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## EVALUATION OF OILSEED RADISH (*Raphanus sativus* L. var. *oleiformis* Pers.) OIL AS A POTENTIAL COMPONENT OF BIOFUELS

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### KEYWORDS

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### ABSTRACT

The growing interest in alternative fuels based on plant oils has led to the search for new plant species. Given this, during 2015–2020, oil from 12 varieties of oilseed radish was studied using standard research protocols. The average content of the dominant fatty acids in the oils studied was: [cis-9] oleic (C 18:1) 33.95% (Cv = 14.2%), [cis-9,12] linoleic (C 18:2) 16.20% (Cv = 20.8%), [cis-13] erucic (C 22:1) 15.18% (Cv = 17.9%), [cis-9, 12, 15]  $\alpha$ -linolenic (C 18:3) 13.33% (Cv = 18.5%) and palmitic (C 16:0) 5.42% (Cv = 18.5%), with a monounsaturated fatty acid content of 59.69% and a ratio of polyunsaturated/monounsaturated fatty acids of 0.508. The studied varieties were ranked in the order of increasing suitability as a component of biofuels: ‘Zhuravka’ < ‘Raiduha’ < ‘Lybid’ < ‘Olga’ < ‘Iveya’ < ‘Ramonta’ < ‘Alpha’ < ‘Tambovchanka’ < ‘Fakel’ < ‘Snizhana’ < ‘Sabina’ < ‘Nika’. The technological suitability of oil from the ‘Zhuravka’ variety was confirmed based on analysis of its physicochemical parameters when subjected to polymerization (at 280 °C) and oxypolymerization (at 120 and 150 °C). Under these conditions the basic parameters of the oil varied within the technological limits that determine its suitability for thermodynamic combustion processes in systems with controlled pressure and temperature.

### INTRODUCTION

Fossil fuel reserves are non-renewable and finite. Several researchers have reported clear indications of depleting fossil fuel resources. According to estimates, the global recoverable oil reserves are diminishing at a rate of 4 billion tonnes per annum. Even if it is assumed that the depletion of these reserves continues at the present rate, it is projected that all of these reserves will be exhausted by 2060 (Corrêa, 2019; Silva Neto et al., 2021; Souza Santana, 2021; Saini et al., 2021; Pereira et al., 2022; Saleem, 2022).

According to the forecasts of the International Energy Association (IEA), the world production of biofuels will increase by 2030 to 92–147 million tons of energy equivalent of oil. The annual growth rate of biofuel production will be 7–9%. It is expected that by 2030 the consumption of biofuels in the countries of the European Union (EU) will increase by 13–18 times compared to

current indicators (ANP, 2020; Brown et al., 2020; Global Biofuels..., 2022). Europe is currently the biggest consumer of bio-based diesel (i.e., biodiesel called fatty acid methyl ester or FAME and renewable diesel or HVO) in the world. This is driven by the EU’s targets for renewable energy in transportation coupled with a dominant share of diesel in this sector. Both factors will continue through to 2030, resulting in increased demand for bio-based diesel, from 17.9 million tonnes (20.6 billion litres) in 2020 to 22.9 million tonnes (27.1 billion litres) in 2030. In Latin America where, along with Asia, the growth in consumption of diesel by 2030 is projected to be the highest in the world, demand for biodiesel will grow as well from 7.4 million tonnes (8.4 billion litres) currently to 12.7 million tonnes (14.5 billion litres) by 2030 (Global Biofuels..., 2022). Furthermore, to reduce dependency on petroleum, several international agencies and governments aim to use biofuels to supply 25% of their transportation

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energy by 2050 (Bhandari & Sessa, 2020; Global Biofuels..., 2022; Ilić & Ödlund, 2022; Malins & Sandford, 2022). A number of national biofuel programmes have been implemented to reduce importation of fossil fuels to enhance the security of national fuel supplies (Valdivia et al., 2016; ANP, 2020; Souza Santana, 2021; Rezende et al., 2021; Ramos et al., 2022; Tavares et al., 2022).

A number of crops are grown specifically for biofuel production and are known as energy crops. These vary according to geography: for example, corn, soybeans, willows and switchgrass are common energy crops in the United States; rapeseed, wheat, sugar beet and willows are preferentially grown in northern Europe; sugarcane is grown in Brazil; palm oil and *Miscanthus giganteus* are grown in Southeast Asia; and sorghum and cassava are grown in China (Anand & Khanna, 2019; Lacerda et al., 2020; Sala et al., 2022). Brazil is one of the world leaders in the production of biofuels from plant oils. For this purpose, Brazil uses soybean (*Glycine max* (L.) Merr.), sunflower (*Helianthus annuus* L.), peanut (*Arachis hypogaea* L.), castor bean (*Ricinus communis* L.), corn (*Zea mays* L.), Barbados nut (*Jatropha curcas* L.), cottonseed (*Gossypium* spp.), rape (*Brassica napus* L.), babassu (*Attalea speciosa* Mart.), muriti (*Mauritia flexuosa* L. f.), African oil palm (*Elaeis guineensis* Jacq.) and macaúba palm (*Acrocomia aculeata* L.) (Bhandari & Sessa, 2020; Silva Mamede et al., 2020; Rezende et al., 2021; Tavares et al., 2022). Ukraine also uses a wide range of crops (more than 20 species) for biofuel production, of which the most popular are members of the cruciferous family (including spring and winter rape, white mustard, oilseed radish and camelina) (Blume et al., 2018; Kaletnik et al., 2021; Tsytsiura, 2019, 2020, 2021a,b).

Raw materials are needed to increase the production of biofuels. The problem of the shortage of raw materials will intensify as processing capacities in Europe increase. The average utilization of biodiesel production capacity introduced in the EU in recent years is only 75–80% (Souza Santana, 2021; Saleem, 2022). In addition, climate change, which means a decrease in the adaptability of several widespread bioenergy crops, suggests a search for alternative crops with a high biofuel potential (Karmakar & Halder, 2019; Ramos et al., 2022). In recent years, the replication of such crops has significantly expanded the resistance of new species but assessment of their potential has been insufficiently explored (Puricelli, 2020; Pasha et al., 2021; Torroba, 2021; Neupane et al., 2022). This applies especially to the issues of finding out the technical parameters of oil suitability for application in classic diesel engine schemes (Faria et al., 2018; Brauna et al., 2020; Zulqarnain et al., 2021; Ilić & Ödlund, 2022; Tavares et al., 2022). It was for these reasons that the aim of our research was to study oilseed radish as an agricultural crop with a high potential for oil production, which is considered as a possible component of mixed biofuels (de Andrade Ávila & Sodr , 2012; Faria et al., 2018).

## MATERIAL AND METHODS

Seed of 12 highly productive oilseed radish (*Raphanus sativus* L. var. *oleiformis* Pers.) varieties was used for the investigation: ‘Alpha’, ‘Olga’, ‘Ramonta’, ‘Iveya’, ‘Fakel’, ‘Raiduha’, ‘Zhuravka’, ‘Snizhana’, ‘Nika’, ‘Tambovchanka’, ‘Lybid’ and ‘Sabina’. The

varieties were of different selection and of different ecological and geographical origin (temperate-continental, continental, moderately arid zones). The zonal technology of oilseed radish cultivation was applied: sowing date of April 8–12, sowing rate of 1.5 million germinable seeds ha<sup>-1</sup>, row width 30 cm, fertilizer rate N<sub>60</sub>P<sub>60</sub>K<sub>60</sub> as the most technologically effective option in the pre-sowing application (Tsytsiura, 2022 a, b).

