# Characterization of High Blended Palm Biodiesel Fuel Properties with Chemical Additive

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# Characterization of High Blended Palm Biodiesel Fuel Properties with Chemical Additive

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**Palm biodiesel-diesel blended fuel feasibility at high blending ratio was investigated in this study through characterization of blend properties with additives. Diethyl ether (DEE) has been used as an oxygenated additive with the blended fuel B50 (50% biodiesel + 50% diesel) at different ratios of 2%, 4%, 6% and 8%. Blended fuel properties with DEE additives were tested and evaluated according to ASTM fuel standard specifications. The results of this study is essential to qualify the trend of change of the different fuel properties with increasing additive ratio which can serve the researchers who work on biodiesel fuels to indicate the fuel suitability for diesel engine applications according to fuel standards. The results show slight improvement in density and acid value with significant decrease in viscosity by about 25% at 8% additive ratio which meets the blended fuel standard ASTM D7467. The maximum decrease in pour and cloud points are 6°C and 2°C at 8% additive ratio, accompanied by about 2.6% decrease in energy content of B50 for each 2% DEE additive ratio.**

**Key words:** Additive, diesel, diethyl ether, fuel property, palm biodiesel.

As global fuel prices rise and environmental change resulting from the burning of fossil fuels becomes more serious, it has become urgent to utilize alternative and eco-friendly (i.e. carbon neutral) energy sources. At the same time it has been estimated that oil production will reach its peak by the next few years. Therefore, it is necessary to find alternative sources of renewable energy to meet the requirement of the modern life energy consumption. Bio-energy can be considered a carbon neutral renewable energy that can be utilized to contribute in the reduction of carbon dioxide emissions. Due to the advantage associated with the biodiesel fuel biodegradability and renewability, it has received a great deals of attention in the last decade [1]. Biodiesel is synthesized usually vi the transesterification of triacylglycerls (vegetable oils) in the presence of low molecular alcohol and it composed of fatty acid methyl ester [2]. Currently, the mandates of blended biodiesel-diesel fuel usage are mostly based on a blending ratio up to 20% biodiesel in many countries around the world. Furthermore, the most viable option to use the blended fuel at high blending ratio as an alternative fuel for mineral diesel is the usage of fuel additives.

The sustainability of biodiesel and the availability of its feedstocks will be the crucial determinants of biodiesel fuel popularization [3]. Palm oil tree is a tropical perennial plant which grows well in lowland humid places. As a comparison, palm oil crop has the highest oil yield among the other biodiesel feedstocks, producing about 5950 litre of oil per hectare annually. On the other hand sunflower, soybean and jatropha can produce only up to 952, 446 and 1892 litre of oil per hectare annually, respectively [4]. It has been found from the literatures that the feedstock cost alone represents 75% to 80% of the overall cost for biodiesel production [5–7]. Accordingly, the selection of feedstock with high oil yield is vital to ensure low biodiesel production cost.

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Biodiesel fuel is a mixture of mono-alkyl esters (saturated and unsaturated long chain fatty acid) generally has poor cold flow properties higher density, viscosity and acid value compared to mineral diesel. The pour and cloud point (cold flow properties) are used to evaluate fuel cold flow operability as these properties affect the utilization of the fuel particularly, in the regions with cold climate conditions [8].

The fuel density is an important parameter for various performance aspects in diesel engine. The output power of the engine influence of change in fuel density due to the different injected fuel mass, as the fuel measured by volume in the fuel injection system [9]. The higher kinematic viscosity of the used fuel can result in undesired consequences, like engine deposits and poor atomization of fuel during spraying as well as wear on injectors and fuel pump elements which required additional energy for fuel pumping [10,11]. The energy content of fuel directly influence the output engine power [12,13]. Due to the lower energy content of biodiesel compared to mineral diesel, the fuel additives usage most not worsens this property. The usage of fuel additives with low energy content with blended fuel can cause a drastic reduction in the fuel energy content if it is adopted at high additive ratio. Therefore, the fuel energy content is considered as one of the important technical issues in the usage of biodiesel-diesel blended fuel. The previous studies that conducted on fuel energy content measurement are very limited and there are no details about the measurement methods and procedures. Furthermore, information concerning the palm biodiesel energy content and its blend with diesel at the present of additives remains scarce.

