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Physical Properties of Biodiesel-Diesel Blends with Butyl Levulinate Additive and their Emission Characteristics from Diesel Engine

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Butyl levulinate (BL) is one of the promising chemicals for biofuel generation especially as an additive for fuel-blending. The BL can be used as a chemical additive for biodiesel-diesel blend in diesel engine. The physical properties (i.e., density, viscosity, and calorific value) and emission characteristics of palm-oil derived biodiesel-diesel blends (fuel blends) (i.e., B7, B10, B15, and B20) with and without the addition of BL were determined in this work. The analysis of gas emission from the combustion of biodiesel-diesel blends in diesel engine was conducted using gas analyser. The effect of varying the volume percentage of BL at 1 %, 3 %, 5 %, and 7 % in the fuel blend was studied in this work using B15 biodiesel-diesel blend as the selected sample. Blended fuel with addition of BL was shown to have improved the fuel blend viscosity while maintaining the density within the optimum range. The calorific value of the fuel blend showed a small reduction with an increase in the percentage of biodiesel in the fuel blend. This indicated that the combustion performance and the energy produced from the varying percentage of biodiesel in the biodiesel-diesel blends would not vary significantly. Therefore, the effect of adding BL on this property was not further investigated. The concentrations of nitrogen oxide (NOx) and carbon monoxide (CO) in the gas emission from the biodiesel-diesel blends showed only a slight increase as the percentage of biodiesel in the blend increased. With the addition of the BL additive, these concentrations showed some levels of reduction. In summary, the presence of BL in the palm oil biodiesel-diesel fuel was demonstrated to have reduced the viscosity of the blend by 4.4 to 6.9 %, and reduced the concentrations of CO and NOx by 19.26 % and 12.22 % during the engine combustion.

1. Introduction

The transportation industry is now growing substantially year by year and has increased the consumption of fuels. Most countries are still relying heavily on conventional fossil fuels, which continue to increase the greenhouse gas (GHG) emission. The release of GHG has negative effects on the ecosystem and the environment. The annual increase in vehicle production has caused the fossil fuel supplies to run out steadily and contribute to severe environmental pollutions (Yusoff et al., 2018). Numerous alternative fuels have been discovered to replace fossil fuel and reduce the net GHG emissions. In transportation sector, biodiesel is the most promising alternative energy source that has been studied to replace fossil fuels. Biodiesel offers many advantages including renewability, biodegradability, sustainability, and carbon neutrality (Yusoff et al., 2021). The primary positive impact of biodiesel is its carbon-neutrality, resulting in no contribution to GHG (Chuah et al., 2022). The plentiful of palm oil in Southeast Asia region has promoted the production of palm oil-based biodiesel to reduce the reliance on fossil fuels. Operating a pure biodiesel (B100) in an unmodified diesel engine is impractical as it affects the engine performance due to the incompatibility of the biodiesel properties (Venkatesan et al., 2012). The physical properties of biodiesel affect the unmodified diesel engine performance

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in many ways, including affecting the fuel atomization, clogging the piston ring, and damaging the injector (Shrivastava et al., 2021). Therefore, biodiesel needs to be blended with diesel fuel to ensure its properties are compatible for utilization in the unmodified diesel engine.

In Malaysia, the Ministry of Plantation Industries and Commodities has phased in B5 (5 % biodiesel + 95 % diesel fuel) mandate and is currently phasing in B7 (Szulczyk and Khan, 2018). High biodiesel percentage is expected to be blended with diesel in the future and this requires an addition of fuel additive to ensure the blended fuel properties are within the standard specifications. Fuel additive is a specialty chemical that is commonly used in the commercial fuel blend to convene up the most wanted performance level. There are several types of fuel additives available today and each of these chemicals deliver a different advantage on fuel blend and diesel engine. The common fuel additives were metal based additives, cetane number improver additives, antioxidant additives, and oxygenated additives (Kumar et al., 2018). BL is categorized as oxygenated additives, which are specifically under furanic fuel oxygenate (Ahmad et al., 2022). Oxygenated fuel additives are a low-carbon chemical with higher oxygen content, which promotes fuel combustion. The most common oxygenate fuel additives used commercially are petroleum-based (Mujtaba et al., 2020) and hence, is still contributing to the use of fossil fuels. Bio-based fuel oxygenates and furanic fuel oxygenates therefore serve as a potential green additive since they are derived from lignocellulosic biomass (Hassan et al., 2023). In the work reported by Wu et al. (2023), it was stated that longer carbon chains in levulinate have a notable impact on diesel properties and emissions. BL was used in this work as an oxygenated fuel additive in palm oil biodiesel-diesel blends. It was observed in Ahmad et al. (2022) that the loading of BL in diesel fuel was limited up to 20 %. Using this finding as a basis, our research examined the impact of low BL loading in palm oil biodiesel-diesel blend on fuel properties and emission profile.