### Determination of proximate composition

The content of moisture, ash, lipid, protein and fibre in the oilseed radish seeds was determined by the AOCS method (2017) and expressed on an absolutely dry weight basis.

### Solvent extraction (SE)

Oilseed radish seed powder for chromatographic analysis was prepared according to Zhao et al. (2017) by grinding portions of the seeds in a grain mill (BiOloMix N-700Y) for 25 s. The seed powder (1000 g) was subsequently soaked in 5000 mL of n-hexane for 5 h at 25 °C and filtered. The residue obtained was again extracted with 5000 mL of n-hexane. The supernatants from both steps were collected, combined and concentrated using a rotary evaporator under vacuum at 40 °C to remove n-hexane. The oil obtained was weighed and stored at 4 °C prior to analysis.

### Determination of physicochemical properties

The research was conducted using the most widespread oilseed radish variety in the region, ‘Zhuravka’, during 2015–2020 in the certified and accredited laboratory of the quality of raw oil and fat of Vinnitsa Oil Seeds Crushing Factory (private joint stock company). All determinations were made in quadruplicate. Oil from the seeds of this variety, obtained by the cold pressing method, was used for the analyses. A Klarstein Olivia cold press with an internal filtration system was used. Additionally, the oil was settled for 24 h before analysis and passed through a filter of non-woven carbon fibre material (Karbopon brand).

According to the tested and standard methods, the following oil indicators were determined: density at 20 °C (ASTM D7042-04), refractive index (ASTM D1218), oil colour and rotation of the plane of polarization at 23 °C (Paquot & Hauntfenne, 1992), specific viscosity at 20 °C (ASTM D445), kinematic viscosity at 20 °C (ASTM D445), relative surface tension (ASTM D971-12), carbon residue (wt.%) (ASTM D4530), net calorific value (ASTM D240), solidification temperature (ASTM D97), flash point (ASTM D93), solubility in organic solvents (ASTM F739), acid value (ASTM D974), content of free acids as a percentage of oleic acid (according to the results of chromatography of the fatty acid composition), saponification value (ASTM D664), ether value (Firestone, 2013), iodine value (ASTM D5768), rhodan value (Paquot & Hauntfenne, 1992), amount of water-insoluble fatty acids (Firestone, 2013), amount of unsaponifiable matter (Paquot & Hauntfenne, 1992) and sulphur content (ASTM D5453).

To evaluate the change in the physicochemical properties of the oil, it was polymerized by thermal heating at 280 °C (an industrial 500 mL high-pressure blender stirred autoclave vessel chemical hydrothermal synthesis reactor was used). Changes in the physicochemical properties of oil during its oxypolymerization (heating of

oil with oxygen purging) were also studied using the same device as during polymerization, with oxygen supplied under a pressure of 1 atm when heated at two modes of 120 and 150 °C within half an hour. Oil without oxypolymerization was heated to 120 °C and held at this temperature for half an hour. Polymerization and oxypolymerization of oil were carried out taking into account methodical approaches in accordance with Rinaldi et al. (2017). The main physicochemical parameters of polymerized and oxypolymerized oil were studied during its long-term heating for 1, 2 and 3 h in the same laboratory equipment. As a control, a polymerized oil sample without additional heating was used.

### Determination of the fatty acid composition

The fatty acid composition of the seed oils of the above-mentioned varieties was determined by the method of gas–liquid chromatography using a Shimadzu GC 2014 chromatograph (Japan) (according to Clancy, 2013;

Hübschmann, 2018) with methyl heptadecanoate standard at a concentration of 9.8 mg mL<sup>-1</sup>. Samples were prepared using approximately 15 mg of product (oil), 200 µL of standard solution containing 9.8 µg of methyl heptadecanoate per 1000 µL and 1 mL of heptane (solvent). The configuration was set: SPL-2014 injector, FID-2014 flame ionization detector + TCD-2014 thermal conductivity detector. Identification of fatty acids was carried out by comparing the chromatograms obtained with those of such standard solutions as methyl esters of fatty acids (C<sub>6</sub>–C<sub>24</sub>).

Coefficients of ER (elongation ratio, Equation 1), DR (desaturation ratio, Equation 2), ODR (oleic desaturation ratio, Equation 3), LDR (linoleic desaturation ratio, Equation 4), and saturated to unsaturated fatty acid ratio (Equations 5 and 6) were estimated according to Velasco et al. (1998) and Pleines & Friedt (1988). Fatty acid ratios were estimated according to Blume et al. (2018).

$$ER = \frac{(\%)C20:1 + (\%)C22:1}{(\%)C20:1 + (\%)C22:1 + (\%)C18:1 + (\%)C18:2 + (\%)C18:3} \quad (1)$$

$$DR = \frac{(\%)C18:2 + (\%)C18:3}{(\%)C20:1 + (\%)C22:1 + (\%)C18:1 + (\%)C18:2 + (\%)C18:3} \quad (2)$$

$$ODR = \frac{(\%)C18:2 + (\%)C18:3}{(\%)C18:1 + (\%)C18:2 + (\%)C18:3} \quad (3)$$

$$LDR = \frac{(\%)C18:3}{(\%)C18:2 + (\%)C18:3} \quad (4)$$

Where:

(%)C20:1 and (%)C22:1 – content of the corresponding fatty acid in %.

$$S/U = \frac{\text{Saturated fatty acids}}{\text{Unsaturated fatty acids}} \quad (5)$$

$$PU/MU = \frac{\text{Polyunsaturated fatty acids}}{\text{Monounsaturated fatty acids}} \quad (6)$$

### Terminology of oil components

International terminology (CODEX, 2020) was used for the components of oilseed radish vegetable oil found during the analysis.

### Soil and climatic conditions of research

The research was carried out during 2015–2020 on the research field (arranged by coordinates 49° 11' 31" N, 28° 22' 16" E) located in the zone of the Right-bank Forest-Steppe of Ukraine. The soil cover of the research field was represented by grey forest soils with the following agrochemical parameters (for the period of crop rotation): humus 2.02–3.20%, mobile forms of nitrogen 67–92 mg kg<sup>-1</sup>, phosphorus 149–220 mg kg<sup>-1</sup> and potassium 92–126 mg kg<sup>-1</sup> with metabolic acidity of the soil solution (pHKCl) 5.5–6.0. The temperature regime and the humidification regime for the period of research for the growth of oilseed radish plants had significant

differences. This allowed analysis of the influence of weather conditions on the fatty acid composition of oil in oilseed radish varieties. According to the weather conditions, the stress effect on seed formation in oilseed radish plants for the years of observation (2015–2020) can be placed in the next decreasing row for 2015: hydrothermal coefficient (HTC) (Equation 7) = 0.230–0.613) – 2017 (0.349–0.806) – 2016 (0.682–0.893) – 2020 (0.649–1.474) – 2019 (1.003–1.555) – 2018 (1.349–3.124).

$$HTC = \sum R \times (0.1 \times \sum t_{>10})^{-1}$$

Where:

ΣR – the amount of precipitation (mm) over a period with temperatures above 10 °C,

Σt>10 °C – the sum of effective temperatures over the same period.

