Improvement of Blended Biodiesel Fuel Properties with Ethanol Additive

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Abstract

Industrial and transportation sectors are the higher energy consumer sectors in the world. As the main fuel used in these sectors now is the expensive depleting fossil fuels which available only in a certain region of the world, there is an urgent need to find out an alternative fuel to fulfill the energy demand of the world. Biodiesel as alternative fuels, are being used as an effective alternative for diesel and can blend together as they have comparable fuel properties. The feasibility of biodiesel production from palm oil was investigated with respect to its fuel properties and blending characteristics with petroleum diesel. Though biodiesel can replace diesel satisfactorily, problems related to fuel properties persist. In this study an oxygenated additive ethanol (E) was added to palm oil biodiesel POME-diesel blend B50 (50% POME + 50% diesel) in the ratios of 1%, 2%, 3% and 4% 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-diesel blended fuel properties can serve the researchers who work on biodiesel fuels to indicate the fuel suitability for diesel engines according to fuel standards. The results showed slight improvement in acid value, significant viscosity and density. Maximum decrease in pour point by 2 ^{o}C at 3% ethanol, on the other hand maximum decrease in energy content about 4.3% at 4% ethanol compare to blended fuel B50.

Keywords: *Palm oil biodiesel, Blending, Ethanol, 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]. Biodiesel is composed of fatty acid methyl esters (FAME) and is synthesized usually via vegetable oils (triacylglycerols) transesterification with low-molecular-weight alcohols [2]. The current mandates regarding the use of biodiesel around the world are mostly based on a biodiesel–diesel blend up to 20% biodiesel. The additive is the most visible option to introduce the biodiesel–diesel blended fuel at a high biodiesel blending ratio as an alternative fuel for mineral diesel.

The availability and sustainability of biodiesel feedstocks will be the crucial determinants in the popularization of biodiesel [3]. 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 [4]. From the literature, it has been found that feedstock alone represents 75%-80% of the overall biodiesel production cost [5–7]. 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 [8].

Fuel injection systems measure fuel by volume, and thus, engine output power influence by changes in density due to the different injected fuel mass [9]. 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 [10, 11]. The fuel energy content has a direct influence on the engine power output [12, 13]. 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. Use of additive that have less energy continent with blended fuel 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.

The higher concentration of oxygen in biodiesel improves lubricity, combustion and reduces emissions while it slightly increases NOx. Low-level blends of ethanol can further reduce the emissions and can decrease viscosity [14]. However, drawbacks of E-diesel include reduced energy content [15], cetane number [16], flash point [16], lubricity [17] and immiscibility of ethanol in diesel [16, 18]. A recent study [17] explored the utility of ethanol-biodiesel-diesel blends (EB-diesel) as a means to mitigate the miscibility issues of E-diesel. The disadvantages of E-diesel were substantially reduced or eliminated in the case of EB-diesel prepared from 5% ethanol and 20% biodiesel (soybean oil methyl esters) in ultra low sulfur diesel (LSD) fuel [17]. A later study [19] revealed that 3% ethanol, 2% biodiesel (sunflower oil methyl esters), and 95% low sulfur diesel improved the pour point (PP) of the resultant blend. In general, EB-diesel blends resulted in reduced CO and HC exhaust emissions versus neat LSD. Also elucidated were the effects of blending ethanol with biodiesel (E-biodiesel) in a 6:4 ratio on the PP, kinematic viscosity, and flash point (FP). Specifically, the PP of biodiesel was reduced from 3 ^{o}C to 9 ^{o}C, kinematic viscosity (40 ^{o}C) was reduced from 4.22 to 1.65mm2/s, and FP was reduced from 187 to 14 ^{o}C after blending with ethanol [19].

Analogously, [20, 21] a blend of ethanol and biodiesel prepared from Madhuca indica oil (MME) and poultry fat (PFME) exhibited better fuel properties versus unblended biodiesel. Where the reduction in cloud point and pour point was 4 ^{o}C and 3 ^{o}C for MME and 6 ^{o}C and 4 ^{o}C for PFME respectively, when blended with 20% of ethanol, with reduction in CO, lower NOx emissions and decrease in smoke emissions on an average without affecting the thermal efficiency.

