Energies **2014**, *7*, 4364-4380; doi:10.3390/en7074364

OPEN ACCESS

energies

ISSN 1996-1073

www.mdpi.com/journal/energies

Article

Influence of Chemical Blends on Palm Oil Methyl Esters' Cold Flow Properties and Fuel Characteristics

Obed M. Ali [1,*], Talal Yusaf [2], Rizalman Mamat [1], Nik R. Abdullah [3] and Abdul Adam Abdullah [1]

[1] Faculty of Mechanical Engineering, Universiti Malaysia Pahang, 26600 Pekan, Pahang, Malaysia; E-Mails: rizalman@ump.edu.my (R.M.); adam@ump.edu.my (A.A.A.)

[2] National Center for Engineering in Agriculture (NCEA), Faculty of Engineering and Surveying, University of Southern Queensland, Toowoomba, 4350 QLD, Australia; E-Mail: yusaft@usq.edu.au

[3] Faculty of Mechanical Engineering, Universiti Teknologi MARA, UiTM Shah Alam, 40450 Shah Alam, Selangor, Malaysia; E-Mail: nikrosli@salam.uitm.edu.my

* Author to whom correspondence should be addressed; E-Mail: obedmajeed@gmail.com; Tel.: +60-179-833-023; Fax: +60-9424-2202.

Received: 25 February 2014; in revised form: 28 June 2014 / Accepted: 2 July 2014 / Published: 8 July 2014

Abstract: Alternative fuels, like biodiesel, are being utilized as a renewable energy source and an effective substitute for the continuously depleting supply of mineral diesel as they have similar combustion characteristics. However, the use of pure biodiesel as a fuel for diesel engines is currently limited due to problems relating to fuel properties and its relatively poor cold flow characteristics. Therefore, the most acceptable option for improving the properties of biodiesel is the use of a fuel additive. In the present study, the properties of palm oil methyl esters with increasing additive content were investigated after addition of ethanol, butanol and diethyl ether. The results revealed varying improvement in acid value, density, viscosity, pour point and cloud point, accompanied by a slight decrease in energy content with an increasing additive ratio. The viscosity reductions at 5% additive were 12%, 7%, 16.5% for ethanol, butanol and diethyl ether, respectively, and the maximum reduction in pour point was 5 °C at 5% diethyl ether blend. Engine test results revealed a noticeable improvement in engine brake power and specific fuel consumption compared to palm oil biodiesel and the best performance was obtained with diethyl ether. All the biodiesel-additive blend samples meet the requirements of ASTM D6751 biodiesel fuel standards for the measured properties.

Keywords: butanol; diethyl ether; energy content; ethanol; palm oil biodiesel

1. Introduction

Decreasing fossil fuel supplies and increasing energy demands, together with the growing effects of greenhouse gas emissions from fuel combustion have led to the growing importance placed on the investigation of biodiesel. Mineral diesel fuel is only available in specific lands around the World, and their sources have very nearly reached their maximum production [1]. On the other hand, biodiesel is a renewable fuel produced from various vegetable oil feedstocks and animal fats [2,3]. The properties of biodiesel are comparable to ordinary diesel fuel with enhanced lubricity properties [4] and reduced pollutant emissions [5,6]. The rapid increase in biodiesel usage as a diesel fuel alternative is restricted by its higher viscosity, which affects the current fuel injection systems and causes poorer fuel vaporization. Furthermore, they are constricted by their cold climate properties [7,8]. The most suitable and economical way to improve both the low-temperature fuel properties of biodiesel and engine performance is the treatment with chemical additives. This technology is applied widely throughout the biodiesel industry [9]. Biodiesel is composed of fatty acid methyl esters (FAME) and is usually synthesized via transesterification of vegetable oils (triacylglycerols) with low-molecular-weight alcohols [10]. In regards to the use of biodiesel around the World, the current mandates are based mainly on a blend of diesel-biodiesel fuel [11]. The most acceptable option to make the biodiesel available as a stand-alone fuel alternative to ordinary diesel is with the use of additives [9]. Biodiesel (a mixture of monoalkyl esters of saturated and unsaturated long chain fatty acids) in general has a higher pour point (PP) and cloud point (CP), acid value and density as well as kinematic viscosity compared to mineral diesel. The low temperature flow properties (PP and CP) are used to characterize the fuel cold flow operability because the fuel utility is affected by the pour point, especially in colder regions around the World [12]. The higher oxygen concentration of biodiesel improves combustion, lubricity and reduces exhaust emissions, while it slightly increases NO_x emissions [12,13]. A small portion of ethanol (E) additive can promote emission reductions and decrease the viscosity [14]. However, the drawbacks of E-additive use include a reduction in fuel energy content [15], flash point, cetane number [16], lubricity [17] and immiscibility of the blended ethanol-biodiesel fuel [18,19].

Recent studies [20,21] have revealed that biodiesel fuel prepared from poultry fat methyl ester (PFME) and *Madhuca indica* oil (MME) exhibit better fuel properties when blended with ethanol compared to pure biodiesel. They found that the reductions in pour point and cloud point were 4 °C and 6 °C for PFME and 3 °C and 4 °C for MME, respectively, with 20% ethanol blending. Similarly, ethanol was used in amounts up to 4% to improve the properties of palm oil methyl ester (POME) [22]. Other experimental studies were conducted to estimate the influence of ethanol utilization as an additive to biodiesel-diesel blends from soybean [23,24] and sunflower oil biodiesel [25] on the direct injection diesel engine performance, exhaust emissions and combustion efficiency. Their results indicate that the brake specific fuel consumption (BSFC) is slightly reduced compared to blended biodiesel fuel. Extreme reduction in exhaust smoke with ethanol is observed at higher engine loads. Hydrocarbon emissions (HC) and nitrogen oxide emissions (NO_x) for blended fuel with ethanol are

slightly higher, on the other hand, there was a slight reduction in carbon monoxide (CO). However, the use of ethanol as an additive to biodiesel blended fuels might result in reductions of both HC and NO_x emissions from a diesel engine [26], where ethanol-biodiesel was blended with biodiesel at 5%, 10% and 15% by volume. A 4-cylinder direct injection diesel engine was used to conduct this test. Diethyl ether (DE) is an excellent ignition improver with a low auto-ignition temperature [27] and can be used with biodiesel fuels to reduce the NO_x exhaust emissions. Furthermore, it can enhance the cold engine starting and improve the ignition for emulsions of diesel and water [28]. Other studies used the DE with biodiesel blends to improve the performance and emissions of a diesel engine. To the best of the authors' knowledge, none of the previous researchers investigated the effect of DE on the biodiesel fuel properties.

The aim of this study was to evaluate the improvement of properties of palm oil methyl ester with the addition of ethanol (E), butanol (BU) and diethyl ether (DE) as additives and the influence of increasing the blend of chemical additives on the reduction of biodiesel fuel energy content. Furthermore, the effect of the chemical additive type on improving engine power and fuel consumption was investigated.