Different chemical additives were used in the previous studies to improve biodiesel properties from various feedstocks. Many researchers try alcohol additives like methanol, ethanol and butanol, other researchers used ether additives like diethyl ether and diemthyl ether. Oxygenated additives like diethyl ether (DEE) can be use with blended biodiesel-diesel fuel to suppress NOx emissions. It can be considered as an excellent ignition enhancer with low auto-ignition temperature [14,15]. Blend of diesel with 5% DEE was the most effective blend to improve the engine performance and emissions [16]. Same ratio of DEE additive was suggested with blended fuel of soybean biodiesel-diesel B30 with more reduction of CO emission and smoke compared to B30 [17].

Other studies investigated the blend of diethyl ether with biodiesel fuel from various feedstocks to reduce the engine emissions. Blend of DEE with biodiesel from rubber seed at low ratios was efficient in reducing the engine emissions with better engine performance [18]. Same results were obtained with karanja biodiesel [19] and jatropha biodiesel [20] at 15% DEE additives. Another studies showed that 20% DEE is the optimum ratio for better engine performance and emissions with pongamia biodiesel [21] and thevetia peruviana biodiesel [22,23]. On the other hand, 2% DEE with fish oil biodiesel gave the higher reduction in all exhaust emissions when running the engine with exhaust gas recirculation (EGR) [24].

All the surveyed studies mainly focused on the effect of adding diethyl ether with biodiesel fuel on engine performance and exhaust emissions. Furthermore, blend of balm biodiesel with mineral diesel up to 40% biodiesel B40 has been used directly as a fuel for diesel engine without any engine modification [25]. Accordingly, the aim of this study is to investigate the ability of using blend of palm biodiesel-diesel fuel at high blending ratio B50 with diethyl additive as a fuel for the existing diesel engines alternative to mineral diesel. The fuel properties with diethyl ether at different additive ratios have been measured and characterizes compared to fuel standard specifications.

## MATERIALS AND METHODS

Biodiesel fuel from palm oil was provided by commercial company (Buly Services) in Selangor, Malaysia. Mineral diesel fuel was supplied by commercial fuel manufacturer. Blended fuel was prepared by adding 50% palm oil biodiesel to 50% mineral diesel. The blend was mixed continuously using magnetic stirrer at 2000 rpm for 20 minutes. Then, diethyl ether additive was added to the blend at low stirring rate of 1000 rpm. The mixtures were stirred continuously for additional 20 minutes and left for 30 minutes to reach equilibrium at room temperature before it were subjected to any test. The use of DEE has also some limitations, such as lower lubricity, reduced ignitability and cetane number, higher volatility and lower miscibility [24] which may lead to increased unburned hydrocarbons emissions. Therefore, DEE was adding at small proportions of 2%, 4%, 6% and 8% by volume to blended fuel, which corresponded to B50-DE2, B50-DE4, B50-DE6 and B50-DE8 fuels, respectively.

The prepared fuel properties were measured according to ASTM standard method specification shown in Table 1. Furthermore, the heating value of blended fuel which not specified in the biodiesel standards ASTM D6751 and have a minimum value of 35 MJ/kg in EN 14213 was determined by Oxygen Bomb Calorimeter model 6772 (Parr instrument company, USA). In these calorimeter systems, the heat leak is precisely measured during the calorimetric pre-period. This evaluation results in an estimate of the effective, average temperature of the calorimeter surroundings. This temperature value is then used throughout the test interval to provide the calorimeter heat leak correction. It harnesses the computing power of the controller, with no additional hardware costs, to provide heat leak correction capability that is almost identical to the approach used when non-electronic thermometry and manual calorimetric techniques are employed.