Other experimental investigations [22, 23] were conducted to evaluate the effects of using ethanol as additives to soybean biodiesel/diesel blends on the performance, emissions and combustion characteristics of a direct injection diesel engine. The tested fuels denoted as

B20E5 (20% biodiesel and 80% diesel in vol.) with 5% ethanol and (B30E5) 30% biodiesel and 70% diesel in vol.) with 5% ethanol. The results indicate that, compared with blended fuel, there is a slightly lower brake specific fuel consumption (BSFC). Drastic reduction in smoke is observed with ethanol at higher engine loads. Nitrogen oxide (NOx) emissions and hydrocarbon (HC) emissions are slightly higher for blended fuel with ethanol, but carbon monoxide (CO) is slightly lower. However, the blended fuels with ethanol could lead to reduce both of NOx and HC emissions of a diesel engine [24], where biodiesel was blended with 5%, 10% and 15% by volume of ethanol and tested in a 4-cylinder direct-injection diesel engine.

Palm biodiesel-diesel blends up to B40 can be directly used in diesel engines without making any engine modifications [25]. Therefore, the first objective of the current study was to characterize the properties of the palm oil methyl esters (POME) and blended fuel B50, including the energy content and low temperature operability. The second objective was to improve the low temperature operability of blended fuel B50 through the addition of a small portion of ethanol additive. Of additional interest was a comparison of B50-E fuel properties at different additive portion to the ASTM D6751 [26] and EN 14214 [27], the American and European biodiesel standards, respectively. The low temperature operability of the resulting B50-E blends was ascertained through measurement of cloud point (CP) and pour point PP. Also of interest was the influence of ethanol addition on the kinematic viscosity (40 ^{o}C), density (15 ^{o}C), acid value (AV), and energy content of blended fuel B50.

2. Materials and Method

Palm oil biodiesel (POME) was supplied by local commercial company in Selangor, Malaysia. Diesel fuel was provided by a commercial fuel manufacturer. Samples of palm oil methyl ester and petroleum diesel were prepared as B50 (50%vol. POME + 50%vol. diesel) through mixed and blended using electrical magnetic stirrer shown in Figure 1(a). The mixtures were stirred continuously for 20 minutes. Then, ethanol (E) was added into the blended fuel at low stirring rate. The mixtures were stirred continuously for additional 20 minutes and left for 30 minutes to reach equilibrium at room temperature before they were subjected to any test. The use of E has also some limitations, such as lower lubricity, reduced ignitability and cetane number, higher volatility and lower miscibility [28] which may lead to increased unburned hydrocarbons emissions. Therefore, E was added in small proportions of 1%, 2%, 3% and 4% by volume to blended fuel, which corresponded to B50-E1, B50-E2, B50-E3 and B50-E4 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 [29]. 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 [30]. 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.

Kinematic viscosity measurements were made with a Digital Constant Temperature kinematic 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.

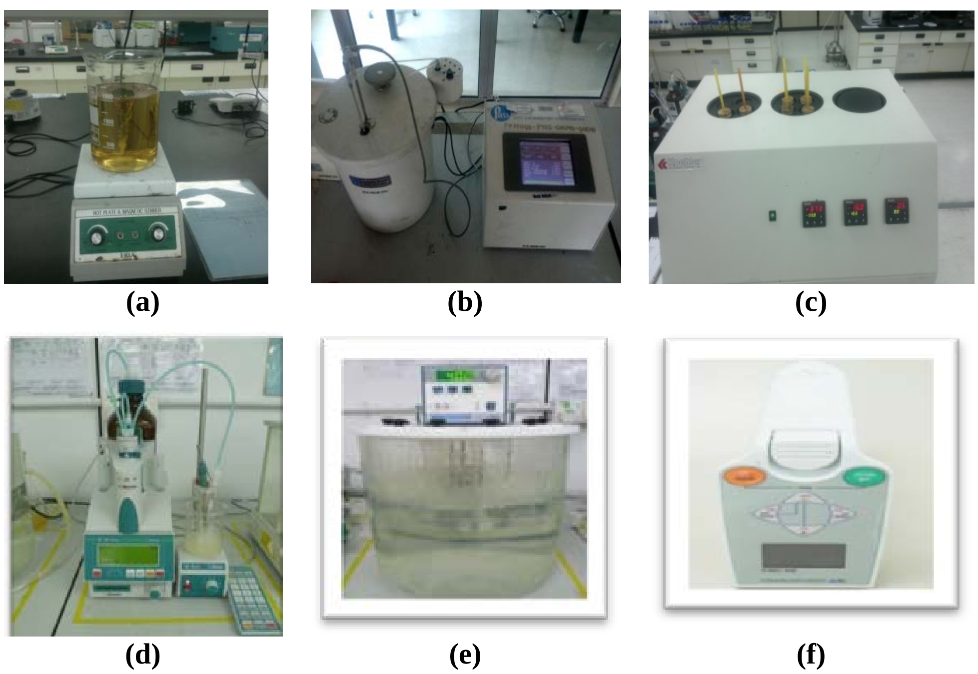

Figure 1. Analytical Instruments used to Measure Fuel Properties; (a) Magnetic Stirrer, (b) Density Meter, (c) Viscosity Bath, (d) Acid Value & Acidity Tester, (e) Oxygen Bomb Calorimeter, (f) Cloud and Pour Point Measuring Equipment

