Effects of Diethyl Ether Additives on Palm Biodiesel Fuel Characteristics and Low Temperature Flow Properties

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Abstract

Diesel engines are widely used in almost all walks of life and cannot be dispensed with in the near future. As the fossil fuels now mainly used in diesel engine and continually depleting accompanied by increasing consumption and prices day by day, there is a need to find out an alternative fuel to fulfill the energy demand of the world. Alternative fuels like biodiesel, are being used as an effective alternative to diesel. The feasibility of biodiesel production from palm oil was investigated with respect to its fuel properties. Though biodiesel can replace diesel satisfactorily, problems related to fuel properties persist. In this study an oxygenated additive diethyl ether (DEE) was blended with palm oil biodiesel (POME) in the ratios of 2%, 4%, 6% and 8% and tested for their properties improvement. These blends were tested for energy content and various fuel properties according to ASTM standards. Qualifying of the effect of additive on palm biodiesel fuel properties can serve the researchers who work on biodiesel fuels to indicate the fuel suitability for diesel engines according to fuel standards. Blends of DEE in POME resulted in an improvement in acid value, viscosity, density and pour point with increasing content of DEE, accompanied by a slight decrease in energy content of biodiesel.

Keywords: *Palm biodiesel, Diethyl Ether, Energy Continent, Diesel, Fuel properties*

1. Introduction

Because bioenergy renewability and considered carbon–neutral, the bioenergy utilization can contribute to the carbon dioxide emissions reduction. Recently biodiesel has received a great deal of attention because of the advantages associated with its biodegradability and its classification as a resource for renewable energy [1, 2]. Biodiesel is composed of fatty acid methyl esters (FAME) and is synthesized usually via vegetable oils (triacylglycerols) transesterification with low-molecular-weight alcohols [3]. The current mandates regarding the use of biodiesel around the world are mostly based on a biodiesel–diesel blend. The additive is the most visible option to introduce the biodiesel as complete alternative fuel for mineral diesel.

The availability and sustainability of biodiesel feedstocks will be the crucial determinants in the popularization of biodiesel [4]. The oil palm is a tropical perennial plant and grows well in lowland with humid places. Compared with other biodiesel feedstocks, oil palm is the highest oil yield crop, producing on average about 5950 liters of oil per hectare annually. Sunflower, canola, soybean, and jatropha can only produce up to 952, 1190, 446, and 1892 liters of oil per hectare annually, respectively [5]. From the literature, it has been found that feedstock alone represents 75%-80% of the overall biodiesel production cost [6–8]. Therefore, selecting the high oil yield feedstock is vital to ensure low production cost of biodiesel. Biodiesel (a mixture of mono-alkyl esters of saturated and unsaturated long-chain fatty acids) generally has a higher cloud and pour point (CP and PP), density, and kinematic viscosity as well as the acid value compared to diesel. The cold flow properties (CP and PP) are used to characterize the cold flow operability of a fuel because the pour point of a fuel affects the utility of the fuel, especially in cold climate conditions [9].

Fuel injection systems measure fuel by volume, and thus, engine output power influence by changes in density due to the different injected fuel mass [10]. Thus, density is important for various diesel engine performance aspects. The use of fuel with a high kinematic viscosity can lead to undesired consequences, such as poor fuel atomization during spraying, engine deposits, wear on fuel pump elements and injectors, and additional energy required to pump the fuel [11, 12]. The fuel energy content has a direct influence on the engine power output [13, 14]. The biodiesel energy content is less than that of mineral diesel, therefore using of additive most not worsen the energy continent of the POME fuel. Because biodiesel has lower energy content compared to diesel resulting from its chemical structure, the blending of biodiesel with additive that have less energy continent usually causes the energy content of the fuel to decrease depending on the additive energy continent and portion. Currently, the energy content is one of the major technical issues in the use of biodiesel–diesel blends, as it relates to the engine power. The conducted researches on measuring the energy content very little and didn't indicate the methods and equipment's used for measurement. However, information concerning the energy content of palm oil biodiesel and its blending with additive remains scarce.

Diethyl ether (DEE), an oxygenated additive can be added to diesel/ biodiesel fuels to suppress the NOx emission. DEE is an excellent ignition enhancer and has a low auto ignition temperature [15]. It is an aid for cold starting and ignition improver for diesel water emulsion [16]. Iranmanesh, *et al.*, in their experimental study found that 5% of DEE with diesel blend was the most effective combination based on performance and emission characteristics [17]. Similarly, Qi et al. [18] conclude that brake specific fuel consumption (BSFC) is slightly lower when adding 5% of DEE with B30 (30% soybean biodiesel and 70% diesel in vol.), accompanied by more reduction of CO emission, smoke and similar NOx emission compara to B30.

