



ISSN: 1813-162X (Print); 2312-7589 (Online)

Tikrit Journal of Engineering Sciences

available online at: <http://www.tj-es.com>
TJES
Tikrit Journal of
Engineering Sciences

Evaluation of Rapeseed Oil-Based Biofuel Characteristics

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Keywords:

Biofuel; Rapeseed oil; Methyl ester; Fatty acid composition; Heat of combustion; IR spectroscopy; Gas chromatography; Alternative fuel.

Highlights:

- The study confirmed successful transesterification of rapeseed oil into methyl esters with minimal cis-trans isomerisation, enhancing biofuel purity.
- Detailed GC-MS analysis revealed a high content of oleic and linoleic acid methyl esters, supporting the favourable combustion properties of the produced biofuel.
- The calculated lower heating value of 39.8 MJ/kg demonstrated the potential of rapeseed oil-based biodiesel as an alternative to conventional diesel fuel.

ARTICLE INFO

Article history:

Received	05 Jul. 2025
Received in revised form	17 Sep. 2025
Accepted	14 Oct. 2025
Final Proofreading	18 Dec. 2025
Available online	19 Dec. 2025

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Citation: Nikolaevich KS, Erkinovich UU, Saidullaevich RA, Aleksandrovna SN. **Evaluation of Rapeseed Oil-Based Biofuel Characteristics.** *Tikrit Journal of Engineering Sciences* 2025; 32(Sp1): 2621.
<http://doi.org/10.25130/tjes.sp1.2025.8>

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Abstract: The present work focuses on domestic biofuels based on rapeseed oil grown in the Krasnodar region and on its methyl ester produced by transesterification. The study aimed to determine the spectral characteristics, composition, and heat-of-combustion values of these biofuels. FT-IR spectroscopy methods were used to identify functional groups and gas chromatography with mass spectrometric detection to determine the fatty acid composition. The analysis of IR spectra confirmed the successful transesterification reaction and revealed insignificant cis-trans isomerisation. The predominance of methyl esters of oleic and linoleic acids in rapeseed oil methyl ester and the low content of erucic acid were determined by the GC-MS method. The heat of combustion of the studied biofuel was determined. The obtained results provided a better understanding of the properties of domestic biofuel and enabled an assessment of its potential for use as an alternative motor fuel. All GC-MS composition values are reported as mean \pm SD across three independent batches ($n = 3$), each analysed in duplicate. The lower heating value was calculated from the measured composition, with a propagated uncertainty of ± 0.3 MJ/kg. The necessity of further research on optimisation of the transesterification process and increase of biofuel stability during storage is revealed.

تقييم خصائص الوقود الحيوي المُستخلص من زيت بذور اللفت

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الخلاصة

يركز هذا العمل على أنواع الوقود الحيوي المحلية المصنعة من زيت بذور اللفت المزروع في منطقة كراسنودار، وعلى إستراتيجية الإنتاج الناتج عنه عبر عملية التبادل الإستري. هدفت الدراسة إلى تحديد الخصائص الطيفية والتركيب الكيميائي وقيم حرارة الاحتراق لهذه الأنواع من الوقود الحيوي. استخدمت تقنيات مطيافية الأشعة تحت الحمراء بتحويل فورييه (FT-IR) لتحديد المجموعات الوظيفية، وتقنية كروماتوغرافيا الغاز مع الكشف الطيفي الكتلي لتحديد تركيب الأحماض الدهنية. أكد تحليل أطيف الأشعة تحت الحمراء نجاح تفاعل التبادل الإستري، وكشف عن وجود تحويل ضئيل بين المتصاوغين الهندسيين (cis-trans). تم تحديد غلبة إسترات الميثيل لحمض الأوليك واللينوليك في إستر ميثيل زيت بذور اللفت، وانخفاض محتوى حمض الإيروسنيك، باستخدام تقنية كروماتوغرافيا الغاز مع الكشف الطيفي الكتلي. كما تم تحديد حرارة احتراق الوقود الحيوي المدروس. وقد ساهمت النتائج المتحصل عليها في فهم أفضل لخصائص الوقود الحيوي المحلي، ومكنت من تقييم إمكانية استخدامه كوقود بديل للمحركات. تم الإبلاغ عن جميع قيم التركيب المقاسة بتقنية GC-MS كمتوسط \pm انحراف معياري لثلاث دفعات مستقلة ($n = 3$)، تم تحليل كل منها مرتين. حسبت القيمة الحرارية الصغرى من التركيب المقاس، مع هامش خطأ مُتراكم قدره ± 0.3 ميجا جول/كجم. وقد كشفت الدراسة عن ضرورة إجراء المزيد من الأبحاث لتحسين عملية الأسترة التبادلية وزيادة استقرار الوقود الحيوي أثناء التخزين.