This work focused on the physical properties which were density, dynamic viscosity, and calorific value, while for the gas emission analysis, the concentrations of the released CO and NOx were measured. Density and calorific value are useful for gauging the fuel's weight and internal energy from combustion, while fuel viscosity indicates fluidity in the injector flow, ensuring ideal fuel delivery for engine efficiency. BL used as fuel additive aimed to enhance complete combustion, with CO and NOx levels serving as indicators, as these measurements would sufficiently signify complete combustion in diesel engine, with CO_2 and HC emissions being minimal. The investigation was performed on fuel blends of varying volume percentages of biodiesel at a fixed BL loading, and a study on the effects of varying the volume percentages of BL in B15 as the selected fuel blend was also investigated.

2. Material and Methods

2.1 Material

Palm oil biodiesel was produced and collected from Fima Biodiesel Sdn. Bhd. located in Port Klang, Selangor, Malaysia. The commercial B7 fuel blend (7 % palm oil biodiesel + 93 % diesel) without addition of fuel additive purchased from a diesel supplier located at Bestari Jaya, Selangor, Malaysia was used to serve as the reference blend. The fuel additive butyl levulinate (BL, ≥98 wt%) was purchased from Sigma-Aldrich.

2.2 Preparation of Fuel Blends

The B7 fuel blend was used as the initial blend. The palm oil biodiesel sample was blended with the B7 fuel blend sample to prepare different fuel blend samples of 10 %, 15 %, and 20 % of biodiesel volume percentages. The fuel blends were labelled as B10, B15, and B20 respectively, in which the capital "B" refers to biodiesel and the number succeeding the letter B is the volume percentage of the biodiesel. The homogeneous blended fuel was prepared by mixing using a magnetic stirrer at 300 rpm for 30 min at room temperature. The effect of fuel additive on fuel blend was studied by adding BL as fuel additive. The fuel blends samples (B7, B10, B15, and B20) were prepared at a constant volume of 200 mL and 5 % of BL was added into each sample and labelled as B7-5, B10-5, B15-5, and B20-5, respectively. B15 fuel blend was used for further analysis on the effects of BL loading variation using 1 %, 3 %, 5 %, and 7 % BL content, which were labelled as B15-1, B15-3, B15-5, and B15-7, respectively. The range of 1 – 7 % used in the investigations was based on the effect of lower and upper limit of 5 % BL loading in the biodiesel-diesel blend. All fuel blend samples with and without additives was left at room temperature for 3 days to observe for any possible separation. These samples were analysed to determine their physical properties (density, dynamic viscosity, calorific value) and gas emissions (CO, NOx) in diesel engine.

2.3 Analysis of Fuel Blends

The density (ρ) was determined using the mass (m) of each sample at constant volume (V). The fuel blend was set at a constant volume of 40 mL, and then weighed to obtain the density (in g/mL). The dynamic viscosity, which is a measure of the minimum forces needed to move a fluid, was determined using a digital viscometer to obtain the shear stress and shear strain. Each fuel blend was set for a constant volume of 20 mL to prevent any spillage during the spindle rotating while the measurement was taken. The viscosity analysis was operated at room temperature and using a single spindle for every sample. The data of shear stress and strain were obtained from the viscometer and the dynamic viscosity value was calculated and presented in mPa.s. The calorific value, which indicates the amount of energy released from the combustion process, was analysed using bomb calorimeter. The sample was poured into the sample cup and the weight of the sample was recorded and inserted into the control panel of bomb calorimeter. The temperature inside the calorimeter chamber slowly increased until the sample was completely burned. The final calorific value was obtained in J/g. For the emission testing, the diesel engine with a single piston diesel engine that operated at constant average speed of 1,800 rpm was used for the combustion. The engine was started and left for 20 to 30 min to maintain the engine speed and to remove the residue fuel inside the diesel engine. 80 mL of fuel blend sample was filled into the diesel engine for the combustion process to take place. A gas analyser was installed next to the diesel engine and its probe was placed at the engine exhaust for the gas emission analysis. As the sample was 75 % consumed, the gas emission reading was recorded by the gas analyser. All the sample analyses were repeated to obtain an average data.

