer (200 rpm) and stainless steel container of 20 l volume were used. The change of volume of blends obtained was negligible.

2.4. Bench Motor Setup and Procedure of Testing

Comparative motor testing of blended fuels was carried out using the bench setup based on serial compression ignition engine VW 1.9TDI ALH of Volkswagen (Germany) production. The engine is equipped with turbocharger and electronically controlled high-pressure fuel pump; its main technical parameters are given in the Table 1. Bench setup also includes electric balancing machine (type DS 742-4/N), control panel and necessary equipment for measuring of engine work parameters and testing conditions. Five-component gas analyzer AUTOTEST-02.03P, which is mounted into exhaust gas line, performs control of the level of harmful gas emissions.

The torque T (N·m) and the fuel consumption per unit time G_f (kg/h) at the constant known crankshaft rotation frequency n (min^{-1}) are the main characteristics of diesel engine work, which are directly determined during bench testing. From these results of direct measurements one can calculate the following diesel engine performances.

The effective engine power (kW) is determined according to Eq. (2):

$$N_e = \frac{T \cdot n}{9550} \quad (2)$$

Table 1

Technical parameters of VW 1.9TDI ALH engine

Parameter	Value
Engine capacity, l	1.9
Number of cylinders	4
Nominal effective power (at crankshaft rotation frequency 3750 rpm), kW	66
Maximal torque (at crankshaft rotation frequency 1900 rpm), N·m	210
Piston stroke, mm	95.5
Compression ratio	19.5
Minimal cetane number of fuel	49

Brake specific fuel consumption (g/(kW·h)) is calculated as follows:

$$g_e = \frac{G_f \cdot 10^3}{N_e} \quad (3)$$

The engine efficiency is equal to

$$\eta_e = \frac{3.6 \cdot 10^3}{g_e \cdot Q_l} \quad (4)$$

where Q_l is a lower heating value of fuel (MJ/kg).

Q_l value is calculated from measured higher heating value of fuel (HHV) Q_h and content of hydrogen (H , wt %) in the sample [37]:

$$Q_l = Q_h - 0.2122 \cdot H \quad (5)$$

Content of hydrogen in the samples of esters is determined from their fatty acid composition, calculated from chromatograms.

Lower heating value for fuel blends is calculated from known densities and lower heating values of petroleum-derived and bio-derived components:

$$Q_l^{mix} = \frac{Q_l^{bd} \cdot \rho_{bd} \cdot v_{bd} + Q_l^{md} \cdot \rho_{md} \cdot v_{md}}{\rho_{mix}} \quad (6)$$

where Q_l^{bd} and Q_l^{md} are the lower heating values of biocomponent (ethyl or butyl esters) and mineral component, respectively, MJ/kg; ρ_{bd} , ρ_{md} , ρ_{mix} are the densities of biocomponent, mineral component and mixture, respectively, kg/m³; v_{bd} and v_{md} are the volume fractions of biocomponent and mineral component, respectively.

Also fuel consumption per unit time in volume units (l/h) can be calculated:

$$V_f = \frac{G_f \cdot 1000}{\rho_f} \quad (7)$$

where ρ_f is the density of fuel blend, calculated as volume additive from known densities of corresponding biocomponent and mineral fuel, kg/m³.

Besides the listed power characteristics, content of harmful gaseous emissions in the exhaust gas (CO₂, CO in per cents as well as NO_x and unburned hydrocarbons CH in ppm) is determined as environmental performances of diesel engine work.

Testing procedure involved carrying out one at a time motor experiment with full fuel feed at the crankshaft rotation frequency of 1900 rpm, corresponding to the maximal torque value according to specification of engine manufacturer. This enabled us to measure two so-called maximal torque characteristics of diesel engine, working on the range of fuel blends of E-series (ethyl esters) and B-series (butyl esters). Such approach provides sufficiently valuable information on the engine performance and does not require high inputs of fuel.

Motor experiments for all mixed fuels of both series, as well as for pure mineral diesel were carrying out

at fuel injection timing angle θ value equal to 22° of crankshaft rotation to top dead center. This value was previously determined as optimal both for petroleum diesel fuel and ethyl esters of sunflower and rapeseed oils during motor tests, conducted by our groups on another bench setup on the basis of soviet tractor diesel engine D21A [29]. Almost the same value of θ of 23° was also found as optimal for both mineral diesel and ethyl esters with ethanol content up to 5 % in another bench testing on the same setup [30].

Ecological performances of diesel engine work were determined as average value of harmful emissions content in exhaust gas during the entire testing time for each individual fuel blend.

3. Results and Discussion

3.1. Peculiarities of Alkali

Transesterification of Sunflower Oil by *n*-Butyl and Ethyl Alcohols

Synthesis of butyl esters by alkali transesterification can be complicated by saponification of glycerides or butyl esters, occurring in the presence of water. Soap formation in butanol media is more intense as compared with shorter chain alcohols. This is due to low polarity of butyl alcohol and thus good solubility of glycerides in the later. On the other hand, water strongly suppresses formation of alkoxide-anions (reaction 1) being real active species in alkali-catalyzed transesterification reaction. In case of alkali TE with *n*-butanol even tenths of a percent of water brought in reaction media with raw materials can greatly slow down the process, leading to low yield of FABE. Moreover, soap formation reduces the concentration of alkali catalyst while fatty acids salts formed prevent spontaneous settling of separate glycerol layer due to stabilization of emulsion of transesterification products [38]. Using alkali metal alkoxides as catalyst provides high concentration of alkoxide-anions and uptake of water from reaction media, consuming on its hydrolysis.

