

V. Ribun¹, S. Kurta¹, T. Gromovy², O. Khatsevich¹

Improving the Technology Synthesis and Properties of Biodiesel

¹*Prekarpathian National Vasyl Stefanyk University, Ivano-Frankivsk, Ukraine, kca2014@ukr.net, ribun.vika@gmail.com*

²*Institute of Surface Chemistry of the National Academy, of Sciences of Ukraine, Kyiv, Ukraine, grotu@ukr.net*

Existing technologies for the synthesis of active additives to motor fuels are quite complicated. Therefore, improvement of the technology of biodiesel fuel synthesis in order to increase the cetane number and improvement of other diesel fuel characteristics with combustion activators is an urgent problem. Raw materials for the biodiesel production are vegetable oils methanol and ethanol with the alkaline or acid catalyst usage. The use of ethyl esters of long-chain fatty acids of rapeseed oil as biodiesel has a number of advantages compared with the methyl ester use [2]. Thus, biodiesel fuel was synthesized by transesterification of rapeseed oil with absolute ethanol (99.9 %), which was dehydrated with calcium oxide (95 %) freshly prepared, using sodium ethoxide as a catalyst [3]. In order to achieve a high degree of mixing of a heterogeneous system, which consists of natural oil and ethyl alcohol, a specially synthesized non-ionic emulsifier was used as a reagent. The technological features of this type of a rapeseed oil transesterification process were studied and the main characteristics of the new diesel fuels such as fractional composition and molecular mass were estimated using the chromatographic method and mass spectrometry. The yield of biodiesel from rapeseed oil increases from 85 - 90 % to 95 - 98 % without waste fraction of glycerol (10 - 15 %).

Key words: rapeseed oil, reesteriation, catalyst, sodium ethanol, biodiesel, cetane number, fractional composition, chromatography, mass spectrometry, MMP-molecular weight distribution.

Article acted received 04.09.2018; accepted for publication 15.09.2018.

Introduction

Biodiesel (BD), which is a methyl or ethyl esters of higher fatty acids, makes an alternative to petroleum diesel fuel (BF). The world DB production reaches 10 million tons and continues to increase rapidly. According to the current forecasts world biofuel production should increase to 150 million tons by 2030. Since Ukraine is poor in petroleum resources but rich in rapeseed and sunflower oil, biodiesel production is promising for our country. Biodiesel is produced by homo- or heterocatalytic transesterification of oils and fats with methanol. Germany is a leader in biofuel production while Ukraine is known as a producer of oilseeds only [1].

An increase in the cetane number of petroleum diesel can be achieved by adding a small amount of 5 - 10 % of natural oils to motor fuels [2]. But the best results are achieved when transesterification of natural oils with alcohols, which is based on the chemical reaction between triglycerides of natural oils and methanol or ethanol. This reaction is known as alcoholysis. The obtained product is a mixture of ethyl and methyl esters of fatty acids. Vegetable oils and methanol are used as

reagents for the biodiesel production. The reaction is carried out using an alkaline homogeneous catalyst. The use of bioethanol in the biodiesel production is rather difficult, since absolute ethanol must be used [3], but in this case, the main reagents for the biodiesel synthesis are natural renewable sources. Despite the fact that the cost of ethanol is higher, its use has some advantages such as better mixing than methanol and being less toxic [4]. Compared with methyl esters, ethyl esters have higher oxidation stability [5], less iodine number and the best lubricating qualities and are less aggressive to the car fuel system. In addition, the ethyl esters have lower cloud points [6], and another carbon atom increases the heat of combustion and the cetane number. Estimation of exhaust gases (determination of the amount of NO, CO₂ and soot) indicates a less negative effect of ethyl esters on the environment compared to methyl esters [7].

Usually homogeneous alkaline catalyst is used for transesterification of vegetable oils. Sodium and potassium hydroxides or their alkoxides are most commonly used. Although alkoxides are more expensive, their usage significantly reduces the amount of water produced as a result of the reaction [8]. Also homogeneous basic catalysts are highly reactive under normal conditions. On the other hand, they have certain

disadvantages as they cannot be reused and are difficult to remove from the reaction system [9]. Several authors show examples of the use of heterogeneous catalysts of vegetable oil alcoholysis - mixtures of metal oxides [10], ion exchange resins [11], heteropolyacids [12] and so on. Due to the presence of different phases during the reaction, a number of difficulties can be faced. Such a process requires more severe reaction conditions, namely higher temperatures (up to 200 °C), higher pressure (up to 25 atm.), Higher catalyst concentrations and more ethanol in ethanol/oil ratio (> 30: 1) in order to achieve the desired ester yield [13]. Although the possibility of reusing heterogeneous catalysts is one of the advantages, their activity with each use decreases. Only a few catalysts do not lose their activity [14], so industrial ethanolysis is carried out by heterogeneous catalysis. Thus, the selection of new homogeneous catalysts and technological conditions for the biodiesel synthesis by alcoholysis, is an urgent problem.

I. Experimental

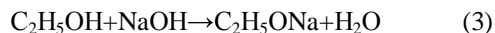
Biodiesel was obtained by transesterification of rapeseed oil (SSTU ISO 5509-2002) with absolute ethanol (to prevent the presence of additional water in the reaction system) using sodium ethoxide. Ethanol was absolved using specially-prepared calcium oxide (95% CaO). The purity of the absolute ethanol reaches 99.9% [2]. To improve the mixing of rapeseed oil with other reagents, a nonionic emulsifier was used. Sodium ethoxide is an extremely reactive compound that reacts violently with water, forming a caustic alkali and ethanol:



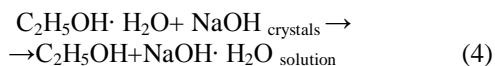
Sodium ethoxide can be synthesized by the interaction of metallic sodium with ethanol, but this reaction as a byproduct contains a strong reducing agent and flammable hydrogen, which prevents the further alcoholysis of higher fats:



Therefore, we have chosen another way of synthesis, which is based on shifting the equilibrium of the reversible reaction of sodium hydroxide with ethyl alcohol in the direction of the formation of sodium ethanol:

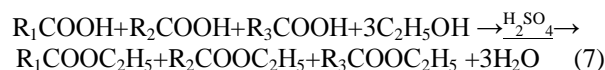
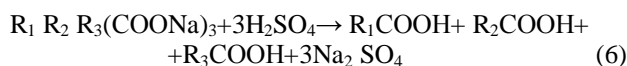
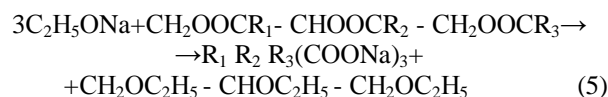


At the same time, when using 94-96% ethyl alcohol, the reaction of its absolute to 99.9% is formed with the formation of sodium crystalline hydrate:



The shifting of the equilibrium is achieved by the excess of absolved ethanol in the system and by distillation of water. The NaOH:C₂H₅OH ratio is about 1: 2-3. The reaction was carried out under laboratory conditions at a temperature of 78 – 82 °C. As a result of the reaction crystalline ethanolate is formed, which is used for the biodiesel synthesis.

