

FACILE METHODS FOR DIESEL/BIODIESEL BLEND RATIO DETERMINATION IN RUBBER SEED METHYL ESTER

CHAN JING HUI¹, SITI NORHAFIZA MOHD KHAZAAI^{1*}, LILIWIRIANIS NAWI¹, SARAH LAILA MOHD JAN¹, NURUN NADHIRAH MD ISA¹, SITI RAIHAN ZAKARIA² AND GAANTY PRAGAS MANIAM³

¹Faculty of Applied Sciences, Universiti Teknologi MARA, Pahang Branch, 26400 Bandar Tun Abdul Razak Jengka, Pahang, Malaysia. ²Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia. ³Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang Al-Sultan Abdullah, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia.

*Corresponding author: ctnorhafiza@uitm.edu.my

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Abstract: Biodiesel is recognised as a highly sustainable alternative bioenergy to mitigate the adverse impacts of fossil fuel use. Blending biodiesel into diesel fuel at specific ratios has been mandated in various countries. In this regard, the study intends to determine the diesel or biodiesel blend ratio in rubber seed methyl ester using several facile methods. The processes of acid-catalysed esterification and base-catalysed transesterification were employed to produce 92.60% rubber seed methyl ester. A series of diesel/biodiesel blends of B20, B40, B60, and B80 were prepared by mixing the biodiesel with pure diesel. Euro 5 (B7) was obtained from the local petrol station for analysis. B80 showed the highest value for several tested parameters, including an acid value of 0.3927 mg KOH/g, a peroxide value of 8.7464 meq/kg, and a density of 0.8701 g/cm³. Meanwhile, Euro 5 (B7) achieved the highest refractive index and UV absorbance values at 1.4601 nD and 0.927, respectively. Moreover, good linearity was observed for all tested parameters with R² values between 0.9097 and 0.9993, validating them as strong indicators for the determination of blend ratio, except for the refractive index, which showed an R² value of 0.6366. However, all tested parameters met the criteria outlined in the EN/ASTM standard methods. Thus, this study helps to provide an approach for related industries to validate the percentage blend claims made by other parties in minimal time.

Keywords: Diesel or biodiesel blending, rubber seed methyl ester.

Introduction

Along with the development of industrialisation and urbanisation in this contemporary world, energy—especially fossil fuel—plays a significant role. Their emissions containing carbon dioxide, sulfur dioxide, nitrogen oxides, and particulates give rise to acute environmental problems such as greenhouse gases, air pollution, and climate change. Note that continued and frequent use of petroleum exacerbates air pollution, as it contributes to global warming by releasing more carbon dioxide into the atmosphere. Rubber Seed Oil (RSO), derived from *Hevea brasiliensis* seeds is a promising non-edible oil for biodiesel production due to its abundance and renewability, as it is a byproduct of the rubber industry (Blagodatsky *et al.*, 2016;

Oyekunle *et al.*, 2024). Moreover, with a high oil content of 50% to 60%, it is compatible with existing fuel infrastructure and can reduce greenhouse gas emissions when blended with fossil diesel (Khazaai *et al.*, 2017; Sugebo *et al.*, 2021). Additionally, since it does not compete with food production, it potentially lowers biodiesel costs (Kumar *et al.*, 2022).

Biodiesel has gained increased attention worldwide as a promising alternative fuel for diesel-based engines due to the benefits of reduced greenhouse gas emissions, sulfur-free content, higher oxygen supply, biodegradability, less smoke and particulate matter production, non-toxicity, and sustainability (Chia *et al.*,

2022). Esterification is commonly used to produce biodiesel from feedstock with high free fatty acid content, such as Palm Fatty Acid Distillate (PFAD), RSO, or Waste Cooking Oil (WCO), using either homogeneous or heterogeneous acid catalysts with water as a byproduct (Alsultan *et al.*, 2021).