3. Results and Discussion

3.1 Density

A fuel blend with a higher density value has a higher energy per unit volume, which increases the power output (Wu et al., 2023). Figure 1a below shows the density values of the fuel blends without and with fuel additive (5 % of BL). The density data for the fuel blends were almost constant with only minor increment as the percentage of biodiesel was increased from 7 % to 20 %. The addition of BL as fuel additive has slightly improved the properties of sample by increasing the density value. The graph shows that the fuel blends with additive had a higher density value compared to their corresponding raw fuel blends. The B15 fuel blend was found to have shown the highest density increment after the addition of BL. The density values of the fuel blends were attributed by both the biodiesel and BL as both chemicals have a higher density value compared to the diesel fuel itself, as reported by Hoang (2021). The samples of up to B15 fuel blend without additive showed that the density value was within the European Standards (EN 16709) range of 0.82-0.86 g/mL (Đurišić-Mladenović et al., 2018). Although the density of the B20 fuel blend was out of the EN 16709 specification range, the value was considered acceptable based on American Society for Testing and Material (ASTM D7467), since no limit in density value is specified in this standard (Moser et al., 2015). The effect of different percentages of additive on density was further studied using B15 fuel blend, which is shown in Figure 1b. The density of B15 fuel blend increased as the fuel additive percentage increased from 1 % to 7 %. The highest density value for B15 fuel blend was 0.98 g/mL, shown in 7 % BL, but this value exceeded the standard range. Therefore, only 1 to 3 % of BL addition is considered acceptable for the fuel blends based on the density value.

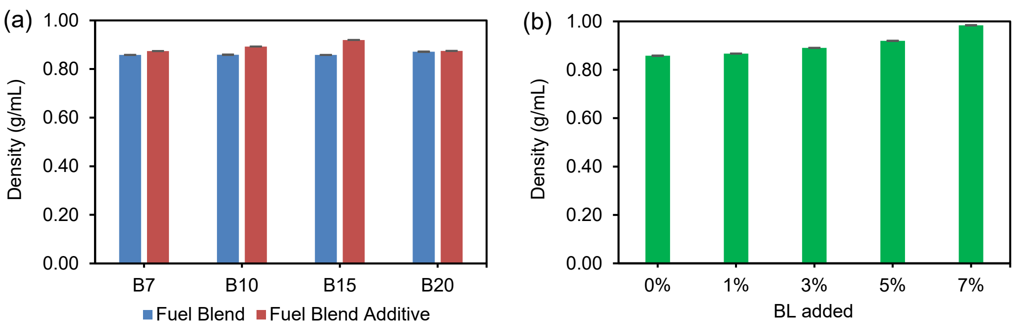

Figure 1: (a) Density of fuel blend with and without additive at different biodiesel-diesel blend, and (b) density of B15 fuel blend with different percentage of additive

3.2 Dynamic Viscosity

The flow characteristics of fuel are critical for fuel injection into the combustion chamber in a high-speed diesel engine operation. The injection duration is between 0.001 and 0.002 s, and the diameter of the droplet cannot exceed 0.025 mm throughout this time to preserve the quality of the fuel combustion (Wu et al., 2023). Biodiesel has a higher viscosity compared to diesel fuel and it affects the physical properties of the fuel blend (Hoang, 2021). Figure 2a below shows the dynamic viscosity of various fuel blends without and with 5 % BL additive. The viscosity of biodiesel-diesel mixture increased slightly as the volume percentage of biodiesel increased from

7 % to 20 %. As stated by Wu et al. (2023), the addition of BL in fuel blends improves the flow properties by improving the fuel blend's viscosity, which affects the fuel supply rate, fuel atomization, combustibility rate, and fuel lubricity, as the addition of BL would lower the viscosity of the fuel blends. The addition of BL into the fuel blends enhanced the flow properties by reducing the viscosity while maintaining the value within the range set by the standard. It was also noted that the viscosity of B15 and B20 did not show much difference between each other, both with and without the addition of BL. The B15 fuel blends was further used to study the effect of different percentages of BL on viscosity and the results are shown in Figure 2b. The dynamic viscosity of B15 fuel blend decreased as the volume percentage addition of BL was increased from 1 % to 7 %. The addition of BL into the fuel blend improved the fuel atomization by reducing the viscosity down to within the standard range, which is between 1.1 and 3.5 mPa.s at 40 °C (Mostapha et al., 2022). Based on this, addition of BL of above 3 % was needed to keep the viscosity within the standard range.

