

CHEMMOTOLOGY

ALTERNATIVE FUELS OF PLANT ORIGIN. DETERMINATION OF FRACTIONAL AND CHEMICAL COMPOSITIONS

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The fractional compositions of fatty acid methyl esters from rape and sunflower oils were determined by the method in GOST 2177–99. The data obtained can be used to calculate the characteristic temperatures and thermophysical parameters of biofuels. The difference in the boiling points of the esters and their vapors was established. The ingredients of the biofuels and their fractions were determined by gas-liquid chromatography. Fuels of plant origin evaporate in a narrow temperature range so that the fatty acid methyl esters are distributed very unevenly over all fractions. The results obtained can be used to create an adequate mathematical model of evaporation of biofuel in the diesel cylinder.

The physicochemical properties of fuels, particularly the chemical composition, have a large effect on the environmental and economic characteristics of diesels. The following groups of hydrocarbons are contained in traditional petroleum diesel fuels as ingredients: paraffins, naphthenes, olefins, dienes, and aromatics [1]. The volatility, boiling point, cetane number, ignition lag time, and dynamics and efficiency of combustion are essentially a function of the group hydrocarbon composition.

The molecules of alternative fuels of plant origin – lube oils and their derivatives – have a slightly different structure. Plant oils consist of fatty acid glycerin esters [2]. They all contain triglycerides, which are mono-, di-, or tribasic as a function of the composition of the fatty acids forming them.

Table 1

Indexes	Rapeseed oil [3]	Rapeseed oil triglycerides	Erucic acid methyl ester	ROME [3]
Approximate overall formula	$C_{57}H_{101.6}O_6$	$C_{61}H_{108}O_6$	$C_{23}H_{44}O_2$	$C_{19}H_{35.2}O_2$
Molecular mass, kg/kmole	883	961	352	296
Heat value (low),* MJ/kg	36.7	37.3	38.6	37.1
Cetane number	~44	–	–	52–56
Density at 15°C, kg/m ³	916	–	–	882
Viscosity at 20°C, mm ² /sec	75	–	–	6–8
Note.	*Determined with the D. I. Mendeleev equation.			

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Table 2

Indexes	SOME	RME	ROME		EMKOR-I	EMKOR-II	Diesel fuel (winter)
			vapor phase	liquid phase			
Density at 20°C, kg/m ³	886	877	–	882	880	877	830
Distillation, °C							
IBP	–	–	325	355	323	310	158
5%	–	325	330.5	356	329	–	–
10%	332	303	333	358	335	330	199
30%	335.5	335.5	334.5	363	337.5	335	245
40%	–	–	335.5	368	–	–	–
50%	337	337	337.5	375	340	337	258
60%	–	–	340.5	388	–	–	–
70%	339	339.5	343	416	345	341.5	288
80%	–	–	344	–	–	–	–
90%	–	345	314	–	352	348	313
97.5%	–	–	–	–	348	354	330*
θ , °C/%	0.117	0.108	0.167	–	0.167	0.192	1.52
$t_{av,v}$, °C	336	336.3	337	–	339.4	336	248
Note.	96% distills off.						

The physicochemical properties of the rapeseed oil used as fuel [3] and the triglycerides in it, whose molecules contain fatty acid radicals: erucic C22:1, oleic C18:1, and linoleic C18:3, are reported in Table 1. With respect to some of them (molecular weight, lowest heat of combustion, etc.), rapeseed oil is similar to heavy fuels for marine diesels.

Alternative fuels based on rapeseed oil fatty acid methyl esters (ROME) have become more common [3, 4]. They are obtained by transesterification of rapeseed oil triglycerides with methanol in the presence of a catalyst [2]. Some physicochemical properties of erucic acid methyl ester and ROME are reported in Table 1.

Let us determine the distillation cut points – one of the fundamental properties of a fuel on which its ability to form a fuel-air mixture in the diesel's cylinder depends [5].