2. Biodiesel Fuel Properties

Biodiesel is a renewable and environmentally friendly alternative to mineral diesel fuel [29,30]. It is obtained through the transesterification of vegetable oils or animals fats, with short chain alcohols such as methanol and ethanol. It gives comparable engine performance to that of fossil diesel and can be utilized pure or blended with mineral diesel [31,32]. Biodiesel is non-flammable, non-explosive, biodegradable and nontoxic, with a high flash point compared to mineral diesel. Furthermore, its use results in a reduction in many toxic exhaust emissions. The absence of soot, sulphur oxide (SO_x) and particulate is nearly absolute, and a reduction in polycyclic aromatic hydrocarbon emissions can be observed. The oxygen content in biodiesel is 10%–15% [31,33] by weight with a typically high cetane number compared to mineral diesel fuel, which leads to higher combustion efficiency [34,35]. The cetane number is an indicator of auto ignition quality for the fuel. An increase in cetane number causes a shorter ignition delay. This results in less fuel being injected during the premix burn and more during the diffusion burn portion, thus reducing the cylinder pressure rise, which may result in lower cylinder temperatures [36]. These characteristics lead to a complete combustion of biodiesel fuel with lower exhaust emissions compared to mineral diesel. However, biodiesel has a higher density, kinematic viscosity, pour point and cloud point than mineral diesel fuel. On the other hand, the energy content of biodiesel is about 12% lower than that of mineral diesel fuel on a mass basis, resulting in lower engine speed and power [37–39]. The fatty acid profile of the feedstock is one of the major determinants of its energy content [1]. The output engine power is influenced directly by the fuel energy content [40,41] as well as by the density changes due to the different mass of fuel injected, as the injection systems measured fuel by volume [42]. Therefore, density is important for different aspects of diesel engine performance. Furthermore, high viscosity can lead to larger fuel droplets, a narrower injection spray angle, lower quality vaporization and higher in-cylinder fuel spray penetration [43,44]. On the other hand, the use of a high kinematic viscosity fuel can cause undesired consequences like poor atomization of fuel during the spraying period, engine deposits, injectors and

fuel pump elements wear and additional power required to the fuel pumping [45]. In general, the biodiesel fuel viscosity is typically higher than that of mineral diesel, and it is significantly influenced by the compound structure of biodiesel [46]. The use of biodiesel fuel as an alternative to mineral diesel can significantly reduce the exhaust emissions such as the overall carbon dioxide (CO_2) life cycle [47], carbon monoxide (CO), particulate matter (PM), sulphur oxides (SO_x), and unburned hydrocarbons (HC) [48]. Moreover, biodiesel has higher nitrogen oxide (NO_x) emissions [49,50]. The major disadvantages of biodiesel fuel are fuel injector coking, engine compatibility [43], and high production costs [37]. The effects of oxidative degradation (auto oxidation) resulting from contact with atmospheric air during prolonged storage periods presents a legitimate concern in terms of maintaining biodiesel fuel quality [51].

Typically, biodiesel fuels have poor cold flow characteristics compared to mineral diesel fuel, which limits their use in cold climate regions [52]. Mineral diesel fuels are affected by the growth and agglomeration of crystals of paraffin wax when the ambient temperatures fall below the cloud point of the fuel. These solid crystals may lead to start-up problems such as clogging of the filter when the ambient temperatures drop to about −10 °C to −15 °C [53]. While the cloud point of mineral diesel is reported to be around −16 °C, typically biodiesel has a cloud point of nearly 0 °C, thus restricting its use to ambient temperatures higher than freezing [54,55].

3. Methodology

3.1. Materials

Palm oil methyl ester (POME) was supplied by a local commercial company from a processing plant located in Selangor, Malaysia. Ethanol (99.5; <0.02 mass% water) butanol (99.5%; <0.05 mass% water) and diethyl ether (99.5%; <0.05 mass% water) were purchased from a chemicals supplier. The properties of POME and the chemical additives were reported in Table 1 [31,56]. All chemicals were immediately used when received from the supplier and then stored in the chemical lab after the first use.

Table 1. Properties of chemicals and POME.

Property	Ethanol	Butanol	Diethyl ether	POME
Chemical Formula	C_2H_5OH	$C_4H_{10}O$	$C_4H_{10}O$	-
Molecular Weight (g/mole)	46.07	74.12	74.12	-
Carbon weight%	52.2	64.8	64.8	76.2
Hydrogen weight%	13.1	13.6	13.6	12.6
Oxygen weight%	34.7	21.6	21.6	11.2
Specific Gravity @ 20 °C	0.790	0.8100	0.714	0.880 *
Boiling point, °C	78	116	34.6	-
Freezing point, °C	−114.1	−89.5	−116	-
Viscosity (cSt) @ 20 °C	1.52	3.64	0.34	4.61 **
Flash point, °C	16.6	35	−45	135
Auto ignition temperature, °C	363	343	160	-
Vapour Density, (Air = 1)	1.59	2.6	2.55	-
Heating value (MJ/kg)	29.7	33	34	38.6

* density measured at 25 °C; ** The viscosity measured at 40 °C.

3.2. Fatty Acid Composition

Fatty acid composition of palm oil methyl ester (POME) was determined using gas chromatography (model 6890, Agilent Technologies, Santa Clara, CA, USA). The gas chromatography (GC) analysis was conducted using helium as a carrier gas with a flow rate of 1.1 mL/min. The GC equipped with FID detector and Agilent 19091S-433 column (30.0 m length × 0.25 μm film thickness × 0.25 mm diameter). The column conditions were as follows: initial flow 1.1 mL/min, head pressure 17.63 psi, average velocity 31 cm/s. The injector temperature was 240 °C, and the detector temperature was 250 °C. The oven temperature was initially held at 140 °C for 2 min, then increased to 220 °C at 8 °C/min.

3.3. Preparation of POME-Chemicals Blends

Ethanol, butanol and diethyl ether were blended with POME at 1.0%, 3.0% and 5.0% by volume (vol%), respectively. Nine samples of palm oil methyl esters and chemical additives listed in Table 2 were prepared through blending and mixing using an electrical magnetic stirrer. Briefly stated, chemical additives were added into POME at a low stirring rate. The mixtures were continuously stirred for 20 min then left for 30 min at room temperature to reach equilibrium state before they were utilized in any test. The chemical additives usage also has some limitations, such as reduced ignitability and cetane number of the fuel, lower lubricity, lower miscibility and higher volatility [57] which may result in increased emissions of unburned hydrocarbons. Therefore, chemical additives were introduced in low portions.

Table 2. Types of blended fuel.