Various researchers tried the blends of DEE with biodiesel to reduce emissions. The addition of DEE with rubber seed biodiesel in lower percentage improved the engine performance and emission characteristics [19]. This has again been agreed with Karanja oil methyl ester blend where, 15% DEE was the effective combination [20]. Likewise, (Sivalakshmi, S. and Balusamy, T.) [21] concluded that 15% DEE is found to be the optimum blend with Jatropha oil methyl ester (JOME) on the basis of performance and emission characteristics. However, Pugazhvadivu, *et al.*, [22] found experimentally that 20% of DEE addition was more beneficial in reducing NOx compared to other combination when using Pongamia biodiesel and diethyl ether as a fuel. Similarly, (Kannan, T. K. and Marappan, R.) in their experimental works [23, 24] agreed that the blending ratio of 20% DEE gives better performance and lesser emissions than other combinations when added to the Thevetia Peruviana biodiesel. On the other hand, Chen, *et al.*, [25] stated that fish oil biodiesel (BOF), with 2% blend of DEE gave the maximum percentage of reduction of all emission pollutants and suggested as the best option for running the engine with EGR.

None of the previous studies investigate the effect of DEE on fuel properties. Therefore, the first objective of this study was to characterize the properties of the palm oil methyl esters (POME), including the energy content. The second objective was to investigate the fuel properties of POME-DEE blends at different ratios for compliance with current mandates. DEE was added in the ratio of 2%, 4%, 6% and 8% to the POME to improve the fuel properties and meet the fuel standard requirement.

2. Materials and Method

All Palm oil biodiesel (POME) was supplied by local commercial company in Selangor, Malaysia. Samples of palm oil methyl ester and DEE were prepared through mixed and blended using electrical magnetic stirrer shown in Figure 1(a). Briefly, DEE was added into palm oil methyl ester at low stirring rate. The mixtures were stirred continuously for 20 minutes and left for 30 minutes to reach equilibrium at room temperature before they 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 [25] which may lead to increased unburned hydrocarbons emissions. Therefore, DEE was adding at small proportions of 2%, 4%, 6% and 8% by volume to POME, which corresponded to B-DE2, B-DE4, B-DE6 and B-DE8 fuels, respectively.

The acid value, cloud point, pour point, density, and kinematic viscosity were determined according to ASTM D-664, ASTM D-2500, ASTM D-97, ASTM D1298 and ASTM D-445, respectively. In addition, 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 14214 was determined by Oxygen Bomb Calorimeter model 6772 (Parr instrument company, USA). In these calorimeter systems shown in Figure 1(b), 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 shown in Figure 1(c) 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) shown in Figure 1(d) was used to measure the acid value.

Kinematics viscosity measurements were made with a Digital Constant Temperature kinematics viscosity bath shown in Figure 1(e), while the density is measured by using Portable Density/Gravity Meter shown in Figure 1(f). 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. It was observed that the kinematics viscosity of POME was found to be about 1.2 times of diesel at $40^{o}C$.