Cloud point is defined as the temperature at which a cloud of wax crystals first appears in a liquid form when the liquid is cooled under certain conditions. PP is defined as the lowest temperature at which a liquid can flow; the PP apparatus and procedure adopted were according to the ASTM D 97 standard method. The test apparatus manufactured by Koehler instrument company K46195 (USA) was used for the cloud and pour point measurements.

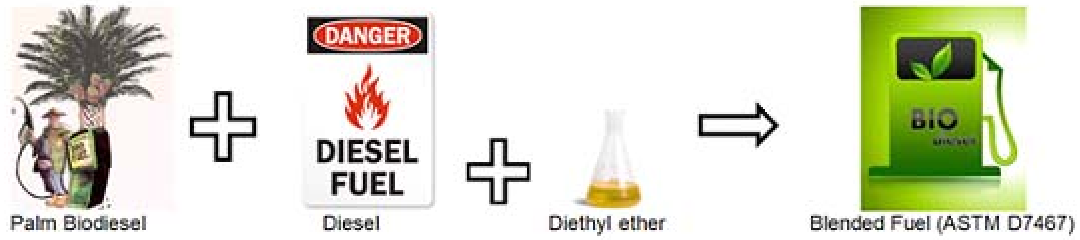
Acid number or neutralization number is a measure of free fatty acids contained in a fresh fuel sample. Free fatty acids (FFAs) are the saturated or unsaturated monocarboxylic acids that occur naturally in fats, oils or greases but are not attached to glycerol backbones [26]. Fatty acids vary in carbon chain length and in the number of unsaturated bonds (double bonds). Higher amount of free fatty acids leads to higher acid value [27]. Acid value is expressed as mg KOH required for neutralizing 1 g of FAME. Higher acid content can cause severe corrosion in the fuel supply system of an engine. The acid value is determined using the ASTM D664 and EN 14104. The test apparatus manufactured Metrohm 785 (USA) was used to measure the acid value.

Kinematic viscosity measurements were made with a Digital Constant Temperature kinematic viscosity bath, while the density is measured by using Portable Density/Gravity Meter. High viscosity leads to problem in pumping and spray characteristics (atomization and penetration, etc.). The inefficient mixing of oil with air contributes to incomplete combustion.

## RESULTS AND DISCUSSION

### Analysis of biodiesel properties

The results of properties measurement for palm biodiesel fuel and its blend with diesel B50 are listed in Table 2. These results evaluated compared to the fuel standard limits for each property as shown in the table. It is obvious from these results that palm oil biodiesel has the higher pour point, cloud point, density, kinematic viscosity and acid value, and the lowest for mineral diesel. However, the fuel energy content for palm biodiesel was the lowest with the higher value for mineral diesel. The pour point temperature for palm biodiesel was very high compared to that of mineral diesel which limits the usage of the fuel in cold climate regions [28,29].



The additive selection to oxygenate the fuel mostly depend on fuel blending properties, economic feasibility and additive toxicity [24]. Based on these parameters, in the current study diethyl ether has been selected as a fuel additive for blended palm biodiesel B50. The additive was added at increasing ratios to evaluate the trend of change of different fuel properties.

**Cloud point and Pour point results**

Table 2 shows that palm oil biodiesel fuel has the higher pour point of 14 °C compared to -14 °C for mineral diesel which is the lower among the measured fuel samples. The pour point for blended fuel B50 reduced by 12 °C compared to pure biodiesel due to the blending effect with diesel. Further improvement in pour point of blended fuel B50 is observed with increasing diethyl ether additive ratio in the blend since the freezing points of DEE (-117.4 °C) are substantially below the temperature at which biodiesel typically undergoes solidification.

Addition of DEE to B50 slightly affected CP by 1 °C decrease at 8% DEE addition, while increasing DEE content from 0 to 8% resulted in a dramatic decline in PP. This due to the significant different chemical structure of diethyl ether compared to diesel and biodiesel fuel which lead to the disruption of crystalline growth at sub-ambient temperature. Fig. 1 shows the variations of the PP for the blended fuel B50 with the volumetric percentage of the DEE. The minimum value of PP for B50 was -4 °C when adding 8% DEE. The low-temperature properties of biodiesel does not indicated in ASTM and EN standards as it related to climatic conditions.