Since rapeseed oil, which contains less amount of unsaturated acid residues (75 – 80 %) than sunflower (85 – 95 %), was used as raw material. An emulsifier of a noninogenic type (2 – 5 %) that makes the mixture (emulsion) of rapeseed oil and alkaline homogeneous was added to the reaction mixture. In a three-necked flask with a mechanical stirrer, a reflux condenser and a thermometer was placed rapeseed oil and crystalline sodium ethoxide. The reaction mass at constant stirring was heated to 75 – 82 °C. Subsequently, an absolute (99.9%) ethyl alcohol was added to provide an excess of ethanol to an oil at a ratio of 1: 4-6. This ratio is the most suitable for the reaction. After 1-2 hours, sulfuric acid was added to the reaction mass to neutralize the reaction mass and transfer the salts of higher fatty acids (soap) to insoluble in organic matter sodium sulfates and higher fatty acids that react with excess ethanol. The reaction proceeds in a slightly acidic medium. Synthesis can be described by the following equations:



A reaction mixture consisting of two phases was separated (the liquid phase is decanted, and solids are separated by a vacuum filtration).

The following methods were used to study the characteristics of biodiesel: a colorimetric method for determining optical density and light transmission; aerometric methods for determination of density and refractometric method for determining the refractive index. The fractional disintegration method (SSTU ISO 3924 or ASTM D 86 or EN ISO 3405) was used to determine the fractional composition of biodiesel. Chromatography with additional methanol esterification was used to determine the composition and molecular weight of the biodiesel fraction (according to DSTU ISO 5509-2002. Vegetable oils - Method for determination of fatty acid composition). Gas chromatograph "Crystal 2000M" with a fiery-ionization detector and temperature programming was used. We also used the mass spectrometric methods of MALDI-ToF and LDI-ToF matrix-activated laser desorption/ionization and laser desorption/ionization to study obtained biodiesel.

II. Analysis and discussion of research results

According to [16], rapeseed oil contains residues of more than 30 higher fatty acids, the main of which are given in Table 1.

Thus, based on the chromatographic data of rapeseed oil and biodiesel before and after additional esterification

Table 1[16]

Standardized content of fatty acid esters and glycerol in rapeseed oil of different varieties

Acid	Old sorts, %	New sorts, %	Content, %
Palmitic saturated acid C ₁₅ H ₃₁ COOH	2	2	2.5-6.0
Stearic saturated acid C ₁₇ H ₃₅ COOH	1.7	1.3	≤ 3
Oleic <u>monounsaturated</u> acid CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOH	12-16	56-65	50-67
Linoleic <u>polyunsaturated</u> acid CH ₃ (CH ₂) ₃ (CH ₂ CH=CH) ₂ (CH ₂) ₇ COOH	10-15	18-32	16-30
Linolenic <u>polyunsaturated</u> acid CH ₃ CH ₂ CH=CHCH ₂ CH=CHCH ₂ CH=CH(CH ₂) ₇ CCOOH	10-13	8-10	6-14
Arachidonic <u>polyunsaturated</u> acid C ₁₉ H ₃₁ COOH	-	-	≤ 5
Erucic <u>monounsaturated</u> acid CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₁₁ COOH	45-52	0-5	≤ 2

Table 2

Decoding of chromatogram data of rapeseed oil and biodiesel, before and after methylation with methanol using the method of DSTU ISO 5509-2002

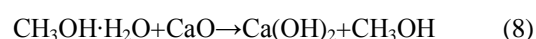
№	Asids	Boiling temperature, C°	Methoxylated rapeseed oil, %	Non- methoxylated biodiesel, %	Methoxylated biodiesel, %
0	X1- unidentified (<C ₁₀)	135-158	0.0	10.7	9.87
1	Capric acid C ₉ H ₁₉ COOH	268	0.21	0	0.001
2	Lauric acid C ₁₁ H ₂₃ COOH	298	0.23	0	0.001
3	Myristic acid C ₁₃ H ₂₇ COOH	326	0.21	0	0.001
4	Pentadecanoic acid C ₁₄ H ₂₉ COOH	339	0.23	0	0.001
5	Palmitic acid C ₁₅ H ₃₁ COOH	351	4.14	4.12	4.16
6	Stearic acid C ₁₇ H ₃₅ COOH	383	1.44	1.43	1.45
7	Oleic acid C ₁₇ H ₃₃ COOH	360	65	56.15	56.76
8	Linoleic acid C ₁₇ H ₃₁ COOH	230	18.18	17.8	17.86
9	Linolenic acid C ₁₇ H ₂₈ COOH	184	9.29	9.78	9.85
10	Arachidonic acid C ₁₉ H ₃₁ COOH	170	0.49	0.02	0.04
11	Erucic acid C ₂₁ H ₄₁ COOH	381	0.49	0.01	0.0

with methanol, we can draw some conclusions (Table 2 and Figure 1). According to Table 2, it can be concluded that the starting material contains a large number of glycerol esters and saturated and unsaturated fatty acids, with a length of the carbon chain from C₉ (caprine) to C₂₁ (erucic acid). The most detectable is olein (64.1 %) and linoleic (18.18 %), in the amount of 82.28 %. But the rapeseed oil does not contain a compound with fewer carbon atoms than C₁₀ (capric acid) with a boiling point lower than 268 °C.

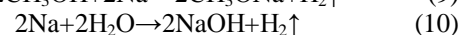
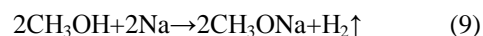
But we must take into account that the chromatograph is calibrated on the methyl esters of the corresponding acids. The chromatographic sample is

prepared according to following reactions.

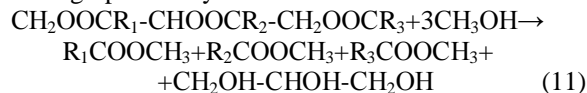
1. At first, absolutisation of methanol with calcium oxide was performed:



2. Synthesis of sodium methoxide in absolute methanol:



3. Method of methyl ester synthesis: 2-3 drops of oil are dissolved in 1.9 cm³ of hexane and add 0.1 cm³ (5-10%) of sodium methoxide solution in methanol (2 mol/l). After stirring for 2 minutes, the reaction mixture is definded for 5 minutes and filtered through a paper filter. A solution of fatty acid methyl esters is ready for chromatographic analysis



Thus, a solution of sodium methoxide in methyl alcohol (2.3 %) acts as a catalyst for transesterification

with methanol, while a by-product of glycerol is formed. Its amount can range up to 10 – 22 % .

