Improvement of fuel properties for palm oil methyl ester (POME) biodiesel blends using organic germanium as additives

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Abstract. Biodiesel is a clean-burning alternative fuel but it is susceptible to lower calorific value due to autoxidation in the presence of oxygen, which hinders its widespread use. Organic germanium Ge-132 is a prospective solution to this problem. It is expected that Ge-132 may affect the energy content of blending biodiesel. This paper presents an experimental investigation of the effect of Ge-132 addition to palm biodiesel on physicochemical properties. Three concentrations including 5ppm, 8ppm and 10ppm added to BD20 to study their fuel physical characteristics effect. The fuel and additive was blend by using ultrasonic emulsifier for 2 minutes before experiment. The results show that BD20 with additive Ge-132 produced 0.48%–1.07% higher density and 0.7%–1.7% higher kinematic viscosity and 0.09%–0.6% higher calorific value compared to BD20 without the additive. The higher calorific value blending biodiesel attribute by the carbon content on Ge-132. Compared to BD20, the blended biodiesel with additive Ge-132 produce higher density, kinematic viscosity and calorific value which attribute the increase the performance and better fuel consumption.

1. Introduction

Changes in lifestyle and population growth lead to increased energy consumption. Major energy consumers are electricity generation and transport sectors. Diesel engine is an integral part of these two sectors around the world. Compare to petrol; diesel is the most versatile fuel burning because it is simpler, more efficient, and more economical. The increase in the price of fossil fuels, having limited fossil fuels and environmental issues has encouraged the exploration of alternative fuel sources such as biodiesel.

Biodiesel, which is denoted as BD100, is defined as a long chain fatty acid mono-alkyl ester (FA) generally produced from plant oils, animal fat or other lipids [1]. The benefits of biodiesel over petroleum diesel fuel are it has better lubricity, derived from renewable feedstocks, and biodegradable, lower toxicity, no sulphur or aromatic content, higher point, positive energy balance and reduced emissions [2-5]. Additionally biodiesel is corrosive and can attack metals, which contribute to the presence of oxygen moieties, auto-oxidation, the increased polarity of biodiesel, and its hygroscopic nature [6]. After Indonesia, Malaysia is the world’s largest producer and exporter of palm oil [7]. Currently, Malaysia offers a huge contribution to the production and export of palm oil in the world, which is 39% and 44%, respectively. [8]. The use of feedstock biodiesel produced from palm oil minimizes the dependence of the country on foreign oil. This paper focuses on a 20% blend of palm oil methyl ether to promote a higher percentage of biodiesel blending since the mandatory use of B5 is
effective in a different region of Malaysia. Furthermore, the fuel handling and delivery system is not required to modified while using the biodiesel in blending form [9]. Biodiesel also has some disadvantage, such as lower calorific value, higher molecular weight, lower volatility and a higher pour point compared to diesel. These drawbacks attribute to poor atomization and lead to incomplete combustion [10]. In this paper, the effect of the Ge-132 as additive with a different concentration on the basic fuel properties of BD20 were studied and compared. The results also compared with BD20 without additive as well as diesel fuel.

Fuel additives are one of the important role in fulfilling international fuel standards and real-time biodiesel problems. With additives in biodiesel, properties of fuel can be improved, which could contribute to improve the performance and reduction of exhaust emissions from the engine. The additive will be selected in view of the issues of biodiesel fuel, for example, density, toxicity, viscosity, energy content, economic feasibility, additives solubility, auto-ignition temperature, flash point, and cetane number for the fuel blending process.

Many researchers investigated the implementation of Palm Oil Methyl Ester (POME) and additive to improve the fuel properties of the blending fuel. Table 1 shows the researchers whose documented their research outcome, which present development in the fuel properties of blending biodiesel BD20 with different additives.

### Table 1. BD20 fuel blending with different additives

| Feed stock of biodiesel | Additives | Density at 15°C (kg/m³) | Viscosity at 40°C (cSt) | Calorific value (MJ/kg) | Cetane number | Ref. |
|------------------------|----------|-------------------------|------------------------|------------------------|---------------|-----|
| Palm oil (BD20)        | 5% Ethanol | 833                     | 3.23                   | 43.08                  | 46            | [11]|
| Palm oil (BD20)        | 5% n-butanol | 833                     | 3.39                   | 43.43                  | 47            | [11]|
| Palm oil (BD20)        | 5% DEE   | 832                     | 3.37                   | 43.41                  | 52            | [11]|
| Palm oil (BD20)        | 2% Methanol | 837                     | 2.31                   | 40.21                  | -             | [12]|
| Palm oil (BD20)        | 2% Ethanol | 838                     | 2.37                   | 40.53                  | -             | [12]|
| Palm oil (BD20)        | 2% DEE   | 840                     | 2.35                   | 39.65                  | -             | [12]|
| Palm oil (BD20)        | BHA antioxidant | 840                   | 4.06                   | 43.79                  | -             | [13]|
| Palm oil (BD20)        | BHA antioxidant | 840                   | 4.06                   | 43.82                  | -             | [13]|