Fuel	POME (vol%)	E (vol%)	BU (vol%)	DE (vol%)
B100	100	0	0	0
B-E1	99	1	0	0
B-E3	97	3	0	0
B-E5	95	5	0	0
B-BU1	99	0	1	0
B-BU3	97	0	3	0
B-BU5	95	0	5	0
B-DE1	99	0	0	1
B-DE3	97	0	0	3
B-DE5	95	0	0	5

3.4. Fuel Properties Measurements

3.4.1. Density Measurement

The engine specific fuel consumption is influenced by fuel density due to the different mass of fuel injected [42]. Therefore, density is important for different performance aspects of the diesel engine. Density was measured at 25 °C according to ASTM D1298 [58] using a Portable Density/Gravity Meter, which is a microprocessor controlled system with an LED display. It has a range of 0.0000–2.0000 g/cm^3

with an accuracy of ±0.001 g/cm^3. It was important to clean the measuring cell before and after each measurement series, to ensure accurate data.

3.4.2. Kinematic Viscosity Measurement

High kinematic viscosity of fuel can result in pumping problems and fuel spray characteristics (penetration and atomization, *etc.*). The inefficient mixing of fuel with air leads to incomplete combustion. Kinematic viscosity was measured using a constant temperature digital kinematic viscosity bath, according to the ASTM D445 method using a Cannon-Fenske Routine viscometer as mentioned in ASTM D446 for transparent liquids with size No. 100 which is used for the kinematic viscosity range 3–5 mm^2/s [58]. The determination of viscosity is conducted at a temperature of 40 ± 0.1 °C.

3.4.3. Acid Value Measurement

The engine fuel supply system may suffer strong corrosion resulting from the rise in the fuel acid value content. An increase in the amount of free fatty acids results in higher fuel acid value [59]. Acid value is represented as the required mg KOH to neutralizing 1 g of FAME. Acid value was measured using a Metrohm test apparatus (Riverview, FL, USA) model 785, according to ASTM D664 [58]. This method gave a detection limit of 0.01%. Analysis of the samples was done in duplicate.

3.4.4. Energy Content Measurement

The energy content was measured using an Oxygen Bomb Calorimeter (from Parr Instrument Co., Moline, IL, USA) model 6772. In these calorimeter systems, the leak of heat from the oxygen bomb to the water in the bucket is measured accurately during the pre-period of calorimetric using electronic thermometer. This evaluation leads to the prediction of the average effective surroundings temperature of the calorimeter. Then, to provide the heat leak correction of the calorimeter, this temperature value is used throughout the interval of test. It harnesses the controller computing power, with no extra hardware costs, to provide the correction capability of the heat leak that is almost identical to the approach used when employing the techniques of non-electronic thermometry and manual calorimetric.

3.4.5. Cloud Point and Pour Point Measurement

The cloud point (CP) represents the temperature at which a wax crystal cloud is first seen in a liquid when the liquid undergoes the cooling process under certain conditions. Pour point (PP) represents the lowest temperature at which a liquid can flow. Cloud point (CP) and pour point (PP) were measured in accordance to ASTM D2500 and ASTM D97, respectively [58]. The test equipment, model K46195, manufactured by the Koehler Instrument Company (Bohemia, NY, USA) was used for the measurement of cloud point and pour point. The values of CP and PP were rounded close to the complete degree. For a higher degree of precision, the resolution of pour point measurements was 1 °C instead of the specified increment 3 °C. For a greater degree of accuracy, each experiment was conducted in triplicate.

3.5. Engine Test

The fuels engine tests were conducted with a naturally aspirated type water cooled 4-cylinder Mitsubishi 4D68 diesel engine with a compression ratio of 22.4:1, total displacement 1.998 dm^3, bore to stroke ratio 0.89 and mechanically controlled fuel injection system distributor. A schematic diagram of the experimental engine setup and the engine test bed are illustrated in Figures 1 and 2 respectively. The engine was coupled with an eddy current dynamometer with a capacity of 150 kW controlled by a Dynalec controller; measuring and controlling the effective torque and engine speed. The tests were conducted at half open throttle and variable engine speed from 1500 to 3500 rpm with constant increments of 500 rpm. The s tested in the diesel engine at 5% percentage with POME, accordingly, the tested fuel includes palm oil methyl ester (B100), B-E5, B-BU5, B-DE5 and mineral diesel. The engine is equipped with an exhaust gas recirculation system; however, in this experiment the EGR mode is set to OFF.

Figure 1. Schematic diagram of experimental engine setup: (1) diesel fuel tank; (2) biodiesel fuel tank; (3) drain valve; (4) fuel filter; (5) fuel pump; (6) pressure transducer; (7) EGR valve; (8) dynamometer, (9) gas analyser; (10) in-cylinder pressure transducer; (11) Orion 1624 DAQ; (12) crank angle encoder.

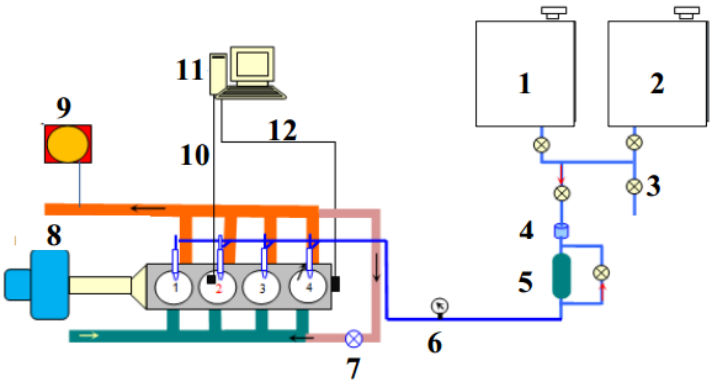
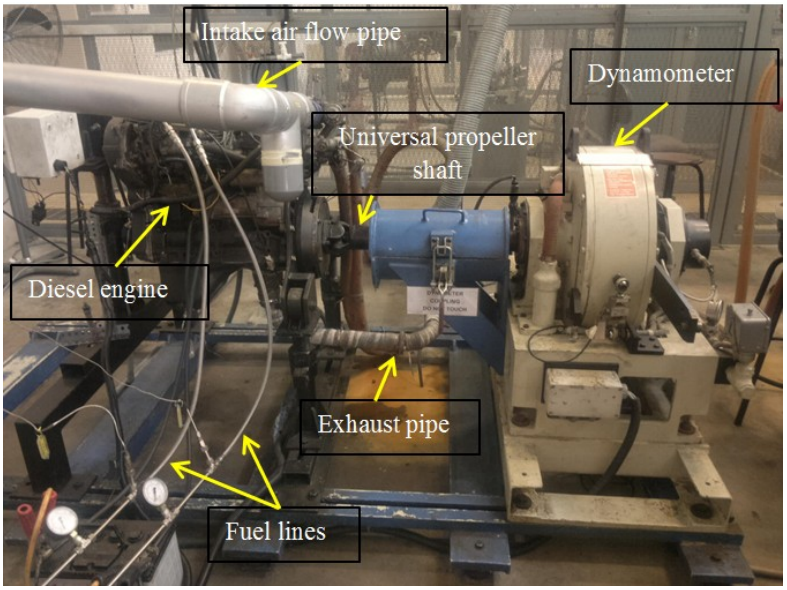


Figure 2. Experimental engine test bed.