According to Vlăduț et al. (2018),  $HTC > 1.6$  indicates excessive humidity,  $HTC 1.3–1.6$  – humid conditions,  $HTC 1.0–1.3$  – slightly arid conditions,  $HTC 0.7–1.0$  – arid conditions and  $HTC 0.4–0.7$  – very arid conditions.

### Statistical analysis

The data obtained were analysed using analysis of variance (ANOVA) with determination of the share of influence of factors in the dispersion scheme (Wong, 2018). Tukey's HSD test in R (version R statistic i386 3.5.3) with multiple comparisons of the parameter means at the 99.9%, 99% and 95% family-wise confidence levels were used. In evaluating the obtained array of multiple values, standard indicators were used for analysing variable data (multi-year and genotypic components:  $\mu$  – mean,  $\sigma$  – standard deviation,  $C_v$  – coefficient of variation).

TABLE 1. Average chemical composition of the seeds of the 12 varieties of oilseed radish investigated (content in absolutely dry matter,  $\pm$  standard deviation (based on the results of the multi-year assessment 2015–2020)) ( $\mu \pm \sigma$ , %).

Seeds	Moisture	Protein	Lipid	Fibre	Ash
Content (%)	$6.57 \pm 1.17$	$23.6 \pm 3.8$	$37.1 \pm 3.5$	$17.0 \pm 1.6$	$5.2 \pm 1.1$

The average lipid content in absolutely dry matter was 37.1%, which is higher than among other crops. With a potential seed yield of up to 2–3.0 t ha<sup>-1</sup> (Tsytsiura, 2019), the possible output of oil is 650–1000 kg ha<sup>-1</sup>. The results of the chromatographic analysis (Table 2) showed that seed of all varieties of oilseed radish possess a high content of oleic (18:1; 31.95–36.28%), linoleic (18:2; 15.06–16.89%), linolenic (18:3; 12.08–14.92%), gondoic (20:1; 7.89–9.26%) and erucic (22:1; 14.79–17.80%) fatty acids. This corresponds to the general profile of the ratio of fatty acids in cruciferous oil. The most common among the fatty acids listed in the composition of Brassicaceae plant seed oil are oleic (18:1), linoleic (18:2), linolenic (18:3), gondoic (20:1) and erucic (22:1) (Ratanapariyanuch et al., 2013). The results for the fatty acid composition were similar to those previously obtained in the recent studies of Blume et al. (2018), Fadhil et al. (2020), Stevanato & Silva (2019), Stevanato et al. (2020) and de Mello et al. (2021) and in the earlier studies of Domingos et al. (2008), Andrade Ávila & Sodr  (2012), Chammoun et al. (2013) and Zhao et al. (2017). The fatty acid composition obtained here is closest to the results of Blume et al. (2018) and Domingos et al. (2008). However, a number of features different from their results are worth noting. In particular, the significance of the differences in fatty acid concentrations within the varieties of different

## RESULTS AND DISCUSSION

The object of research was oilseed radish (*Raphanus sativus* L. var. *oleiformis* (synonymous name *oleiferus*) Pers.) defined as a species of radish (*Raphanus sativus* L.), genus *Raphanus* L., subtribe II Raphanusae DC., tribe 5 Brassiceae Hayek, in the family Brassicaceae, order Capparidales, class Dicotyledoneae (Francis et al., 2021). According to the results of some studies, it belongs to the group of species convar. *oleiferus* L., a group of varieties of oilseed radish with the following characteristics: plants are annual (95–110 days of vegetation), the taproot is not formed, it is grown to produce oil from the seeds and for forage purposes, and vegetative and generative organs are similar to the forms of root crops (Tsytsiura, 2019). Oilseed radish has long been used as forage and green manure in Europe and South Africa. The proximate composition of seed in tested varieties is shown in Table 1.

ecological and geographical origin in the presence of a wider spectrum of cis-isomers of fatty acids was established. According to Singer et al. (2016), this type of fatty acid profile indicates the high-amplitude nature of temperature and moisture variation during the period of seed formation and filling. At the same time, the differences between oilseed radish varieties were proven statistically: the level of significance for the majority of fatty acids (linoleic,  $\alpha$ -linolenic, arachidic, gondoic, eicosadienoic, eicosapentaenoic, behenic, erucic, docosadienoic) was  $p < 0.01$ . For nervonic acid, this level was  $p < 0.001$ , and for myristoleic and palmitoleic acids, the differences in content between varieties were insignificant. For the rest of the fatty acids, the significance of the differences between varieties was  $p < 0.05$ .

Among the full list of the fatty acids identified, five varieties contained no octanoic acid (8:0); undecanoic (11:0), elaidic (18:1) and eicosapentaenoic acids (20:5) were absent in four varieties each; and two varieties had no geneicosanoic acid (21:0). These same acids were also not identified in oilseed radish in the studies by Blume et al. (2018) and Domingos et al. (2008). Such results allow us to ascertain a wider range of fatty acids in the composition of oilseed radish than was noted and to form a classification of varieties according to the suitability of their oil for biofuel use.

TABLE 2. Oil fatty acid composition of different oilseed radish (*Raphanus sativus* var. *oleifera*) varieties (based on multi-year assessment 2015–2020) ( $\mu \pm \sigma$ , %).