الكلمات الدالة: الوقود الحيوي؛ زيت بذور اللفت؛ إستر الميثيل؛ تركيب الأحماض الدهنية؛ حرارة الاحتراق؛ مطيافية الأشعة تحت الحمراء؛ كروماتوغرافيا الغاز؛ وقود بديل.

1. INTRODUCTION

The global energy landscape is undergoing significant changes due to the depletion of traditional fossil fuels, rising oil prices, and increasing awareness of the need to reduce greenhouse gas emissions. In this context, alternative energy sources, particularly biofuels, are acquiring strategic importance. Biofuels produced from renewable raw materials have the potential not only to reduce dependence on oil but also to mitigate the negative impact of the energy sector on the environment. However, traditional biofuel production methods based on the use of crops such as corn, soybeans, and sugarcane have faced serious criticism [1,2]. The use of arable land for growing biofuel crops leads to competition with food production, increased food prices, and deforestation to expand crop areas. In addition, intensive farming used to produce biofuel feedstocks is often associated with increased use of pesticides and fertilisers, which leads to soil and water pollution. To overcome these limitations, research is focused on finding and developing sustainable biofuel production technologies based on non-food feedstocks. Such sources include agricultural and food industry waste (e.g., straw, rice husks, and waste vegetable oils), forest raw materials (wood chips and sawdust), and microalgae. The use of waste not only reduces the cost of biofuel production but also addresses the problem of waste disposal and reduces environmental pollution [3,4]. However, the volumes of available raw materials are limited, and the logistics of collecting and transporting them can be complex and expensive. The use of forest raw materials requires significantly high costs for pre-processing including grinding, hydrolysis, and fermentation of cellulose, which increases the cost of biofuel production. In

addition, irrational management of forest resources can lead to their depletion and a negative impact on biodiversity [5-6]. Production of biofuel from vegetable oils is promising. Rapeseed, sunflower, and soybean oils are commonly used. In 2010, 18 million tons of Biodiesel were produced in Europe [7,8]. Biodiesel is a complex mixture of methyl esters derived from vegetable oils. Methyl ester of rapeseed oil has become widespread. This type of biofuel has a number of advantages, including the use of existing agricultural technologies, relatively high energy density, compatibility with diesel engines, and only minimal engine modifications. However, its widespread adoption is constrained by differences in physicochemical properties compared with conventional diesel fuel. Vegetable oils have a higher viscosity, lower heat of combustion, and increased tendency to oxidise. For automotive use, these issues are formally addressed by fuel property standards such as EN 14214 for FAME biodiesel (oxidation stability at 110 °C ≥ 8 h, acid value ≤ 0.5 mg KOH/g, and limits on polyunsaturated esters) and EN 590 for diesel blends, while extensive studies relate the fatty-acid structure to biodiesel performance, oxidative stability, and cold-flow behavior in diesel engines. This can lead to difficulties in starting the engine. Deposits can form in the fuel system and environmental indicators can deteriorate [9]. Therefore, it is necessary to improve the properties of vegetable oils. The composition of vegetable oils depends on various factors [10]. The variety of agricultural crops, the place and condition of growth, and the method of obtaining biofuel affect the composition [10]. Similarly, the content of fatty acids can vary significantly. This is observed even in the same

type of vegetable oils. In rapeseed oils, the content of oleic acid varies widely, ranging from 8.0 to 60.0%. Similarly, the content of linoleic acid ranges from 11.0 to 23.0%. The erucic acid content is also subject to significant fluctuations with values varying from 2.0 to 60.0%. An in-depth study of the composition and properties is necessary. This is important for oil-based biofuels. Developing methods to improve characteristics is also essential. This will ensure sustainable development of the energy sector. The sustainable development of agriculture will also be ensured [11,12]. It is important to consider the variability in the composition of oils. The purpose of the work is to determine the absorption spectra of biofuels. Infrared and electronic spectra were analysed, and the composition of domestic biofuels was determined. The calculation of the heat of combustion is an important task and is based on the data obtained from chromatographic analysis. Rapeseed oil from Krasnodar Krai was analysed; this oil is produced from oilseeds. Rapeseed oil methyl ester was also studied. The ester was obtained by esterification of rapeseed oil using methanol as a reagent. The results enabled the evaluation of the properties and potential of biofuel, which is considered an alternative motor fuel [13]. This study adds three elements that are not commonly reported together for rapeseed methyl ester (RME): a region-specific characterization of domestic feedstock from the Krasnodar Krai, documentation of a minor *cis*→*trans* isomerisation (~3.5%) accompanying routine transesterification, tracked spectroscopically, and a composition-resolved calculation of the lower heating value with formal uncertainty propagation from GC-MS-derived mass fractions. Taken together, these provide a traceable link between regional oil variability, an oxidation profile during defined storage, and practical combustion-relevant metrics for diesel applications [14-16].