3. Results and Discussions

3.1. Analysis of Biodiesel Properties

The measured fuel properties of the POME and blended fuel B50 are listed in Table 1and compare to the biodiesel specifications, including in ASTM D6751 standard. The PP, CP, kinematic viscosity, density and acid value for B50 were significantly higher than those of the mineral diesel and lower than those of POME, while the heating value was lower than that of mineral diesel and higher than that of POME. In general the blended fuel B50 presented satisfactory fuel properties that satisfied most biodiesel specifications. The PP value of B50 was about 2^{o}C, a property that limited the beneficial use of this blended in cold climates [31], [32].

The selection of additives for oxygenating the fuel depends on economic feasibility, toxicity, fuel blending property, additive solubility, flash point of the blend, the viscosity of the blend, solubility of water in the resultant blend, and water partitioning of the additive [28]. Based on the fuel blending properties, toxicity and economic feasibility ethanol was selected. There are a number of fuel properties that are essential to the proper operation of a diesel engine. Ethanol (E) was further added to B50 at different volumetric ratios (varied from 0% to 4% in steps of 1%) to study the variations in the CP, PP, density, heating value, acid value and kinematic viscosity of the B50-E blends.

Table 1. Properties of POME Compared to the Biodiesel Specifications

Property	Unit	POME	B50	ASTM D6751
Acid Value	mg KOH/g	0.49	0.33	0.5 max
Viscosity at 40 ^{o}C	mm^{2}/s	4.6116	4.0	1.9-6.0
Density at 15 ^{o}C	kg/m^{3}	880.8	863.4	880
CP	^{o}C	14	4	---
PP	^{o}C	14	2	---
Heating Value	MJ/kg	38.6	42.7	----

3.2. Cloud Point and Pour Point Results

B50-E blends have improved low temperature operability compared to unblended B50 since the freezing point of E (-114 ^{o}C) are substantially below the temperature at which biodiesel typically undergoes solidification.

Addition of E to B50 slightly affected CP by 1 ^{o}C decrease, while increasing E content from 0 to 4% resulted in a non regular decline in PP. Figure 2 shows the variations of the PP for blended fuel B50 with the volumetric percentage of the E. The minimum value of PP for B50 was 0 ^{o}C at 3% E. The low-temperature property of biodiesel does not indicate in ASTM and EN standards as it related to climatic conditions.

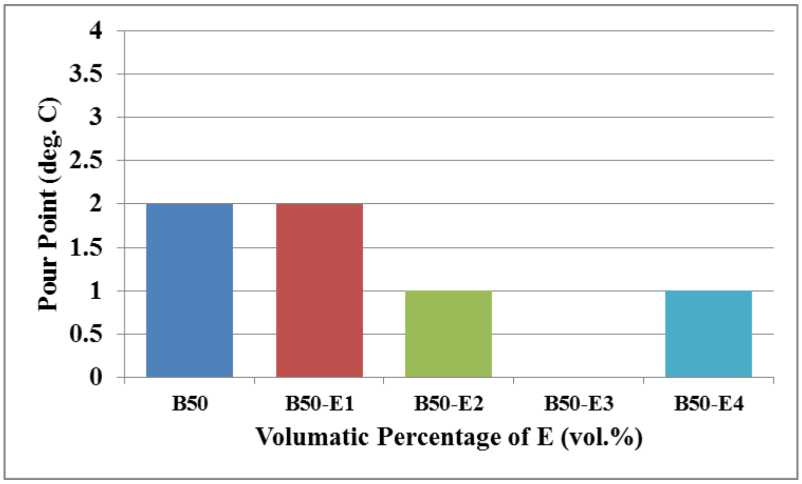

Figure 2. Variation in PP with the Volumatric Percentage of DEE (vol.%) for POME

3.3. Density Results

The densities of B50-E blended fuel produced in this study are very close to each other and in the range of 860–863.4 kg/m3 for B50-E4 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. Figure 3 presents the variety of density values for B50 with E Portion. It is clear that the density of the fuel decreases with rising of E portion in the mixture. The density of the B50-E blend decreased linearly with a higher volumetric percentage of the E, indicating that the additivity for the volume. Excellent agreement between the measured and estimated values of the density of the B50-E blends at 15 ^oC is given by:

$$\text{Density (kg/m3)} = -0.84x + 863.64 \qquad R^2 = 0.965 \qquad (1)$$

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

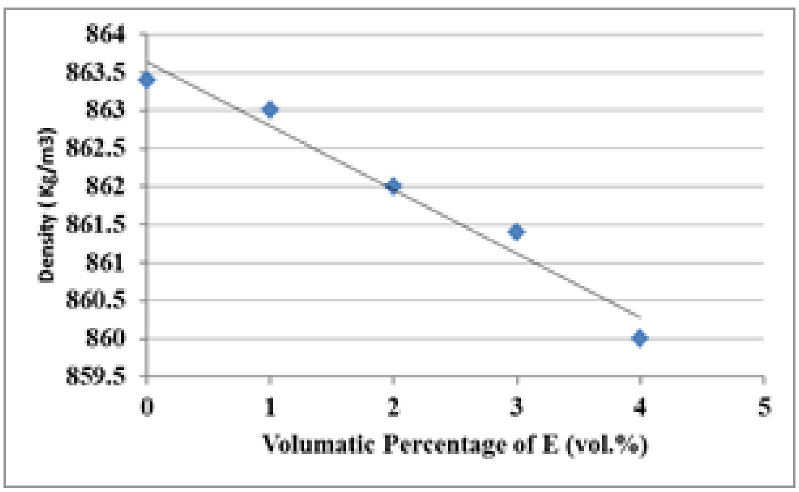

Figure 3. Variation in Density with the Volumatric percentage of DEE (vol.%) for POME

These results are in agreement with a previous study [33] that determined blends of microalgae oil biodiesel and its blends with petroleum diesel. The density of the B50-E blends can satisfy the specifications for diesel and biodiesel blends, listed in the standards.

3.4. Viscosity Results

The viscosities of blended fuel vary in the range of 3.6 and 4.0 mm2/s for B50-E4 and B50 respectively. All B50-E blend, as well as B50, satisfied the kinematic viscosity specification contained in ASTM D6751. The viscosity of the blend increases as the E portion increases in the fuel mixture as observed from Figure 4. Similar to density, the kinematic viscosity of the B50-E blend decreased linearly with a higher volumetric percentage of the E. The kinematic viscosity at 40 ^{o}C can be described by Eq. (2) for the B50-E blends, with a linear relationship:

$$\text{Viscosity (mm2/s)} = -0.101x + 4.0255 \qquad R^2 = 0.9856 \qquad (2)$$

Where x is the volumetric percentage of the E (vol.%). Likewise density, the kinematic viscosity of the B50-E blends are in agreement with a previous study [33] that determined blends of microalgae oil biodiesel and its blends with petroleum diesel.

The density and kinematic viscosity of the B50-E blends can satisfy the specifications for diesel and biodiesel blends, including ASTM D975, ASTM D7467 and EN 14213 for all the studied ethanol portions.

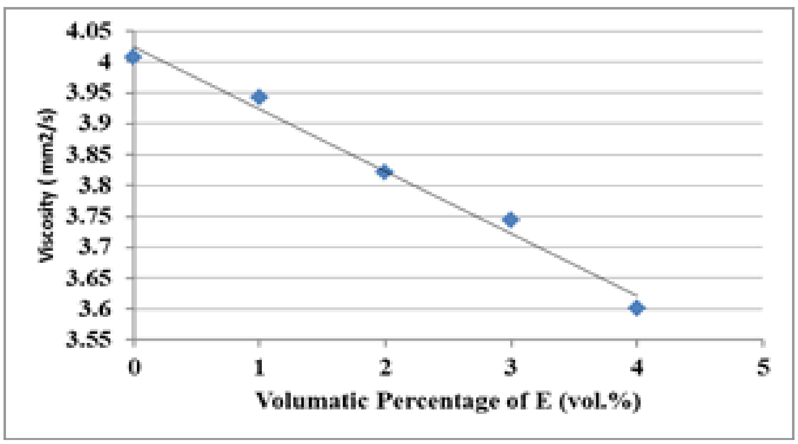

Figure 4. Variation in Viscosity with the Volumatric Percentage of DEE (vol.%) for POME

3.5. Acid Value

Addition of E to the blended fuel B50 improved the acid value (AV) of the fuel, where slight reduction in AV was achieved by increasing E 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 [34, 35]. Figure 5 shows acid value profile of B50-E blends, the acid value decrease by approximately 3% at 4% E additive, by volume with a maximum acid value for B50 was 0.33 mg KOH/g. This was expected, as E will dilute the free fatty acids present in POME, resulting in a reduction in AV. The acid value of the B50-E blend satisfies the requirement of ASTM D6751-06 and EN 14104 Standard for all blending ranges.