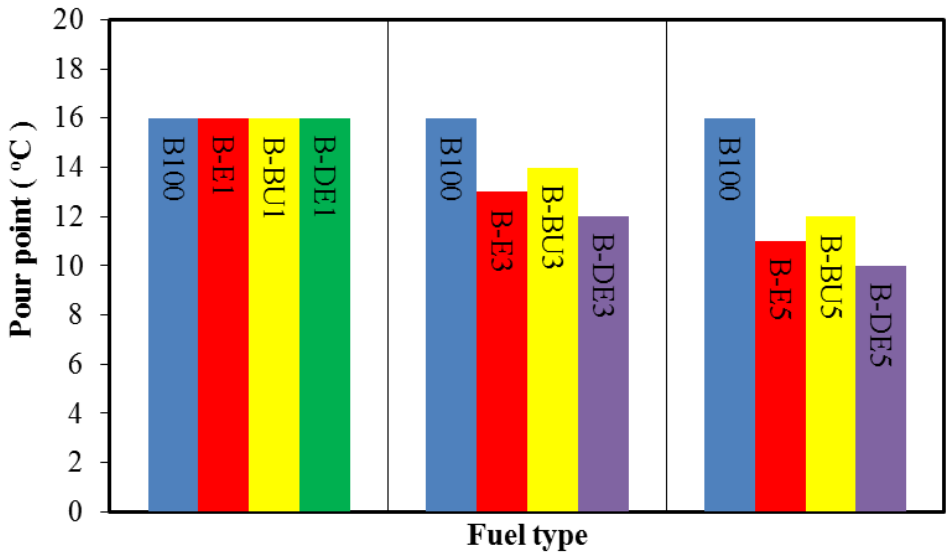
4. Results and Discussion

The tests results reveal that palm oil methyl ester shows the higher pour point, a property that limited the benefits of the biodiesel utilization in cold climates [56,57]. This is due to the predominance of saturated fatty acids in palm oil biodiesel as shown from the fatty acid composition analysis results present in Table 3. Furthermore, all POME-chemical's blends improved the pour point (PP) compared to unblended POME. This may be attributed to the low freezing points of ethanol (−114.1 °C) butanol (−89.5 °C) and diethyl ether (−116 °C) which are substantially lower than the temperature at which biodiesel typically undergoes solidification. Furthermore, POME pour point was improved by increasing the additive ratio in the blend. A significant difference in PP among additive types was detected at 5% blending ratio with 11 °C, 12 °C and 10 °C for ethanol butanol and diethyl ether respectively; compared to pure palm oil methyl ester. Figure 3, shows that, the minimum PP temperature was with diethyl ether which is about 5 °C lower than that of palm oil methyl ester.

Table 3. Fatty acid composition of palm oil biodiesel by GC.

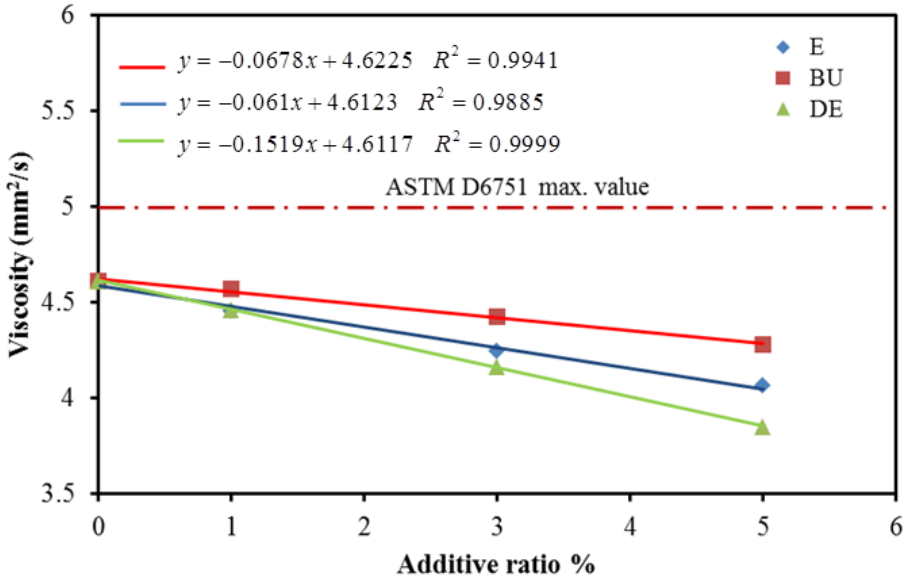
No.	Fatty Acid	Structure	Formula	Molecular Mass	POME (%)
1	Lauric	12:0	$C_{12}H_{24}O_2$	200	0.3
2	Myristic	14:0	$C_{14}H_{28}O_2$	228	1.0
3	Palmitic	16:0	$C_{16}H_{32}O_2$	256	43.3
4	Palmitioleic	16:1	$C_{16}H_{30}O_2$	254	0.1
5	Margaric	17:0	$C_{17}H_{34}O_2$	270	0.1
6	Stearic	18:0	$C_{18}H_{36}O_2$	284	5.4
7	Oleic	18:1	$C_{18}H_{34}O_2$	282	49.2
8	Arachidic	20:0	$C_{20}H_{40}O_2$	312	0.4
9	Eicosenoic	20:1	$C_{20}H_{38}O_2$	310	0.1
Saturation		-	-	-	50.6
Unsaturation		-	-	-	49.4
Total		-	-	-	100.0

Figure 3. Variation in palm oil methyl ester pour point with increasing blending ratio for different additives.



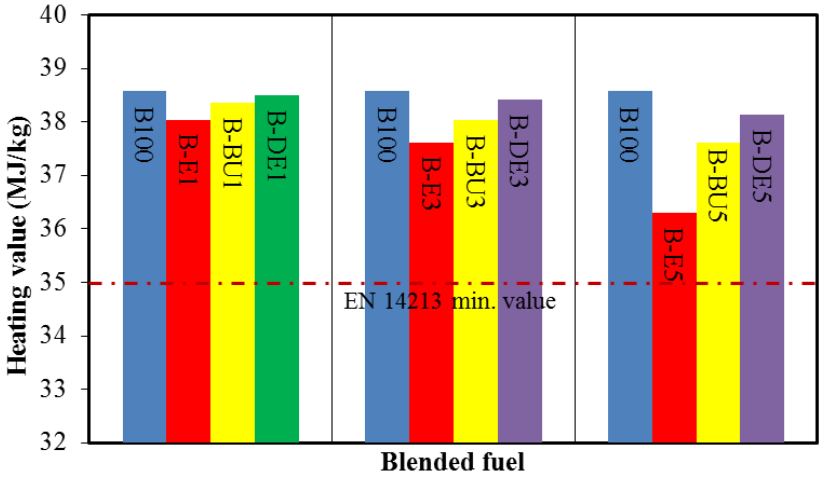
Blending chemical additives with POME reduced kinematic viscosity at 40 °C, as short-chain alcohols and ether have significant low kinematic viscosities compared to biodiesel. The kinematic viscosities at 20 °C of ethanol, butanol and diethyl ether are 1.52, 3.64 and 0.23 mm^2/s, respectively; therefore, blends of POME were least viscous with diethyl ether and most viscous with butanol as shown in Figure 4. For 5% blends with ethanol, butanol and diethyl ether the exhibited kinematic viscosities at 40 °C were 4.06, 4.28 and 3.85 mm^2/s, respectively. The decrease in the biodiesel viscosity with additives results in a better atomization and fuel spray shape. These finer droplets of the fuel lead to good mixing with air, which results in improving combustion. All blends, as well as pure POME, meet the kinematic viscosity requirement indicated in ASTM D6751 standard [58]. Furthermore, as the chemical additives ratio increased, the kinematic viscosity of the fuel decreased. These reductions were higher for diethyl ether and lower for butanol. The decrease in the kinematic viscosity of the POME-additive blend changed linearly with the additive volumetric percentage and could be represented by a correlation equation for each additive as shown in Figure 4. These results are in agreement with a prior study [21] which indicates that blends of ethanol and *M. indica* oil biodiesel exhibited lower kinematic viscosities in comparison to unblended *M. indica* oil methyl esters.