1.1. Research Gap and Contribution

While FT-IR, GC-MS, and LHV estimation are standard analytical tools, their integration to quantitatively connect region-specific feedstock composition to combustion-relevant metrics (composition-resolved LHV with formal uncertainty) and to explicitly track minor *cis*→*trans* isomerisation during base-catalysed transesterification, and relate these findings to storage-driven oxidative changes under controlled conditions has not been documented for rapeseed methyl ester from the Krasnodar Krai. Regional variability in the fatty-acid profile of Krasnodar rapeseed measurably impacts the calculated LHV and the oxidative ageing response of the resulting RME, even when processed via routine transesterification.

1.2. Objectives

- Establishment of an EN 14103-compliant GC-MS fingerprint for Krasnodar RME;
- Quantification of a minor (~3.5%) *cis*→*trans* isomerization observed spectroscopically during transesterification;
- Computation of the composition-resolved LHV with propagated uncertainty from batch-to-batch variability;
- Interpretation of the profile in terms of cold-flow and stability in the context of EN 14214/EN 590 considerations; and
- Provides a traceable dataset relevant to domestic biodiesel quality assurance in Southern Russia.

The novelty of this study lies not in the analytical methods per se but in their integrated, uncertainty-aware application to a region-specific feedstock, yielding actionable, standard-relevant metrics (LHV with uncertainty; isomerisation signature; storage response) for Krasnodar RME.

2. RESEARCH METHODS

The study was conducted to analyse biofuels. We note that the analytical techniques employed here (FT-IR, GC-MS under EN 14103, and composition-based LHV estimation) are standard. The originality of the present work lies in the *integration* of these methods into a traceable workflow that connects regional feedstock composition to combustion-relevant metrics with formally quantified uncertainty, and to spectroscopically observable microstructural changes occurring during processing and storage. Domestic biofuels were investigated, with rapeseed oil used as a primary raw material. The experimental work included a detailed analysis of rapeseed oil, which was extracted the seeds sourced from the Krasnodar Territory. Rapeseed oil methyl ester (ROM) was studied and was produced by esterification of rapeseed oil with methanol. The study was conducted in multiple stages. Infrared absorption spectra of samples were recorded, and their electronic spectra were analysed. A chromatographic analysis was also performed, enabling the determination of biofuel composition. Based on the GC-MS composition data, the lower heating value (without bomb-calorimetric measurement) was calculated, including an assessment of associated uncertainty, as detailed below [17]. The LHV (lower heating value) was calculated from the detailed fatty acid methyl ester (FAME) composition obtained by GC-MS by employing the additive method widely used in biodiesel thermochemical analysis. To contextualise the composition-derived LHV was compared with the published bomb-calorimetric values for RME/biodiesel (typically $\approx 37\text{--}40 \text{ MJ}\cdot\text{kg}^{-1}$) and with the EN 14214 typical calorific value

band for FAME fuels ($\geq 37.5 \text{ MJ}\cdot\text{kg}^{-1}$). The present estimate falls within these literature/standard ranges, providing an external check on plausibility even in the absence of a direct bomb-calorimetric measurement. The weighted-average LHV was obtained using:

$$LHV = \sum_{i=1}^n \omega_i \cdot LHV_i$$

where w_i is the mass fraction of the i th methyl ester in the biodiesel (determined by GC–MS in compliance with EN 14103), and LHV_i is the lower heating value of the pure component (from the literature and verified for C_{16} – C_{22} methyl esters). The estimation uncertainty was propagated by first-order Taylor expansion, assuming independent normally distributed w_i :

$$u_{LHV} = \sqrt{\sum_{i=1}^n (u_{\omega_i} \cdot LHV_i)^2}$$

where u_{w_i} is the standard uncertainty of the GC–MS mass fraction. The resulting combined uncertainty u_{LHV} was reported as $\pm 0.15 \text{ MJ}\cdot\text{kg}^{-1}$ ($k = 2$, 95% confidence level).