Blending has been widely applied to enhance biodiesel fuel properties in recent years. Some crucial fuel properties for its use in engines, including flash point, kinematic viscosity, density, and cetane number, can be easily enhanced through multiple fuel blends (Razzaq *et al.*, 2020). Consequently, the vital attributes of biodiesel and its blends are employed as input data for predicting engine combustion models. They verify biodiesel concentration in diesel/biodiesel blends by fluorescence spectroscopy and X-ray spectrometry. They reported density as a simultaneous function of blend percentage to forecast the biodiesel blend (Khazaai *et al.*, 2023).

According to the Malaysian Biofuel Industry (Blending Percentage and Mandatory Use) Regulations (2019), biofuel blends are mandatory for specified activities only. A specific blend level of biodiesel is needed to guarantee the intactness of engine parts. On the other hand, the variation of blend level in biodiesel influences several critical fuel properties, including viscosity, density, flash point, moisture content, and flow point, which in turn affects market prices (Khazaai *et al.*, 2020). Thus, biodiesel blends in the market must comply with their specifications based on their labels and disprove the fraudulent claims made about the biodiesel ratio by producers. Such fraud could affect monetary gains and losses in the fuel markets. Consequently, facile methods for determining biodiesel/diesel blend levels must be developed to obtain reliable data on the physical properties of the related blends, as claimed.

The specific objectives of this research are to prepare biodiesel via acid-catalysed esterification and base-catalysed transesterification from RSO and determine the blend level of diesel

or biodiesel using several physicochemical properties and instrumental analyses, including Gas Chromatography-Mass Spectroscopy (GC-MS) and UV-Vis spectrometer. The tested parameters included acid value, peroxide value, density, and refractive index, chosen for their simple procedures that allow quicker testing.

Materials and Methods

Rubber seeds were obtained from the Rubber Industry Smallholders Development Authority (RISDA). The rubber seed shells were cracked to obtain the kernels. Correspondingly, the kernels were roasted in an oven at 100°C overnight to remove moisture. The dried kernels were ground into a fine powder (Wint *et al.*, 2019). Ultrasonic-Assisted Solvent Extraction (UASE) was applied to extract RSO from the kernel powders. The ultrasound bath was preheated to 60°C. Each flat-bottom cylindrical flask containing kernel powders and n-hexane solvent in a ratio of 1:3 was placed in the ultrasound bath for 24 hours (Wint *et al.*, 2019). Rotatory evaporation under vacuum at 60°C to 65°C was employed to remove n-hexane from the extracted RSO.

The 80 g of extracted RSO was added into a 1 L flat bottom flask with a magnetic stirrer. Esterification was carried out with a methanol-to-oil molar ratio of 25.74:1, 2 wt.% of H₂SO₄, and a stirring rate of 750 rpm at 63.04°C for 2.5 hours. Correspondingly, the reacted mixture was then transferred to a separating funnel to separate into two layers. The esterified RSO was added into a 1 L flat bottom flask with a magnetic stirrer. Transesterification was carried out with a methanol-to-oil molar ratio of 9:1, NaOH of 0.5 wt.%, and a stirring rate of 750 rpm at 63°C for 1.5 hours. The reacted mixture was then transferred to a separating funnel to separate into two layers. Subsequently, the biodiesel layer was heated to remove all the solvent and water.

Characterisation of Biodiesel

Samples for GC analysis were prepared by mixing about 20 mg of FAME with 400 µL of methyl heptadecanoate (C₁₇) using a

micropipette. The concentration of methyl heptadecanoate, which acted as an internal standard, was 10 mg/mL using n-heptane as solvent. The column used for GC analysis was an HP-5MS (length 30 m × internal diameter 0.25 mm × thickness 0.25 μm). Each sample was set with an injection volume of 0.6 μL for each analysis. Note that helium was used as the carrier gas with a linear velocity of 40 cms⁻¹. The oven temperature was programmed to start at 190°C with a 2-minute holding time, then ramped at 10°C/min until it reached 230°C, followed by a final 8-minute holding time (Zawadzki *et al.*, 2007; Zhen *et al.*, 2022).

