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RESEARCH ARTICLE

The Effect of Diesel/Biodiesel Blend Ratio on Physical-Chemical Properties of Biodiesel

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ABSTRACT - Biodiesel is a highly sustainable alternative to alleviate fossil fuel shortages and environmental concerns. Many countries have adopted the practice of blending biodiesel into diesel at specific ratios. This study focused on the effect of different biodiesel-diesel blend ratio in terms of acid value, saponification value, peroxide value, and iodine value, and analysed by using Ultraviolet-Visible (UV-Vis) spectroscopy. A series of diesel-biodiesel blends of B20, B40, B60, and B80 were prepared by mixing the biodiesel produced by refined, bleached, and deodorized palm oil through transesterification reaction with pure diesel. Based on the result, the FTIR spectrum showed a slight change in intensity and wavenumber for some possible functional groups but retained the same main characteristic peaks such as C=O, C-O, and OCH_3. Predominant compound in biodiesel is oleic acid. Furthermore, acid value, saponification value, iodine value, and peroxide value increased from Euro 5 (B7) to B80 with linear regression (R^2) of 0.9817, 0.9971, 0.7521, and 0.9911, respectively. The absence of aromatic compounds in biodiesel causes a decrease in the absorbance of UV light from Euro 5 to B80. Yet, tested parameters were positively accepted according to ASTM - D6751 standard method. Hence, determining the physicochemical properties of blend ratio is vital for industries to counter false claims economically and effectively.

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1. INTRODUCTION

Biodiesel, derived from a renewable source, possesses environmentally friendly qualities and the stability to naturally regenerate over time. It offers several advantages, including non-toxicity, non-flammability, reduced tailpipe emissions, low sulfur, biodegradability, and engine durability, which is like petroleum diesel fuel [1]. The main goal of utilizing biodiesel blend is to reduce carbon footprint from various sectors. Currently, approximately 80% of the world's energy relies on fossil fuels, and 98% of them produce carbon [2]. Fossil fuel additives such as benzene, toluene, and ethylbenzene lead to the release of carcinogens. One in five deaths worldwide is caused by fossil fuel pollution. Fossil fuel pollution caused 350,000 premature deaths in the United States in 2018, with states such as Pennsylvania, Ohio, and West Virginia having the highest number of deaths per capita [3]. Therefore, alternative biofuels are keen to replace fossil fuels. This can be done by blending diesel with biodiesel. For instance, when 20% of biodiesel is reacted with 80% of diesel, it is known as B20. The implementation of B20 on-road, alongside a B7 mandate for the industry, is projected to prevent emissions equivalent to 3.88 million tonnes of CO_2 per year [4]. This program may contribute to lowering national greenhouse gas emissions rather than solely as a market strategy to support palm oil prices.

Therefore, plotting different physicochemical values against different blend ratios can help to determine the ratio's efficiency. In this research, palm-based biodiesel is characterized in terms of acid value, saponification value, peroxide value, and iodine value, and analyzed by Fourier Transform Infrared Spectroscopy (FTIR) and gas chromatography-mass spectroscopy (GC-MS). Then, different diesel-biodiesel blend ratios are determined in terms of acid value, saponification value, peroxide value, and iodine value, and analyzed by using ultraviolet spectroscopy. Nationwide is implementing higher biodiesel content in fuels such as B5, B7, B10, and B20 not only to solve environmental problems, but also to increase energy security. However, there is a concern regarding the accuracy of blend ratios, which is known as false claims. False claims not only disrupt the integrity of the biodiesel market, but also lead to increased costs for end-users, and cause problems in engine performance. The selection of biodiesel blends by consumers does not automatically invalidate engine warranties, as Paccar offers coverage for engines that meet ASTM D6751 specifications [5]. Thus, this study will evaluate a rapid and accurate method is required to determine blend ratios. The testing parameters of the diesel-biodiesel properties should be easy with factual results.