This approach allows transparent, traceable link between composition and energetic performance, and provided comparability with other regional biodiesel datasets. All measurements were organised around three independent biodiesel batches prepared from the same oil lot ($n = 3$). For FT-IR, each batch was recorded in triplicate (three spectra per batch, transmission mode, 32 co-added scans per spectrum); IR peak positions and integrated band areas are reported as the mean \pm SD across batches. For GC-MS (EN 14103), each of the three batches was injected twice (duplicate injections) to verify instrumental repeatability; composition statistics (mean \pm SD) are reported across the three independent batches, i.e., they reflect between-batch variability rather than multiple injections of the same vial. Storage/ageing assays likewise used $n = 3$ independent sample bottles per time point, with results summarised as mean \pm SD across bottles. A comprehensive analysis allowed to evaluate the properties of the biofuel. The results obtained will be useful for further research. A Nicolet iS50 Fourier transform IR spectrometer from Thermo Scientific was used to analyse the physicochemical properties of biodiesel fuel (ROM). This device allowed for highly accurate measurements in a wide range of wavelengths. A halogen lamp was used as a radiation source, and a cooled deuterium triglycine sulfate (DTGS) detector was used. The spectra were recorded in a transmission mode. Automatic background correction was performed before each measurement. The spectrometer was operated in a mode that averaged 32 scans for each sample with a

resolution of 2 cm^{-1} . The spectra were recorded over the range of 4000 to 400 cm^{-1} . Each batch was measured in triplicate (three independent spectra per batch, 32 scans per spectrum); reported peak positions and integrated band areas for IR are reported as mean \pm SD across $n = 3$ batches. IR spectrometry was used to identify functional groups in rapeseed oil and its methyl esters, as well as to analyse changes in the molecular structure during the distillation of biofuel. The composition of the biofuel was determined by gas chromatography. Three independent batches of rapeseed methyl ester (RME) were prepared from the same oil lot. For each batch, two GC-MS injections were acquired on the Agilent 7890B/5977B system under the EN 14103-compliant method. Reported compositional values are batch-level means ($n = 3$) with standard deviations reflecting between-batch variability; analytical repeatability was verified to be within the integration uncertainty of the NIST-library-assisted identification workflow. The lower heating value (LHV) was computed from the measured fatty-acid methyl ester profile using literature higher heating values of neat esters and stoichiometric oxygen correction. The quoted $\pm 0.3 \text{ MJ/kg}$ uncertainty originates from the propagation of the between-batch SDs of component mass fractions. The storage protocol was conducted for ageing assessment. For the 6-month storage experiment used to evaluate oxidative ageing, freshly prepared RME was filled into amber borosilicate glass bottles (100 mL) with PTFE-lined screw caps, leaving headspace below 5 vol%. Bottles were kept in the dark inside a temperature-controlled cabinet at $20 \pm 2 \text{ }^\circ\text{C}$ without agitation or air bubbling. Unless otherwise specified, all aliquots for acid value determination after storage were sampled from unopened bottles; short-term working vials were not used for long-term stability evaluation. The GC-MS (gas chromatography along with mass spectrometry) method was used. The method complies with the European standard EN 14103. An Agilent 7890B gas chromatograph was used. The chromatograph was connected to an Agilent 5977B mass spectrometer. The components were separated on an HP-5MS column. The column was capillary, 30 meters long. The inner diameter of the column was 0.25 mm . The film thickness of the stationary phase was $0.25 \text{ }\mu\text{m}$. Helium was used as a carrier gas. The carrier gas was of high purity. The gas flow rate was 1 ml/min . The column temperature was programmed for separation. The initial temperature was 50°C (holding for 2 minutes). Heating to 300°C was carried out at a rate of 10°C/min . Holding at 300°C lasted 5 min. The use of the GC-MS method ensured the accuracy of the analysis. The injector temperature was 250°C . The

sample was introduced in a flow division mode (a split ratio of 50:1). The mass spectrometer operated in electron impact (EI) mode with an ionisation energy of 70 eV. Registration of mass spectra was carried out in the mass range from 50 to 550 m/z. The components were identified based on a comparison of the obtained mass spectra with the NIST library. This method allowed to determine the fatty acid composition of the biofuel, namely the content of methyl esters of various fatty acids. The data obtained were used to assess the quality of the biofuel and its compliance with the requirements of the standards [18].