Fatty acid methyl esters are distilled at a residual pressure of 0.133-0.399 kPa [2], which decreases the boiling point of the esters to values at which thermal decomposition does not occur. The decomposition zone of palmitic and stearic acid methyl esters is defined by a temperature of 202-207°C and pressure of 2.66-5.32 kPa [6].

Let us examine the results of determining distillation of rapeseed oil fatty acid methyl esters (ROME) and Ukrainian sunflower oil fatty acid methyl esters (SOME) and RME biofuel manufactured in Germany. As noted in [7], the thermophysical properties of fuels can be calculated with the distillation results after determining the volume-average $t_{av,v}$, weight-average $t_{av,w}$ and mole-average $t_{av,m}$ distillation temperatures and the average values t_{av} of these temperatures.

The volatility and individual performance characteristics of fuels are usually evaluated with the method in GOST 2177–99. In distillation of methyl ester compositions, the conditions (water temperature in the condenser, heating rate, temperature correction for ambient pressure, etc.) corresponded to the GOST.

In determining the distillation of ROME, a thermocouple was additionally placed in the flask for distillation at a distance approximately 15 mm from the bottom, which ensured determination of the distillation temperature of 0 to 70% of the esters. The distillation results are reported in Table 2. The fractional compositions of the Polish ester EMKOR (rapeseed oil acid methyl ester) used as an additive to BIODIESEL diesel fuel [8] and winter diesel

Table 3

Fraction of distillation of fuel, %	Δt_m , deg	Δt_a , deg
IBP	30	15.5
5	25.5	16.3
10	25	17.2
20	–	20.3
30	28.5	23.6
40	32.5	24.9
50	37.5	24.9
60	47.5	25.7
70	73	25.1

fuel DZ are also reported there [5]. According to DSTU 3868–99 (Ukraine), winter diesel fuel should have the following physical properties: density $\leq 840 \text{ kg/m}^3$ at 20°C , distillation: 50% at $\leq 280^\circ\text{C}$, 96% at $\leq 370^\circ\text{C}$.

In analyzing the fractional distillation data for SOME, RME, ROME, and EMKOR, we note that the fatty acid methyl esters distill in a very narrow temperature range: $325\text{--}350^\circ\text{C}$, similar to the temperature range of distillation of narrow crude cuts. When a temperature of 325°C is attained near the steam pipe, approximately 85% of DZ fuel distills off.

The distillation curve is frequently used for calculating some physical properties of fuels [5, 7]. The $t_{av.v}$ and slope θ of the fractional distillation curve calculated with the following equations are reported in Table 2 for fuels of plant and petroleum origin:

$$t_{av.v} = \frac{t_{10} + t_{30} + t_{50} + t_{70}}{4}$$

$$\theta = (t_{70} - t_{10}) / 60$$

where t_{10} , t_{30} , t_{50} , t_{70} are the distillation temperatures of 10, 30, 50, and 70 vol. % of the fuel, determined with the fractional distillation curve.

By analogy with petroleum fuels [5, 7], knowing $t_{av.v}$, $t_{av.w}$, $t_{av.m}$, and t_{av} can be found with the corresponding temperature corrections. As Table 2 shows, for SOME, RME, and ROME fuels, the value of θ varies from 0.108 to $0.167^\circ\text{C}/\%$, which allows estimating the correction [7, Figs. 1-36] as equal to zero in a first approximation and writing:

$$t_{av.v} \approx t_{av.m} \approx t_{av.mol} \approx 336.5^\circ\text{C}$$

For petroleum fuels, some of their physical properties – specific heat capacity, enthalpy, etc. – can be represented as a function of factor K , which determines the chemical nature of the petroleum product [5, 7].