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2. METHODS AND MATERIAL

The transesterification of 150 g of palm oil, methanol to oil ratio, (12:1) and 1.2 wt% of potassium hydroxide (KOH) was carried out in a 500 mL three-neck round bottom flask with a magnetic stirrer, condenser, and thermometer, immersing in a water bath within 1 h at 60 °C. After the overnight stand, the separation of the two phases was observed. The top layer of transparent yellowish liquid will be methyl ester (crude biodiesel), and the second layer of deep yellow liquid will be the by-product of glycerol. Synthesized methyl ester contained impurities such as glycerol, unreacted methanol, soap, and other unfiltered contaminants. To obtain pure biodiesel, the biodiesel was washed with distilled water. Glycerol was carefully discarded, and warm water was slowly poured into the synthesized biodiesel. The separating funnel was capped tightly, the separately funnel was turned upside down 4-5 times to let the water soak up the impurities and let it settle for 30 min. Water appeared cloudy for the first washing. Hence, the washing was repeated several times until the water became clear or the pH of biodiesel became 7 is necessary. The biodiesel of palm oil was split to produce 4 different concentrations of diesel- biodiesel with a ratio of blend levels as B20 (10% biodiesel, 90% petroleum diesel), B40 (40% biodiesel, 60% petroleum diesel), B60 (60% biodiesel, 40% petroleum diesel), and B80 (80% biodiesel, 20% petroleum diesel). This blending was used to test their variation in acid value (EN 14214), saponification value, iodine value, and peroxide value (ASTM D6751) together with Euro 5 (B7). The methyl ester yield was determined following the European regulation procedure EN 14103 by comparing the identified methyl ester peaks with the respective internal standard [6].

3. RESULTS AND DISCUSSION

By using gas chromatography-mass spectroscopy (GC-MS), the highest methyl ester conversion was 95.67%. The results showed that biodiesel employed in this study predominantly comprised oleic acid, which was 29.45% of the relative content. The fatty acid composition in biodiesel is saturated, accounting for 34.38% of the overall fatty acid content, with palmitic acid being the highest among the saturated fatty acids at 20.84%. According to Bôas and Mendes [7], different raw materials exhibit different fatty acid compositions, and these compositions play a crucial role in determining the compositions of biodiesel produced. Palm oil is primarily composed of oleic acid, followed by palmitic acid. Same observation biodiesel produced in this study also exhibits a high content of oleic acid and palmitic acid.

According to Figure 1, the Fourier Transform Infrared Spectroscopy (FTIR) spectrum for refined, bleached, and deodorized palm oil (RBDPO) and biodiesel, there are minor differences. They retain the same main peaks in their spectrum as the biodiesel product is chemically like its precursor (RBDPO). In the range of 3006 cm^{-1} to 2853 cm^{-1}, which main groups in both compounds. Also, for both spectra, the main characteristic peaks were shown at about 1740 cm^{-1}, which is C=O stretching for the ester carbonyl group as both fatty acid methyl ester (FAME) and palm oil consists of fatty acids with RCOO structure. For both RBDPO and biodiesel, another possible functional group present at 1159cm^{-1} to 1196cm^{-1} is C-O stretching in the form of the OCH_3 group. At 1436 cm^{-1} to 1462 cm^{-1} is CH_3CH_2 functional group. About 722 cm^{-1} and 870 cm^{-1} are -CH_2 aromatic blending and =C-H alkenes bending, respectively, and the possible functional groups at 1097 cm^{-1} to 1117 cm^{-1} for both palm oil and biodiesel are C-O alkoxy esters stretching, ethers, and C-O-C stretching [8, 9]. However, there are some differences between RBDPO and biodiesel spectrum. When RBDPO is converted to biodiesel, there is a slight change in intensity and wavenumber for the same possible functional groups, for instance, peaks of 1463 cm^{-1}, 1376 cm^{-1}, and 1236 cm^{-1} were shifted to 1462 cm^{-1}, 1361 cm^{-1}, and 1244 cm^{-1}, respectively due to the change in chemical structure or environment during transesterification process. Also, the wavenumber above 3006 cm^{-1} is due to resides, RBDPO has more resides owing to their carbon origin, which showed the presence of high energy storage in the compound [9]. Fatty acid methyl ester (FAME) does not contain an -OH group. However, the FTIR spectrum of biodiesel shows the presence of -OH groups, indicating the presence of water residues [10]. The occurrence of -OH groups in FAME may be attributed to several factors. Firstly, there might be a certain amount of by-product glycerol present in the methyl ester. Additionally, there could be residual water that did not evaporate during the biodiesel drying process. When water reacts with esters, it initiates a hydrolysis process, resulting in the formation of free fatty acids and alcohol. Furthermore, during storage, oxidation may occur, leading to the formation of oxidation products such as alcohol.