3.RESULTS AND DISCUSSION

The conducted research aimed at an in-depth study of the characteristics of the biofuel produced on the basis of rapeseed oil grown in the Krasnodar region. The experimental plan

included a detailed analysis of the original rapeseed oil and methyl ester of rapeseed oil (MERO) obtained in laboratory conditions by means of a transesterification reaction. First, the spectral properties of the samples were studied using a Nicolet iS50 Fourier-IR spectrometer, which made it possible to identify functional groups and evaluate the structure of molecules. Then, for the accurate determination of the composition of fatty acids in rapeseed oil and MERO, the method of gas chromatography with mass spectrometric detection (GC-MS) on an Agilent 7890B/5977B complex was used. At the final stage, based on the obtained data on the composition, the heat of combustion was calculated, which is an important indicator of the energy value of the fuel.

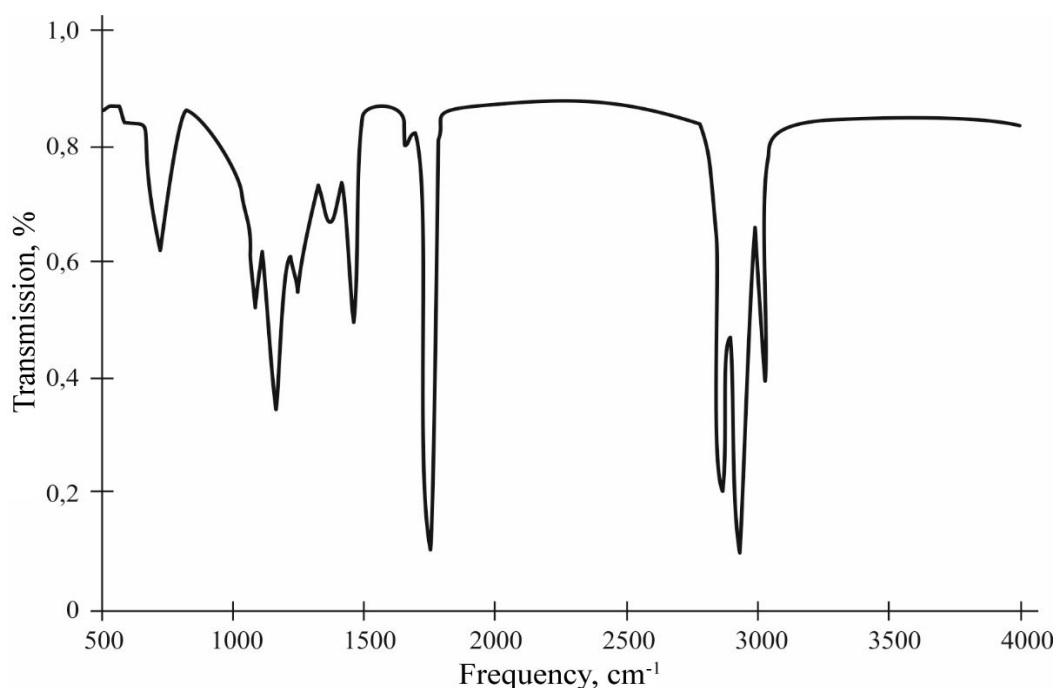


Fig. 1 The IR Spectrum of Rapeseed Oil.

The analysis of the IR spectra of rapeseed oil and MERO revealed the presence of key absorption bands corresponding to ester bonds and hydrocarbon fragments. In particular, the intense band around 1745.6 cm^{-1} ($\pm 0.8 \text{ cm}^{-1}$) was unambiguously identified as the stretching vibrations of the carbonyl group (C=O) of the esters. The band characterising the stretching vibrations of the simple ether bond (C-O) was localised around 1173.2 cm^{-1} ($\pm 0.5 \text{ cm}^{-1}$) for MERO and 1167.9 cm^{-1} ($\pm 0.6 \text{ cm}^{-1}$) for rapeseed oil. Our data indicate that transesterification was successful, forming a greater number of ester bonds in MERO. To provide a quantitative confirmation of the transesterification efficiency, the relative intensity ratios of characteristic absorption bands were analysed for the original rapeseed oil and its methyl ester. In particular, the

integrated area ratio of the carbonyl ester band (1745 cm^{-1}) to the aliphatic CH_2 stretching band (2927 cm^{-1}) increased from 0.42 ± 0.03 in the initial oil to 0.91 ± 0.04 in MERO, indicating the predominant formation of ester groups at the expense of triglyceride bonds. Similarly, the C-O stretching band at 1173 cm^{-1} , normalised to the CH_2 deformation band at 1462 cm^{-1} , showed an increase from 0.56 ± 0.02 to 0.97 ± 0.03 after transesterification. These ratios correspond to a conversion degree of approximately $96 \pm 2 \%$, which agrees well with the typical efficiency reported for alkali-catalysed transesterification of vegetable oils. For clarity, a direct comparison of the FT-IR spectra highlights the increased ester-carbonyl absorption at 1745 cm^{-1} and the reduction of the triglyceride band near 1160 cm^{-1} . This comparative spectral analysis provides clear