CN:DB*	Fatty acid/ variety (C <sub>n</sub> )	'Raiduha'	'Zhuravka'	'Lybid'	'Fakel'	'Ramonta'	'Tambovchanka'	'Alpha'	'Olga'	'Iveya'	'Sabina'	'Nika'	'Smizhana'
C 8:0 $< 2e-3^*$	Octanoic xxx (26.8)	0.16± 0.05	0.36± 0.08	0.21± 0.09	0.11± 0.05	0.00 (trace)	0.00	0.00	0.00	0.00 (trace)*	0.00	0.00	0.00 (trace)
C 11:0 $< 2e-3^*$	Undecanoic (32.4)	0.33± 0.07	0.55± 0.11	0.18± 0.05	0.14± 0.04	0.11± 0.07	0.15± 0.06	0.00	0.00	0.00 (trace)	0.00	0.00	0.00 (trace)
C 14:0 $< 2e-1^{ns}$	Myristoleic (22.8)	0.07± 0.04	0.07± 0.04	0.08± 0.03	0.06± 0.05	0.04± 0.03	0.06± 0.02	0.06± 0.02	0.07± 0.01	0.04± 0.02	0.04± 0.01	0.05± 0.01	0.03± 0.01
C 16:0 $< 2e-4^*$	Palmitic (18.5)	5.11± 0.78	4.68± 0.89	5.06± 1.11	5.00± 1.23	5.02± 1.17	5.08± 1.09	5.33± 0.87	5.22± 0.85	5.12± 1.26	4.84± 1.41	4.76± 0.59	5.02± 0.64
C 16:1 $< 2e-1^{ns}$	Palmitoleic (23.3)	0.13± 0.03	0.14± 0.05	0.15± 0.04	0.15± 0.03	0.11± 0.04	0.08± 0.02	0.12± 0.03	0.10± 0.02	0.07± 0.02	0.09± 0.01	0.10± 0.05	0.12± 0.02
C 18:0 $< 2e-3^*$	Stearic (16.9)	2.60± 0.33	2.37± 0.51	2.46± 0.30	2.03± 0.44	2.12± 0.29	2.21± 0.39	2.24± 0.67	2.29± 0.55	2.26± 0.51	2.13± 0.41	2.11± 0.67	2.13± 0.59
C 18:1 $< 2e-3^*$	Elaidic (17.1)	0.08± 0.02	0.18± 0.05	0.05± 0.01	0.11± 0.02	0.14± 0.01	0.07± 0.02	0.00	0.00 (trace)	0.00	0.00	0.00 (trace)	0.00
C 18:1 $< 2e-3^*$	[cis-9] Oleic (14.2)	33.53± 4.38	33.19± 3.89	34.08± 3.55	31.95± 5.14	31.34± 4.89	33.72± 5.17	35.91± 4.87	33.59± 6.17	33.27± 5.91	34.97± 5.17	34.62± 4.14	36.28± 4.96
C 18:2 $< 2e-6^{**}$	[cis-9,12] Linoleic (20.8)	15.22± 3.56	15.53± 3.25	15.06± 3.24	16.81± 3.51	15.70± 4.11	17.08± 4.09	16.19± 3.77	16.90± 3.52	16.61± 3.78	16.89± 4.05	16.12± 4.26	16.23± 3.77
C 18:3 $< 2e-6^{**}$	[cis-9, 12, 15] $\alpha$ - Linolenic (18.5)	12.40± 2.21	12.08± 2.39	13.01± 2.49	13.10± 2.56	13.28± 2.93	12.26± 2.54	13.66± 2.49	13.84± 2.72	14.92± 2.84	14.42± 2.41	14.03± 1.98	12.97± 1.95
C 20:0 $< 2e-6^{**}$	Arachidic (27.9)	0.96± 0.17	0.91± 0.11	0.94± 0.14	0.66± 0.10	0.76± 0.20	0.79± 0.27	0.70± 0.31	0.72± 0.19	0.71± 0.23	0.75± 0.29	0.71± 0.34	0.63± 0.31
C 20:1 $< 2e-6^{**}$	Gondoic (22.7)	9.15± 2.07	8.48± 2.05	8.84± 2.03	9.12± 1.99	8.92± 1.84	8.55± 1.77	8.12± 1.71	8.06± 1.92	7.92± 1.87	7.89± 2.19	9.14± 2.29	9.26± 1.67
C 20:2 $< 2e-5^{**}$	[cis-11, 14] Eicosadienoic (32.6)	0.47± 0.14	0.39± 0.17	0.26± 0.14	0.28± 0.12	0.40± 0.15	0.28± 0.10	0.33± 0.09	0.41± 0.11	0.21± 0.08	0.32± 0.11	0.20± 0.14	0.24± 0.09
C 20:3 $< 2e-3^*$	Eicosatrienoic (25.2)	0.13± 0.06	0.12± 0.04	0.10± 0.02	0.10± 0.03	0.12± 0.03	0.08± 0.02	0.15± 0.03	0.13± 0.03	0.08± 0.03	0.07± 0.03	0.05± 0.01	0.08± 0.03
C 20:4 $< 2e-3^*$	Arachidonic (24.5)	0.12± 0.03	0.14± 0.02	0.14± 0.03	0.12± 0.04	0.13± 0.05	0.15± 0.02	0.10± 0.03	0.11± 0.03	0.10± 0.04	0.05± 0.01	0.05± 0.02	0.07± 0.02
C 20:5 $< 2e-7^{**}$	[cis-5,8,11,14,17] Eicosapentaenoic (21.7)	1.24± 0.27	1.11± 0.22	1.08± 0.31	1.02± 0.24	1.37± 0.29	0.97± 0.23	0.00	0.00	0.00	0.00	0.00 (trace)	0.00 (trace)
C 21:0 $< 2e-4^*$	Geneicosanoic (28.3)	0.00 (trace)	0.46± 0.09	0.00 (trace)	0.00 (trace)	0.00	0.36± 0.07	0.00	0.44± 0.13	0.39± 0.10	0.32± 0.12	0.00 (trace)	0.33± 0.09
C 22:0 $< 2e-7^{**}$	Behenic (29.8)	0.37± 0.11	0.41± 0.07	0.39± 0.14	0.08± 0.03	0.28± 0.10	0.07± 0.02	0.32± 0.12	0.24± 0.09	0.30± 0.12	0.00 (trace)	0.31± 0.07	0.00 (trace)
C 22:1 $< 2e-7^{**}$	[cis-13] Erucic (17.9)	15.20± 2.07	15.95± 2.18	15.93± 2.79	16.70± 2.56	17.80± 2.75	15.59± 2.92	17.66± 3.02	15.74± 3.09	16.18± 2.93	15.73± 2.38	16.30± 2.49	14.79± 2.37
C 22:2 $< 2e-6^{**}$	[cis-13, 16] Docosadienoic (26.7)	0.38± 0.09	0.51± 0.12	0.25± 0.09	0.27± 0.08	0.15± 0.04	0.17± 0.05	0.12± 0.03	0.14± 0.04	0.17± 0.04	0.11± 0.05	0.10± 0.03	0.12± 0.04

C 23:0 < 2e-4*	Tricosanoic (27.5)	0.45± 0.14	0.42± 0.12	0.41± 0.09	0.39± 0.17	0.42± 0.11	0.42± 0.08	0.47± 0.09	0.44± 0.07	0.46± 0.08	0.43± 0.12	0.39± 0.08	0.46± 0.17
C 24:0 < 2e-4*	Lignoceric (28.1)	0.44± 0.24	0.52± 0.27	0.31± 0.11	0.39± 0.18	0.57± 0.17	0.14± 0.05	0.34± 0.16	0.34± 0.14	0.45± 0.09	0.33± 0.11	0.38± 0.14	0.41± 0.24
C 24:1 < 2e-10**	Nervonic (34.9)	1.46± 0.36	1.43± 0.34	1.01± 0.28	1.41± 0.50	1.22± 0.42	1.72± 0.48	1.18± 0.51	1.22± 0.39	0.74± 0.30	0.62± 0.28	0.58± 0.24	0.83± 0.33
Total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total saturated		11.34	11.65	10.55	9.41	9.87	9.73	9.91	10.31	10.11	9.27	9.01	9.37
Monounsaturated		59.55	59.37	60.06	59.44	59.53	59.73	59.99	58.71	58.18	59.30	60.74	61.28
Polyunsaturated		29.11	28.98	29.39	31.15	30.60	30.54	30.10	30.98	31.71	31.43	30.25	29.35
Total unsaturated		88.66	88.35	89.45	90.59	90.13	90.27	90.09	89.69	89.89	90.73	90.99	90.63
ER		0.285	0.286	0.285	0.294	0.306	0.277	0.257	0.270	0.271	0.263	0.282	0.269
DR		0.323	0.323	0.323	0.341	0.332	0.336	0.337	0.349	0.355	0.348	0.334	0.326
ODR		0.451	0.453	0.451	0.483	0.479	0.465	0.454	0.478	0.487	0.472	0.465	0.446
LDR		0.449	0.438	0.463	0.438	0.458	0.418	0.458	0.450	0.473	0.461	0.465	0.444
S/U		0.128	0.132	0.118	0.104	0.110	0.108	0.110	0.115	0.112	0.102	0.099	0.103
PU/MU		0.489	0.488	0.489	0.524	0.514	0.511	0.502	0.528	0.545	0.530	0.498	0.479