Among alkoxides of low-molecular alcohols only methoxides, being commercially available products, can be regarded as promising industrial-scale catalyst for FABE production. Lab-scale method preparation of alkoxides of longer-chain alcohols by the way of direct reaction of alkali metal with corresponding alcohol [23, 25] can not be considered as valuable for large-scale BD production. However, using of methoxide for TE indirectly involves methyl alcohol, utilized in their industrial production, in the process of biobutanol-based BD manufacturing. The later may also contain significant fraction of methyl esters.

Recently high efficiency of butoxide-contained dried butanol solution for alkali synthesis of FAE was shown [38]. Alkali solution, prepared in the same way, was used in current work in the process of TE of vegetable oil by butanol. This allows to utilize all advantages of dry alkali synthesis of FAE on alkoxides, based on only KOH and n-butyl alcohol as initial raw stuff.

Results of TE of refined sunflower oil by butanol are given in Fig. 1. The process was carried out at molar ratio of alcohol to oil (R_{AO}) equal to 4.5 at ambient temperature (288–289 K) without any heating of reagents. The amount of alkali catalyst in terms of K^+ was 0.95 % relative to oil mass. Settling of reaction products also occurred at 288 K. When using dried solution of catalyst yield of FAE determined immediately after stirring reaches 66 % during first 2 min and then slowly grows with the synthesis time up to 82 % after 40 min. Sufficiently lower yields of esters were obtained in synthesis on KOH (synthesis time is 40 min).

In all syntheses on potassium butoxide, spontaneous formation of separate layer of glycerol by-product was observed. Yields of butyl esters after full separation of GL noticeably increased and were almost the same (90–93 %) independent of stirring time. When KOH was used as the catalyst, nor GL separation neither FAE yield growth after settling were observed.

It is worth emphasizing that spontaneous dividing of reaction mixture to ester and glycerol phases is an

aspect of crucial importance in alkali synthesis of FAE. It provides removing of not only glycerol by-product, but also most of alkali catalyst from ester layer. However, there is not sufficient information about spontaneous separation of products of FAE alkali synthesis in published literature. One can meet information [7] about glycerol layer (GL) appearance at certain set of reaction conditions in products of rapeseed oil transesterification by butanol on KOH. However, no quantitative data of GL yield or its composition is reported. To provide the FAE separation removing of excess butanol and various ways of neutralization of transesterification products by acids can be used [7, 39].

Observed spontaneous dividing of TE products had unusual peculiarities, namely, formation of primary GL (marked as GL1 in Fig. 1b) occurred directly during the stirring of mixture in reaction flask. It was highly basic dense residue on bottom of the later. GL1 mass gradually grew over the course of synthesis. Secondary glycerol layer (GL2) formed after 24 h of settling. It was slightly yellow, high-dense, strongly basic and contained only traced amounts of FAE and butanol. Mass of GL2 changed in antitactic manner with mass of GL1. Total amount of glycerol layers (TGL) was slightly higher in shorter synthesis, which may be due to varying composition of GL1 depending on synthesis duration. It should be emphasized that maximal theoretical amount of potassium-contained pure glycerol formed from oil is about 11 % of its mass.

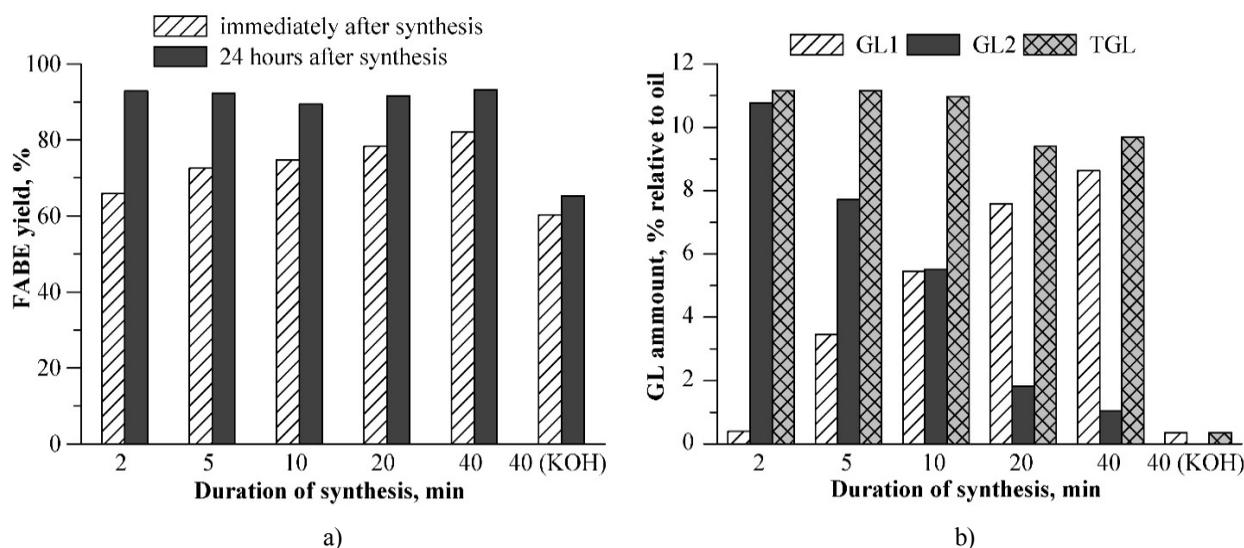


Fig. 1. Results of TE of refined sunflower oil by butanol: FAE yield (a) and peculiarities of GL distribution (b)