In the experimental part it was shown that we synthesized biodiesel in another way, according to reactions 1-7. At the same time, initially, the formation of fatty acid sodium salts (soap) as it is shown in the reaction 5 and glycerin ethyl esters. After neutralizing of soap with sulfuric acid, the corresponding fatty acids are formed by reaction 6, which subsequently react with absolute ethanol and form fatty acid ethyl ester by reaction 7 (biodiesel). Since all these reactions are consistent in one reactor, after filtration and separation of

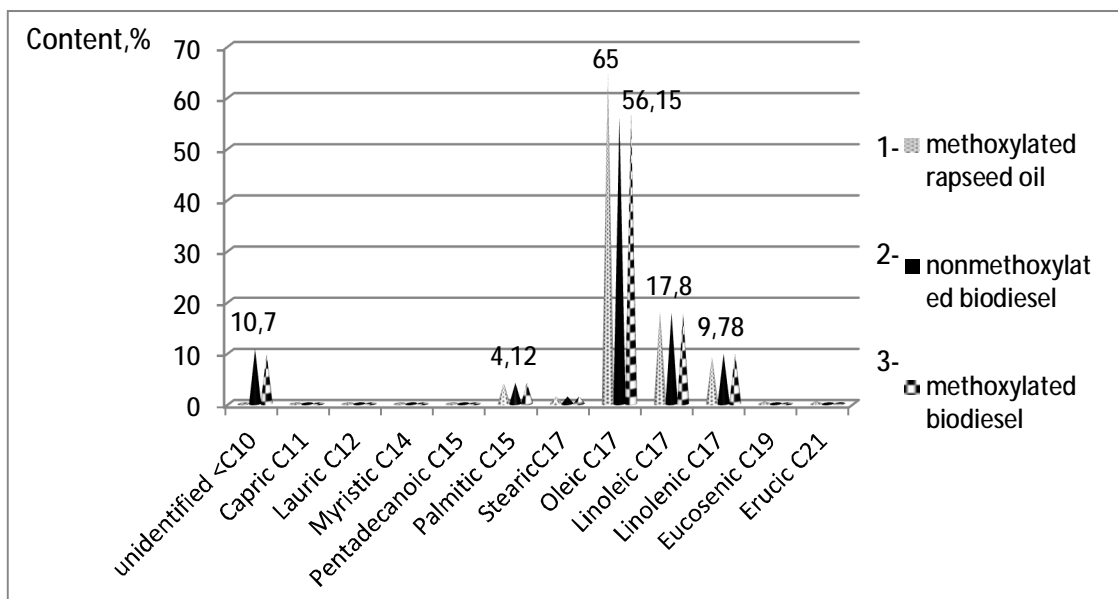


Fig. 1. Chromatographic of methoxylated rapeseed oil, nonmethoxylated biodiesel and methoxylated biodiesel.

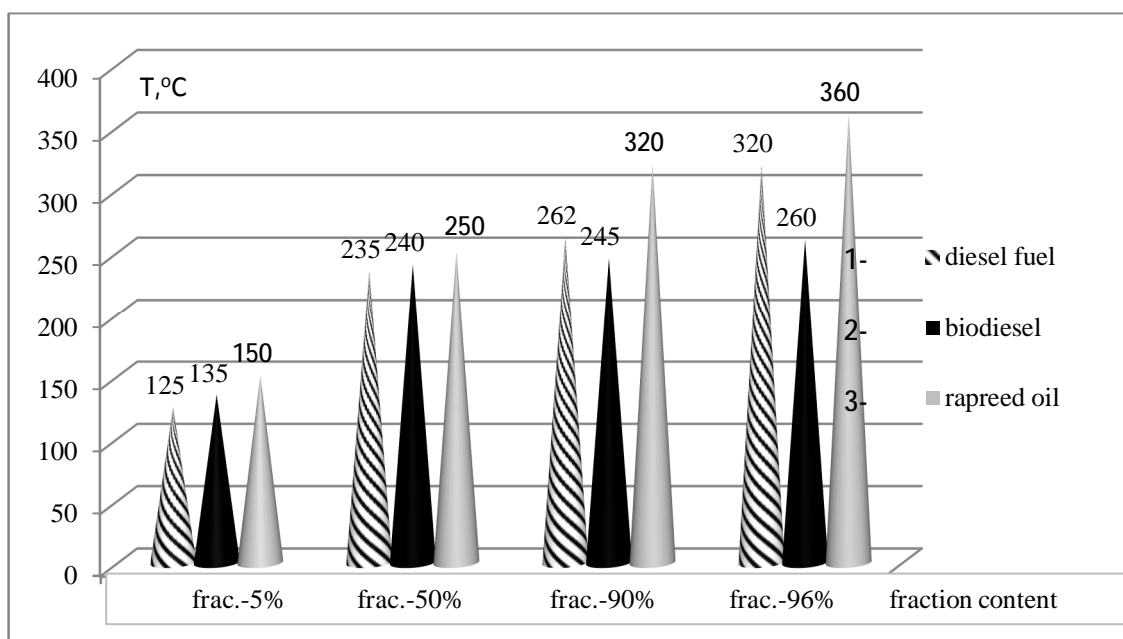


Fig. 2. Histograms of fractional composition (5% / 50% / 90% / 96%), 1-DF-oil diesel fuel, 2-BD-biodiesel, 3- rapeseed oil.

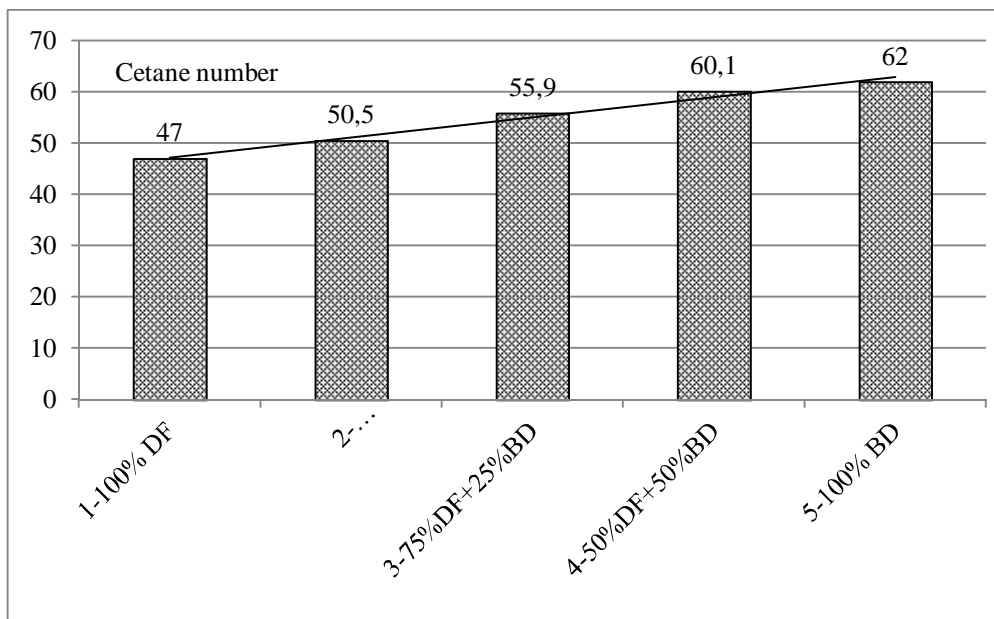


Fig. 3. Histograms of the cetane number: 1-DP - diesel fuel, 2 - diesel fuel mixture of 95% and 5% rapeseed oil, 3 mixture of BP 75% and 25% biodiesel, 4 - mixture of BP 75% and 25% biodiesel, 5 – biodiesel.