\*Trace – the concentration was less 0.01%; \*carbon number (CN) per double bond (DB); \*\*level Pr (>F) for a given fatty acid to compare between oilseed varieties (Tukey HSD test results, significance codes: \*\*\*\*, 0.001; \*\*\*, 0.01; \*\*, 0.05; ns, non-significant); \*\*\*average share of the influence of hydrothermal conditions of vegetation (%) on the fatty acid content in the two-factor ANOVA system (A – year conditions, B – variety with an assessment of the content of the corresponding fatty acid).

The variability of the values of the concentration of the corresponding fatty acids by the value of the presented standard deviation was ranked for varieties in the range from 7.6 to 53.7%. The variability was due to both annual variance and internal variability within the limits of the results obtained from four-fold repetition of determinations, taking into account the general error of the experiment. The level of variation was consistent with the generalized results of Velasco et al. (1998), Mendal et al. (2002), Andrade Ávila & Sodr  (2012) and Wendlinger et al. (2014). It should be noted that according to the amino acid composition of other cruciferous crops (statistical long-term data according to Giakoumis (2018)), in terms of dominant fatty acids, oilseed radish oil contains (as a percentage of comparison with the concentration) 25% more myristoleic acid than in rapeseed, spring bittercress, camelina, and 42.9% more than in white mustard. The oleic acid content is 43.0% lower than that of rapeseed and 26.9% lower than that of spring bittercress, but 17.6% higher than that of white mustard and 1.5 times higher than that of camelina. In terms of erucic acid content, radish oil is second only to white mustard (40.1% reduction). The content of linoleic acid is 7.3% less than that in camelina; 16.6% and 21.8% less, respectively, than in rapeseed and spring bittercress; and greater by 14.3% than in white mustard. The linolenic acid content is 1.8 times greater than that of rapeseed and 50.0% more than that of spring bittercress, but on the same level with white mustard and 55.7% less than that of camelina.

It has also been established that hydrothermal conditions during seed formation and filling affect the fatty

acid composition in the context of the respective varieties. For example, for the years of radically contrasting temperature and humidity conditions in terms of the hydrothermal coefficient (HTC) parameter – 2015 (very arid conditions) and 2018 (excessive humidity) – for three oil radish varieties, ‘Raiduha’, ‘Zhuravka’ and ‘Lybid’, the fatty acid profile is shown in Figure 1.

This confirms the complex nature of the formation of the fatty acid composition of the seeds of cruciferous family oilseeds (Velasco et al., 1998; Andrade Ávila & Sodr , 2012; Blume et al., 2018; Kralji  et al., 2018) and requires a careful assessment of the quality of the oil obtained and consideration of possible interval changes in the concentration of the corresponding acids depending on the hydrothermal conditions of the period of seed formation and filling and the impact of these processes on the quality and biofuel suitability of the oil produced.

In addition, the share of the influence of hydrothermal conditions of the vegetation of oilseed radish on the fatty acid composition of its oil was determined in the dispersion scheme of year-variety-relevant fatty acid-random (not accounted for) factors. The influence value thus obtained ranged from 16.9% for stearic acid to 34.9% for nervonic acid. The determined nature of the effect allows evaluation of the fatty acid components of the oil for plasticity and stability and, in the future, prediction of the approximate fatty acid composition of the oil of this variety based on its genotypically characteristic structure and weather conditions during the period of seed formation.

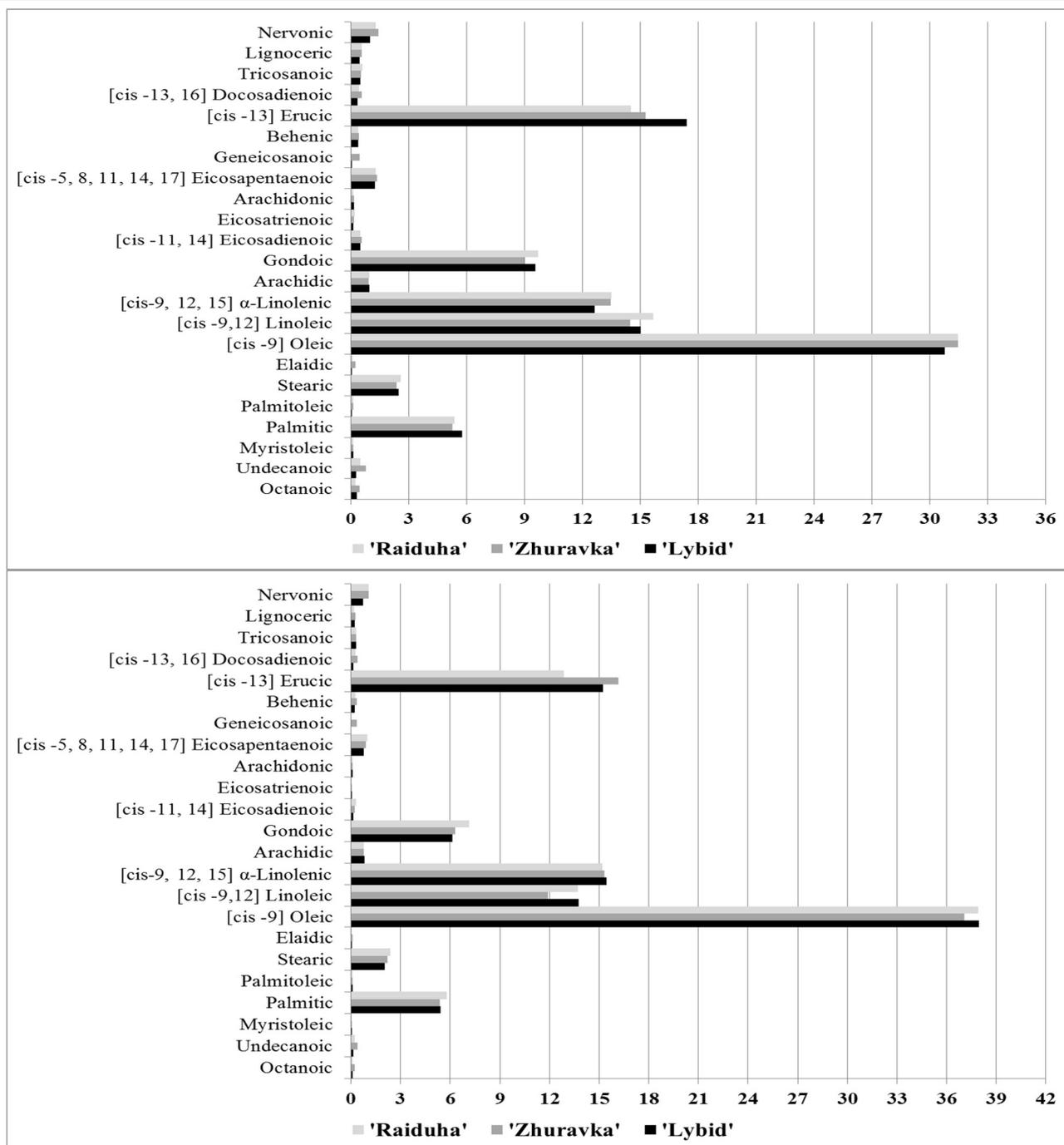


FIGURE 1. Fatty acid profile of oil of oil radish varieties (top position for 2015 conditions, bottom position for 2018 conditions).