TE of unrefined sunflower oil was carried out at R_{AO} in the range of 3–7.5 at ambient temperature about 295–296 K and synthesis duration of 5 min. Amount of catalyst used was the same as in case of TE of refined oil

(0.95 % relative to oil in terms of K^+). Settling of reaction products occurred also at ambient temperature. Yield of FAE, measured immediately after synthesis, expectedly increased with increasing of alcohol to oil ratio, reaching

82 % at $R_{AO} = 7.5$ (Fig. 2a). Observed character of reaction products dividing was more complex than during TE of refined oil. GL1 formed in sufficiently lower amounts (Fig. 2b). Masses of GL2 also were lower, especially in synthesis at low R_{AO} values (3 and 4.5). At the same time, additional tertiary GL (GL3) formed during settling of products of this synthesis. Its nature was completely different as compared with GL2. It also was strongly basic but has intense brown color and contained more than 30 % of FABE and sufficiently high amount of butyl alcohol. In case of synthesis at equimolar ratio of reagents GL3 appeared after removing of GL2. In products of TE at $R_{AO} = 4.5$ both GL2 and GL3 formed simultaneously during settling overnight. Therefore, yield of esters after GL2 separation was not measured for this synthesis.

Different chemical nature of secondary and tertiary glycerol layers forming in alkali synthesis of FABE on potassium butoxide is clearly demonstrated by their FTIR-spectra (Fig. 3). Spectrum 1 of sunflower oil butyl esters, distilled under vacuum, contains intense bands at nearly 3000 and 1736 cm^{-1} , inherent to stretching vibrations of C–H bonds of sp^3 -hybridized atoms of carbon chain and to stretching vibrations of C=O bonds of carbonyl group, respectively. The same bands of slightly lower intensity are also present in spectrum 2 of EL. It also contains butanol and products of partial conversion of TG – mono- and diglycerides. Their presence is reflected by wide low-intense band of valance vibrations of O–H bonds in the range of 3100–3600 cm^{-1} .

The later band in FTIR-spectrum 3 of GL3 is far more intense due to the presence of glycerol and higher concentration of butanol in tertiary glycerol layer. A band

nearly 1030 cm^{-1} , which is native to alcohol C–O bonds, is clearly presented in the spectrum of the sample. Intense absorbance nearly 1730 cm^{-1} indicates high concentration of carboxyl groups, contained both in molecules of FABE and non-converted mono- and diglycerides. In contrast, samples of GL2 (both for refined and unrefined oil) do not absorb in this region, but they have an intense band in the region of absorbance of alcohol C–O bonds. In addition, spectra 4 and 5 of GL2 do not contain band at 1564 cm^{-1} , which is inherent to potassium soaps and well resolved in spectrum 3 of GL3. It means that soaps accumulate mostly in the GL3 and do not transfer into GL2. Finally, it should be mentioned, that FTIR-spectra 3 and 4 of both samples of GL2 repeat completely the shape of spectrum 6 of pure glycerol. Thus, secondary glycerol layer, which forms upon alkali TE of vegetable oil by butanol on potassium butoxide, appears to be valuable by-product of FABE synthesis. Due to water absence in reaction mixture and higher acidity of glycerol as compared to n-butyl alcohol, GL2 is believed to be fairly pure solution of potassium glyceroxide in glycerol. One can meet information that sodium glyceroxide in the form of solution in glycerol efficiently catalyzes TE of vegetable oil by methanol [40]. So, it can be assumed that GL2 can also be useful as alkali catalyst for BD production.

Although effective TE of vegetable oils by ethanol is possible on alkali metal hydroxides as is, in current study we used both dried and non-dried solution of KOH in ethyl alcohol to synthesize FAEE. Removing of water from the alkali catalyst solution should have contributed to forming of potassium ethoxide. However, it was difficult to estimate the amount of water removed and thus the yield of alkoxide.