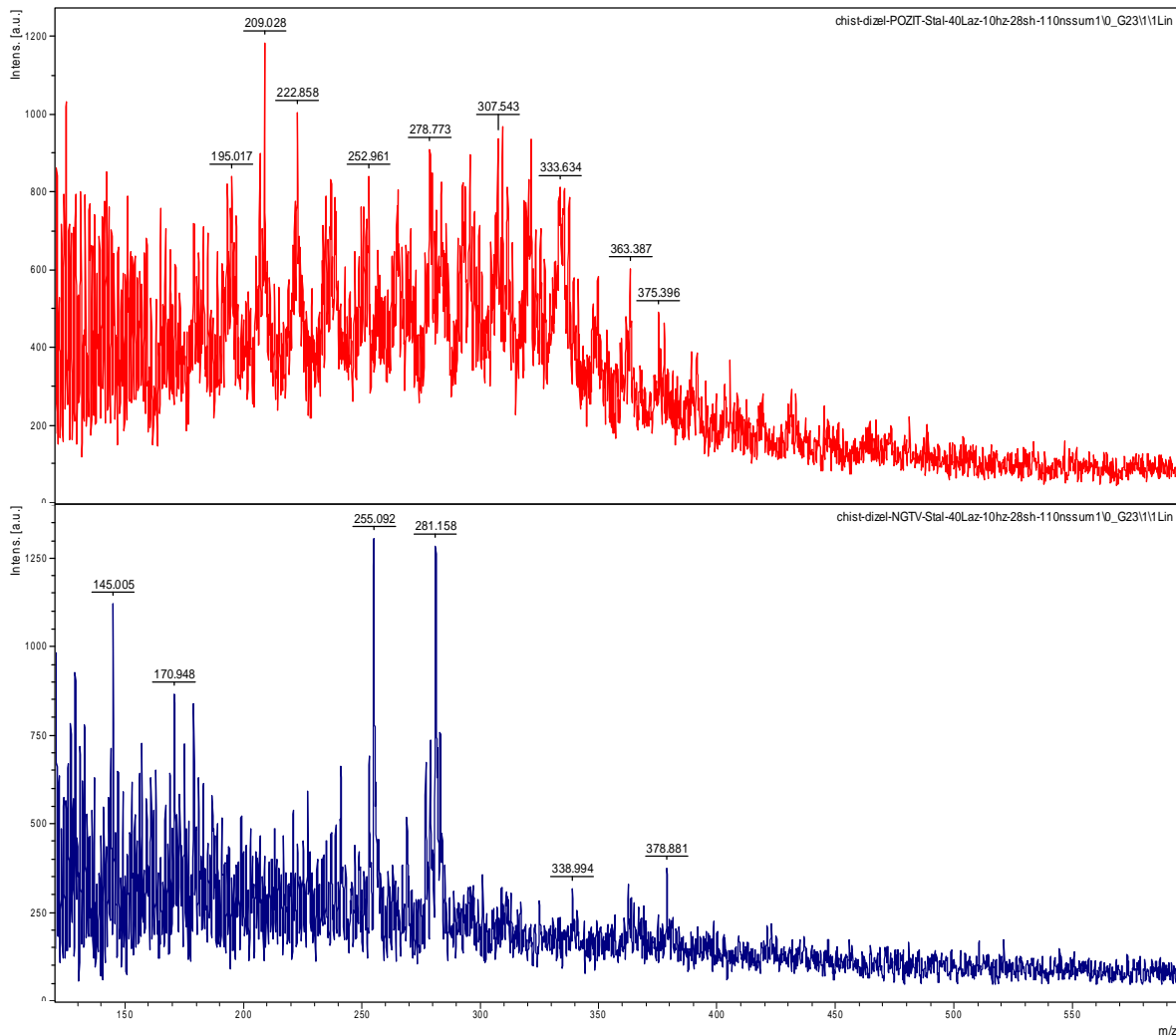


Fig.4. Mass spectrum of petroleum diesel fuel brand (DP-L49Euro-2) analyzed on the device AutoFlex II LRF 20 BrukerDaltonics (IHP NAS of Ukraine Kiev).

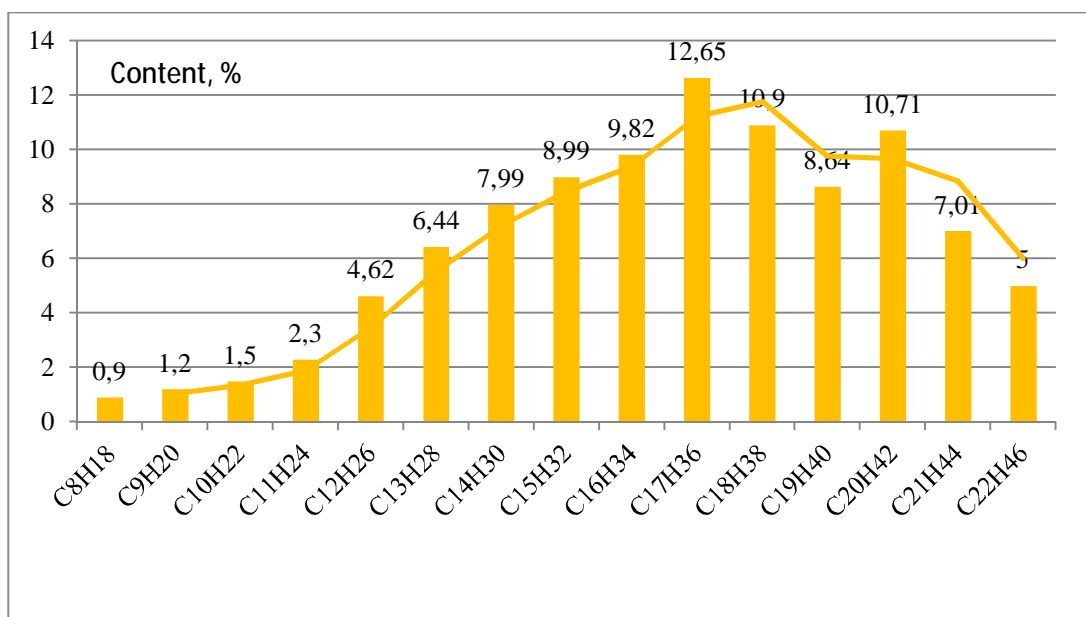


Fig. 4.1. Molecular-mass distribution of fractions of DP-oil diesel fuel on the basis of petroleum diesel oil masses) were obtained using the autoflex II mass spectrometer LRF 20 Bruker Daltonics.