Figure 2 indicate the graph of parameters tested for the series of biodiesel/diesel blends. The acid value represents the quantity of free fatty acids present in the fuel sample. It shows increasing value because biodiesel contains a larger quantity of acid components such as mineral acids from the production process, residual free fatty acids from the hydrolysis process, and oxidation byproducts [11,12]. All the diesel-biodiesel blend samples meet the EN 14214 acid value requirement. Besides that, correlation coefficient of the relationship between acid value with biodiesel/diesel blends is 0.9817. Meanwhile, the saponification value also increased from Euro 5 to B80. The acidity test is the direct reaction of free fatty acids, but saponification is the reaction involving the hydrolysis of triglycerides. Hydrolysis of triglycerides produces free fatty acids; these free fatty acids then react with base to form soap. Thus, a high saponification value indicates an incomplete reaction of transesterification. Although correlation coefficient shows strong relationship (R^2=09971) between saponication with biodiesel/diesel blends. Triglycerides are only present in biodiesel, thus, increased biodiesel content increases saponification value [13, 14].

Both iodine value and peroxide value also increased from Euro 5 to B80. The iodine value test is the test for the quantity of unsaturated fatty acids, peroxide value test is the test for oxidation stability. Biodiesel derived from triglycerides has more double bonds compared to petrodiesel, a higher number of double bonds results in higher reactivity with oxygen and metal ions [15]. Thus, they will be less stable and easy to degrade. All the iodine values are acceptable because they are within the standard limit of 120 mg/g. Meantime, peroxide values give strong correlation coefficient relationship (R^2=0.9911) with biodiesel/diesel blends. Acid value, saponification value, and peroxide value show a p-value of less than 0.05, indicating a strong correlation with biodiesel content. Only iodine value gives moderate correlation with biodiesel content.