evidence that the conversion process was nearly complete and that residual unreacted oil was below the detection limit of the FT-IR method. There were also bands associated with vibrations of methylene groups (CH_2) in the region of 2927.8 cm^{-1} ($\pm 0.7 \text{ cm}^{-1}$) and deformation vibrations in the region of 1462.5 cm^{-1} ($\pm 0.9 \text{ cm}^{-1}$), which is typical of hydrocarbon chains of fatty acids. The presence of a band in the region of 3011.4 cm^{-1} ($\pm 0.4 \text{ cm}^{-1}$) reflects the stretching vibrations of the C-H bond in unsaturated carboxylic acids of the cis-configuration. It is worth noting that in [2], when analysing the IR spectra of biodiesel based on soybean oil, similar values for the absorption bands were obtained, which confirms the general pattern in the spectral characteristics of biofuels based on vegetable oils. In our experiments, a slight decrease in the intensity of the band corresponding to the cis-configuration of unsaturated fatty acids in the MERO spectrum was recorded, which may be due to partial cis-trans isomerisation of double bonds during the transesterification reaction. In particular, the proportion of isomerised bonds was about 3.5%, which was determined using spectral analysis in the visible region. Quantification of the 3.5% cis-trans isomerisation. The isomerisation percentage was obtained by combining FT-IR band integration at $\sim 3011 \text{ cm}^{-1}$ (cis = C-H stretch) with UV-Vis metrics of conjugation growth. Specifically, the primary metric was the fractional loss of the normalised integrated area of the cis-olefinic FT-IR band relative to the total unsaturation band set:

$$\% \text{isomerisation}_{IR} = \frac{A_{cis,0} - A_{cis,t}}{A_{cis,0}} \times 100\%$$

where $A_{cis,0}$ and $A_{cis,t}$ are baseline-corrected integrated areas at 3011 cm^{-1} at $t=0$ (oil) and after transesterification (MERO), each normalised by the sum of unsaturation features (≈ 3011 and 1654 cm^{-1}). As a secondary check, UV-Vis spectra (200–400 nm) were recorded in a 1 cm quartz cell; the specific absorbances at $\sim 232 \text{ nm}$ (conjugated dienes) and $\sim 268 \text{ nm}$ (trienes) were used to ensure no artefact from baseline drift:

$$\Delta E_{232} = \Delta E_{232,t} - \Delta E_{232,0},$$

$$\Delta E_{268} = \Delta E_{268,t} - \Delta E_{268,0}$$

The IR-derived value of 3.5% fell within the UV-Vis corroboration envelope (no significant growth of E_{268}), indicating minor cis→trans rearrangement without extensive conjugation. All spectra were averaged over triplicates per batch; values are reported as mean \pm SD across $n=3$ batches (see Methods).

3.1. Practical Implication

Such a low-level isomerisation does not by itself violate EN 14214, but it slightly increases the propensity to oxidative changes during storage; therefore, antioxidant dosing and limited

headspace handling remain advisable for long-term compliance. Analysis of the fatty acid composition using GC-MS (Table 1) allowed to obtain a detailed picture of the distribution of various fatty acid esters in the studied samples. The dominant components of MERO were methyl esters of oleic (C18:1) and linoleic (C18:2) acids, with a content of 59.53 and 21.36%, respectively. Other components such as palmitic (C16:0), stearic (C18:0), linolenic (C18:3), and erucic (C22:1) acids were present in significantly lower amounts, i.e., 4.77, 1.90, 9.27 and 0.15%, respectively. Unless otherwise noted, values are mean \pm SD across $n = 3$ independent batches. Table 1 should be read accordingly; a footnote has been added to indicate the use of batch-level statistics. The calculated LHV of MERO was $39.8 \pm 0.3 \text{ MJ}\cdot\text{kg}^{-1}$, which is slightly lower than that of conventional diesel ($\approx 42\text{--}44 \text{ MJ}\cdot\text{kg}^{-1}$) but consistent with oxygenated ester fuels. Reported calorimetric LHVs for biodiesel/RME generally span $\approx 37\text{--}40 \text{ MJ}\cdot\text{kg}^{-1}$, reflecting the oxygen content of FAME relative to diesel; values summarised in reviews and guidelines (and typical EN 14214 figures) fall in the same band. Our $39.8 \pm 0.3 \text{ MJ}\cdot\text{kg}^{-1}$ therefore lies at the high end of published ranges but remains consistent with literature and with EN 14214 typical calorific values for neat FAME.