S. Imtenan et al [11] measured the properties BD20 with addition 5% of ethanol and stated that by adding the additive, the density of the blend biodiesel fuel decreases from 837 kg/m³ to 833 kg/m³, viscosity from 3.62 cSt to 3.23 cSt and calorific value from 43.71MJ/kg to 43.08MJ/kg. Fattah, I.R et al. [13] carried out some investigations into the effect of antioxidant on palm biodiesel BD20; they found that the additive BHA and BHT increase the value of density and viscosity. However, the calorific value of the blend decrease from 43.92MJ/kg to 43.79MJ/kg (BHA) and 43.82MJ/kg (BHT). Vedaraman, N. et al. [12] highlights the properties of BD20 with an addition of 2% DEE as an additive and found the significant improvement in the energy content of the fuel blend. The calorific value was an increase from 39.21MJ/kg to 39.65MJ/kg.

The BD20 blended biodiesel which contained of 20% waste frying oil biodiesel and 80% diesel fuel with additive manganese oxide and cobalt oxide nanoparticles were studied by M. Mehregan & M. Moghiman [14]. Based on the experimental results, the brake specific fuel consumption and the brake thermal efficiency of nanoparticles blended fuel were considerably enhanced while the NOX and CO emission were appreciably decreased compared to those of base fuel.

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Choi et al. [15] studied the effect addition of the antioxidants and the final result reveal the improved the oxidation stability of biodiesel without affecting much in the density and kinematic viscosity. For the addition antioxidant showed the best results by reducing NO (0.8% lower on average), CO (10.8% lower on average) and HC emission (32.9% lower on average).

One reasonable solution to lower the resistance of biodiesels against lower energy content and autoxidation without through a complicated process is to treat them with Ge-132 [16]. Bis-carboxyethyl germanium sesquioxide (Ge-132) also noted with chemical formula $C_{6}H_{10}O_{7}Ge_{2}$ is the additive to introduce to enriches with an oxygen content that can improve the thermophysical properties such as flash point, density, cetane number, calorific value, viscosity and boiling point. On the other hand, Ge-132 also capable easily attach to oxygen molecules that can improve the fuel properties of the biodiesel blending. In this regard, the objective of this article to study the fuel properties effect of Ge-132 as additive on BD20.

2. Methodology
The study used five types of fuel, including mineral diesel (D100), biodiesel palm (BD100), BD20 (biodiesel 20% blend with 80% mineral diesel), BD20 (biodiesel 20% blend with 80% mineral diesel and 5ppm Ge-132), BD20Ge8 (biodiesel 20% blend with 80% mineral diesel and 8ppm Ge-132), and BD20Ge10 (biodiesel 20% blend with 80% mineral diesel and 10ppm Ge-132). For preparing the blending fuel, Ultrasonic emulsifier (Hielscher UP400S) was set at 50% amplitude and 0.5 cycles for 2 minute to prevent harmful the fuel chemical properties and fuel element. Mixing process should take no longer than 2 minutes to avoid harmful chemical properties and the element itself. The temperature was kept between 30°C - 32°C to maintain the chemical properties [17].

Table 2 shows a list of equipment used in the characterisation of fuels. The testing was repeated three times and was wisely recorded.

| Properties          | Equipment                              | Manufacturer                | Standard method | Accuracy         | B6–BD20 U.S. (ASTM D7467-08) |
|---------------------|----------------------------------------|-----------------------------|-----------------|-----------------|-----------------------------|
| Density             | Portable Density/Specific Gravity Meter DA-130N | MRC laboratory equipment manufacturer, Israel | ASTM D127     | ±0.1 kg/m³     | N/S                         |
| Kinematic viscosity | Cannon-Fenske Column and Oil Bath      | Thomas scientific, US.      | ASTM D 445     | ±0.35%          | 1.9–6.0                     |
| Calorific value     | C2000 basic calorimeter – automatic    | IKA, UK                     | ASTM D 240     | ±0.1%           | N/S                         |

Remark: N/S= not specific. Data obtained from Ref. [18]

The fuel density measurement was conducted at 20°C, according to ASTM D127, using a portable density meter (model DA-130N). A Cannon-Fenske Column and Oil Bath was used to measure the fuel kinematic viscosity at a constant temperature of 40°C ± 0.1, according to ASTM D-445. The IKA apparatus model C2000 basic calorimeter-automatic was used to measure the calorific value based on ASTM D240 standard. All the fuel blending was measure with the strict ASTM method as prescribed by manufacturer. Those tests were directed under controlled room temperature, pressure and relative humidity to ensure that the data is not affected by environmental errors.
3. Results and discussion

Table 3. Presents the results for fuel properties testing through experiments.

| Properties    | Unit       | D100  | BD100 | BD20  | BD20Ge5 | BD20Ge8 | BD20Ge10 |
|---------------|------------|-------|-------|-------|---------|---------|----------|
| Density       | Kg/m³      | 829   | 875   | 838   | 842     | 845     | 847      |
| Viscosity     | mm²/s      | 3.61  | 4.91  | 4.05  | 4.08    | 4.11    | 4.12     |
| Calorific value | MJ/kg     | 44.8  | 39.9  | 43.92 | 43.96   | 44.15   | 44.21    |

3.1 Density

![Figure 1](Figures/density.png)

Figure 1. Graph showing the density of each fuel samples.