Table 3

Decoding of diesel fuel mass spectra C_nH_{2n+2}

№ з/п	MM	Cn		formula	intensity index	fractional content	
		exper.	theor.			2000 од.	%
1	114	8.2	8	C ₈ H ₁₈	6.7	12.2	0,9
2	128	9.3	9	C ₉ H ₂₀	12.2	24.3	1,2
3	145	10.2	10	C ₁₀ H ₂₂	75.64	56.67	1,5
4	156	11.1	11	C ₁₁ H ₂₄	60.7	103.79	2,3
5	170	12.3	12	C ₁₂ H ₂₆	57.13	111.4	4,62
6	184	13.2	13	C ₁₃ H ₂₈	85.77	168.26	6,44
7	195	14.4	14	C ₁₄ H ₃₀	75.64	174.68	7,99
8	209	14.9	15	C ₁₅ H ₃₂	77.1	196.463	8,99
9	222	16.1	16	C ₁₆ H ₃₄	92.85	236.768	9,82
10	240	17.4	17	C ₁₇ H ₃₆	96.13	294.503	12,65
11	255	18.2	18	C ₁₈ H ₃₈	77.84	226.63	10,9
12	268	18.8	19	C ₁₉ H ₄₀	67.84	208.269	8,64
13	281	20.2	20	C ₂₀ H ₄₂	91.73	289.378	10,71
14	296	21	21	C ₂₁ H ₄₄	21.42	172.614	7,01
15	307	22.12	22	C ₂₂ H ₄₆	46.42	112.969	5,00
16	324	23.3	23	C ₂₃ H ₄₈	31.26	17.225	1,33
Σ	128-324	9-27		C ₈₋₂₃ H ₁₈₋₄₈	6.7-96.13	1406.119	100

insoluble sulfates, we obtain a homogeneous mixture of rapeseed fatty acid ethyl esters and glycerol ethyl ethers, which can also be used as biodiesel, since they have similar characteristics.

To confirm this, we conducted a chromatographic analysis of this biodiesel, processed the data and obtained the following results, which are presented in Figure 1. The most obvious difference in the composition of rapeseed oil and obtained biodiesel is evident in the re-esterification of ethanol under the specified conditions. So the content of ethanol and oleic acid esters-56.15 % in biodiesel is 10.85 % less than in the raw rapeseed oil (65%). At the same time, on the chromatogram, a peak of new unidentified substances appears (10.7 %, $T_{cp} =$

135 -158 ° C), before capric acid (C11, $T_{boiling} = 268$ °C), (Table 2, Fig. 1). Moreover, this substance does not disappear even after additional methoxylation of our biodiesel with methyl alcohol Tab.2. and (fig.1, p.3). Ssynthesized biodiesel can contain simple glycerol ethyl ethers with boiling points below 250 °C. All other components in three samples are almost the same (Table 2, Fig. 1)

As can be seen from Fig. 2, biodiesel (curve 2) actually contains only two fractions (5% distilled at 135 °C, which confirms our assumptions about the possible content of glycerol ethyl ethers with a boiling point = 135 - 158 °C.

All other fractions are also distilled at the same

temperature: 50 % at 240 ° C, 90 % at 245 ° C, 96 % at 260 °, which confirms our previous assumptions about the two main fractions of our biodiesel. In contrast, oil diesel and rapeseed oil consist of at least 3 to 4 fractions, the latter being distilled at significantly higher temperatures of 320 - 360 ° C

Biodiesel must meet DSTU 6081: 2009 "Motor fuels. Methyl esters of fatty acids, oils and fats for diesel engines. Specifications". This standard is harmonized with European Standard EN 14214: 2003. According to this standard, the cetane number of diesel fuel should be equal to 45-60 units. Therefore, we measured the cetane

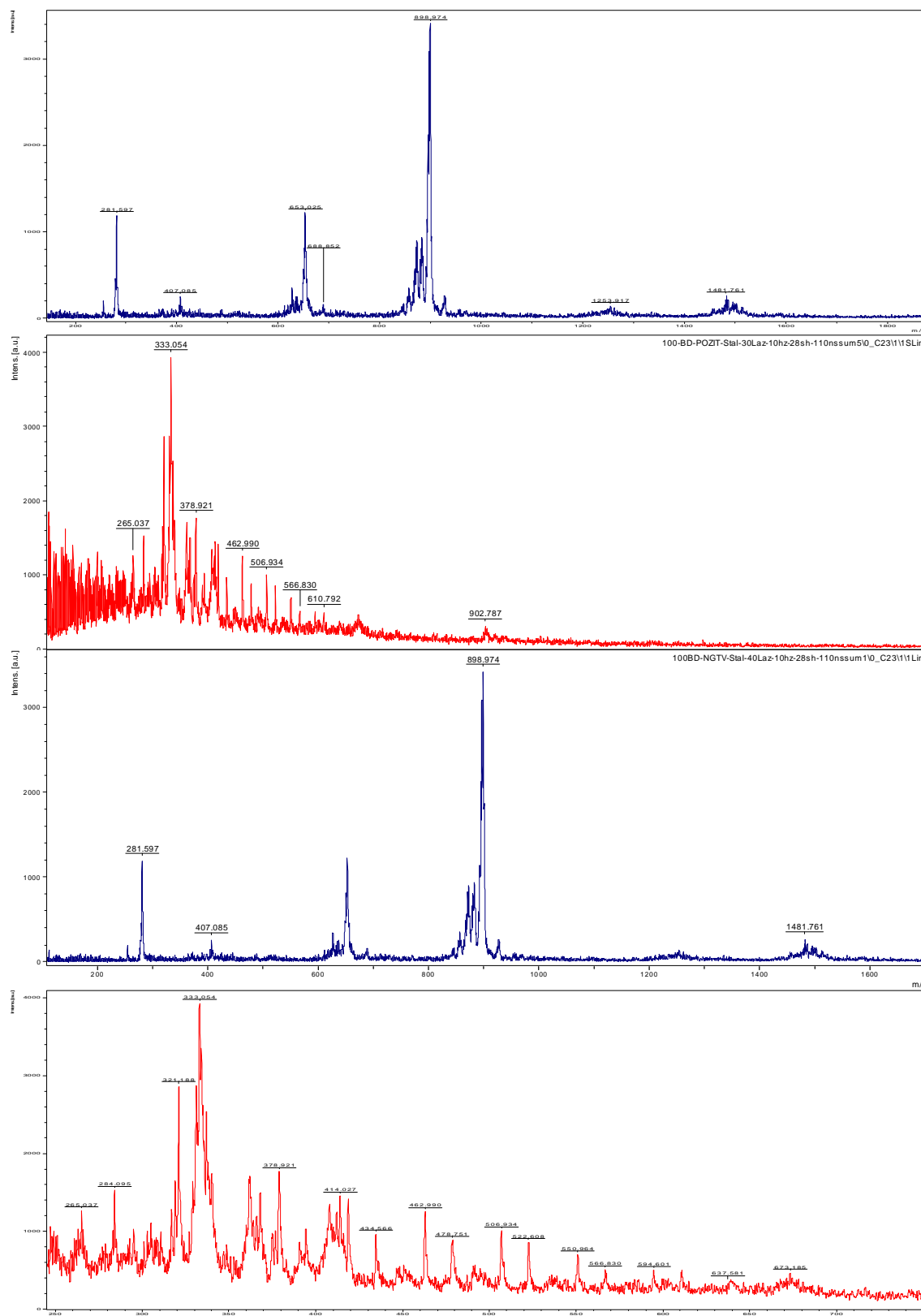


Fig. 5. Mass spectrum of biodiesel, synthesized by re-esterification of rapeseed oil with ethanol, analyzed on the device Autoflex II LRF 20 BrukerDaltonics (IHP NAS of Ukraine Kiev).

Table 4

Decoding of biodiesel fuel mass spectra $C_nH_{2n+1}COOC_2H_5 + CH_2CHCH_2(OC_2H_5)_{1-3}$.