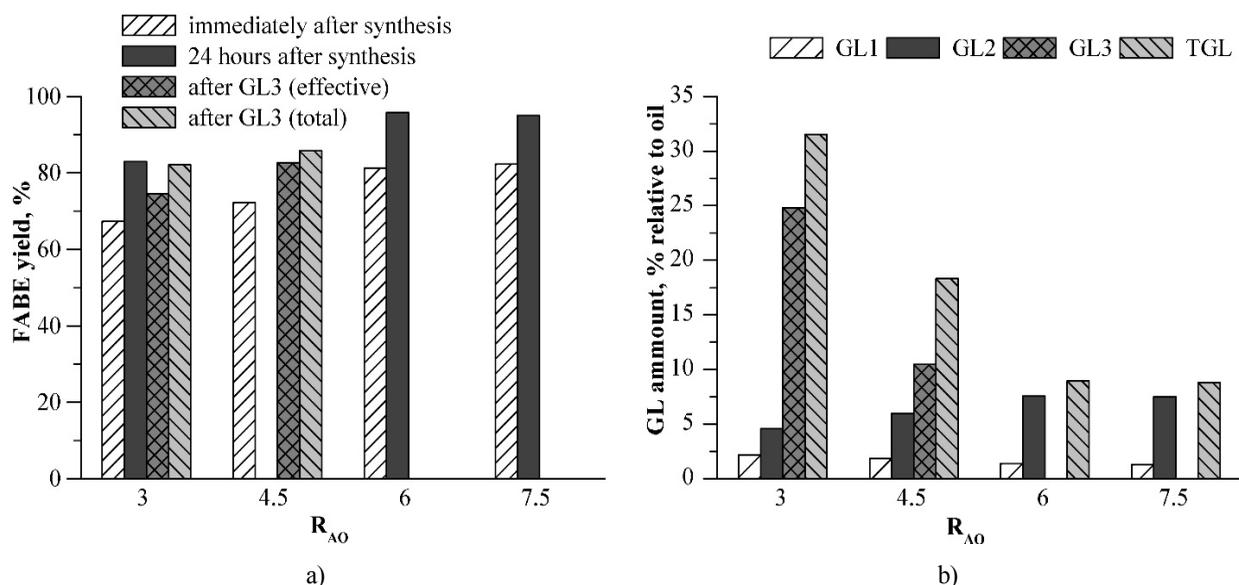


Fig. 2. Results of TE of unrefined sunflower oil by butanol: FABE yield (a) and peculiarities of GL distribution (b)

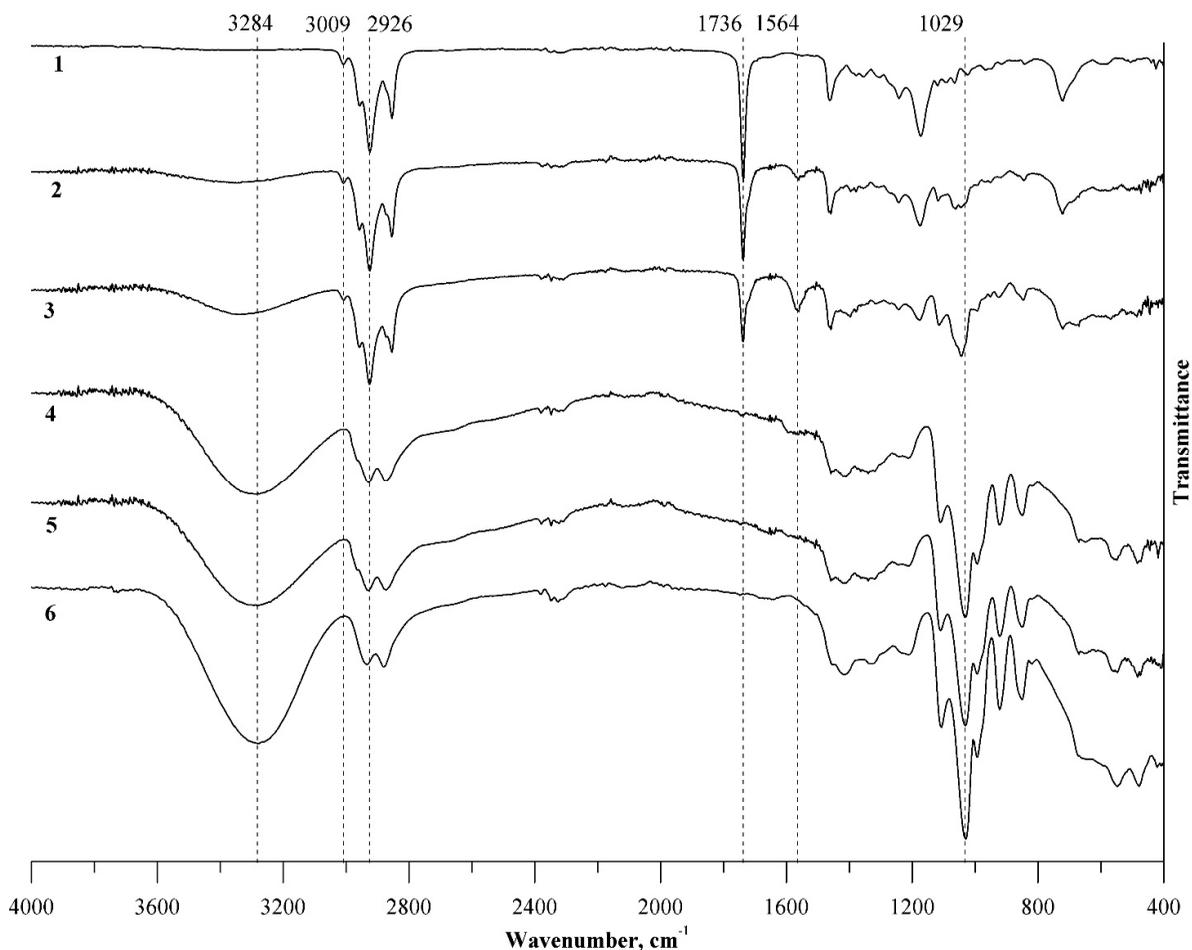


Fig. 3. FTIR-spectra: FAE distilled under vacuum (1); EL (2), GL3 (3) and GL2(4) after TE of unrefined oil; GL2 after TE of refined oil (5); pure glycerol (6)