**Table 1.** ASTM standard methods for properties measurement

| Property | ASTM Method |
|---|---|
| Acid Value | ASTM D-664 |
| Viscosity | ASTM D-445 |
| Density | ASTM D1298 |
| Cloud point (CP) | ASTM D-2500 |
| Pour point (PP) | ASTM D-97 |

**Table 2.** Properties of pome and b50 compared to the biodiesel specifications

| Property | Unit | B100 | D | B50 | ASTM D6751 | EN 14213 |
|---|---|---|---|---|---|---|
| AcidValue | mg KOH/g | 0.49 | 0.16 | 0.33 | 0.5 max | 0.5 max |
| Viscosity at 40 °C | $mm^2/s$ | 4.62 | 3.8 | 4.0 | 1.9-6.0 | 3.5-5 |
| Densityat 20°C | $kg/m^3$ | 880 | 847 | 863 | 900 | 860-900 |
| CP | °C | 14 | -8 | 4 | - | - |
| PP | °C | 14 | -14 | 2 | - | - |
| Heating Value | MJ/kg | 38.57 | 45.2 | 42.7 | - | 35 min |

**Density results**

Table 2 shows that palm oil biodiesel fuel has the higher density of 880 $kg/m^3$ compared to 847 $kg/m^3$ for mineral diesel which is the lower among the measured fuel samples. The density for blended fuel B50 reduced to 863 $kg/m^3$ due to the

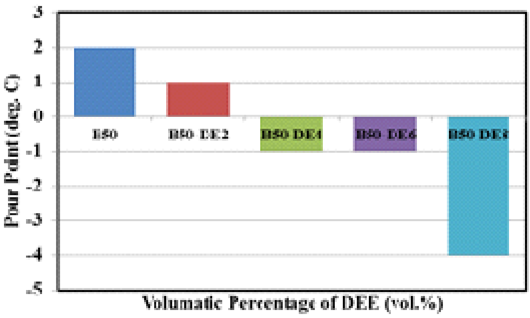



**Fig. 1.** Variation in PP for blended fuel B50 with the volumetric Percentage of DEE (vol.%)

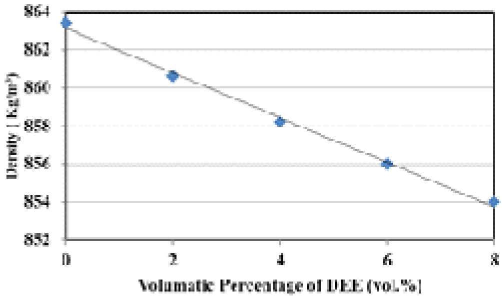



**Fig. 2.** Variation in Density for blended fuel B50 with the volumetric Percentage of DEE (vol.%)

blending effect with diesel. Further improve in density of blended fuel B50 is observed with increasing diethyl ether additive ratio in the blend since the density of diethyl ether additive is substantially below that of diesel and biodiesel fuel.

The densities of B50-DEE blended fuel produced in this study are very close to each other and in the range of 854–863.4 kg/m$^3$ for B50-DE8 and B50 respectively. They are suitable for the ASTM and EN standards and slightly higher than those of the diesel fuel 847 kg/m$^3$. Fig. 2 presents the variation of density values for B50 with DEE portion. It is clear that the density of the fuel decreases with rising of DEE portion in the mixture. The density of the B50-DEE blend decreased linearly with a higher volumetric percentage of the DEE, indicating that the additivity for the volume. This is due to the lower density of diethyl ether (714 kg/m$^3$) compared to diesel and biodiesel as shown in Table 2. Excellent agreement between the measured and estimated values of the density of the B50-DEE blends at 20 $^o$C is given by:

Density (kg/m$^3$) = -1.17x + 863.12 $R^2$ = 0.9957 ...(1)

Where x is the volumetric percentage of the diethyl ether additive (vol.%).