We will determine factor K for biofuel with the equation:

$$K = 1.216 \sqrt[3]{t_{av}} / \rho_{15}^{15}$$

where

$$\rho_{15}^{15} = \rho_4^{20} + 5\beta$$

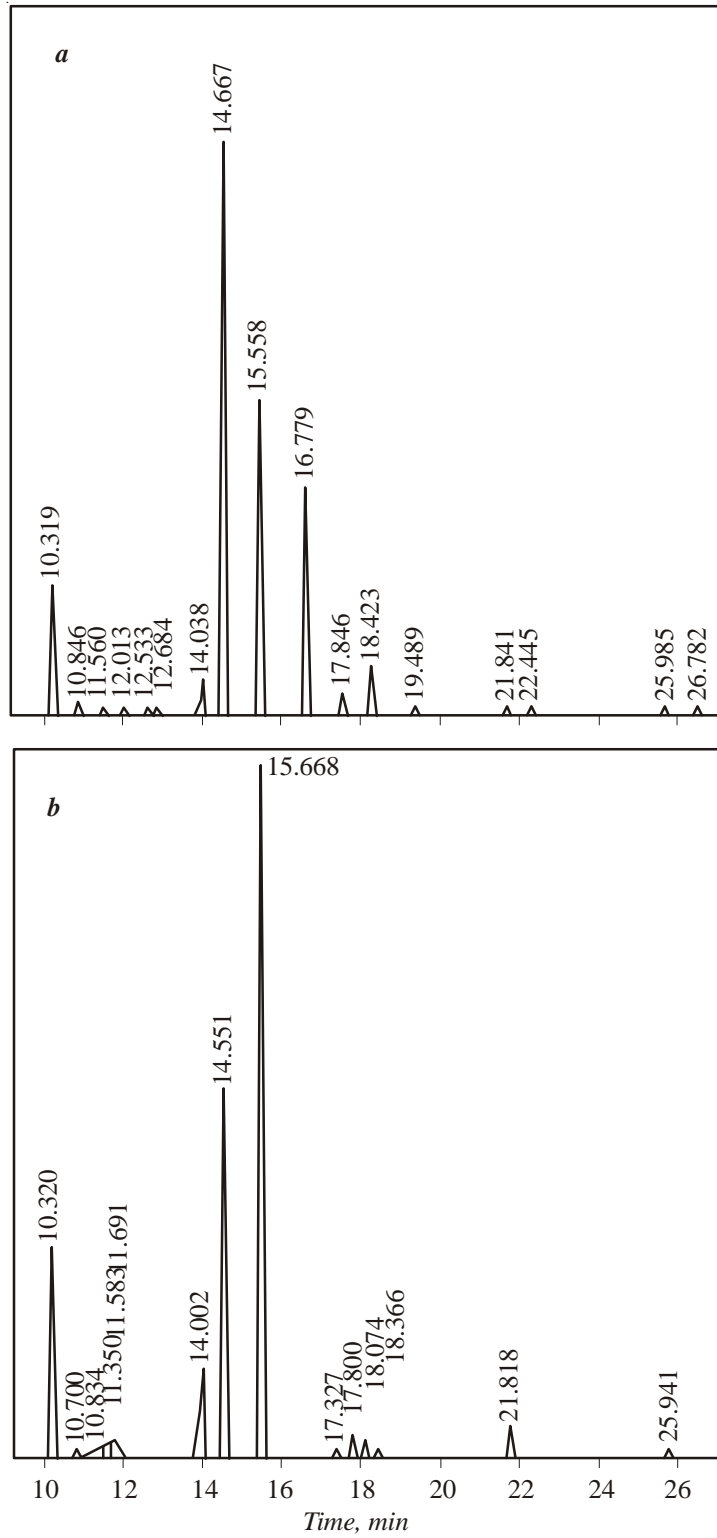


Fig. 1. Chromatograms of RME (a) and SOME (b) biofuels.

$$\beta = (18.28 - 13.2\rho_4^{20})10^{-4}$$

At $r_{20} = 877\text{-}886 \text{ kg/m}^3$ and $t_{av} = 336.5^\circ\text{C}$, $K = 11.6\text{-}11.7$, which is close to the values for naphthene-base petroleum products.

The curves of the difference in the liquid and vapor (around the steam-diversion pipe) as a function of the distillation fraction are shown in Table 3: biofuel Δt_m and diesel fuel Δt_d [8]. For diesel fuel, this difference increases monotonically in the segment from the initial boiling point (IBP) to distillation of 40% of the fuel from 15.5 to 24.9°C, and then remains constant.