Figure 4. Variation in palm oil methyl ester kinematic viscosity with increasing blending ratio for different chemical additives.



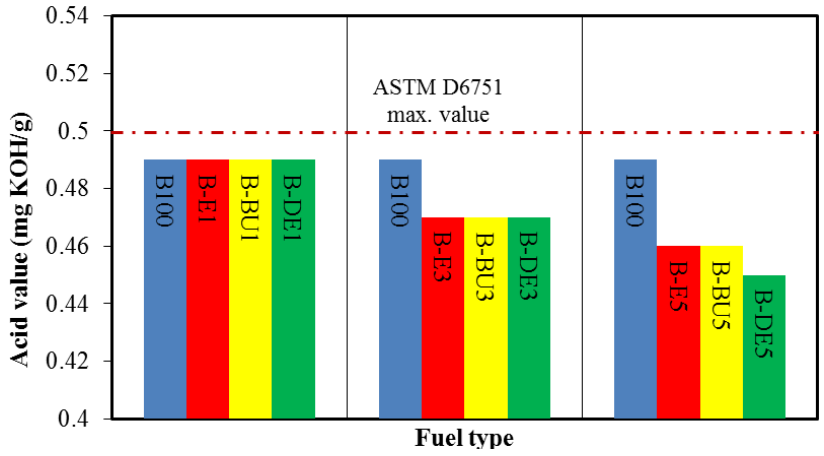
Heat of combustion is the amount of heating energy liberated by the combustion of a unit value of fuel [60]. The addition of chemical additives to POME resulted in a slight reduction in energy content compared to unblended POME, as these additives have less energy content. The ASTM D6751 standard does not specify the heating value of the fuel [58] while it is prescribed in EN 14213 with a minimum of 35 MJ/kg (biodiesel for heating purpose) [61]. POME heating value slightly decreased with the increase in the volumetric percentage of the additive as shown in Figure 5. Furthermore, palm oil methyl ester exhibited a lower heating value with ethanol compared to butanol and diethyl ether. All fuel blends as well as neat POME, satisfying the EN 14213 biodiesel standard requirement for all ranges of blending.

Figure 5. Variation in palm oil methyl ester heating value with increasing blending ratio for different chemical additives.



The addition of alcohol and ether to POME slightly improved the AV as shown in Figure 6, this was anticipated as alcohol and ether will dilute the existing free fatty acids in POME, leading to a reduction in acid value. A slight divergence was noticed between the different additive types. All biodiesel-additive blends meet the requirement of biodiesel fuel standard ASTM D6751 which states that the maximum acid value for biodiesel fuel is 0.50 mg KOH/g [58].

Figure 6. Variation in palm oil methyl ester acid value with increasing blending ratio for different additives.



Fuel density decreased with the addition of alcohol and ether to POME as shown in Figure 7. The density of POME was lower with diethyl ether and higher with ethanol. For 5% blends, ethanol, butanol and diethyl ether exhibited densities at 15 °C of 877.6, 876 and 873.4 kg/m^3, respectively. The density at 25 °C can be described by a correlation equation for each additive as presented in Figure 7. It is obvious that the POME-additive blend density linearly changed with the additive volumetric percentage. The ASTM D6751 standard does not specify the density of the biodiesel fuel [58]; however, the density value is indicated in the range of 860–900 kg/m^3 in the European standard EN 14214 [62]. All blends, as well as pure POME, meet the density requirement indicated in EN 14214 standard specifications.

Figure 7. Variation in palm oil methyl ester density with increasing blending ratio for different additives.

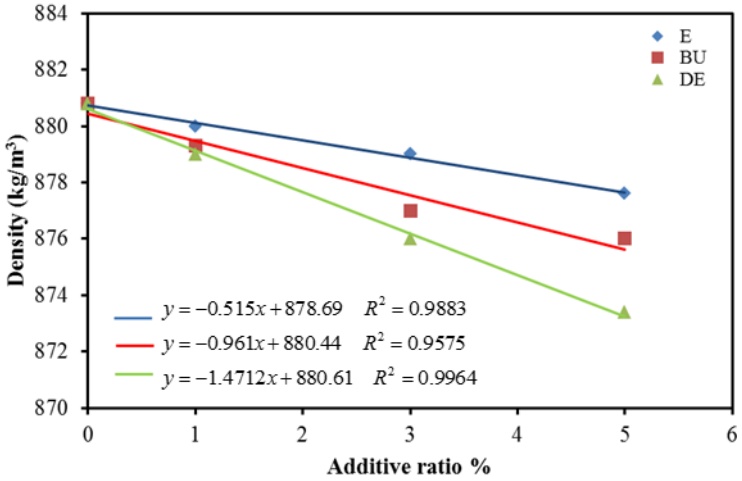


Figure 8 illustrates the variation in engine brake power at increasing speed for different fuel samples. The results show that the measured engine power for diesel fuel is higher than that of B100 and B100 with 5% of different additives. At 2500 rpm, the engine brake power for diesel and B100 fuels were 24.3 kW and 21.4 kW, respectively. This difference in brake power is due to the high energy content of mineral diesel (45.21 MJ/kg) compared to palm biodiesel fuel (38.57 MJ/kg) [37–39]. As a comparison, the engine brake power is lower by about 11% with biodiesel compared to diesel fuel. However, the measured engine brake power for B100 fuel increased with additives. The engine brake power measured at 2500 rpm engine speed for B100 was 21.8, 21.9 and 22 with ethanol, butanol and diethyl ether respectively at 5% additive ratio, which is slightly different. This difference in the trend of increasing engine power with POME and various additives is due to the effect of two conflicting factors, the effect on reducing the fuel viscosity which improves the fuel spray and the fuel energy content reduction effect. Diethyl ether has a lower viscosity and higher energy content compared to other additives, resulting in higher engine brake power.