According to the fatty acid composition, the ratio of saturated to unsaturated fatty acids in all varieties studied had a small interval ratio of 9.01–11.65:88.35–90.99 (%). Among the unsaturated fatty acids, monounsaturated fatty acids prevailed, with the average value for varieties according to their ratio to polyunsaturated acids being 59.69:30.34 (%) with an average share of saturated acids of 9.97%. The established differences in fatty acid composition led to a corresponding spread of values according to the main fatty acid ratios (Equations 1–6). Thus, Blume et al. (2018) indicated that a very large amount of polyunsaturated fatty acids will significantly reduce the oxidative stability of obtained fuel and oil presents a mixture had a large number of different fatty acids. For this reason, some coefficients are useful for more accurate assessment of the qualitative composition of

different oil types: ER, DR, ODR and LDR. These ratios show the relationship between different groups of fatty acids with similar properties and probably could show activity of the respective desaturase or elongase (Atabani et al., 2013). Biodiesel fuel can be divided into two types, heavy and light (which can be used as additive to aviation fuel), according to length of the carbon chain (Blume et al., 2018). The biggest difficulty in assessing fatty acid composition is large number of various fatty acids, each of which has specific properties. Fuel obtained from certain types of oil should have a small carbon number (preferably not more than 18); therefore, the content of mono- and polyunsaturated fatty acids with a short chain (such as C 18:2, C 18:3) is important. On the other hand, a very large amount of polyunsaturated fatty acids will significantly reduce the oxidative stability of the fuel

(Firestone, 2013). Also, to assess the results of the chromatographic analysis, S/U (saturated fatty acids/unsaturated fatty acids) and PU/MU (polyunsaturated fatty acids/monounsaturated fatty acids) proportions are used as indicators (Blume et al., 2018). At the same time, in the practice of evaluating oils for biofuel (Clancy, 2013; Shah et al., 2013; Faria et al., 2018), preference should be given to oils with a high content of unsaturated fatty acids (primarily monounsaturated) and also the lowest value of such fatty acid ratios as PU/MU, ER and DR. The highest LDR value has been found due to the highest content of linolenic acid (C18:3), which could indicate reduced oxidative stability (Blume et al., 2018).

According to the indicated dataset and considering as the resulting indicator PU/MU (Fadhil et al., 2020), the investigated varieties of oilseed radish can be placed in the following order of increasing suitability of its oil as a biofuel component: 'Zhuravka' < 'Raiduha' < 'Lybid' < 'Olga' < 'Iveya' < 'Ramonta' < 'Alpha' < 'Tambovchanka' < 'Fakel' < 'Snizhana' < 'Sabina' < 'Nika'. It should also be noted that the high content of erucic acid (14.80–17.80%) allowed this oil to be classified as not suitable for food purposes and determined the importance of its application for bioenergetics. The results for the oil's fatty acid composition were confirmed by cluster analysis (Figure 2).

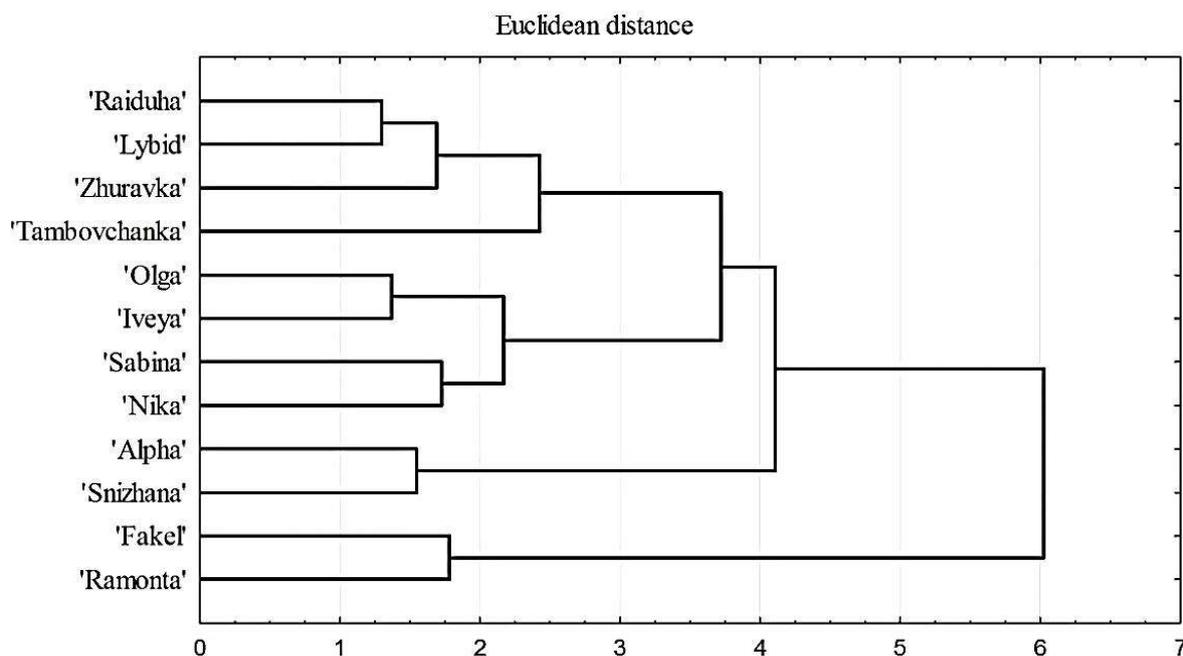


FIGURE 2. Cluster analysis of 12 oilseed radish varieties by fatty acid content of their oil (full linkage method for the 2015–2020 dataset).

This cluster analysis confirmed the significance of the differences between the studied varieties in the concentration of individual fatty acids according to the seven groups of Euclidean distances determined in the clustering of data according to the full linkage method scheme. It also indicated the proximity of varieties that were in neighbouring positions in a certain range of

suitability of their oil for biofuel use. That confirmed the reliability of the conducted ranking of varieties.

Together with the study of the fatty acid composition of the oil, the importance of assessing its physical and physicochemical constants is noted (Mat et al., 2020). The data of such assessments are presented in Tables 3 and 4.