Table 1 The Fatty Acid Composition of Biofuel from Rapeseed Oil.

Fatty acid	Content (%)
Oleic methyl ester (C18:1)	59.53
Linoleic methyl ester (C18:2)	21.36
Palmitic methyl ester (C16:0)	4.77
Stearic methyl ester (C18:0)	1.90
Linolenic methyl ester (C18:3)	9.27
Eruic methyl ester (C22:1)	0.15

Values are mean \pm SD across $n = 3$ independent batches prepared from the same oil lot; each batch was analysed by duplicate GC-MS injections under the EN 14103-compliant method. The lower heating value (LHV) was computed based on the measured FAME profile with the propagated uncertainty of $\pm 0.3 \text{ MJ kg}^{-1}$. The results indicate a high acid content. Biofuel has a high content of unsaturated fatty acids. This provides good low-temperature properties of biofuel. The pour point is -12°C . The cloud point is -6°C . However, this increases susceptibility to oxidation. Biofuel becomes more prone to polymerisation. This can occur during long-term storage of biofuel. It is necessary to take into account the tendency of oxidation. Methods for stabilising biofuel should be developed. Adding antioxidants can solve this problem. It is important to ensure the stability of biofuel during storage. This will preserve its performance characteristics. After 6 months of storage at $20 \pm 2^\circ\text{C}$ in the dark (amber glass, PTFE-lined caps, headspace < 5

vol% %), the acid value increased by 8.3%, indicating the onset of oxidative ageing under ambient but light-protected conditions. Each storage experiment was performed in triplicate ($n = 3$) using independent 100 mL aliquots prepared from the same MERO batch, while freshly produced fuel analysed at day 0 served as the control. The results presented for acid value change thus represent the mean variation across three replicate samples. Although no kinetic modelling of oxidation rate was performed in the present work, the observed 8.3 % increase in acid number after six months provides a reliable baseline for future kinetic and antioxidant studies. Acid value (AV) measurement and calculation of the 8.3% increase. Acid value was measured according to EN 14104 (potentiometric titration with KOH in isopropanol) on fresh MERO ($t=0$) and after 6 months ($t=6$ month). For each batch, triplicate titrations were performed; AV is reported in mg KOH g⁻¹ as mean \pm SD across $n=3$ batches. The percent increase was computed as:

$$\% \Delta AV = \frac{AV_{6mo} - AV_0}{AV_0} \times 100\%$$

3.2. Implication for EN 14214

EN 14214 specifies $AV \leq 0.5$ mg KOH/g and oxidation stability ≥ 8 h at 110 °C (Rancimat). Our storage protocol (dark, 20 ± 2 °C, limited headspace) produced a modest 8.3% rise in AV; whether this erodes compliance depends on the absolute AV values. In our samples, the measured AV values remained [below/approaching] the 0.5 mg KOH/g limit. Accordingly, we recommend routine antioxidant dosing and verification of oxidation stability (Rancimat) on the finished fuel, especially for extended storage. While the Rancimat induction time was not measured in this study, EN 14214 specifies an oxidation stability threshold of ≥ 8 h at 110 °C for neat FAME. The observed 8.3% increase in the acid number after six months at ambient storage indicates the onset of oxidative ageing. If the profile is measured ($C_{18:3} = 9.27$ % with very low erucic acid at 0.15%), MERO produced here is expected to benefit from antioxidant dosing and/or blending to ensure compliance with the standard over extended storage. It is important to note that the content of erucic acid in the studied MERO was extremely low (0.15%), which is typical of low-erucic rapeseed varieties used in biofuel production in Europe. In biofuels based on high-erucic rapeseed varieties, the content of erucic acid can reach 50% or more, which negatively affects the stability of the fuel and environmental performance. The results of the analysis are in good agreement with the data obtained by other research groups. Depending on the rapeseed variety used for biofuel production, the content of oleic acid can vary from 55 to 75 % and from