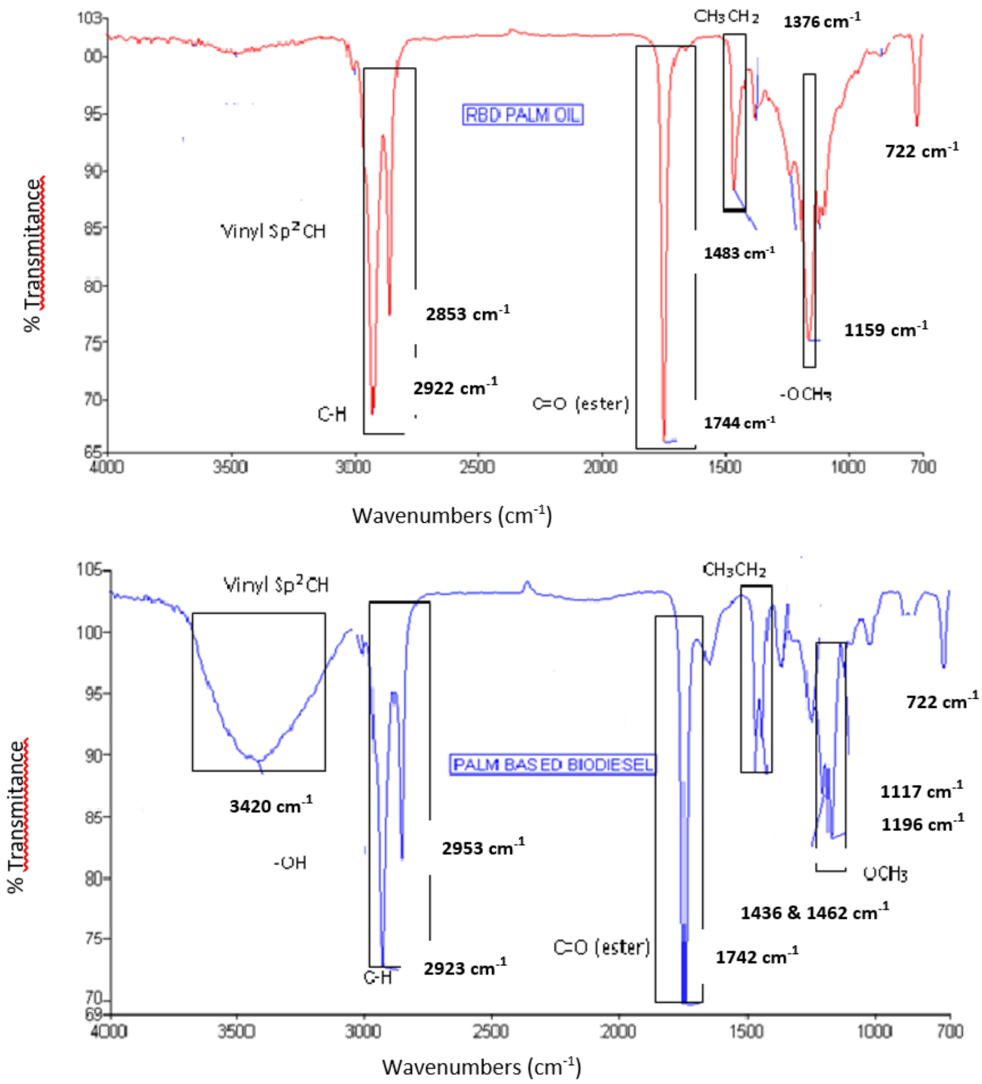
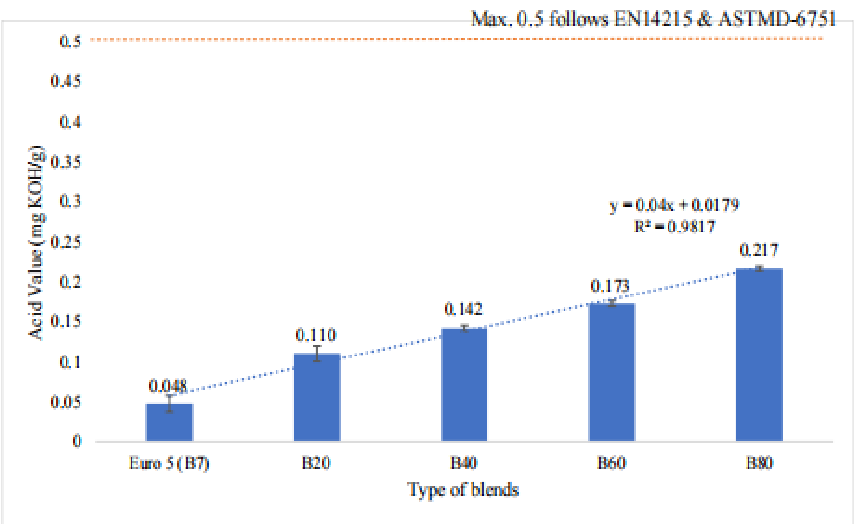
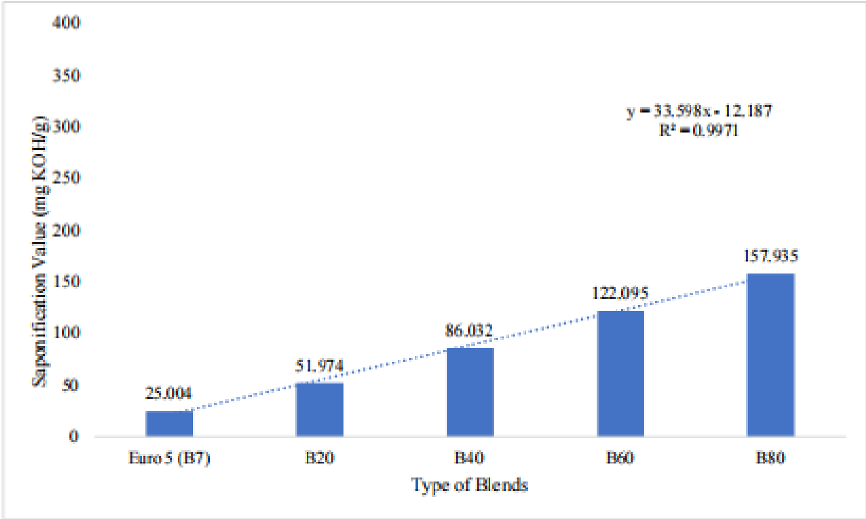