For ROME, Δt_m is higher and is constant ($\sim 25^\circ\text{C}$) in the segment from the initial boiling point to distillation of 20% of the fuel and then monotonically increases to 73°C in distillation of up to 70% of the fuel. This is due to the heavier fractional composition and lower volatility of the ROME composition, so that higher temperatures and a larger amount of heat are required for its conversion from the liquid to the vapor state in injection.

During fractional distillation of ROME, SOME, and RME, samples of the 0-10, 10-50, and 50-90% cuts were collected. These samples and samples of the biofuels were analyzed on a Shimadzu GC-14B chromatograph using

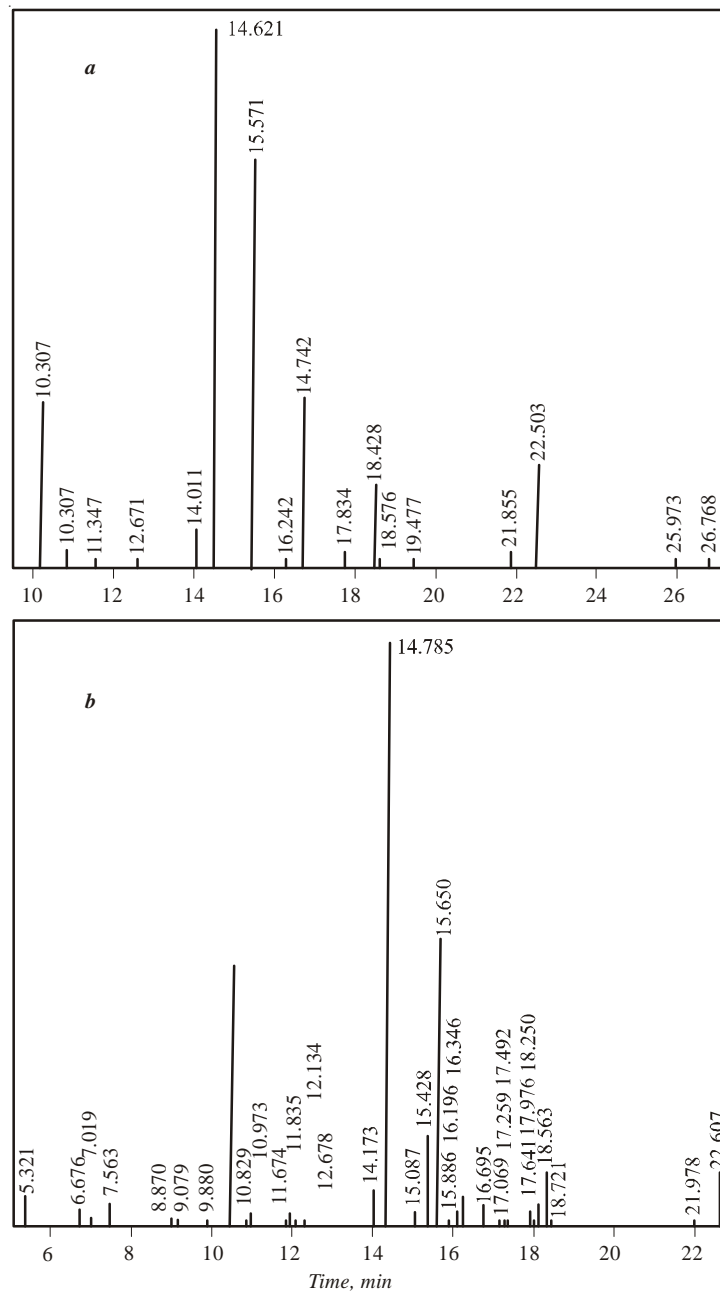


Fig. 2. Line chromatograms of ROME biofuel (a) and its 0-10% cut (b).

a quartz capillary column (60 m long, 0.32 mm in diameter) packed with HP-23 sorbent with particles 0.25 mm in diameter. The detector temperature was 250°C, the evaporator temperature was 240°C, and linear programming of the column thermostat temperature elevation was from 160 to 225°C. The carrier gas (hydrogen) flow rate at a pressure of 65 kPa was 1 ml/min. The sample volume – a solution of fatty acid methyl esters in cyclohexane – was 1 mm³.