Blending of Diesel/Biodiesel

Upon the complete purification of biodiesel, a series of diesel/biodiesel blends [Euro 5, B20 (20B: 80D), B40 (40B: 60D), B60 (60B: 40D), B80 (80B: 20D)] was prepared by mixing the corresponding volumes of pure diesel and pure biodiesel. The tested parameters were evaluated according to the standards of acid value (EN 14214), peroxide value (ASTM D6751), density (ASTM D1480/81), and refractive index (ASTM D1218). On the other hand, methyl ester yield was determined in accordance with the European regulatory procedure EN 14103. This involved comparing the identified methyl ester peaks with those of the corresponding internal standard.

UV-Vis Absorbance

Each sample of pure diesel and blends was diluted in three repeats. Consequently, the UV absorption spectra of all samples were measured using a single-beam and general-purpose

spectrophotometer. The absorption spectra of samples were scanned in the range of 190 nm to 350 nm with 1 nm intervals using standard 1 cm quartz cuvettes (Zawadzki *et al.*, 2007).

Results and Discussion

Characterisation of Biodiesel

Qualitative analysis of the biodiesel produced from transesterification was conducted using GC-MS. Based on the results in Table 1, unsaturated FAME, which is methyl oleate at 35.00%, was the main component present in the biodiesel derived from RSO. This characteristic may decrease the temperature and lower the cloud point and cetane number. Additionally, feedstock that contains more unsaturated fatty acids works better in cold climates (Khazaai *et al.*, 2024). On the other hand, Pandiangan *et al.* (2021) reported that the main ester present in RSO biodiesel was methyl oleate at 47.81%, which supported the present findings.

Meanwhile, the results indicated that methyl palmitate, at 15.08%, was the major saturated FAME discovered in the biodiesel, which agreed with other findings (Ibrahim *et al.*, 2021). There were many other FAMES present in the biodiesel, such as methyl myristate, methyl stearate, and methyl arachidate, at 0.11%, 5.86%, and 0.23%, respectively. Koffi *et al.* (2022) stated that the FAME composition can vary due to the location and varieties of the rubber tree from which the seeds were collected. A low saturated FAME content in biodiesel could lead to a decrease in oxidation stability, while a high unsaturated FAME content will make it more resistant to cold (Sugebo *et al.*, 2021).

Table 1: FAME composition of biodiesel from the RSO

Retention Time (min)	Systematic Name	Trivial Name	Molecular Formula	Composition (%)
32.289	Methyl tetradecanoate	Methyl myristate	C ₁₅ H ₃₀ O ₂	0.11
36.587	Methyl hexadecanoate	Methyl palmitate	C ₁₇ H ₃₄ O ₂	7.27
40.713	Methyl 9-octadecenoate	Methyl oleate	C ₁₉ H ₃₆ O ₂	35.00
40.995	Methyl octadecanoate	Methyl stearate	C ₁₉ H ₃₈ O ₂	5.86
45.284	Methyl eicosanoate	Methyl arachidate	C ₂₁ H ₄₂ O ₂	0.23

Acid Value

Euro 5 (B7) achieved the lowest acid value of 0.0707 mg KOH/g, while B80 had the highest acid value of 0.3927 mg KOH/g compared to other biodiesel blends. The acid values for blends B20, B40, and B60 were 0.1728 mg KOH/g, 0.2513 mg KOH/g, and 0.3534 mg KOH/g, respectively. As a result, the acid value of the blends increased from Euro 5 (B7) to B80 as the biodiesel content in the blends increased due to the fatty acid content in the biodiesel. The strong correlation coefficient of the relationship between acid value and biodiesel content was 0.9833, as shown in Figure 1. All the diesel/biodiesel blend samples met the ASTM D7467 acid value requirement.