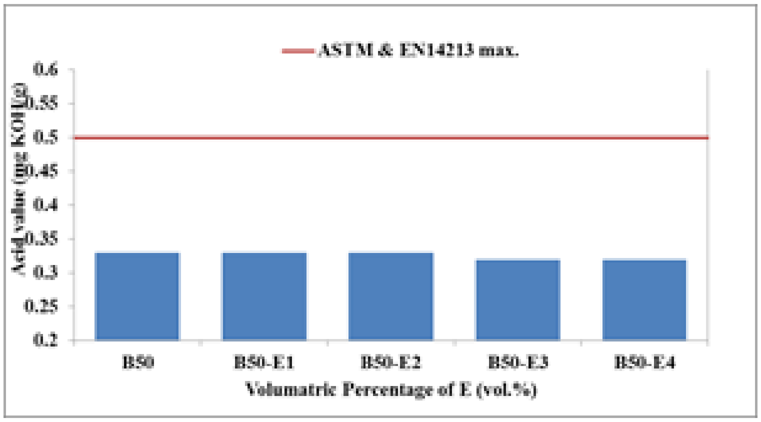

Figure 5. Variation in Acid Value with the Volumatric Percentage of POME (vol.%) for POME-diesel Blends

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 [36]. 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 [29]. Figure 6 shows that the heating value of the B50-E blend decreased slightly with increasing volumetric percentage of the E. A minimum heating value for B50-E4 was 40.9 MJ/kg, which is 4.3% less than the heating value of the blended fuel B50. The heating value of the B50-E blend satisfies the requirement of EN 14213 Standard for all blending ranges.

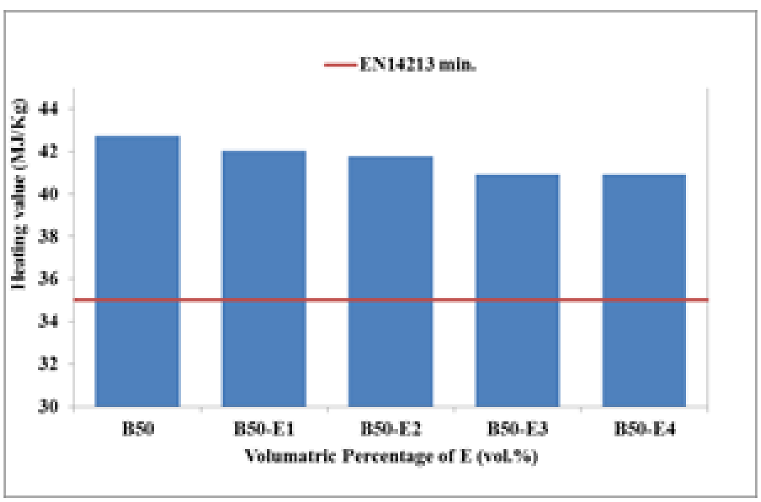

Figure 6. Variation in Heating Value with the Volumatric Percentage of POME (vol.%) for POME-diesel Blends

4. Conclusions

The objective of this study was to characterize how the key fuel properties changed when ethanol was added to palm oil methyl esters-diesel blends B50. According to the experimental results; the density and kinematic viscosity of the B50-E blend significantly decreased with the increase of E concentration in the blended fuel and displayed satisfactory fuel properties for all blending ranges. Similarly, the acid value of B50-E blends slightly improved with increasing E content. Likewise, increasing E content in the blended fuel B50 resulted in a significant difference in low temperature performance, with a maximum decrease in pour point by 2^{o}C for B50-E3 compare to B50. On the other hand, there was a slight difference in the cloud point of the blends by 1 ^{o}C. In general, the heating value decreases slightly with increasing E portion in the blends. B-E4 has the minimum heating value 4.3% less than the heating value of the blended fuel B50, which is still satisfying the limits of the EN 14213. Finally, B50-E 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 suitable choice when considering biodiesel diesel blended fuel with additives.

Acknowledgements

The authors would like to acknowledge to University Malaysia Pahang for the financial support under MTUN-CoE Research Grand RDU121201.

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