TABLE 3. Average values of physical and physicochemical indicators of oil for 12 varieties of oilseed radish (*Raphanus sativus* var. *oleifera*), 2015–2020.

Sample of oil	Organoleptic properties										
	Colour (Lovibond, 1 in.)		Transparency		Colour (iodine scale)		Odour		Taste		
	Y25.00, R2.00 - Y35.00, R2.60		Absolute transparency after 24 h		30–40		Light radish hue		Soft, satisfying with a radish taste		
	Physical indicators ( $\mu \pm \sigma$ )										
	Density at 20 °C, kg m <sup>-3</sup>	Refractive index at 20 °C	Rotation of the plane of polarization at 23 °C, °	Specific viscosity at 20 °C, mm <sup>2</sup> s <sup>-1</sup>	Kinematic viscosity of oil at 20 °C, mm <sup>2</sup> s <sup>-1</sup>	Relative surface tension	Carbon residue (wt.%)	Net calorific value, MJ kg <sup>-1</sup>	Solidification temperature, °C	Flash point, °C	Solubility in organic solvents
Cold pressed oil	0.912 ± 0.047	1.468 ± 0.012	-0.73 ± 0.02	70.39 ± 0.58	77.18 ± 0.55	0.459 ± 0.011	0.31 ± 0.12	37.93 ± 0.29	-11.5 ± 2.0	265.0 ± 23.7	Well soluble
	Chemical indicators ( $\mu \pm \sigma$ )										
	Acid value, mg KOH g <sup>-1</sup>	Content of free acids in % of oleic acid	Saponification value, mg KOH g <sup>-1</sup>	Ether value, mg KOH g <sup>-1</sup>	Iodine value, g I <sub>2</sub> (100 g) <sup>-1</sup>	Rhodan value, g (SCN) <sub>2</sub> (100 g) <sup>-1</sup>	Amount of water-insoluble fatty acids	Amount of unsaponifiable matter, %	Sulphur content (wt.%)		
	3.80 ± 0.30	0.45 ± 0.10	170.0 ± 1.8	168.4 ± 2.1	104.8 ± 2.4	81.4 ± 1.5	92.2 ± 1.8	1.17 ± 0.15	0.0017 ± 0.005		

TABLE 4. Range of values of physical and physicochemical indicators of oil for typical representatives of the cruciferous family (indicators for the period 1950–2018 based on Firestone (2013), Tsytsiura & Tsytsiura (2015), Giakoumis (2018) and Riayatsyah et al. (2022)).

Main indicators	Rapeseed ( <i>Brassica napus</i> subsp. <i>napus</i> )	White mustard ( <i>Sinapis alba</i> L.)	Spring bittercress ( <i>Brassica campestris</i> var. <i>oleifera</i> DC.)	Camelina ( <i>Camelina sativa</i> (L.) Crantz)	Safflower ( <i>Carthamus tinctorius</i> L.)	Soybean ( <i>Glycine max</i> (L.) Merrill)	Linseed ( <i>Linum usitatissimum</i> L. var. <i>intermedia</i> )	Jatropha ( <i>Jatropha curcas</i> L.)
Kinematic viscosity, mm <sup>2</sup> s <sup>-1</sup>	74.6–77.2	66.6–69.7	75.8–78.4	51.2–53.4	65.8–68.4	56.9–57.8	60.8–62.9	57.8–61.3
Acid value	0.1–11.0	0.06–8.5	0.8–7.3	0.5–5.0	0.8–5.8	0.0–5.7	0.5–1.5	8.7–9.8
Iodine value	95–118	79–115	105–122	133–155	138–155	120–141	175–204	98–103
Flash point, °C	255.4–276.1	238.7–257.2	245.9–264.7	183.7–218.5	246.9–277.3	230.7–254.4	220.4–249.8	232.8–247.5
Solidification temperature, °C	0 to -10	-8 to -16	-6 to -8	-14 to -16	-8 to -16	-10 to -18	-16 to -27	0.5 to -1
Carbon residue (wt.%)	0.38–0.51	0.33–0.46	0.39–0.55	0.24–0.32	0.42–0.67	0.44–0.69	0.27–0.41	0.47–0.72
Net calorific value, MJ kg <sup>-1</sup>	37.1–40.2	36.4–38.2	36.8–37.2	36.5–37.0	36.4–37.0	37.0–37.6	36.7–37.0	36.7–37.2

The values of the groups of indicators presented correspond to the interval indicators defined for oil in the species category ‘fodder radish crude oil’ (CERBIO, 2007; Andrade Ávila & Sodr , 2012; Clancy, 2013; Ratanapariyanuch et al., 2013; Faria et al., 2018). According to the specified parameters, the oil from oilseed radish varieties obtained by ordinary cold pressing belongs to the group of semi-drying oils. In comparison to a

number of vegetable oils (the first 7 are most widely used in biofuel practice in the research region, and jatropha oil is gaining popularity (Riayatsyah et al., 2022)), oil from oil radish should be classified as suitable for biofuel use by basic parameters. This is confirmed by both the comparison and the conclusions of a number of studies (Andrade Ávila & Sodr , 2012; Clancy, 2013; Blume et al., 2018; Fadhil et al., 2020; Paricaud et al., 2020).

The positive aspects of this oil include a high calorific value of combustion (one of the highest among cruciferous oils) and a relatively low percentage of carbon residue, which is 0.07–0.20% lower than that of traditional rapeseed and soybean oils. The last factor was positive in view of the predicted use of fuel equipment. The negative aspects include high acidity and lower values of the ‘solidification temperature’ indicator against the background of a significantly higher value of the flash point (265 °C). The interaction of these factors in view of the research of Giakoumis (2018) and Paricaud et al. (2020) limits its use in a single-component version even with the addition of corrective organic additives (Domingos et al., 2008).

According to the presented data, it is expedient to use this oil combined with others in mixed biofuels. At the same time, the optimal version of the mixtures should be

investigated in detail, despite a some combinations containing oilseed radish oil already having been recommended in practice (Pedro et al., 2009; Andrade Ávila & Sodr e, 2012; Clancy, 2013; Faria et al., 2018; Fadhil et al., 2020).

This was confirmed by the results of changes in the basic physical and physicochemical parameters of radish oil during polymerization and oxypolymerization (Table 5). Due to the polymerization of the oil at a temperature of 280 °C, which corresponded to the maximum possible level of the flash point of the oil and its heating in combination with oxypolymerization, it was possible to study changes in the physical and physicochemical parameters of the oil under conditions close to those in a fuel supply system and its preparation before injection into the combustion chamber of an engine.

TABLE 5. Changes in the physicochemical parameters of oxypolymerized and non-oxypolymerized oil of ‘Zhuravka’ variety during polymerization (heating at 280 °C (average value for 4 years of study 2017–2020 ( $\mu \pm \sigma$ )).