Peroxide Value

Referring to Figure 1, Euro 5 (B7) achieved the lowest peroxide value of 1.3883 meq/kg, while B80 had the highest peroxide value of 8.7464 meq/kg compared to other biodiesel blends. The peroxide values for blends B20, B40, and B60 were 3.4708 meq/kg, 4.4426 meq/kg, and 5.6921 meq/kg, respectively.

As a result, the peroxide values of the blends increased from Euro 5 (B7) to B80 as the biodiesel contents in blends increased. Refdi *et al.* (2023) stated that the peroxide level is linked to the unsaturated fatty acids content in the biodiesel, which are prone to react at the double bonds. These double bonds contribute to autoxidation and facilitate the formation of peroxide compounds. Note that the strong correlation coefficient of 0.9598 for the relationship between peroxide value and biodiesel content further supports this relationship.

Density

Meanwhile, Euro 5 (B7) achieved the lowest density value of 0.8264 g/cm³ for the density parameter, while B80 obtained the highest density value of 0.8701 g/cm³ compared to other biodiesel blends. According to Figure 1, the density values for blends such as B20, B40, and B60 were 0.8370 g/cm³, 0.8483 g/cm³, and 0.8602 g/cm³, respectively.

As a result, the density of the blends increased from Euro 5 (B7) to B80 as the biodiesel content in the blends increased. Khazaai *et al.* (2023) revealed that biodiesel has a higher density than pure diesel due to the presence of longer fatty acid carbon chains. Biodiesel molecules possess stronger intermolecular attractions, such as dispersion forces and dipole-dipole attractions, than petrochemical molecules. These forces pull the chains of biodiesel closer to one another, increasing the mass of molecules contained in each volume (Akhiehiero *et al.*, 2019). As expected, the strong correlation coefficient of the relationship between density and biodiesel content was 0.9993. All the diesel/biodiesel blend samples met the ASTM specifications.

Refractive Index

B80 achieved the lowest refractive index of 1.4582 nD, while Euro 5 (B7) obtained the highest refractive index of 1.4601 nD compared to other biodiesel blends, (Figure 1). The refractive indices for blends such as B20, B40, and B60 were 1.4585 nD, 1.4584 nD, and 1.4583 nD, respectively.

As a result, the refractive index of the blends decreased from Euro 5 (B7) to B80 as the biodiesel content in the blends increased. This phenomenon can be explained by the fact that diesel consists of a complex mixture of hydrocarbons, making it denser and more viscous, which causes light to travel slower in the medium compared to the simpler biodiesel molecules with a moderate correlation coefficient (0.6366) between refractive index and biodiesel content (Ashqer *et al.*, 2019). All the diesel/biodiesel blend samples met the ASTM D1218 refractive index requirement.

UV-Vis Absorbance

Benzene, the simplest aromatic compound, exhibits maximum absorption at a wavelength in the vicinity of 255 nm (Akash *et al.*, 2020). At 248 nm, B80 achieved the lowest absorbance value of 0.048, while Euro 5 (B7) obtained the highest absorbance value of 0.927 compared to other biodiesel blends. The absorbance values at

248 nm for blends such as B20, B40, and B60 were 0.462, 0.437, and 0.125, respectively.

As a result, the absorbance value of the blends decreased from Euro 5 (B7) to B80 as the biodiesel contents in the blends increased. This decrease in absorbance can be attributed to the decrease in the proportion of the absorbance of aromatic compounds at each wavelength when

they are diluted with biodiesel (Zawadzki *et al.*, 2007). Hence, there is a strong correlation coefficient of 0.9097 between absorbance value and biodiesel content (Figure 1).

Note that all the data collected from each characterisation test is summarised in Table 2. The results for a series of biodiesel/diesel blends were compared to the data from standard methods.