Table 2

Conditions and results of TE of unrefined sunflower oil by ethanol

FAEE synthesis	Conditions of synthesis		Results of synthesis		
	R_{AO}	Catalyst amount, % ^a	FAEE effective yield, %	FAEE total yield, %	TGL, % relative to oil
1	3.0	1.07	74.5	75.4	5.0
2	3.5	1.07	73.4	81.6	27.8
3	4.0	1.07	82.0	88.9	21.8
4	4.5	1.07	87.8	93.4	19.7
5	5.0	1.07	89.8	93.8	15.4
6	4.5	1.07 (KOH) ^b	73.5	82.6	29.0
7	4.5	1.31	93.1	95.2	7.9

Notes: ^a relative to mass of oil in terms of K⁺; ^b non-dried solution of KOH in ethanol

All syntheses (Table 2) were performed without temperature control at ambient temperatures of about 292–293 K. Time of each synthesis was 20 min, ratio R_{AO} varied in the range of 3–5. Dividing of TE products into ester-enriched and glycerol-enriched phases occurred in all experiments after settling overnight at ambient temperature,

but mass of GL formed varied significantly. Formation of clearly defined various glycerol layers was not observed. Only small amounts of dense slightly yellow layer of a nature similar to GL2 settled in the bottom of the funnel. However, it was difficult to collect it quantitatively and separate from main part of GL, having dark brown color

and containing 28–33 % of ethyl esters. Thus, only masses of total glycerol layer, formed during settling, were determined. The formation of GL1 was not fixed either. Some minor amount of residue on reaction flask was not considered as the later.

In synthesis at equimolar reagents ratio (synthesis 1) low yield of ethyl esters and only 5 % of TGL were obtained. When increasing excess of alcohol both effective and total yield of FAEE grew gradually. This was accompanied by decreasing of TGL amount and therefore by lowering of FAEE losses with the later. Using of non-dried solution of KOH (synthesis 6) resulted in low yield and formation and separation of as high as 29 % of glycerol layer. Although increasing of amount of dried catalyst solution (synthesis 7) allowed to achieve high ethyl esters yield, the separation of TE products was not full enough full. Conditions of synthesis 4, which combines using of moderate excess of ethanol and 88 % effective yield of esters, were chosen for further preparation of FAEE batch party.

3.2. Batch Parties of Esters and Fuel Blends Preparation

251 batches of both ethyl and butyl esters of sunflower oil (samples EES and BES, respectively) have been prepared by the way of numerous sequential syntheses (30 min duration, ambient temperature) followed by dividing, residue alcohol removal and washing of products. Another conditions of alkyl esters preparation, as well as some technical characteristics of products obtained are given in Table 3. The measured higher heating value and density (288 K) of mineral diesel fuel used for blends preparation were 45.5 MJ/kg and 845 kg/m³, respectively. HHV of biodiesel samples was found to be close to that of reported in literature for fatty acid methyl or ethyl esters. This characteristic is very close for both methanol and ethanol-based biodiesel samples derived from different vegetable oils and usually varies in the range of 38–41 MJ/kg according to different sources [41–44]. Lesser HHV of esters as compared with petrodiesel is due to the presence of oxygen in their mole-

cules. For example, molecules of butyl oleate and ethyl oleate contain 9.82 and 10.74 % of oxygen, respectively. Lower oxygen content explains the slightly higher heating value of BES.

Kinematic viscosity of EES sample meets requirements of European standard on methyl esters [45] and Ukrainian standards on methyl and ethyl esters [46–47]. This characteristic of BES sample is higher than limited by listed documents 5 mm²/s, however it is within requirements of USA standard on FAME or FAEE as BD [48]. It should be mentioned that higher viscosity of butyl esters as compared to ethyl esters is due to the lengthening of carbon chain of alcohol fragments of their molecules and does not mean lower product quality. Densities of both EES and BES samples are within requirements of the mentioned standards.

Two series of blends marked according to alkyl esters used (E-series for ethanol- and B-series for butanol-based products) were prepared. Each series included 3 mixtures, containing 20, 50 and 80 vol % of biocomponent (mixtures E20, E50, E80 in E-series and B20, B50, B80 in B-series). Pure mineral diesel fuel served as reference sample for both series and corresponded to mixture E0/B0 with zero ester content.

3.3. Comparable Bench Motor Testing

Table 4 summarizes both power and ecological characteristics of diesel engine work during testing. Relative changes of each characteristic comparing with reference sample of mineral diesel fuel are listed for each fuel blend.

Fuel consumption per unit time, expressed in mass units (Fig. 4a, hereafter points on graphs for 0 % of biocomponent correspond to pure mineral diesel fuel), slightly grows for both series when increasing biocomponent content. More noticeable growth up to 7.1 % was demonstrated by E-series of blends, while it was only up to 5 % for blends of B-series. Increasing of volume fuel consumption (Fig. 4b) of all samples, containing butyl esters, do not exceed 2 %. Blends based on ethyl esters demonstrated slightly higher growth of this characteristic. This is due to higher densities of both biocomponents as compared to mineral diesel.