The individual methyl esters of saturated and unsaturated fatty acids with 12-22 carbon atoms in the molecule were used to identify the chromatograms obtained. The basic constituents of the samples identified are in agreement with the data in GOST 30089–93.

The chromatograms of RME and SOME biofuels are shown in Fig. 2, the line chromatograms of samples of ROME and its 0-10% cuts are shown in Fig. 3, and the line chromatograms of the 10-50% cuts of RME and 50-90% cuts of ROME are shown in Fig. 3.

The histograms of the distribution of the basic fatty acids in the plant oil triglycerides in biofuels and their methyl ester cuts are shown in Fig. 4: C16:0 palmitic, C18:0 stearic, C18:1 oleic, C18:2 linoleic, C18:3 linoleic, C22:1 erucic and compounds arbitrarily assigned to residue.

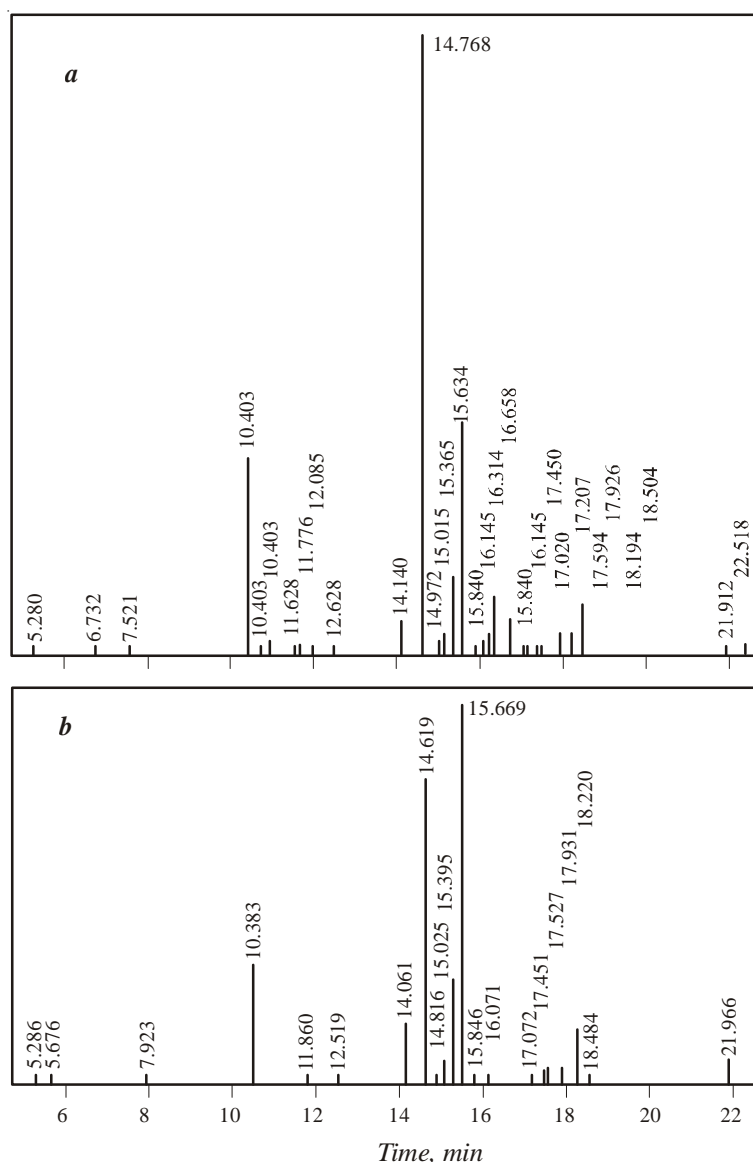


Fig. 3. Line chromatograms of 10-50% cut of RME biofuel (a) and 50-90% cut of ROME biofuel (b).