№ з/п	MM	Cn		Formula	Intensity index	Fractional content	
		Exper.	Theor.			1000 оД.	%
1	135	5	5	$OHCH_2CHOHCH_2OC_2H_5$	7	32.7	3,2
2	147	7	7	$OHCH_2CHCH_2(OC_2H_5)_2$	5	19.21	1,8
3	159	9	9	$OHCH_2CHCH_2(OC_2H_5)_3$	6	50.3	5,0
4	265-284	15	15	$C_{15}H_{28-31}COOC_2H_5$	12	49.88	4,9
5	298-333	16.85	17	$C_{17}H_{30-33}COOC_2H_5$	82	847.7	84,7
6	340	19.21	19	$C_{19}H_{38}COOC_2H_5$	4	10.6	0,1
7	378	21.29	21	$C_{21}H_{42}COOC_2H_5$	3	12.3	0,2
8	394	23.79	23	$C_{23}H_{45}COOC_2H_5$	2	0.71	0,06
9	422	25.07	32	$C_{25}H_{49}COOC_2H_5$	2	0.11	0,01
10	434	27.07	34	$C_{27}H_{53}COOC_2H_5$	2	0.56	0,05
11	462	29.79	43	$C_{29}H_{57}COOC_2H_5$	1	0.16	0,01
12	506	31.21	59	$C_{31}H_{61}COOC_2H_5$	2	0.74	0,07
Σ	135-506	15-59		$C_{5-31}H_{31-61}COOC_2H_5$ $CH_2CHCH_2(OC_2H_5)_{1-3}$	1-82	1025.9	100

Table 5

Decoding of mass spectra of rapeseed oil $(C_nH_{2n+1}COO)_3OCH_2OCHOCH_2$ for synthesis biodiesel

№	MM	Cn	Formula	Intensity index	Fractional content	
					1000 оД.	100%
1	179	1	$(CH_3CO)_3OCH_2OCHOCH_2$	1.2	12.2	0.6
2	216	2	$(C_2H_4-5CO)_3OCH_2OCHOCH_2$	6	12.9	0.91
3	248	3	$(C_3H_5-6CO)_3OCH_2OCHOCH_2$	7	12.4	0.9
4	281	4	$(C_4H_7-9CO)_3OCH_2OCHOCH_2$	5	15.2	0.7
5	320	5	$(C_5H_9-11CO)_3OCH_2OCHOCH_2$	35	136.0	3.3
6	664	15	$(C_{15}H_{28-31}CO)_3OCH_2OCHOCH_2$	45	180.2	10.79
7	885	17	$(C_{17}H_{30-33}CO)_3OCH_2OCHOCH_2$	88	416.65	68.0
8	905	19	$(C_{19}H_{35-37}CO)_3OCH_2OCHOCH_2$	64	262.0	14.3
9	1055	21	$(C_{21}H_{42-43}CO)_3OCH_2OCHOCH_2$	2.0	20	0.5
Σ	179-962	1-19	$(C_{1-21}H_{3-43}CO)_3OCH_2OCHOCH_2$	1.2-88	1151.55	100

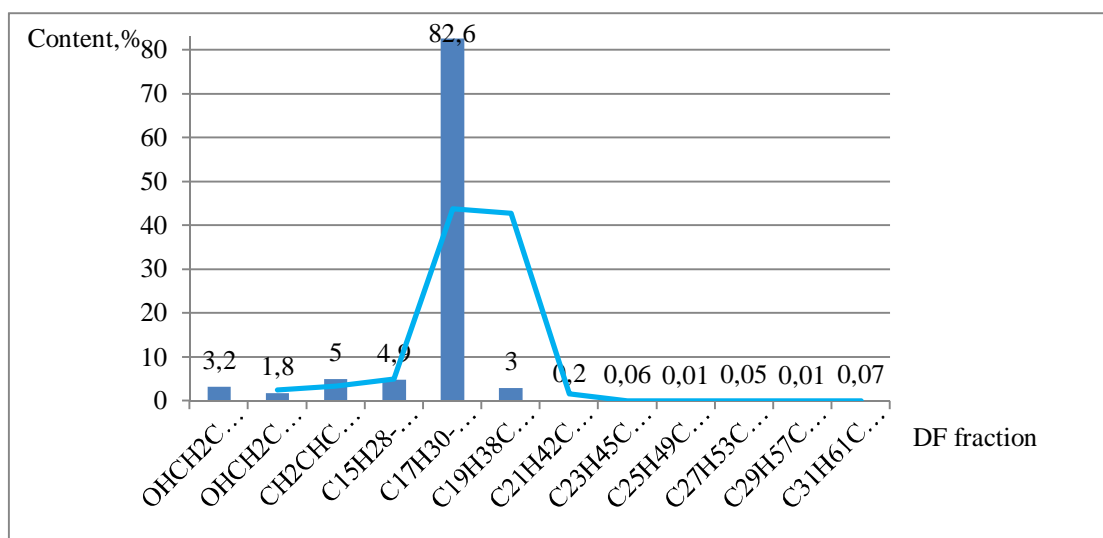


Fig. 5.1. Molecular mass distribution of biodiesel fractions (tab.4) basing of mass spectra of biodiesel, analyzed on the mass spectrometer Autoflex II LRF 20 Bruker Daltonic.

number of biodiesel and its mixtures with oil diesel, presented in Fig. 3. The cetane numbers of 4 samples of

biodiesel (BD) were measured in different ratios in the mixtures with petroleum diesel fuel (BF) (25:75 and

50:50), as well as a mixture of DF with rapeseed oil (95: 5) and compared with cetane number of petroleum diesel fuel without an additives (Fig. 3). Even adding 5 % of peeled rapeseed oil increases cetane number of oil

diesel to 50.5. Adding 25 % of biodiesel (DB) to petroleum diesel fuel (DB) can increase the cetane number to 55.9. The greatest value of the cetane number can be