Variant	Heating, h	Density at 20 °C, kg m <sup>-3</sup>	Refractive index	Acid value	Content of free acids in % of oleic acid	Saponification value	Ether n value	Iodine value
Control variant (heated oil)	-	0.913 ± 0.058	1.471 ± 0.001	3.75 ± 0.50	2.10 ± 0.55	181.15 ± 2.84	175.52 ± 7.35	108.52 ± 2.33
	1	0.928 <sup>c*</sup> ± 0.041	1.472 <sup>ns</sup> ± 0.002	18.30 <sup>a</sup> ± 1.35	9.05 <sup>a</sup> ± 2.15	186.08 <sup>c</sup> ± 3.52	170.43 <sup>c</sup> ± 6.51	93.09 <sup>b</sup> ± 3.45
Heated oil without oxypolymerization up to 120 °C	2	0.931 <sup>c</sup> ± 0.044	1.473 <sup>c</sup> ± 0.003	25.10 <sup>a</sup> ± 1.52	12.55 <sup>a</sup> ± 2.30	189.42 <sup>c</sup> ± 3.85	167.55 <sup>b</sup> ± 5.44	82.82 <sup>a</sup> ± 2.64
	3	0.935 <sup>b</sup> ± 0.051	1.474 <sup>c</sup> ± 0.002	27.95 <sup>a</sup> ± 1.60	14.20 <sup>a</sup> ± 2.70	188.21 <sup>c</sup> ± 2.15	157.71 <sup>a</sup> ± 3.62	71.72 <sup>a</sup> ± 3.52
	1	0.917 <sup>ns</sup> ± 0.035	1.473 <sup>c</sup> ± 0.002	3.50 <sup>c</sup> ± 1.78	1.74 <sup>c</sup> ± 0.16	177.89 <sup>ns</sup> ± 1.53	175.22 <sup>ns</sup> ± 4.10	105.85 <sup>ns</sup> ± 2.83
Oxypolymerized oil at 120 °C	2	0.924 <sup>c</sup> ± 0.041	1.474 <sup>c</sup> ± 0.002	3.65 <sup>ns</sup> ± 1.92	1.82 <sup>c</sup> ± 0.18	180.05 <sup>ns</sup> ± 3.20	175.59 <sup>ns</sup> ± 4.52	97.83 <sup>b</sup> ± 3.15
	3	0.924 <sup>c</sup> ± 0.052	1.474 <sup>c</sup> ± 0.002	3.79 <sup>c</sup> ± 1.87	1.87 <sup>c</sup> ± 0.14	181.55 <sup>ns</sup> ± 2.58	176.89 <sup>ns</sup> ± 3.57	97.47 <sup>b</sup> ± 2.81
	1	0.914 <sup>ns</sup> ± 0.036	1.473 <sup>c</sup> ± 0.002	3.40 <sup>c</sup> ± 1.72	1.75 <sup>c</sup> ± 0.21	179.14 <sup>ns</sup> ± 3.05	174.85 <sup>ns</sup> ± 3.89	103.92 <sup>c</sup> ± 3.92
Oxypolymerized oil at 150 °C	2	0.920 <sup>c</sup> ± 0.053	1.473 <sup>c</sup> ± 0.003	3.48 <sup>c</sup> ± 1.88	1.72 <sup>c</sup> ± 0.28	181.53 <sup>ns</sup> ± 3.28	178.15 <sup>c</sup> ± 4.18	92.56 <sup>b</sup> ± 4.09
	3	0.927 <sup>c</sup> ± 0.067	1.475 <sup>b</sup> ± 0.004	3.59 <sup>c</sup> ± 1.97	1.74 <sup>c</sup> ± 0.37	183.12 <sup>ns</sup> ± 3.91	179.58 <sup>c</sup> ± 4.63	91.72 <sup>b</sup> ± 4.56
	Level Pr (>F) for the Tukey HSD test		< 2e-3*	< 2e-2*	< 2e-3*	< 2e-6**	≈ ns	< 2e-2*

\*Letter indicates appropriate confidence level (in comparison to the control variant): <sup>a</sup> \*\*\*\*, 0.001; <sup>b</sup> \*\*\*, 0.01; <sup>c</sup> \*\*, 0.05; <sup>ns</sup> non-significant.

Considering the results of research by Dahmen & Marquardt (2017) and Tucki et al. (2019) on the behaviour of oil from oil radish under the combination of oxypolymerization and constant heating modes, it can be assessed as stable. Both modes of oxypolymerization at temperatures of 120 and 150 °C showed similar changes in the specific gravity of the oil. Moreover, long-term heating increased this indicator with respect to the control ( $p < 0.05$ ) only when heated for 2 and 3 h. The absence of a

previous oxypolymerization process increased the reaction sensitivity of the oil to long-term heating during polymerization, which led to a significant ( $p < 0.05$ ) indicator of the specific density of the oil already apparent after heating for 1 h.

On the contrary, the refractive index changed more significantly with the heating variants of pre-oxypolymerized oil. Oxypolymerization was also positively reflected in the basic indicators of acid, iodine

and ether numbers and saponification value. Significant changes in the full set of these parameters ( $p < 0.05$ – $0.01$ ) were noted only for preliminary oxypolymerization at 150 °C with heating for 2 and 3 h. The oil without prior oxypolymerization had more significant changes ( $p < 0.01$ – $0.001$ ) in terms of the basic indicators of the physicochemical properties of the oil compared to the control, especially when heated for 3 h.

The obtained results confirmed the suitability of oil from oilseed radish for thermodynamic combustion processes in regulated pressure and temperature systems. Such results are consistent with the data of Chammoun et al. (2013), Ratanapariyanuch et al. (2013), Faria et al. (2018), Brauna et al. (2020), Sala et al. (2022) and Tavares et al. (2022).

However, these conclusions are based not only on analysis of the chemical composition of the oil itself, but also take into account certain transformation processes that the oil undergoes during its stay in the fuel system of a heated engine.

## CONCLUSIONS

Based on comparison of the oil from the seeds of oilseed radish varieties of different breeding, both in terms of the fatty acid composition and its physical and physicochemical properties, this crop should be considered as one of the promising ones for use in the production of multicomponent biofuels. Oil from these varieties, on average, is characterized by a high content of monounsaturated fatty acids (59.69%), especially the highest value of oleic acid (18:1; 33.87%). PU/MU was rather lower – 0.479–0.545 – so the oxidative stability of this oil is high. The other fatty acid ratios (DR – 0.326–0.349, ER – 0.257–0.306, ODR – 0.446–0.487, LDR – 0.418–0.473, S/U – 0.099–0.132) indicate a wide range of potential biofuel use for the oil of this plant species. Particularly valuable in this regard were the varieties ‘Sabina’ and ‘Nika’ with the highest values of oleic acid (18:1; 34.62–34.97%) and an S/U ratio of 0.099–0.102. The possibility of successful use of oil from oilseed radish is also confirmed on the basis of a comparative analysis of its basic properties with those of other oils common in biofuel production. Among the valuable features are a low level of carbon residue (0.31 wt.%) and low sulphur content (0.0017 wt.%), a high calorific value (37.93 MJ kg<sup>-1</sup>) and preservation of the main physical and physicochemical parameters of the oil during high-temperature flow (polymerization), especially against the background of its oxypolymerization. The last factor confirms the possibility of successful use of this oil in closed engine systems. However, the low freezing point, high flash point and higher viscosity values are reasons to recommend its use as a component of mixed biofuels. This direction needs additional scientific study.

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