Density is the ratio of mass over the volume. Fuel injected into the combustion chamber affected by its density and air-fuel ratio [34]. Denser fuel has greater mass in the same volume, and the fuel system injects the fuel into the combustion chamber by volume of the fuel, not by the mass of the fuel. The variation of density for the fuel samples as illustrated in the Figure 1. The diesel fuel was used as a baseline for comparison. It is showed that the BD20 have lower density compared to BD100 due to the molecular weight of biodiesel [19]. When compared to the Ge-132 blending fuels, it was found that the higher concentration Ge-132 in the blending produce higher the density value of the fuel. The result show that the BD20Ge10, BD20Ge8, and BD20Ge5 higher 1.07%, 0.83% and 0.48%, respectively, compared to the BD20. The finding is reliable with findings of past studies by Syafiq Z. et al. [16] who study the performance of Ge-132 in diesel fuel. The Ge-132 additive have significant effect on density fuel that could improve the performance and reduce the consumption of the fuel. Fuel density has directly affected to engine performance characteristics. Density has a significant impact on the engine fuel injection system. The injected timing, injection spray pattern and injection fuel amount are influence by density and compressibility [20, 21].
3.2 Kinematic viscosity

![Figure 2](image)

**Figure 2.** Variation of kinematic viscosity (mm\(^2/s\)) for various fuel blends.

The viscosity of fuel is one of the most important properties because it plays a dominant role in the fuel spray, mixture formation and combustion process. From Fig. 2 reveal the viscosity for biodiesel and various concentration of additive Ge-132. It can be noted that the viscosity of BD100 is 26.47% higher than the viscosity of D100. Addition of a higher viscosity component would increase the viscosity of the fuel sample in BD20. From the Figure 2, it can see that the increasing the amount Ge-132 in BD20 will increase the value of kinematic viscosity. BD20Ge5, BD20Ge8, BD20Ge10 was higher 0.7%, 1.4% and 1.7%, respectively when compare to the BD20.

Like density, viscosity also affects the quality of atomization, the amount of fuel and the penetration. Therefore, it has an impact on the quality of combustion [22]. Low viscosity can cause leakage in the fuel system and the high viscosity that causes a low fuel flows in the engine combustion chamber during the intake stroke and takes a long time to mix with air [23]. As a result, this situation will delay the combustion process. Besides, too high viscosity will increase the engine deposits due to the incomplete combustion. The high viscosity also causes additional problems in cold weather because of viscosity increases as the temperature decreases [24].
3.3 Calorific value

![Figure 3. Variation of the calorific value of tested fuel samples.](image)

Calorific value is also an important fuel's feature, which denotes the amount of heat transferred into the chamber using a chemical reaction during the combustion. It indicates the available energy in the fuel. The higher energy content expected to have high calorific value because it releases higher heat and consequently improves engine performance during combustion. As seen in Figure 3, the highest calorific value belongs to the commercial diesel (44.8 MJ/kg). The calorific value of pure biofuels BD100 is the lowest among the rest (39.9 MJ/kg). BD20Ge5, BD20Ge8, and BD20Ge10 show higher 0.09%, 0.52% and 0.66%, respectively compared to BD20. The main reason for these phenomena is related to the elemental composition of the fuels. The presence of carbon and hydrogen in Ge-132 afect the molecules bonding. The calorific value of fuel increase with a chain length of the molecule [25]. Calorific values of fuel blend give great influence towards engine power output [3]. Higher calorific value means there is more energy content in the fuel blend and will reduce the brake specific fuel consumption of the engine [13, 44].

4. Conclusions
The study on fuel properties for D100, BD100, BD20 and BD20 with additive Ge-132 blend fuels had been concluded into points as followed:

- The effect fuel properties of the B20 with additive Ge-132 were studied.
- Both of pure biodiesel and diesel sample (BD100&D100) meet the ASTM D6751 and ASTM D975 for all tested parameters.
- All blends of the biodiesels (BD20, BD20Ge5, BD20Ge8 and BD20Ge10) meet ASTM standards for biodiesel blends ASTM D7467 specification.
- Compared to BD20, the blended biodiesel with additive Ge-132 produce higher density, kinematic viscosity and calorific value.
- The fuel properties value increase when the concentration additives Ge-132 increase.

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