Table 2: Characterisation of a series of diesel/biodiesel blends

Results						
Test	Euro 5 (B7)	B20	B40	B60	B80	Standard Method
Acid value (mg KOH/g)	0.0707	0.1728	0.2513	0.3534	0.3927	0.5
Peroxide value (meq/kg)	1.3883	3.4708	4.4426	5.6921	8.7464	-
Density (g/cm ³)	0.8264	0.8370	0.8483	0.8602	0.8701	0.86-0.90
Refractive index (nD)	1.4601	1.4585	1.4584	1.4583	1.4582	1.3300-1.5000
UV absorbance value	0.927	0.462	0.437	0.125	0.048	-

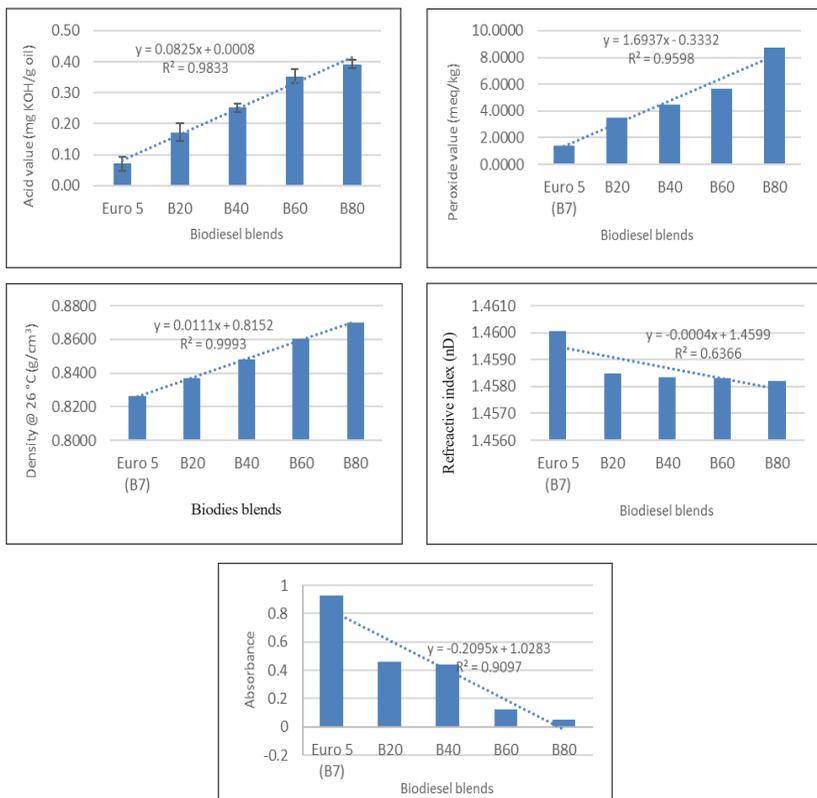


Figure 1: Graph of (a) acid value, (b) peroxide value, (c) density, (d) refractive index, and (e) absorbance at 248 nm against biodiesel blends

Conclusions

In this study, synthesising biodiesel derived from RSO was conducted through acid-catalysed esterification, followed by base-catalysed transesterification, resulting in 92.60% of biodiesel production. Acid-catalysed esterification was performed due to the high levels of free fatty acids in the rubber seed kernel. Based on the results, the acid value, peroxide value, and density of blends from Euro 5 (B7) to B80 increased with the biodiesel content, respectively. As for refractive index and UV absorbance, the values of blends decreased with the biodiesel content from Euro 5 (B7) to B80, respectively.

These findings showed that acid value, peroxide value, density, and UV absorbance value were promising indicators for predicting biodiesel fraction in diesel/biodiesel blends with a good approximation. In comparison, the refractive index was the least promising indicator for diesel/biodiesel blend ratio determination as it had the lowest correlation coefficient. Biodiesel blends derived from RSO met the criteria for tested parameters according to EN/ASTM standard methods.

To conclude, the outlined blend determination methods streamline quality control processes by saving time and yielding monetary gain by refuting inaccurate claims regarding the blend percentage. In the future, additional research and optimisation for sustainability and efficiency of the engine performance in the pursuit of greener transportation fuels will be undertaken, emphasising the potential of other feedstock in biodiesel blends.

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Conflict of Interests Statement

The authors declare that they have no conflict of interest.

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