As Figs. 1 and 2 show, the number and position of the peaks with respect to the time coordinate of the chromatograms are identical for all types of biofuels except for SOME, whose chromatogram has no peak for erucic acid methyl ester. The volume content of the corresponding methyl esters in each biofuel differed (see Fig. 4).

It should be noted that food-grade rapeseed oil with a low erucic acid content is used for manufacture of RME and the Australian standard CNORM C 1190 for biofuel restricts the linolic (less than 15%) and erucic (less than 5%) fatty acid content [9].

As Fig. 4 shows, monounsaturated oleic acid is the basic component of ROME and RME: 52.9 and 62%, respectively. Then come (in decreasing content) polyunsaturated acid methyl esters (26 and 18.2% linolic, 26 and 18.2% linoleic) and saturated acids (4.9 and 4.5% palmitic, 2 and 1.9% stearic). Linolic acid methyl esters are the base in SOME: 58.8%, followed by fatty acid methyl esters: 26% oleic, 6.8% palmitic, and 3.7% stearic.

Let us examine the qualitative and quantitative compositions of the biofuel cuts (see Fig. 2-4). The quantitative content of the basic ingredients of all cuts of the three types of biofuels is shown in the histograms, and the minimum and maximum retention times of the ingredients and amounts of the biofuels and cuts in each sample found in processing the chromatograms are reported in Table 4.

According to the results obtained, new compounds appear in all cuts of the condensate of each fuel in heating, evaporation, and condensation. The fatty acid methyl esters contained in the biofuel are the basic ingredients in all cuts. The ester composition distills in a narrow temperature range; 325-345°C for 90% of RME biofuel.

This can explain the simultaneous transition of several esters with close boiling points to the vapor phase in evaporation of the boiling fuel. As noted in [6], palmitic and stearic fatty acid methyl esters boil at 196 and 215°C at a pressure of 1.995 kPa.

The number of compounds arbitrarily assigned to residue increases in each type of biofuel and its cuts (see Fig. 4). For example, in ROME and RME, identified fatty acid methyl esters are these compounds: saturated – C14:0 myristic, C20:0 arachnic, C22:0 behenic, and unsaturated – C16:1 palmitoleic and C20:1 gadoleic, as well as other compounds which remain to be identified.

In conclusion, we note the following. It is necessary to clearly differentiate distillation of biofuel – methyl ester compositions at atmospheric pressure and the maximum boiling point (~430°C) with a yield of ~80% ROME condensate and evaporation of the biofuel with subsequent decomposition and oxidation of the molecules in the diesel combustion chamber.

Table 4

Biofuel and cuts, %	Number of ingredients	Retention time (min) of ingredients in chromatograph	
		minimum	maximum
SOME	18	6.400	25.941
0–10	21	4.576	26.156
10–50	14	7.480	26.011
50–90	25	4.673	26.121
ROME	16	10.307	26.768
0–10	33	4.762	22.607
10–50	30	4.739	22.580
50–90	45	4.781	33.681
RME	17	10.319	26.782
0–10	28	5.294	22.536
10–50	29	5.280	22.518
50–90	29	5.277	33.657

At the rated duty of 6ChN12/14 diesel ($N_e = 191 \text{ kW}$, $n = 2000 \text{ min}^{-1}$), the pressure and temperature in the combustion chamber at the beginning of fuel injection are 6.9 MPa and 667°C, versus 13.1 MPa and 1185°C at the end. Nevertheless, knowing the chemical composition of the biofuels investigated and the quantitative ratio of