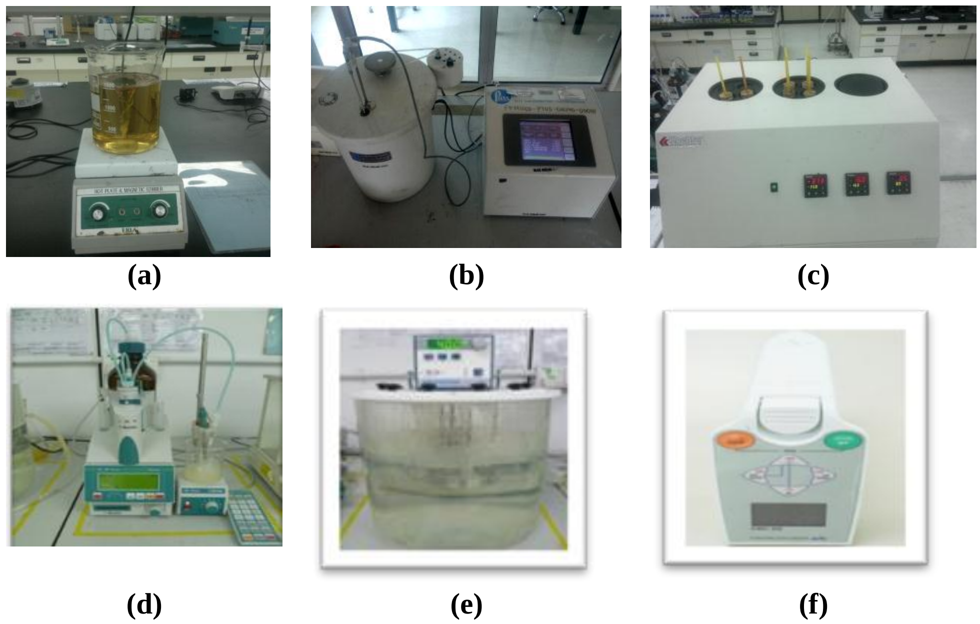

Figure 1. Analytical instruments used to measure fuel properties; (a) Magnetic Stirrer, (b) Density meter, (c) Viscosity bath, (d) Acid value & acidity tester, (e) Oxygen Bomb Calorimeter, (f) Cloud and Pour Point measuring Equipment

3. Results and Discussions

3.1. Analysis of Biodiesel Properties

The measured fuel properties of the POME are listed in Table 1 and compare to the biodiesel specifications, including ASTM D6751 in the United States and EN 14214 in Europe. The PP, CP, kinematics viscosity, density and acid value of the POME were significantly higher than those of the mineral diesel, while the heating value was lower than that of mineral diesel. The POME presented satisfactory fuel properties that satisfied most biodiesel specifications. The PP value of the POME was about 14^{o}C, a property that limited the beneficial use of the POME in cold climates [28, 29].

Table 1. Properties of POME compared to the biodiesel specifications

Property	Unit	POME	ASTM D6751	EN 14213
Acid Value	mg KOH/g	0.49	0.5 max	0.5 max
Viscosity at 40 ^{o}C	mm^2/s	4.6116	1.9-6.0	3.5-5
Density	kg/m^3	880.8	880	860-900
CP	^{o}C	14	---	---
PP	^{o}C	14	---	---
Heating Value	MJ/kg	38.6	----	35 min

The selection of additives for oxygenating the fuel depends on economic feasibility, toxicity, fuel blending property, additive solubility, flash point of the blend, viscosity of the blend, solubility of water in the resultant blend, and water partitioning of the additive [25]. Based on the fuel blending properties, toxicity and economic feasibility Diethyl Ether was selected. There are a number of fuel properties that are essential to the proper operation of a diesel engine. The DEE was further added to POME at different volumetric ratios (varied from 0% to 8% in steps of 2%) to study the variations in the CP, PP, density, heating value, acid value and kinematic viscosity of the POME-DEE blends.

3.2. Cloud Point and Pour Point Results

DEE-POME blends improved low temperature operability compared to unblended POME since the freezing points of DEE (-117.4 ^oC) are substantially below the temperature at which biodiesel typically undergoes solidification.

Addition of DEE to POME does not be affected CP, while increasing DEE content from 0 to 8% resulted in a dramatic decline in PP. Figure 2 shows the variations of the PP for POME with the volumetric percentage of the DEE. The maximum reduction of PP for POME was 7 ^oC when adding 8% DEE. The low-temperature properties of biodiesels not indicated in ASTM and EN standards as it related to climatic conditions.

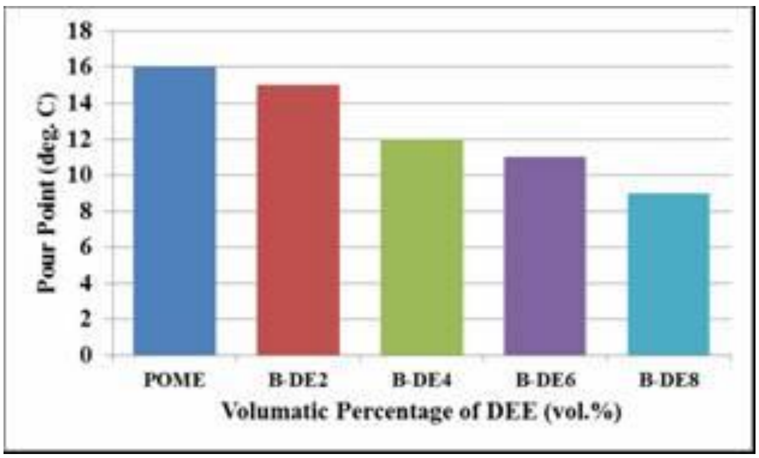

Figure 2. Variation in PP with the volumatric Percentage of DEE (vol.%) for POME

3.3. Density Results

The densities of POME-DEE blended fuel produced in this study are very close to each other and in the range of 0.870.2–0.880.8 kg/m^3 for B-DE8 and POME respectively. They are suitable for the ASTM and EN standards and slightly higher than those of the diesel fuel. Figure 3 presents the density values of the POME. The density of the POME-DEE blend decreased linearly with a higher volumetric percentage of the DEE, indicating that the additivity for the volume. Excellent agreement between the measured and estimated values of the density of the POME-DEE blends at 15 ^oC is given by:

$$\text{Density (kg/m}^3\text{)} = -2.59x + 882.83 \qquad R^2 = 0.9883 \qquad (1)$$

Where x is the volumetric percentage of the DEE (vol.%). The density of the POME-diesel blends can satisfy the specifications for diesel and biodiesel blends, listed in the standards.

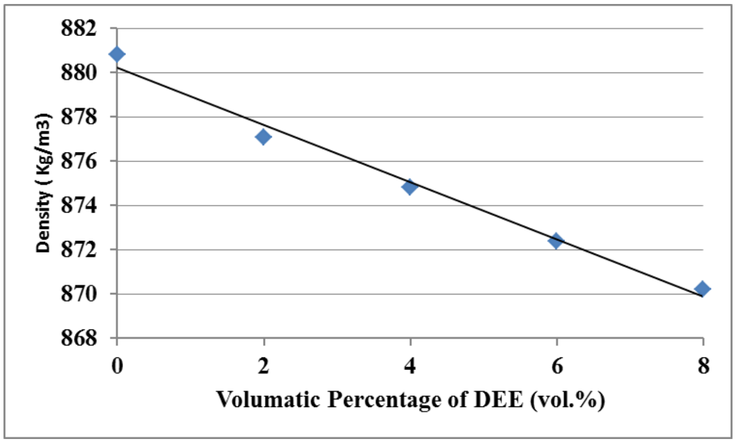

Figure 3. Variation in density with the volumatric percentage of DEE (vol.%) for POME

3.4. Viscosity Results

The viscosities of methyl esters vary in the range of 3.4587, 3.7, 4.007, 4.3151 and 4.611 mm^2/s for B-DE8, B-DE6, B-DE4, B-DE2 and POME respectively. All blends, as well as neat POME, satisfied the kinematic viscosity specification contained in ASTM D6751. But, the viscosity of BDE8 is slightly lower than the limits of the EN14213 standard (3.5 mm^2/s). The viscosity of the blend decreases as the DEE portion increases in the fuel mixture as observed from Figure 4. Similar to density, the kinematic viscosity of the POME-DEE blend increased linearly with a higher volumetric percentage of the DEE. The kinematic viscosity at 40 ^oC can be described by Eq. (2) for the POME-DEE blends, with a linear relationship:

$$\text{Kinematics Viscosity } (mm^2/s) = -0.146x + 4.6028 \qquad R^2 = 0.9983 \qquad (2)$$

The density and kinematics viscosity of the POME-DEE blends up to B-DE6 can satisfy the specifications for diesel and biodiesel blends, including ASTM D975, ASTM D7467, and EN 14213.

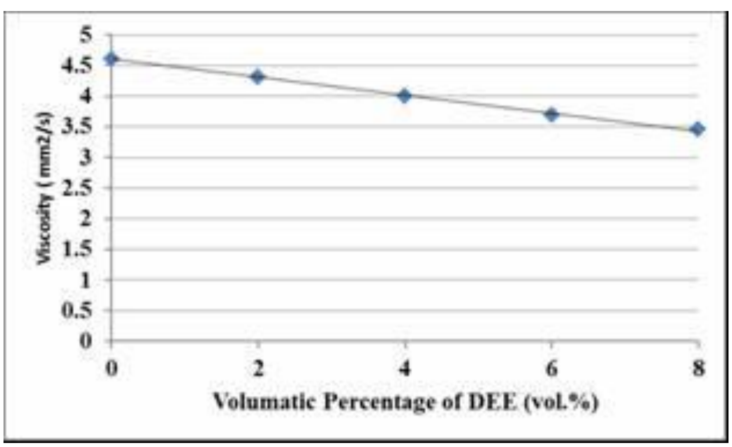

Figure 4. Variation in Viscosity with the volumatric Percentage of DEE (vol.%) for POME

3.5. Acid Value

Addition of DEE to POME improved the AV, and a significant 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 [30, 31]. Figure 5 shows acid value profile of POME–DEE blends. The acid value decrease by approximately 1% to 2% for each 2% of DEE added, by volume with a linear relationship, a maximum acid value for POME 0.49 mg KOH/g. This was expected, as DEE will dilute the free fatty acids present in POME, resulting in a reduction in AV. The acid value of the POME-DEE blend satisfies the requirement of ASTM D6751-06 and EN 14104 Standard for all blending ranges.