These results are in agreement with a previous study [30] that determined blends of microalgae oil biodiesel and its blends with mineral diesel. The density of the B50-DEE blends can satisfy the specifications for diesel and biodiesel blends, listed in the standards.

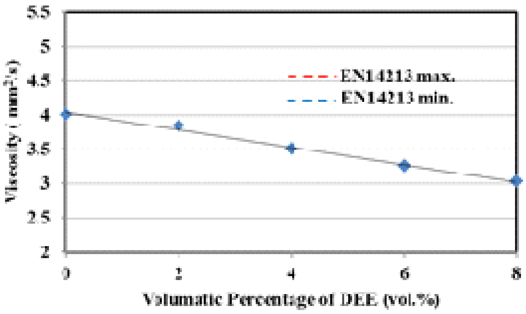



**Fig. 3.** Variation in Viscosity with the volumetric Percentage of DEE (vol.%) for POME

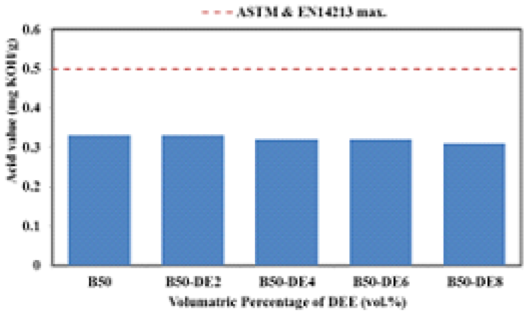



**Fig. 4.** Variation in Acid value for blended fuel B50 with the volumetric Percentage of DEE (vol.%)

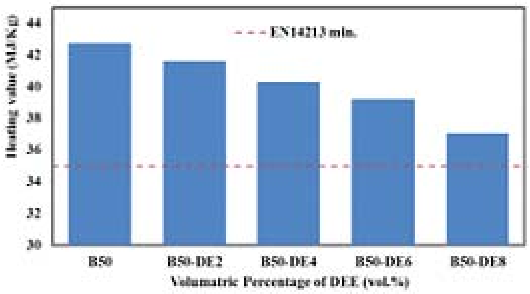



**Fig. 5.** Variation in heating value with the volumetric percentage of DEE (vol.%) for POME-diesel blends

**Viscosity results**

Table 2 shows that palm oil biodiesel fuel has the higher viscosity of 4.62 mm$^2$/s compared to 3.2 mm$^2$/s for mineral diesel which is the lower among the measured fuel samples. The viscosity of blended fuel B50 reduced to 4 mm$^2$/s due to the blending effects with diesel. Further improve in viscosity of blended fuel B50 is observed with increasing diethyl ether additive ratio in the blend since the viscosity of diethyl ether additive is substantially below that of diesel and biodiesel fuel.

The viscosities of blended fuel B50 vary in the range of 3.03 and 4.0 mm$^2$/s for B50-DE8 and B50 respectively. All B50-DEE blends, as well as B50, satisfied the kinematic viscosity specification contained in ASTM D6751. However, the viscosity of B50-DE6 and B50-DE8 is slightly lower than the limits of the EN14213 standard. The viscosity of the blend decreases as the DEE portion increases in the fuel mixture as observed from Fig. 3. This is due to the lower viscosity of diethyl ether (0.24 mm$^2$/s) compared to diesel and biodiesel as shown in Table 1. Similar to density, the kinematic viscosity of the B50-DEE blend decreased linearly with a higher volumetric percentage of the DEE. The kinematic viscosity at 40 $^o$C can be described by Eq. (2) for the B50-DEE blends, with a linear relationship:

Kinematic Viscosity (mm$^2$/s) = -0.1268x + 4.0384, $R^2$ = 0.9924 ...(2)

Where x is the volumetric percentage of the diethyl ether (vol.%).

Likewise density, the kinematic viscosity of the B50-DEE blends are in agreement with a previous study [30] that determined blends of microalgae oil biodiesel and its blends with petroleum diesel.