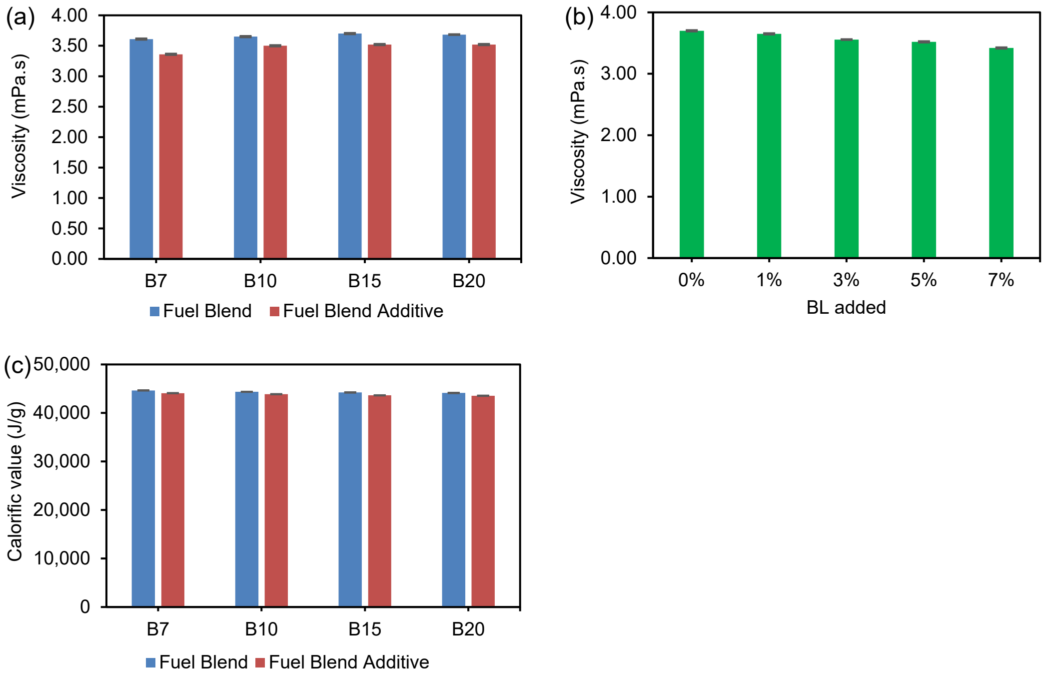

Figure 2: (a) Dynamic viscosity of fuel blend with and without additive at different biodiesel-diesel blend, (b) dynamic viscosity of B15 fuel blend with different percentage of additive, and (c) calorific value of fuel blend with and without additive at different biodiesel-diesel blend

3.3 Calorific Value

Calorific value is an essential property in fuel that determines the combustion quality and engine performance. The higher the calorific value, the higher energy is released by a unit of material, and this improves the engine efficiency. Figure 2c shows the calorific value of fuel blends without and with BL fuel additive. The calorific value of fuel blend decreased slightly as the volume percentage of biodiesel increased. Diesel fuel has a higher calorific value compared to biodiesel and it can produce more energy from combustion process than biodiesel. The addition of BL into fuel blends had also slightly decreased the calorific value as BL has lower calorific value than the diesel fuel. Nonetheless, the overall minor reduction did not significantly affect the amount of energy released by the fuel blends as the calorific value of the samples were between 43.5 and 44.0 MJ/g, which were within the same range as reported in the previous study (Wu et al., 2023), and was also still close to the standard calorific value for diesel fuel, which is 44.5 MJ/g (Singh and Bharj, 2019).

3.4 CO and NOx Emissions

The CO emission of fuel blend without and with BL additive is shown in Figure 3a. The graph shows minor increment of CO emission for the different fuel blends across B7 to B20. With the addition of the 5 % BL into the fuel blend, the CO emission level reduced by between 11.9 % and 12.2 %. The results were consistent with what was observed in a previously reported study, where an oxygenated fuel additive was added (Vijay Kumar et al., 2018). The effect of different percentages of BL in B15 fuel blends on the CO emission is shown in Figure 3b. The graph shows that the CO emission level of B15 fuel blend reduced when higher than 1 % of BL was added, and the CO emission increased slightly as the BL percentage was increased up to 7 %. The addition of 1 % BL into fuel blends contributed 15.67 % reduction of CO while the addition of 7 % BL has a percentage reduction of 2.05 %. More oxygenated additives with a lower energy content were introduced with more fuel being injected into the combustion chamber at high engine loads, which caused partial oxidation of the fuel hydrocarbons and increased CO emissions (Venu and Madhavan, 2017). A small percentage of BL as fuel blend additive delivered quite a notable reduction in the CO emission level.