Figure 8. Engine brake power with mineral diesel fuel, palm oil methyl ester and palm oil methyl ester with different additives at 5% blending ratio (tests conducted at increasing engine speed and half open throttle).

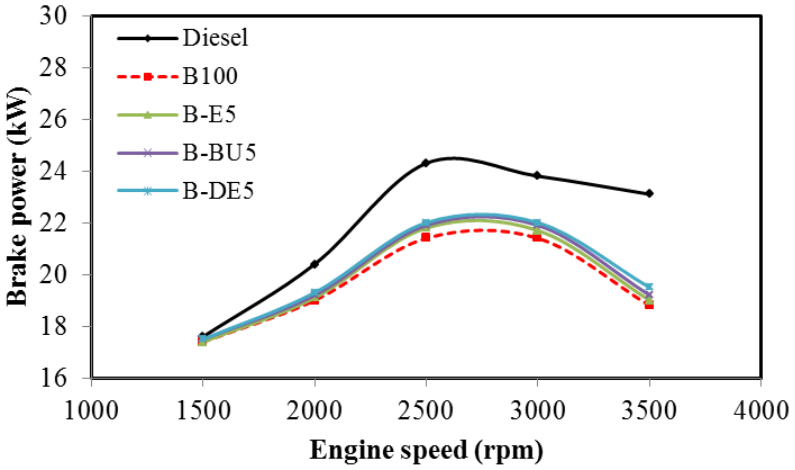
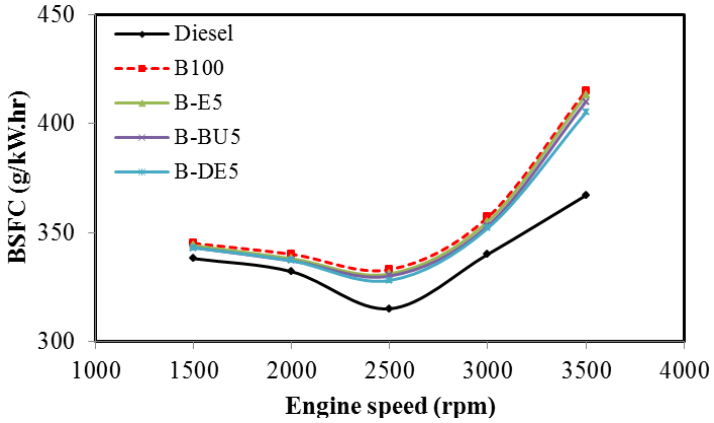


Figure 9 presents the variations in the brake specific fuel consumption (BSFC) with increasing engine speed for the tested fuel samples. At 2500 rpm, the BSFC for diesel and B100 fuel was 315 and 333 g/kWh, respectively. The higher fuel consumption of the B100 fuel mainly related to their lower heating value [63]. However, the BSFCs of B100 decreased to 331, 330 and 328 g/kWh, with 5% of ethanol, butanol and diethyl ether respectively; at the same engine speed, with a slight variance between the different blends. This difference is due to the improvement in engine brake power and the lower density of the additives compared to B100, where the engine fuel system measures fuel on a mass basis.

Figure 9. Brake specific fuel consumption with mineral diesel fuel, palm oil methyl ester and palm oil methyl ester with different additives at 5% blending ratio (the tests conducted at increasing engine speed and half open throttle).



5. Conclusions

The aim of this study was to qualify the changes in the key fuel properties when alcohols and ether are blended with palm oil biodiesel. In summary, addition of ethanol, butanol and diethyl ether can cause a regular low temperature operability improvement of palm oil biodiesel with the increase in additive proportion. Increasing additive content resulted in a significant improvement in pour point with a maximum decrease of 5 °C in pour point at 5% diethyl ether addition compared to pure palm oil methyl ester. Additionally, a statistically significant pour point variation between the different chemical additives was observed as the mean palm oil methyl ester pour point temperature with diethyl ether being around 1 °C less than that with ethanol and 2 °C less than that with butanol at 5% blending ratio. A linear reduction in palm oil biodiesel kinematic viscosity and density was indicated with an increase in the chemical additive blending ratios. The lower viscosity was for blends of biodiesel-diethyl ether blend mixtures with 16.5% reductions at 5% blending ratio compared palm oil methyl ester whereas, biodiesel-butanol blends mixtures were progressively more viscous. The effect of chemical additives on reducing the fuel energy content restricts their use in high blending ratios. The inclusion of additives to palm oil methyl ester slightly reduced the energy content of the fuel. The minimum heating value indicated that when adding 5% ethanol which is 6.35% less than that of neat palm oil biodiesel. A reduction in biodiesel acid value was indicated when increasing the additive content. Furthermore, the acid value for diethyl ether was 0.01 lower than that of ethanol and butanol. Engine test results show that the use of fuel additives with palm oil biodiesel fuel have a noticeable effect on

improving the engine brake power and decreasing specific fuel consumption compared to palm oil biodiesel fuel. Furthermore, the better engine power at lower fuel consumption presented with diethyl ether compared to other additives. Finally, palm oil methyl ester with diethyl ether blend exhibited optimum properties with slightly superior cold flow performance, kinematic viscosity, heating value, acid value and engine performance in comparison to ethanol and butanol, suggesting that diethyl ether may be the most prudent choice among the selected additive-biodiesel blends.

Acknowledgments

This work was supported financially by University Malaysia Pahang under UMP Research Grand (GRS 130307).

Author Contributions

The listed authors contributed together to achieve this research paper; the fuel measurements and analysis were conducted by the corresponding author Obed M. Ali and Talal Yusaf; the fuel engine test and analysis were conducted by Nik R. Abdullah and Abdul Adam Abdullah; the paper was written and revised by Rizalman Mamat.

Abbreviations

POME	Palm oil methyl ester
FAME	Fatty acid methyl esters
CP	Cloud point
PP	Pour point
DE	Diethyl ether
E	Ethanol
BU	Butanol
B100	Pure biodiesel
B-E	Biodiesel-ethanol blend
B-DE	Biodiesel-diethyl ether blend
B-BU	Biodiesel-butanol blend
AV	Acid value

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Demirbas, A. *Biodiesel: A Realistic Fuel Alternative for Diesel Engines*; Springer: London, UK, 2008.
2. Salamanca, M.; Mondragón, F.; Agudelo, J.R.; Santamaría, A. Influence of palm oil biodiesel on the chemical and morphological characteristics of particulate matter emitted by a diesel engine. *Atmos. Environ.* **2012**, *62*, 220–227.