Figure 1. FTIR spectrum for RBDPO and palm-based biodiesel

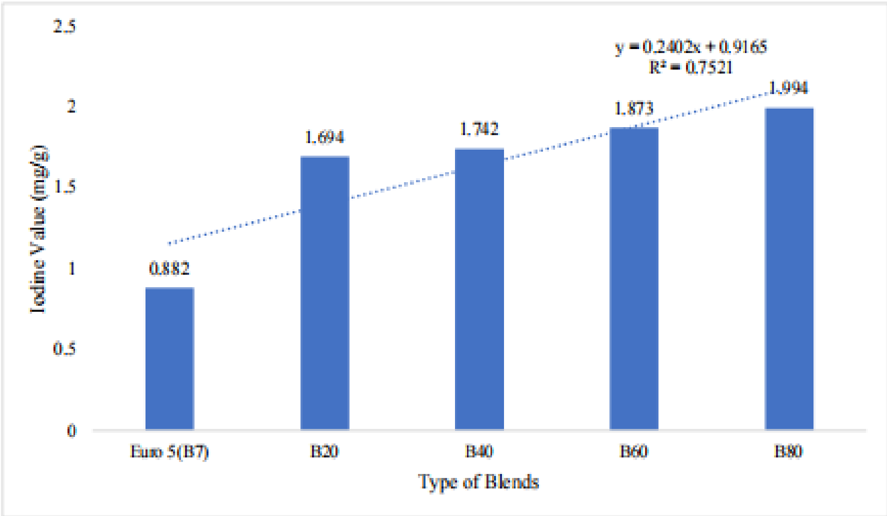


(a)

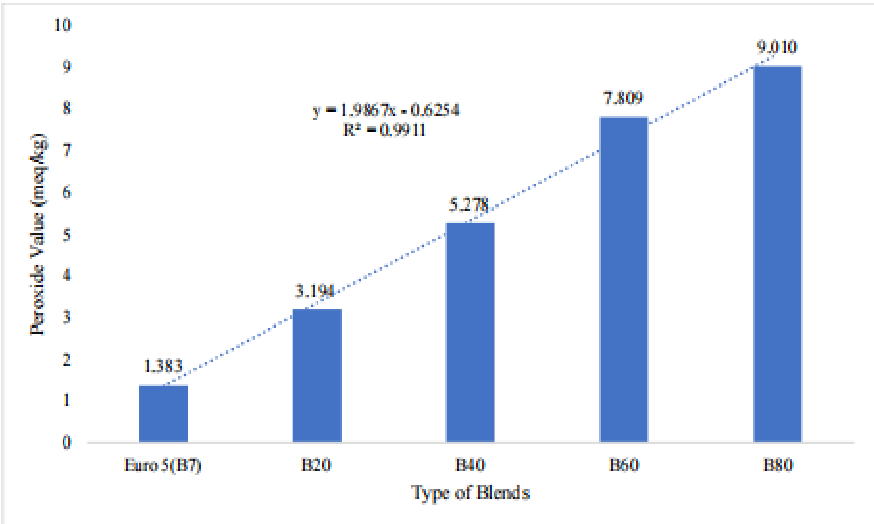
Figure 2. Effect of (a) acid value



(b)



(c)



(d)

Figure 2. (cont.) (b) saponification value, (c) iodine value and (d) peroxide value against type of biodiesel/diesel blends