Table 3

Synthesis conditions and technical characteristics of batches prepared

Characteristic	EES	BES
R _{AO}	4.5	3.0
Catalyst, % of K ⁺ relative to oil	1.07	0.95
Final product yield kg/kg of oil	0.94	0.98
Ester content, %	93.5	91.5
Higher heating value, MJ/kg	39.50	40.15
Kinematic viscosity at 313 K, mm ² /s	4.86	5.85
Density at 288 K, kg/m ³	881	877

Related changes of power and ecological characteristics of diesel engine work on fuel blends

Characteristic	E0/B0 ^a	Change of characteristic in relative % for mixture ^b					
		E20	B20	E50	B50	E80	B80
Fuel consumption by mass, kg/h	12.6	+0.8	+0.6	+4.0	+2.9	+7.1	+5.0
Fuel consumption by volume, l/h	14.9	-0.1	-0.1	+1.8	+1.0	+3.6	+1.9
Torque, N·m	210	-0.8	-1.0	-1.9	-1.5	-2.1	-2.0
Effective power, kW	42	-0.8	-1.0	-1.9	-1.5	-2.1	-2.0
Engine efficiency	0.282	+0.4	0	+0.3	+0.3	+1.2	+1.9
Brake specific fuel consumption, g/(kW·h)	301.6	+1.6	+1.7	+5.9	+4.5	+9.4	+7.1
CO ₂ in exhaust gas, %	11.0	-6.44	-8.2	-13.6	-14.6	-18.1	-19.1
CO in exhaust gas, %	0.3	-23.3	-26.7	-40.0	-43.3	-66.7	-70.0
NO _x in exhaust gas, ppm	1930	-6.2	-6.7	-9.3	-10.9	-16.6	-17.6
CH in exhaust gas, ppm	3.7	-51.6	-61.0	-75.8	-81.2	-86.6	-94.6

Note: ^a absolute value for reference sample; ^b relative change in % as compared with reference sample E0/B0

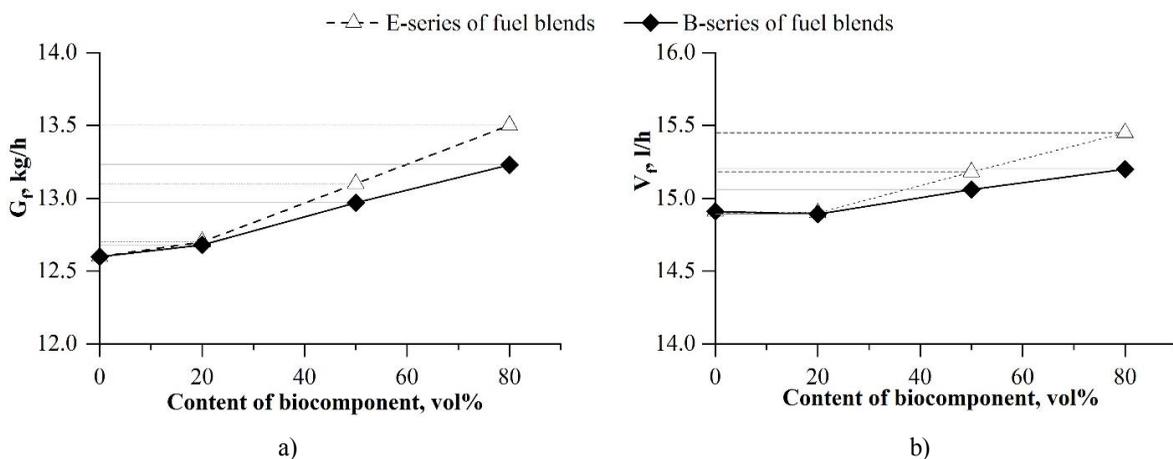


Fig. 4. Changing of fuel consumption by the diesel engine powered by blended fuels and pure mineral diesel: consumption by mass (a) and consumption by volume (b)

Torque of the diesel engine (Fig. 5a) powered by investigated blends decreases very insignificantly when increasing volume fraction of both ethyl and butyl esters. The highest drop of torque from 210 N·m in case of pure petrodiesel (maximal torque according specification of engine manufacturer) by only 2.1 % down to 205.6 N·m was obtained during engine work on mixture E80. As motor testing was performed at the constant crankshaft rotation frequency, changing of engine effective power (Fig. 5b) in both series of blends demonstrates exactly the same trend as changing of engine torque. Obviously, the drop of these power characteristics is due to lower heating value of EES and BES products are less by 7.5 and 5.5 %, respectively, than that of petroleum-derived diesel fuel (Table 3). No significant difference in values of engine torque and engine effective power between E- and B-series of fuel blends was observed. At the same time, the mentioned difference of lower heating values between BES and EES products, as well between both biocompo-

nents and petrodiesel, are more pronouncedly expressed in increasing of fuel consumption by mass (Fig. 4a), rather than in changing of torque and effective power of engine.

The most suitable unifying characteristic for comparison of efficiency of fuels during motor testing under the same conditions is brake specific fuel consumption g_e . It expresses the mass of fuel needed for engine to produce the unit of work. Brake specific fuel consumption of mixture fuels increase with increasing of both ethyl or butyl esters content (Fig. 5d). As the increase in brake specific fuel consumption of blends of E-series is somewhat more noticeable than that of blends of B-series (growth up to 9.4 and 7.1 % for samples E80 and B80, respectively), mixtures on the basis of fatty acid butyl esters appear to be more efficient fuel for diesel engine in testing conditions. On the other hand, there is no difference in g_e between samples E20 and B20, which contain 20 vol % of ethyl and butyl esters, respectively.