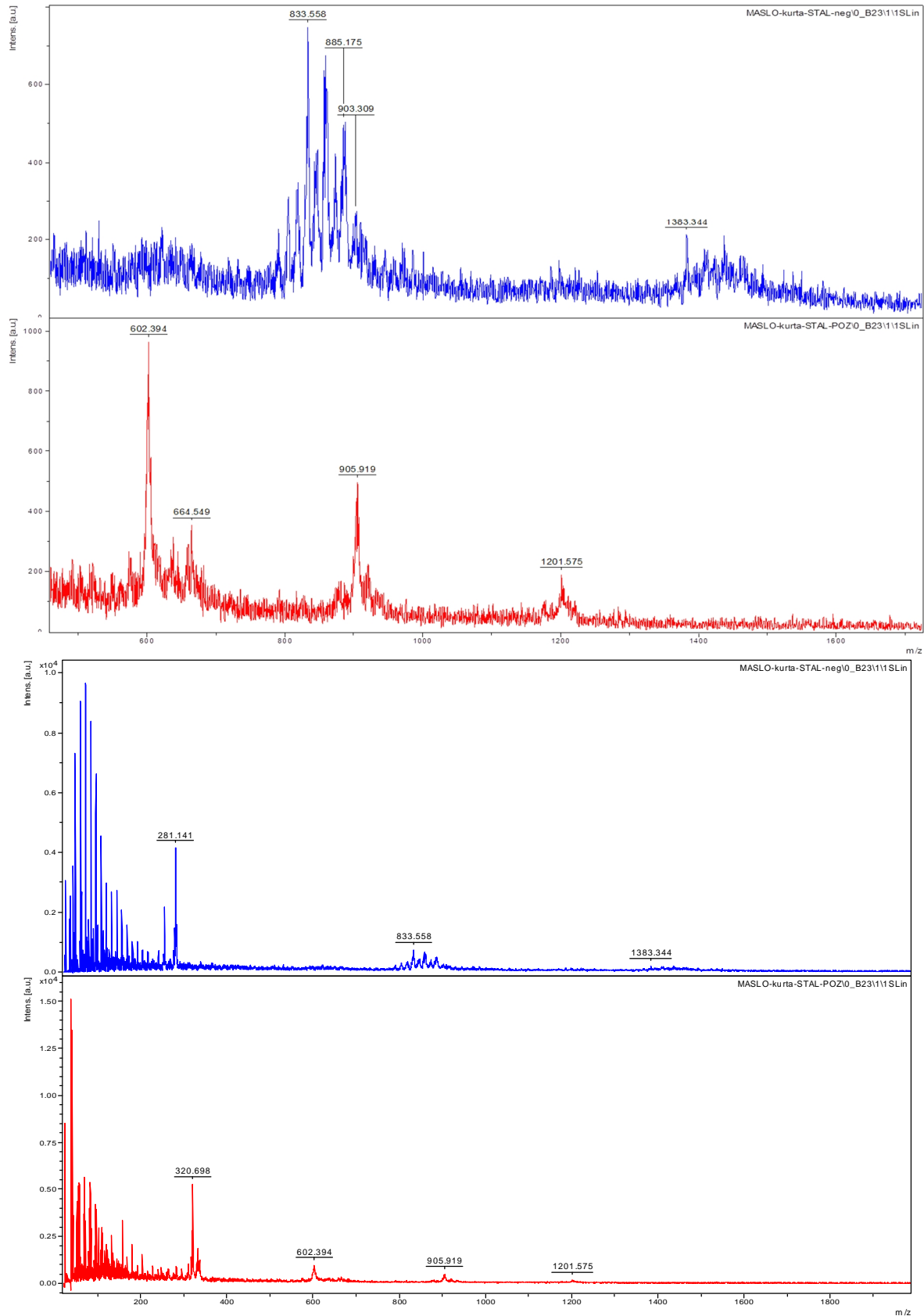


Fig. 6. MAS spectra of rapeseed oil at the attachment of Autoflex II LRF 20 BrukerDaltonics (IHP NAS of Ukraine Kiev).

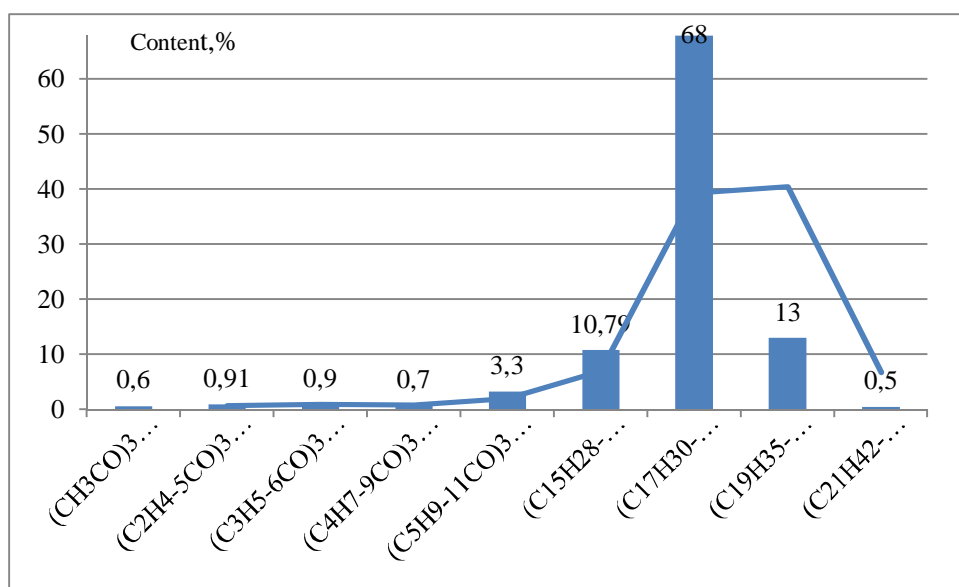


Fig. 6.1. Molecular mass distribution of rapeseed oil fractions based on MAS spectra of rapeseed oil, which are stacked on a mass spectrometer Autoflex II LRF 20 BrukerDaltonics.

achieved by introducing up to 50 % of biodiesel, with the cetane number reaching 60.1, and with 100 % biodiesel content, the cetane number of motor fuel can exceed 62 units, that is, to become of the highest quality and efficiency.

molecular mass and molecular mass distribution of petroleum diesel fuel (DF), and its comparison with the molecular mass distribution of biodiesel (BD) and rapeseed oil (RO) (Fig. 4 , 5.6) and a decoding for the mass spectrum (tab.3.4.5.).

According to Fig. 4 and Fig. 4.1. diesel fuel mass spectra (Table 3), we can conclude that the total molecular mass of diesel fuel fractions make up 70% of saturated hydrocarbons (70%) with the length of the carbon chain (C₁₄-C₂₀) and the molecular weight of 195-281. The molecular weight of the remaining fractions (15 %) below 190 is one (C₁₄), and the molecular weight of 13% fractions is greater than 290 (C₂₀). That is, in the oil sector, we have clearly pronounced 3-4 fractions. Consequently, diesel fuel has a semi-dispersed distribution of molecular weight, which shows the MMP curves in Fig. 4.,4.1. Mass spectra of biodiesel are shown in Fig. 5 and decoded in Table 4.

As can be seen from Table 4 and Fig. 5, the main composition of fractions of biodiesel (89.6 %) is in the range of complex ester with a length of the chain C₁₅-C₁₉ with a molecular weight of biodiesel MMPC₁₅-C₁₇ = 265-340, which is similar to the DP. But biodiesel contains a low molecular weight fraction (10 %) of simple mono- and tri-ethylates of glycerin with a length of the carbon chain C₅-C₉ and a molecular weight of MM = 135 - 159, which is very different from oil diesel fuel (DP), where these fractions in 2 times less (Fig. 4, Table 3). In this case, the high-molecular fraction of C₂₁-C₃₁ in biodiesel is almost-0.32 %.

If we compare the mass spectra of biodiesel and the raw rapeseed oil (Fig. 6 (Fig. 6.1) Table 5), on the basis of which it was synthesized, then in oil we can see up to

93 % of the sum of fractions with length of chain C₁₅-C₃₂ with molecular weight MMC₁₅-C₁₇ = 664 - 1055, which is much higher than in biodiesel by content (89 %) and molecular weight MMBDP = 265-333 (Fig. 5, Table 4).