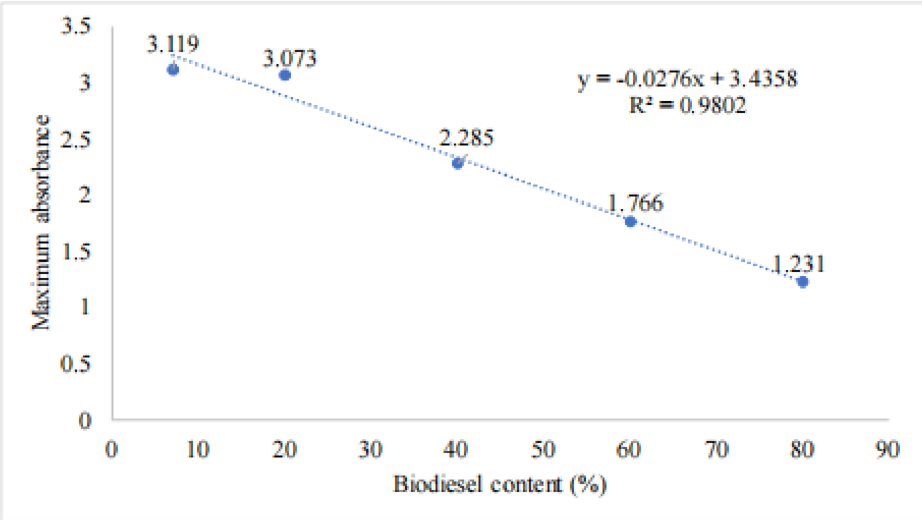


Figure 3. Graph of maximum absorbance against biodiesel content

Polycyclic aromatic hydrocarbons (PAHs) are nearly absent in biodiesel but present in petrodiesel [16]. Thus, the occurrence and absence of aromatic compounds lead to the ability to distinguish diesel and biodiesel by using UV-Vis spectroscopy. When diluted with n-heptane, biodiesel exhibits minimal absorbance in comparison to aromatic compounds at the same frequency [17]. As shown in Figure 3, Euro 5 (B7) exhibits the highest absorbance of 3.119 at 281 nm, B20 has the highest absorbance of 3.073 at 279 nm, B40 has the highest absorbance of 2.285 at 278 nm, B60 has the highest absorbance of 1.766 at 276 nm, while B80 has the highest absorbance of 1.231 at 272 nm. the linearity line fitted for maximum absorbance versus the percentage of biodiesel showed a high coefficient regression of 0.9802. The linearity of absorbance declines with the increasing biodiesel content, primarily because of reduced concentrations of aromatic compounds in diesel duel. Hence, when biodiesel content decreases, there is a rise in the concentration of aromatic compounds in the diesel in the same volume of sample diesel-biodiesel blend fuels. These aromatic compounds absorb UV light, consequently leading to an increase in absorbance.

4. CONCLUSION

In summary, the acid value, saponification value, iodine value, and peroxide value of palm-based biodiesel were determined as 0.2392 mg KOH/g, 179.6418 mg KOH/g, 1.9938 mg I_2/g, and 10.6733 meq/kg, respectively. The Fourier Transform Infrared Spectroscopy (FTIR) revealed slight differences between palm oil and palm-based biodiesel. Surprisingly, the results indicated the presence of -OH groups in the biodiesel, possibly due to residual substances like glycerol and water. Additionally, changes in the strength and position of certain components were observed, suggesting alterations in the biodiesel structure during the production process. This enhances our understanding of the chemical transformation occurring in biodiesel production. Analysis with the aided of Gas Chromatography (GC) library data identified oleic acid as the predominant component in biodiesel, the overall composition of biodiesel has a higher content of saturated fatty acids. Moreover, the acid value, saponification value, iodine value, and peroxide value all exhibited an increasing trend from Euro 5 (B7) to B80, with a moderate and strong correlation with biodiesel/diesel blends. Contradict observation of UV-Vis spectra demonstrated a decreasing trend of maximum absorbance with increasing biodiesel content due to the absence of aromatic compounds in biodiesel.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

AUTHORS CONTRIBUTION

C. Z. Ying (Methodology; Data curation; Writing — review and editing - original draft; Resources)

G. P. Maniam (Conceptualization; Formal analysis; Funding acquisition Visualisation; Supervision)

N. M. Hussin (Methodology; Data curation; Writing — review and editing - original draft; Resources)

S. N. M. Khazaai (Conceptualization; Formal analysis; Writing — review and editing; Visualisation; Supervision)

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