As for the engine efficiency η_e , there was observed insignificant growth of this characteristic when engine was powered by biodiesel blends with high fraction of biocomponent (Fig 5c). However, improvement of η_e was almost negligible and did not exceed 1.2 and 1.9 rel. % for mixtures with maximal fraction of ethyl and butyl esters, respectively (Table 4). The increase of η_e of the engine, powered by biodiesel mixtures, may be caused by slightly higher combustion rate of biofuel/air mixture in cylinders at the same fuel injection timing angle due to the presence of structural oxygen in molecules of esters, which provides its higher homogeneity with fuel during combustion.

All fuel mixtures based on both ethyl and butyl esters demonstrated better ecological performance during the motor testing as compared to pure mineral diesel fuel: the concentration of harmful gaseous emissions (CO_2 , CO, NO_x and unburnt hydrocarbons CH) in exhaust gas regularly decrease while increasing volume fraction of bioderived component (Fig. 6). Almost no difference between two investigated series of mixture fuels was observed. Some advantage of samples of B-series in terms of harmful emissions is barely perceptible and should not be regarded as significant for practice. On the other hand, such a difference can be regularly traced in the whole range of concentrations of esters and may be caused by some intrinsic peculiarities of

burning of FABE as compared with FAEE. Another possible reason of insignificantly lower concentration of environmentally harmful gaseous emissions in combustion products of fuel blends of B-series is different volume of exhaust gases, caused by different mass ratio of fuel to air, consumed by working engine (was not determined during testing).

Anyway, both series of investigated blends show quite essential drop of the content of all listed pollutants in exhaust gases. In case of blends with highest volume fraction of biocomponent such a drop reaches 18.1–19.1 rel. % for CO_2 (Fig. 6a), 66.7–70.0 rel. % for CO (Fig. 6b), 16.6–17.6 rel. % for NO_x (Fig. 6c), and 86.6–94.6 rel. % down to almost zero content for CH (Fig. 5d). It is worth emphasizing the unequivocal decreasing of NO_x emissions with growth of BD fraction content in blends. This fact is in good agreement with results obtained previously by our group during testing of another diesel engine (soviet two-cylinder tractor engine D21A), fueled with FAEE-based fuel blends and pure ethyl esters [29–30]. It should also be emphasized that significant decreasing of NO_x emissions in current study was observed in high-load regime of engine work (at maximal torque of engine). At the same time, one can meet information that NO_x emissions of diesel engine fueled with methanol-derived BD slightly decrease at low loads but increase at high loads [49].

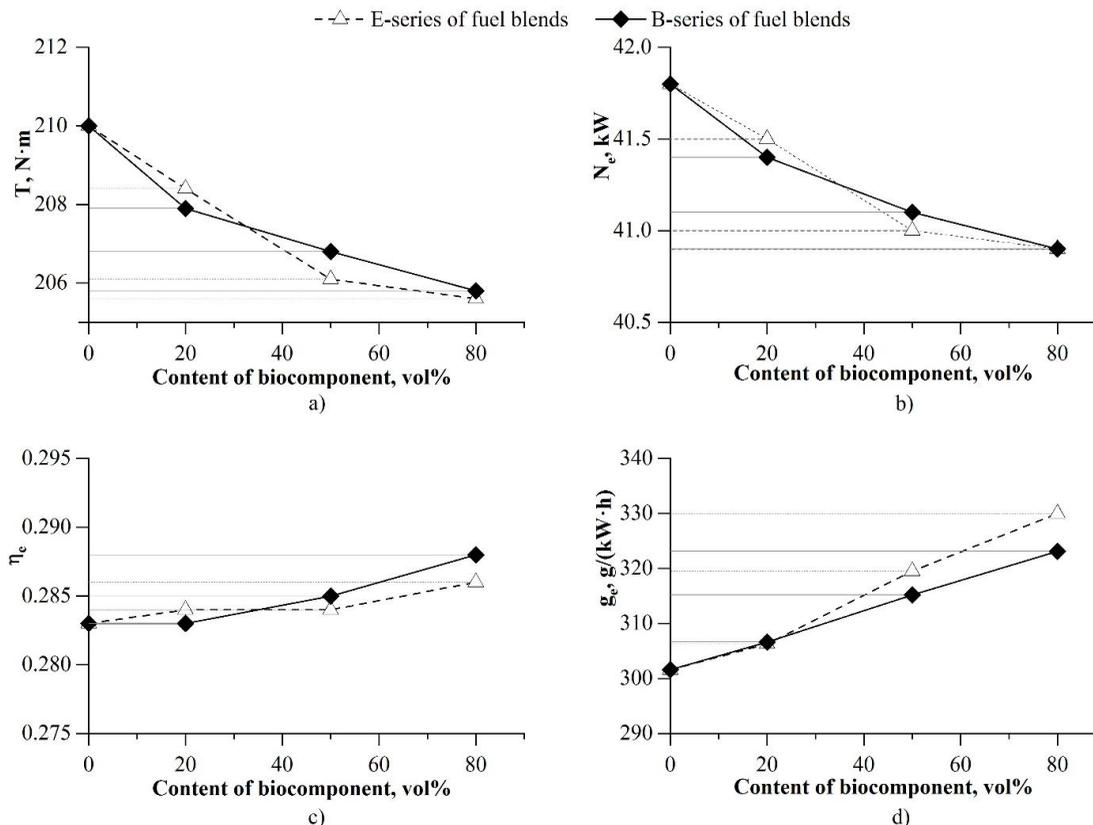


Fig. 5. Changing of power characteristics of the diesel engine powered by blended fuels and pure mineral diesel: torque (a); effective power (b); engine efficiency (c) and brake specific fuel consumption (d)