Molecular mass distribution of rapeseed oil (Fig. 6) shows the presence of three fractions in rapeseed oil C₁₅-C₁₉, boiling at 320 - 360 °C (Fig. 2). This confirms our assumption that our synthesized biodiesel is more mono-dispersed (content of fraction C₁₇ = 82 %), which is seven times more than the content of the same fraction in diesel fuel (12 %). Therefore, the DB has a significantly higher cetane number and combustion efficiency in the automobile engine than the DP, as shown earlier by us in Fig. 3.

Conclusions

1. Thus, it can be construed that with the proposed improved method of re-esterification has several advantages and allows to obtain a new product of biodiesel with unique characteristics.

2. Based on the conducted researches, it was shown that the composition and structure of synthesized biodiesel is significantly different from the composition of the rapeseed oil in the direction of obtaining a more homogeneous composition (2 main fractions-89.6 %) and monodispersed by molecular weight MM BDF C₁₅-C₁₇ = 265 - 333, than petroleum diesel fuel DF (3-4 fractions - 95 %) with a molecular weight MM DF C₈-C₂₃ = 114-324.

3. The main difference between the BDF and the DF is the presence in the BDF of the low molecular weight fraction of mono-, di- and triethylates of glycerol. This significantly increases the cetane number of BDF = 62 in comparison with DF = 47, and the cetane number of mixed compositions DF with rapeseed oil DP\5% rapeseed oil = 50,5, and mixed compositions DF with

BDF, 50DF / 50BDF = 60.1.

3. Thus, on the basis of the obtained results, we confirmed the chemistry and mechanism of the process of re-esterification of rapeseed oil by sodium ethoxide sequentially in alkaline and acidic media, which is described in the work of reactions No.3-7.11, which as a result make it possible to increase the yield of biodiesel from 85 - 90 % in the classical way, up to 95 - 98 % without 10 - 15 % waste from the glycerine fraction, which remains in the form of biodiesel in the form of mono-di- and triethylates of glycerol.

Kurta S.A. - Dr.Sc. Professor of the Department of Chemistry of the Faculty of Natural Sciences;
Ribun V.S. - post-graduate student of the Department of Chemistry;
Hromoviy T. Yu. - Ph.D. chem. Sciences. Laboratory of Mass Spectrometry of Surface of Nanosystems;
Khatsevich O.M. -- Ph.D., Associate Professor, Department of Chemistry, Faculty of Natural Sciences.

- [1]. L. K. Patrylyak, K. I. Patrylyak, M. V. Okhrimenko et al., *Catalysis and petrochemistry*, 20 (2012) 39-44.
- [2]. S. A. Kurta , V. S. Ribun, *Science Review: Scientific Educational Center Warsaw, Poland*, 7 (2017) 4-8.
- [3]. V. Starchevsky, V. Ribun, S. Kurta, O. Khatsevich, *Chemistry & chemical technology*, 8(3) (2018) 346-354.
- [4]. J. M. Encinar, J. F. Gonzalez, J. J. Rodrigues, A. Tegedor, *Energy and Fuels*, 16 (2002) 443-445.
- [5]. J. Cvengros, J. Paligova, Z. Cvengrosova, *European journal of Lipid Science and Technology*, 108 (2006) 629-635.
- [6]. H. Joshi, B. R. Moser, J Toler, T. Walker, *Biomass and bioenergy*, 34 (2010) 14-20.
- [7]. D. C. Drown, K. Harper, E. Frame, *Journal of the American Oil Chemist's Society*, 78 (2001) 579-584.
- [8]. O. S. Stamenkovic, O. V. Velickovic, V. B. Veljkovic, *Fuel*, 90 (2011) 3141-3155.
- [9]. G. Vicente, M. Martinez, J. Aracil, *Bioresource technology*, 92 (2004) 297-305.
- [10]. N. Saravanan, S. Puhan, G. Nagarajan, N. Verdaraman, *Biomass and Bioenergy*, 34 (2010) 999-1005.
- [11]. S. Benjapornkulaphong, C. Ngamcharussrivichai, K. Bunyakiat, *Chemical Engineering Journal*, 145 (2009) 468 – 474.
- [12]. F. R. Abreu, M. B. Alves, C. C. S. Macedo, L. F. Zara, P. A. Z. Suarez, *Journal of Molecular Catalysis A*, 227 (2005) 263-267.
- [13]. N. Shibasaki-Kitakawa, H. Honda, H. Kuribayashi, T. Toda. T. Fucumura, T. Yonemoto, *Bioresource technology*, 98 (2007) 416-421.
- [14]. G. J. Suppes, M. F. Dasari, E. J. Doskocil, P. J. Mankidy, M. J. Goff, *Applied Catalysis A: General*, 257 (2004) 213-223.
- [15]. W. Charusiri, W. Yongchareon, T. Vitidsant, *Korean Journal of Chemical Engineering*, 23 (2006) 349-355.
- [16]. *Pharmaceutical Encyclopedia, Rapeseed Oil*. <https://www.pharmencyclopedia.com.ua/article/1122/ripak>

В.С. Рібун¹, С.А. Курта¹, Т.Ю. Громовий², О.М. Хацевич¹

Удосконалення технології синтезу та властивості біодизельного палива

¹ДВНЗ «Прикарпатський національний університет імені Василя Стефаника» м. Івано-Франківськ,
вул. Галицька 201/320, kca2014@ukr.net, ribun.vika@gmail.com;

²Лабораторія мас-спектрометрії поверхні наносистем Інституту хімії поверхні НАН України м. Київ
вул. Генерала Наумова 17, grotu@ukr.net

Існуючі технології синтезу активних присадок до моторних палив досить складні. Тому удосконалення технології синтезу біодизельного палива з метою покращення цетанового числа та інших показників дизельного палива з добавками біодизелю є надзвичайно важливою проблемою. Сировиною для виготовлення біодизелю слугують рослинні олії, метиловий та етиловий спирти та лужні або кислотні каталізатори. Використання етилових естерів вищих жирних кислот ріпакової олії в якості біодизелю має ряд переваг порівняно з використанням метилових естерів. Тому в даній роботі біодизель був отриманий шляхом переестерифікації ріпакової олії абсолютизованим етанолом (99,9 %) за допомогою спеціально прокаленого оксиду кальцію (95%) та з використанням етаноліату натрію, як реагенту. Для досягнення високого ступеню змішування гетерогенної системи олії з етиловим спиртом при переестерифікації використали спеціально синтезований неіоногенний емульгатор. Було вивчено технологічні особливості такого процесу переестерифікації ріпакової олії та проведена оцінка якості головних експлуатаційних характеристик нових дизельних палив, їх фракційного складу та молекулярної маси за допомогою хроматографічного методу та мас-спектрометрії. Вихід біодизеля з ріпакової олії при цьому зростає з 85 - 90 % за класичним способом до 95 - 98 % , без 10 – 15 % відходів гліцеринової фракції.

Ключові слова: ріпакова олія, переестерифікація, каталізатор, етаноліат натрію, біодизель, цетанове число, фракційний склад, хроматографія, мас-спектрометрія, ММР-молекулярно-масовий розподіл.