3. Ali, Y.; Hanna, M.A.; Cuppett, S.L. Fuel properties of tallow and soybean oil esters. *J. Am. Oil Chem. Soc.* **1995**, *72*, 1557–1564.
4. Yilmaz, N.; Vigil, F.M.; Burl Donaldson, A.; Darabseh, T. Investigation of CI engine emissions in biodiesel-ethanol-diesel blends as a function of ethanol concentration. *Fuel* **2014**, *115*, 790–793.
5. Franco, V.; Kousoulidou, M.; Muntean, M.; Ntziachristos, L.; Hausberger, S.; Dilara, P. Road vehicle emission factors development: A review. *Atmos. Environ.* **2013**, *70*, 84–97.
6. Schröder, O.; Bünger, J.; Munack, A.; Knothe, G.; Krahl, J. Exhaust emissions and mutagenic effects of diesel fuel, biodiesel and biodiesel blends. *Fuel* **2013**, *103*, 414–420.
7. Randazzo, M.L.; Sodré, J.R. Cold start and fuel consumption of a vehicle fuelled with blends of diesel oil-soybean biodiesel-ethanol. *Fuel* **2011**, *90*, 3291–3294.
8. Moser, B.R. Impact of fatty ester composition on low temperature properties of biodiesel-petroleum diesel blends. *Fuel* **2014**, *115*, 500–506.
9. Ali, O.M.; Mamat, R.; Faizal, C.K.M. Review of the effects of additives on biodiesel properties, performance, and emission features. *J. Renew. Sustain. Energy* **2013**, *5*, 012701.
10. Silitonga, A.S.; Ong, H.C.; Masjuki, H.H.; Mahlia, T.M.I.; Chong, W.T.; Yusaf, T.F. Production of biodiesel from Sterculia foetida and its process optimization. *Fuel* **2013**, *111*, 478–484.
11. Steiner, S.; Czerwinski, J.; Comte, P.; Popovicheva, O.; Kireeva, E.; Müller, L.; Heeb, N.; Mayer, A.; Fink, A.; Rothen-Rutishauser, B. Comparison of the toxicity of diesel exhaust produced by bio- and fossil diesel combustion in human lung cells *in vitro*. *Atmos. Environ.* **2013**, *81*, 380–388.
12. Ali, O.M.; Mamat, R. Improving engine performance and low temperature properties of blended palm biodiesel using additives. A review. *Appl. Mech. Mater.* **2013**, *315*, 68–72.
13. Vallinayagam, R.; Vedharaj, S.; Yang, W.M.; Saravanan, C.G.; Lee, P.S.; Chua, K.J.E.; Chou, S.K. Emission reduction from a diesel engine fueled by pine oil biofuel using SCR and catalytic converter. *Atmos. Environ.* **2013**, *80*, 190–197.
14. Fang, Q.; Fang, J.; Zhuang, J.; Huang, Z. Effects of ethanol–diesel–biodiesel blends on combustion and emissions in premixed low temperature combustion. *Appl. Therm. Eng.* **2013**, *54*, 541–548.
15. Shadidi, B.; Yusaf, T.; Alizadeh, H.H.A.; Ghobadian, B. Experimental investigation of the tractor engine performance using diesohol fuel. *Appl. Energy* **2013**, *114*, doi:10.1016/j.apenergy. 2013.06.011.
16. Rahimi, H.; Ghobadian, B.; Yusaf, T.; Najafi, G.; Khatamifar, M. Diesterol: An environment-friendly IC engine fuel. *Renew. Energy* **2009**, *34*, 335–342.
17. Fernando, S.; Hanna, M. Development of a novel biofuel blend using ethanol-biodiesel-diesel microemulsions: EB-diesel. *Energy Fuels* **2004**, *18*, 1695–1703.
18. Satge de Caro, P.; Mouloungui, Z.; Vaitilingom, G.; Berge, J.C. Interest of combining an additive with diesel-ethanol blends for use in diesel engines. *Fuel* **2001**, *80*, 565–574.
19. Li, D.; Zhen, H.; Lv, X.; Zhang, W.; Yang, J. Physico-chemical properties of ethanol-diesel blend fuel and its effect on performance and emissions of diesel engines. *Renew. Energy* **2005**, *30*, 967–976.
20. Joshi, H.; Moser, B.R.; Toler, J.; Smith, W.F.; Walker, T. Effects of blending alcohols with poultry fat methyl esters on cold flow properties. *Renew. Energy* **2010**, *35*, 2207–2210.

21. Bhale, P.V.; Deshpande, N.V.; Thombre, B.S. Improving the low temperature properties of biodiesel fuel. *Renew. Energy* **2009**, *34*, 794–800.
22. Ali, O.M.; Mamat, R.; Abdullah, N.R.; Abdullah, A.A. Effects of blending ethanol with palm oil methyl esters on low temperature flow properties and fuel characteristics. *Int. J. Adv. Sci. Technol.* **2013**, *59*, 85–96.
23. Qi, D.H.; Chen, H.; Geng, L.M.; Bian, Y.Z. Effect of diethyl ether and ethanol additives on the combustion and emission characteristics of biodiesel-diesel blended fuel engine. *Renew. Energy* **2011**, *36*, 1252–1258.
24. Randazzo, M.L.; Sodré, J.R. Exhaust emissions from a diesel powered vehicle fuelled by soybean biodiesel blends (B3–B20) with ethanol as an additive (B20E2–B20E5). *Fuel* **2011**, *90*, 98–103.
25. Aydin, H.; İlkılıç, C. Effect of ethanol blending with biodiesel on engine performance and exhaust emissions in a CI engine. *Appl. Therm. Eng.* **2010**, *30*, 1199–1204.
26. Zhu, L.; Cheung, C.S.; Zhang, W.G.; Huang, Z. Emissions characteristics of a diesel engine operating on biodiesel and biodiesel blended with ethanol and methanol. *Sci. Total Environ.* **2010**, *408*, 914–921.
27. Miller Jothi, N.K.; Nagarajan, G.; Renganarayanan, S. LPG fueled diesel engine using diethyl ether with exhaust gas recirculation. *Int. J. Therm. Sci.* **2008**, *47*, 450–457.
28. Subramanian, K.A.; Ramesh, A. Use of Diethyl ether along with Water Diesel Emulsion in a DI diesel Engine. In Proceedings of the SAE Powertrain & Fluid Systems Conference & Exhibition, San Diego, CA, USA, 21–24 October 2002; doi:10.4271/2002-01-2720.
29. Demirbas, A. Progress and recent trends in biodiesel fuels. *Energy Convers. Manag.* **2009**, *50*, 14–34.
30. Lam, M.K.; Tan, K.T.; Lee, K.T.; Mohamed, A.R. Malaysian palm oil: Surviving the food versus fuel dispute for a sustainable future. *Renew. Sustain. Energy Rev.* **2009**, *13*, 1456–1464.
31. Hoekman, S.K.; Broch, A.; Robbins, C.; Ceniceros, E.; Natarajan, M. Review of biodiesel composition, properties, and specifications. *Renew. Sustain. Energy Rev.* **2012**, *16*, 143–169.
32. Pinto, A.C.; Guarieiro, L.L.N.; Rezende, M.J.C.; Ribeiro, N.M.; Torres, E.A.; Lopes, W.A.; Pereira, P.A.P.; de Andrade, J.B.J. Biodiesel: An overview. *Chem. Soc.* **2005**, *16*, 1313–1330.
33. Krahl, J.; Munack, A.; Schroder, O.; Stein, H.; Bunger, J. *Influence of Biodiesel and Different Designed Diesel Fuels on the Exhaust Gas Emissions and Health Effects*; Technical Paper 2003-01-31 2003; SAE International: Warrendale, PA, USA, 2003; doi:10.4271/2003-01-3199.
34. Knothe, G. Determining the blend level of mixtures of biodiesel with conventional diesel fuel by fiber-optic near-infrared spectroscopy and 1H nuclear magnetic resonance spectroscopy. *J. Am. Oil Chem. Soc.* **2001**, *78*, 1025–1028.
35. Jenkins, C.; Mastbergen, D.S.R. Measurement of the percentage of biodiesel in blends with a commercial dielectric fuel sensor. In Proceedings of the ASME Internal Combustion Engine Division 2006 Fall Technical Conference, Sacramento, CA, USA, 5–8 November 2006; pp. 109–115.
36. Demirbas, A. Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Prog. Energy Combust. Sci.* **2005**, *31*, 466–487.
37. Atabani, A.E.; Silitonga, A.S.; Badruddin, I.A.; Mahlia, T.M.I.; Masjuki, H.H.; Mekhilef, S. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renew. Sustain. Energy Rev.* **2012**, *16*, 2070–2093.