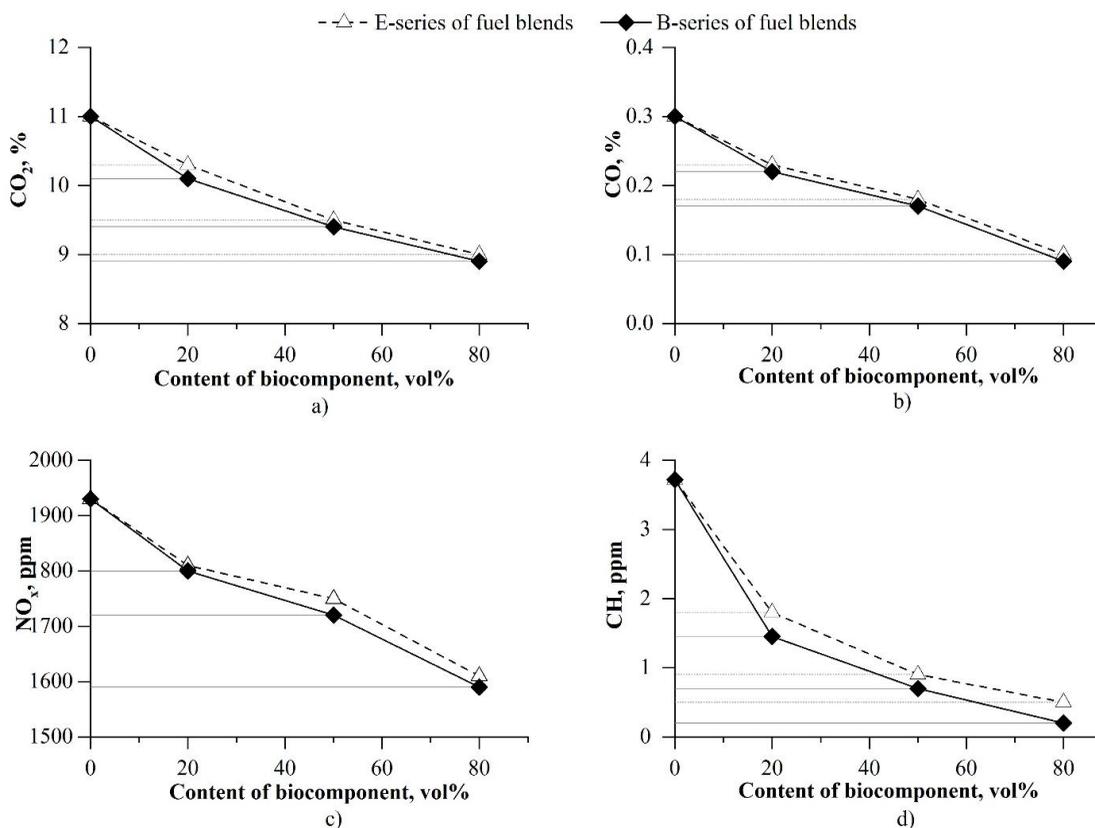


Fig. 6. Changing of harmful emissions content in exhaust gas of the diesel engine powered by blended fuels and pure mineral diesel: CO₂ (a); CO (b); NO_x(c), unburned hydrocarbons CH (d)

4. Conclusions

The alkali TE of sunflower oil by ethyl and *n*-butyl alcohols on alkoxide-contained dried catalyst solution, obtained on the basis of potassium hydroxide, was carried out. For the first time for alkali transesterifications of oils, the spontaneous separation of high pure alkaline glycerol byproduct was observed. Bench testing of diesel engine, fueled by blends on the basis of fatty acid butyl esters with biocomponent content up to 80 vol %, were carried out for the first time. FAFE-based blends demonstrated slightly higher power performances as compared to mixtures containing the same amount of synthesized ethyl esters. Gradual decreasing of harmful emissions with increasing volume fraction of both ethyl and butyl esters was also shown. Notably, the drop of NO_x by 17–18 % at highest content of biodiesel fraction was fixed.

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ЛУЖНИЙ СИНТЕЗ БУТИЛОВИХ І ЕТИЛОВИХ ЕСТЕРІВ ЖИРНИХ КИСЛОТ І ПОРІВНЯЛЬНІ СТЕНДОВІ МОТОРНІ ВИПРОБУВАННЯ СУМІШЕВИХ ПАЛИВ НА ЇХ ОСНОВІ

Анотація. Проведено лужну переестерифікацію соняшникової олії *n*-бутанолом та етанолом на алкогольній осередкованій розчині гідроксиду калію. Виявлено складний характер самочинного розширення продуктів синтезу бутилових естерів, який супроводжувався утворенням трьох відмінних різновидностей гліцеринового шару. Виявлено, що одним з них є високолузний чистий гліцерин. Стендові моторні випробування сумішей біодизеля з дизпаливом продемонстрували децю кращі енергетичні показники бутилових естерів порівняно з етиловими естерами та закономірне зниження шкідливих викидів (CO_2 , CO , NO_x , CH) із збільшенням частки біодизелю в суміші.

Ключові слова: біодизель, лужна переестерифікація, етилові естери жирних кислот, бутилові естери жирних кислот, гліцерин.