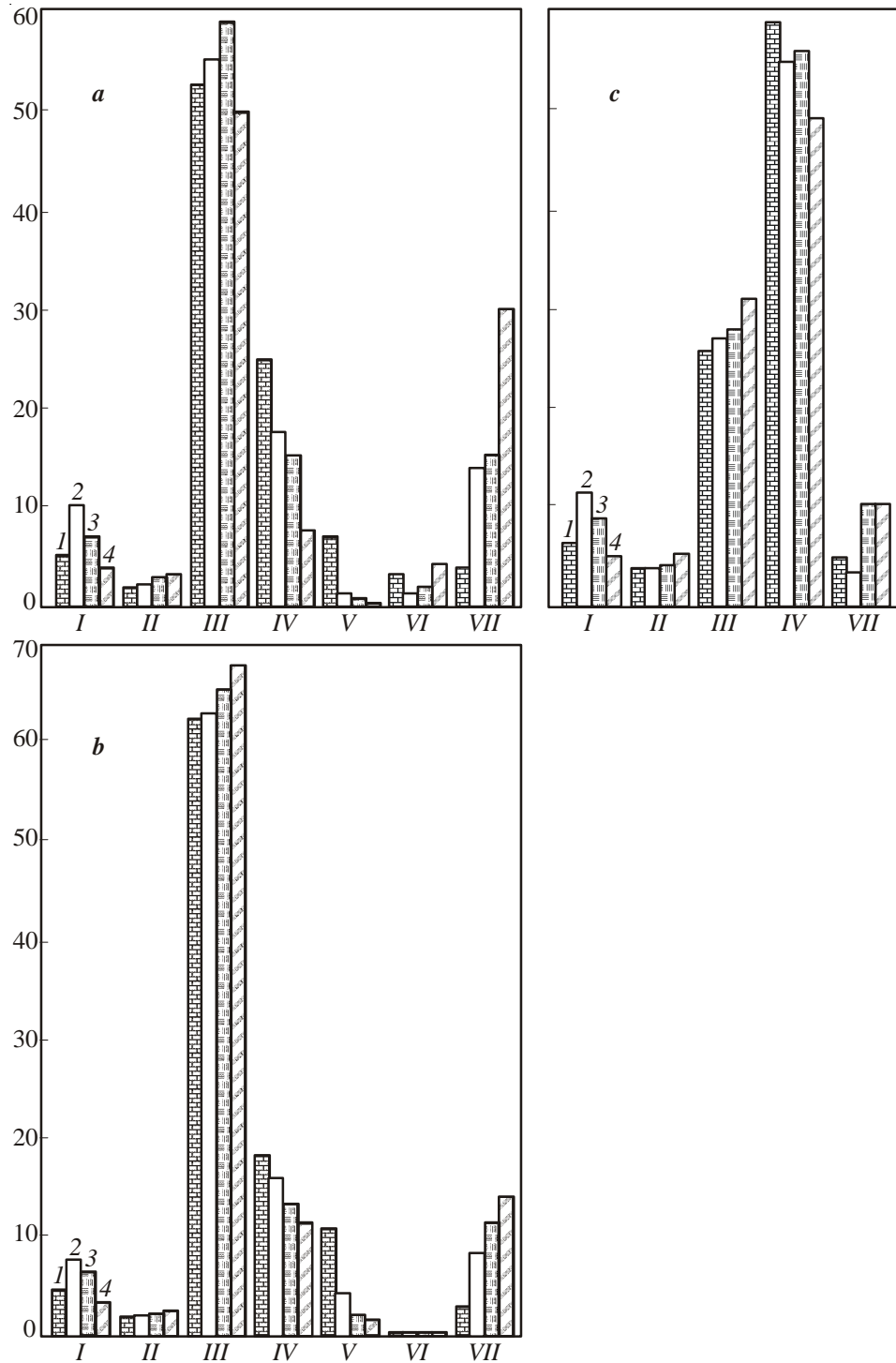


Fig. 4. Histogram of distribution in ROME (a), RME (b), SOME (c) biofuels and their cuts: I, II, III, IV, V, VI) C16:0 palmitic, C18:0 stearic, C18:1 oleic, C18:2 linolic, C18:3 linoleic, C22:1 erucic acid methyl esters; VII) residual compounds; 1) in initial fuel; 2, 3, 4) in 0-10, 10-50, and 50-90% cuts.

ingredients in the cuts of these fuels allows estimating the intensity and completeness of their evaporation, creating a satisfactory mathematical model of pre-ignition preparation of the biofuel for self-ignition and combustion.

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