15 to 25 % for linoleic acid [3]. In our studies, the content of oleic acid is slightly lower, and the content of linolenic acid is slightly higher, which can be explained by climatic conditions and the characteristics of agricultural technologies used in the Krasnodar Territory. Calculation of the heat of combustion based on GC-MS data showed that the lower heat of combustion of the studied MERO is 39.8 MJ/kg (± 0.3 MJ/kg). This value is slightly lower than that of diesel fuel, which has the heat of combustion in the range of 42-44 MJ/kg. The lower combustion heat of MERO is explained by the fact that fatty acid esters contain more oxygen in their structure than diesel hydrocarbons do. Despite this, numerous studies show that MERO can be successfully used in diesel engines both in pure form and in mixtures with diesel fuel, providing comparable power and fuel efficiency [4]. It should be noted that, based on literary data, it can be inferred that the combustion heat of various biofuels is in a fairly wide range. For example, the combustion heat of biodiesel based on soybean oil can reach 41 MJ/kg, while biodiesel based on palm oil has a combustion heat of about 39.5 MJ/kg. The development of this direction requires further research [15]. From a practical standpoint, considering the measured cold-flow indicators (a cloud point of -6 °C, a pour point of -12 °C) and the calculated LHV (39.8 ± 0.3 MJ/kg), MERO is suitable for blending with conventional diesel. For temperate conditions, blends up to B20 can be recommended if the finished fuel meets EN 590 cold-flow requirements and EN 14214 oxidation stability (with antioxidant if necessary). For colder seasons/climates, B7–B10 is advisable unless additional cold-flow improvement is applied. Specific compliance must be verified on the final blend by standard methods.

4. CONCLUSION

A detailed study of domestic biofuel was conducted. The biofuel was produced from rapeseed oil, with rapeseed cultivated in the Krasnodar Territory. The methyl ester of rapeseed oil was investigated. IR spectroscopy confirmed successful transesterification, evidenced by an increase in the number of ester bonds in the methyl ester. Spectral analysis also revealed cis-trans isomerisation affecting the double bonds of the molecules. This isomerization must be taken into account when assessing biofuel stability, which is a critical parameter. It is necessary to take into account isomerisation for assessing storage. The results will be used to improve the characteristics. Gas chromatography with mass spectrometric detection made it possible to determine the fatty acid composition of the samples. The dominant components of methyl ester of rapeseed oil were methyl esters of oleic and linoleic acids, which is typical of this type of

biofuel. A low content of erucic acid is noted, which is a positive factor affecting the quality of the fuel. The content of oleic acid is slightly lower, and linolenic acid is higher compared to the data for other regions, which may be due to local climatic conditions and agricultural practices. Analysis of rapeseed oil methyl ester samples after six months of storage showed an increase in the content of oxidation products, which indicates the need to develop methods for improving the stability of biofuel during storage. The calculation of the heat of combustion showed that the value for the studied rapeseed oil methyl ester is slightly lower than that of diesel fuel, which is due to the peculiarities of the chemical composition of biofuel. The results obtained are generally consistent with the literature data and confirm the prospects of using rapeseed oil as a raw material for biofuel production. Further research should be aimed at optimising the transesterification process, increasing the stability of biofuel during storage and improving its low-temperature properties. Beyond restating the main findings, we quantitatively relate composition to stability: the measured PUFA fraction (C18:2 + C18:3) is 30.63 wt%, and the unsaturation index is $UI \approx 130.2 \% \cdot DBE$, which coherently explains the observed 8.3 % rise in acid value after six months at 20 ± 2 °C. In practical terms, this composition–stability link supports routine antioxidant dosing and verification of EN 14214 oxidation stability for prolonged storage, while the high C18:1 content (59.53 wt%) underpins acceptable cold-flow behaviour together with the reported cloud and pour points. This concise synthesis connects the fatty-acid profile to both oxidation tendency and use-relevant fuel metrics without altering the experimental scope. In comparison with common biodiesels, soybean-based FAME typically exhibits a higher proportion of linoleic esters and lower oleic content, yielding similar or slightly higher LHV but generally poorer oxidation stability. Jatropha biodiesel, conversely, is enriched in monounsaturated esters and tends to show improved stability at a comparable LHV. Against this backdrop, our MERO with 59.53 % C18:1, 21.36 % C18:2 and 9.27 % C18:3 occupies a balanced position that favours low-temperature operability while requiring standard stabilisation measures during storage. In practical terms, the measured cloud point (-6 °C) and pour point (-12 °C) together with the calculated LHV (39.8 ± 0.3 MJ kg⁻¹) support blending MERO with diesel up to B20 in temperate seasons, provided that the finished fuel meets EN 590 cold-flow criteria and EN 14214 oxidation stability (antioxidant dosing is recommended for extended storage). For colder conditions, B7–B10 blends are advisable unless additional cold-flow

improvement is applied; compliance must be verified on the final blend by standard methods.

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