The density and kinematic viscosity of the B50-DEE blends up to B50-DE4 can satisfy the specifications for biodiesel blends, including ASTM D7467. However, B50-DE6 and B50-DE8 fuels had kinematic viscosities below the lower limit specified in EN 14213 (3.5 mm$^2$/s, 40$^o$C) as shown in fig. 9.

**Acid value**

Table 2 shows that palm oil biodiesel fuel has the higher acid value of 0.49 mg KOH/g compared to 0.16 mg KOH/g for mineral diesel, which is the lower among the measured fuel samples. The acid value for blended fuel B50 reduced to 0.33 mg KOH/g due to the blending effect with diesel. Further improve in acid value of blended fuel B50 is observed with increasing diethyl ether additive ratio in the blend.

The addition of DEE to the blended fuel B50 improved the acid value (AV) of the fuel, where slight reduction in AV was achieved by increasing DEE portion. The acid value is determined using the ASTM D664 and EN 14104. Both standards approved a maximum acid value for biodiesel of 0.50 mg KOH/g [31,32]. Fig. 4 shows the acid value profile of B50-DEE blends which decreases by approximately 6% at 8% DEE additive, by volume with a linear relationship. This was expected, as DEE will dilute the free fatty acids present in blended fuel, resulting in a reduction in AV. The acid value of the B50-DEE blend satisfies the requirement of ASTM D6751-06 and EN 14104 Standard for all blending ranges.

**Heating value, heat of combustion**

Heating value (heat of combustion) is the amount of heating energy released by the combustion of a unit value of fuels. One of the most important determinants of heating value is the moisture content of the feedstock oil [33].

Fig. 5 Variation in heating value with the volumetric percentage of DEE (vol.%) for POME-diesel blends

The heating value is not specified in the biodiesel standards ASTM D6751 and EN 14214 but is prescribed in EN 14213 (biodiesel for heating purpose) with a minimum of 35 MJ/kg [26]. Table 2 shows that palm oil biodiesel fuel has the lower heating value of 38.57 MJ/kg compared to 45.2 MJ/kg for mineral diesel, which is the higher among the measured fuel samples. The heating value for blended fuel B50 reduced to 42.7 MJ/kg compared to mineral diesel due to the blending effect with biodiesel. Further reduction in heating value of blended fuel B50 is observed with increasing diethyl ether additive ratio in the blend. Fig. 5 shows that the heating value of the B50-DEE blend decreased slightly with increasing volumetric percentage of the DEE and the minimum heating value recorded for B50-DE8 (37.05 MJ/kg). This is due to the lower heating value of diethyl ether (34 MJ/kg) compared to diesel and biodiesel as shown in Table 2. The heating value of the B50-DEE blend satisfies the requirement of EN 14213 Standard for all blending ranges.

## CONCLUSIONS

The aim of this study was to characterize how the key properties of blended palm biodiesel-diesel fuel B50 change with increasing diethyl ether additives ratio in the blend. The fuel property test results show significant improvement in blended fuel density closed to that of diesel fuel. Significant improve of blended fuel viscosity was observed by increasing additive ratio, with a drastic increase to below the viscosity of mineral diesel at 6% and 8% diethyl ether additive ratios. Slight improve in the blended fuel acid value is observed with increasing additive ratio in the blend. These properties satisfy ASTM standard specifications for all additives ranges. However, adding 6% and 8% DEE to the blended fuel B50 results in fuel viscosity values lower that the limit of EN14213 standard. The cold flow properties of blended fuel improved with increasing additives ratio and the maximum decrease in blended fuel pour point was at 8% additive ratio which is 6$^o$C lower than that of B50. On the other hand, there was a slight difference in the cloud point of the blends by 2 $^o$C at the same additive ratio. However, the energy content of blended fuel worsens with increasing diethyl ether additive ratio in the blend, where the blended fuel energy content reduced by about 13% at 8% additive ratio compared to that of B50 which still satisfy the limits of the EN 14213 standard. Finally, B50-DE4 blends exhibited slightly superior low temperature performance, acid value, viscosity and density with slight lower energy continent in comparison to B50 and may be suggested as prudent choice when considering biodiesel diesel blended fuel.

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