3.6. Heating Value

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 [32]. 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]. Figure 6 shows that the heating value of the POME-DEE blend decreased slightly with increasing volumetric percentage of the DEE, a minimum heating value for B-DE8 was 36.768 MJ/kg. The heating value of the POME-DEE blend satisfies the requirement of EN 14104 Standard for all blending ranges.

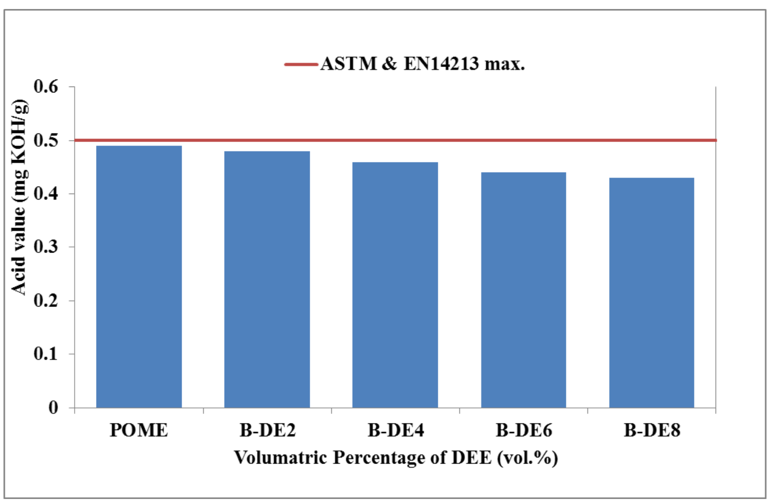

Figure 5. Variation in Acid value with the volumatric Percentage of POME (vol.%) for POME-diesel blends

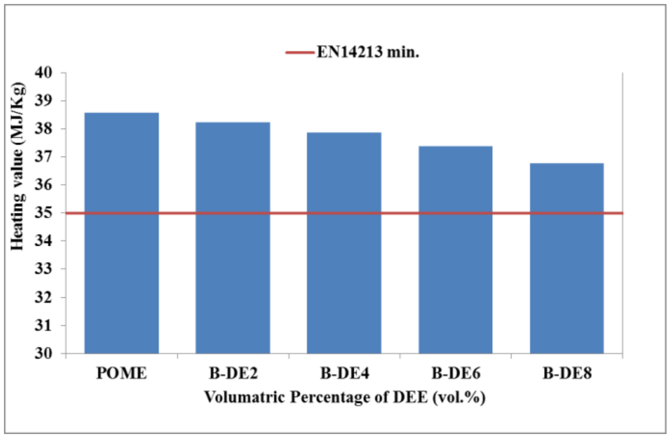

Figure 6. Variation in Heating value with the volumatric Percentage of POME (vol.%) for POME-diesel blends

4. Conclusions

The objective of this study was to characterize how the key fuel properties changed when diethyl ether were blended with palm oil methyl esters. According to the experimental results; the density of the POME-DEE blend decreased with the increase of DEE concentration in the blended fuel and displayed satisfactory fuel properties for all blending ranges. Similarly, the acid value of POME-DEE blends slightly improved with increasing DEE content. However, adding 8% DEE to the POME results in fuel viscosity lower that the limit of EN14213 standard. Increasing DEE content in POME resulted in a statistically significant difference in low temperature performance, with a maximum decrease in pour point by 7 ^{o}C at 8% DEE compare to POME. On the other hand, there was no significant difference in the cloud point of the biodiesel with DEE. In general, the heating value decreases slightly with increasing DEE portion in the blends. B-DE8 has the minimum heating value which is 4.7% less than POME and still satisfies the limits of the EN 14213.

Finally, palm biodiesel with diethyl ether additive exhibited slightly superior low temperature performance, acid value, viscosity and density with slight energy continent in comparison to POME. B-DE6 satisfied both ASTM and EN14213 specifications and may be suggested as the most prudent choice when considering POME-DEE blends.

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