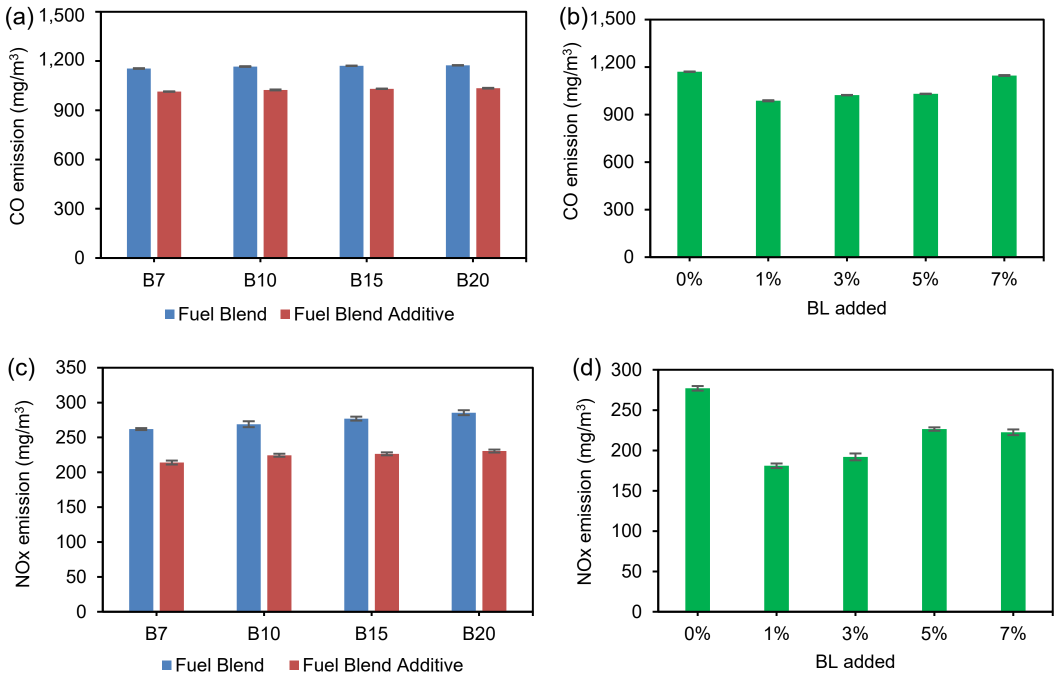

Figure 3: (a) CO and (b) NOx emissions of fuel blend with and without additive at different biodiesel addition, and (c) CO and (d) NOx emissions of B15 fuel blend with different fuel additive percentage

Figure 3c shows the NOx emission level of fuel blends without and with an additional 5 % BL. The NOx emission of biodiesel-diesel increased as the volume percent of biodiesel increased from 7 % to 20 %. The level of NOx emission present in the exhaust gas was affected by the engine operation and volume percent of biodiesel. As stated in Chen et al. (2018), the addition of biodiesel with diesel fuel reduced the NOx emissions level at low engine load and at low engine speed of below 1,000 rpm. The engine speed used in this research was 1,800 rpm and was considered as medium to high speed, which caused the NOx emission level to have increased slightly as the volume percent of biodiesel increased. Previous work reported that that NOx emission increased when biodiesel was present due to its high oxygen content (Xue et al., 2011). The addition of BL as fuel additive in fuel blend had reduced the NOx emission level. The percentage reduction of NOx emission for fuel blends with additives of 1 - 7% was between 16.5 and 19.3 %. The addition of BL helped promote complete combustion and reduce the NOx emission. Previous work reported that oxygenated additive prolonged ignition delay, which resulted in less residual gas temperature, wall temperature, and NOx emission (Venu and Madhavan, 2017). Figure 3d shows the NOx emission level of B15 fuel blend at different percentages of BL. The NOx emission level was significantly decreased as 1 % of BL was added into fuel blend, showing the highest percentage reduction of NOx emission, which was 34.66 %. The NOx emission increased with the increasing percentage of BL from 1 % to 7 %. The BL added caused presence of excess oxygen components in the mixture, which contributed to the increase of the NOx emission. Only a small addition of BL affects the NOx emission.

4. Conclusions

The results show that BL is a potential fuel additive for both the conventional diesel and biodiesel-diesel blends. The increase in biodiesel percentage slightly increased the density and viscosity of the fuel blends. The addition of BL of up to 7% in the biodiesel-diesel fuel increased the density and reduced their viscosity, which were still within the ASTM standard limits. The BL present in the fuel blends did not introduce significant changes to the calorific value. The CO and NOx emissions of BL15 were observed to have reduced by 15.67 % and 34.66 %

with the addition of 1 % of BL. Parameter such as cetane number, flash point, cloud point, pour point, and oxygen content should be tested to obtain more data to further qualify BL as the potential fuel additive.

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