38. Basha, S.A.; Raja Gopal, K. A review of the effects of catalyst and additive on biodiesel production, performance, combustion and emission characteristics. *Renew. Sustain. Energy Rev.* **2012**, *16*, 711–717.
39. Van Gerpen, J.H.; Peterson, C.L.; Goering, C.E. Biodiesel: An alternative fuel for compression ignition engines. In Proceedings of the Agricultural Equipment Technology Conference, Louisville, KY, USA, 11–14 February 2007; pp. 1–22.
40. Karmakar, A.; Karmakar, S.; Mukherjee, S. Properties of various plants and animals feedstocks for biodiesel production. *Bioresour. Technol.* **2010**, *101*, 7201–7210.
41. Sahoo, N.K.; Naik, M.K.; Pradhan, S.; Naik, S.N.; Das, L.M. High quality biodiesel from Thevetia peruviana Juss: Physico-chemical, emission and fuel performance characteristics. *J. Biobased Mater. Bioenergy* **2012**, *6*, 269–275.
42. Bahadur, N.P.; Boocock, D.G.B.; Konar, S.K. Liquid hydrocarbons from catalytic pyrolysis of sewage sludge lipid and canola oil: Evaluation of fuel properties. *Energy Fuels* **1995**, *9*, 248–256.
43. Alptekin, E.; Canakci, M. Determination of the density and the viscosities of biodiesel–diesel fuel blends. *Renew. Energy* **2008**, *33*, 2623–2630.
44. Ejim, C.E.; Fleck, B.A.; Amirfazli, A. Analytical study for atomization of biodiesels and their blends in a typical injector: Surface tension and viscosity effects. *Fuel* **2007**, *86*, 1534–1544.
45. Satyanarayana, M.; Muraleedharan, C. Biodiesel production from vegetable oils: A comparative optimization study. *J. Biobased Mater. Bioenergy* **2009**, *3*, 335–341.
46. Knothe, G.; Steidley, K.R. Kinematic viscosity of biodiesel fuel components and related compounds, influence of compound structure and comparison to petrodiesel fuel components. *Fuel* **2005**, *84*, 1059–1065.
47. Agarwal, A.K. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Prog. Energy Combust. Sci.* **2007**, *33*, 233–271.
48. Carraretto, C.; Macor, A.; Mirandola, A.; Stoppato, A.; Tonon, S. Biodiesel as alternative fuel: Experimental analysis and energetic evaluations. *Energy* **2004**, *29*, 2195–2211.
49. Robbins, C.; Hoekman, S.K.; Ceniceros, E.; Natarajan, M. *Effects of Biodiesel Fuels upon Criteria Emissions*; SAE Technical Paper 2011-01-1943; SAE International: Warrendale, PA, USA, 2011; doi:10.4271/2011-01-1943.
50. Hoekman, S.K.; Broch, A.; Robbins, C.; Ceniceros, E. *Investigation of Biodiesel Chemistry, Carbon Footprint and Regional Fuel Quality*; Clean Technologies and Renewable Energy Center: Reno, NV, USA, 2011.
51. Rawat, D.S.; Joshi, G.; Lamba, B.Y.; Tiwari, A.K.; Mallick, S. Impact of additives on storage stability of Karanja (Pongamia Pinnata) biodiesel blends with conventional diesel sold at retail outlets. *Fuel* **2014**, *120*, 30–37.
52. Smith, P.C.; Ngothai, Y.; Nguyen, Q.D.; O'Neill, B.K. Improving the low-temperature properties of biodiesel: Methods and consequences. *Renew. Energy* **2010**, *35*, 1145–1151.
53. Chandler, J.E.; Horneck, F.G.; Brown, G.I. *The Effect of Cold Flow Additives on Low Temperature Operability Of Diesel Fuels*; SAE Technical Paper 922186; SAE International: Warrendale, PA, USA, 1992; doi:10.4271/922186.
54. Dunn, R.O.; Shockley, M.W.; Bagby, M.O. Improving the low-temperature properties of alternative diesel fuels: Vegetable oil-derived methyl esters. *J. Am. Oil Chem. Soc.* **1996**, *73*, 1719–1728.

55. Knothe, G.; Krahl, J.; van Gerpen, J. *The Biodiesel Handbook*; AOCS Press: Champaign, IL, USA, 2004.
56. Merck Material Safety Data Sheets (MSDS). Available online: http://www.merckmillipore.my/chemicals/msds-search/c_r_ab.s1O_d4AAAEl7otx3CaA (accessed on 22 January 2014).
57. Swaminathan, C.; Sarangan, J. Performance and exhaust emission characteristics of a CI engine fueled with biodiesel (fish oil) with DEE as additive. *Biomass Bioenergy* **2012**, *39*, 168–174.
58. ASTM Biodiesel Specifications. Available online: http://www.afdc.energy.gov/fuels/biodiesel_specifications.html (accessed on 7 July 2014).
59. Akcay, H.T.; Karslioglu, S. Optimization process for biodiesel production from some Turkish vegetable oils and determination fuel properties. *Energy Educ. Sci. Technol.* **2012**, *28*, 861–868.
60. Filemon, A. *Biofuels from Plant Oils*; ASEAN Foundation: Jakarta, Indonesia, 2010; p. 47.
61. Rashid, U.; Anwar, F.; Knothe, G. Evaluation of biodiesel obtained from cotton-seed oil. *Fuel Process. Technol.* **2009**, *90*, 1157–1163.
62. European Committee for Standardization. *European Standard*; EN 14214; CEN: Brussels, Belgium, 2008.
63. Buyukkaya, E. Effects of biodiesel on a DI diesel engine performance, emission and combustion characteristics. *Fuel* **2010**, *89*, 3099–3105.