RBD PALM OLEIN-BASED METHYL/ETHYL ESTERS

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ABSTRACT

In this study, transesterification of refined, bleached and deodorized (RBD) palm olein was carried out with methanol, ethanol and their mixtures at various methanol/ethanol ratios, while maintaining the molar ratio of oil to alcohol at 1:6. Potassium hydroxide was used as the catalyst. The process variables were temperature, methanol/ethanol molar ratio and amount of catalyst. The optimum biodiesel production yield was 98.10% when using a methanol/ethanol molar ratio of 4:2 and an alcohol to oil molar ratio of 6:1, a reaction time of 1 hr and a reaction temperature of 50°C. Physical and chemical properties of all the esters were also obtained and these parameters are reported. The physical properties of esters obtained from this study were found to be comparable with standard biodiesel specification of EN 14214. Analysis was also done to establish the differences in physical properties between biodiesel produced in this work and Malaysian petroleum diesel, data which is vital for blending purposes.

INTRODUCTION

Concerns over decreasing oil reserves, uncertain fuel prices and increasing environmental consciousness have led to growing interest in using renewable energy sources. Biodiesel is a renewable and biodegradable diesel fuel with less harmful emissions than petroleum-based diesel fuel, and can be used in its pure form or blended with petroleum-based diesel.

The most common method for producing biodiesel is by the transesterification of vegetable oils and animal fats. Catalytic transesterification has a long history of development, and biodiesel produced by this method is now available in North America, Europe and Malaysia (Barnwal and Sharma, 2005).

The use of vegetable oils as an alternative renewable fuel to compete with petroleum gained prominence in the beginning of the 1980s (Bartholomew, 1981). A variety of vegetable oils (virgin and waste oils) can be used to produce biodiesel. Rapeseed, soyabean and palm oils are most commonly used to produce biodiesel, although non-edible oils such as those from jatropha and even algae show promise. Rapeseed or canola oil is the primary feedstock for biodiesel production in Europe and Canada, while in the United States, soyabean oil is the main feedstock (Campbell, 2000; Riley, 2004). Of all the world's vegetable oils and fats produced in 2007, palm oil had the largest tonnage (Oil World, 2008). As one of the world's largest palm oil producers and exporters, Malaysia can produce biodiesel from this raw material. It is reported that in 2007, the total crude palm oil production in Malaysia was approximately 15.8 million tonnes (MPOB, 2007). Palm oil is high in saturated fatty acids (at about 50%). Indeed, oil palm gives its name to the 16-carbon saturated fatty acid palmitic acid which is found in palm oil. Mono-unsaturated oleic acid is also a constituent of palm oil.

The alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol and amyl alcohol. However, methanol and ethanol are used most frequently. Ethanol has better solvent properties; it is renewable and more environmental-friendly due to its production from agriculture. However, when ethanol is used in biodiesel production, the formation of an emulsion with the oil makes separation of the ester very difficult. Thus, the use of methanol is preferable because of its low cost, its physical and chemical

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advantages (polar and shortest chained alcohol) (Demirbas, 2005). In the case of methanolysis, the solubility of oil in methanol is less and the reaction is mass-transfer limited. On the other hand, methanol makes a higher equilibrium conversion due to the more reactive intermediate methoxide (Sridharan and Mathai, 1974). During the transesterification reaction, emulsions usually form. In the case of methanolysis, these emulsions quickly and easily break down to form a lower glycerol-rich layer and an upper methyl ester-rich layer. In ethanolysis, these emulsions are more stable and severely complicate the separation and purification of esters (Zhou et al., 2003).

Engine tests demonstrate that methyl esters produce slightly higher power and torque than ethyl esters (Encinar et al., 2002). Some desirable attributes of the ethyl esters over methyl esters are: significantly lower smoke opacity, lower exhaust temperature and lower pour point. The ethyl esters tend to have more injector coking than the methyl esters.

If a mixture of methanol and ethanol is used for the transesterification reaction, then this will take advantage of the better solvent properties of ethanol and desired equilibrium conversion of methanol. Also, esters obtained from a mixture of alcohols may act as a good lubricity additive. Another advantage of using a mixture of methanol and ethanol is, if part of the methanol is replaced by ethanol, there would be less dependency on the synthetic sources for methanol (Issariyakul et al., 2007).

Few studies have been done in biodiesel production using mixtures of alcohols. Kulkarni et al. (2007) transesterified canola oil with methanol, ethanol and various mixtures of methanol and ethanol, using potassium hydroxide (KOH) as a catalyst. It was found that the reaction rate increased because of better solubility of the oil in the alcohol mixture.

In another study, Issariyakul et al. (2007) used fryer grease with methanol, ethanol and a mixture of methanol and ethanol for biodiesel production. To avoid soap formation, a two-stage (acid- and alkali-catalyzed) method was used.

Lang et al. (2001) prepared methyl, ethyl, 2-propyl and butyl esters from canola and linseed oils through transesterification using KOH and/or sodium alkoxides as catalysts.

The present work is motivated by the fact that there is no comprehensive study of biodiesel production from palm olein using methanol/ethanol mixtures. Therefore, the objective of this work was to establish some basic information pertaining to the effect of varying methanol/ethanol ratios at various reaction temperatures and catalyst loading on production yield and important physical properties of the biodiesel. Meanwhile, the physical properties of the products obtained were also compared with those of the biodiesel standard. Finally, the differences were also established between the physical properties of biodiesel produced in this study and Malaysian petroleum diesel.

EXPERIMENTAL

Materials

Palm olein was purchased locally. The acid value, iodine value and water content of the oil were 0.5, 53.2 and 400 ppm, respectively. Pure methanol and ethanol (99%) were obtained from Sigma-Aldrich, Malaysia. Pure KOH (98.9%) was used as a catalyst and obtained from the same company. Similarly, reference standards such as methyl oleate, methyl palmitate, methyl linoleate, methyl stearate, ethyl oleate, ethyl palmitate, ethyl linoleate, ethyl stearate of 99% purity were supplied by Sigma-Aldrich, Malaysia.

Biodiesel Production

Transesterification reactions were performed in a batch system. This consisted of a two-litre jacketed glass vessel equipped with a thermometer and water-cooled condenser. A mechanical stirrer (Kika® Werke) fitted with a stainless steel propeller provided the agitation. Reaction temperatures were established by using hot water circulation and controlled using (LAUDA, RCS and RC6). Initially the reactor was filled with 500 g refined, bleached and deodorized (RBD) palm olein. The catalyst, KOH was dissolved in alcohol, then added to the reactor at the reaction temperature. Agitation was set at a constant speed of 700 rpm throughout the experiment. The reaction was conducted using 100% excess alcohol, i.e. the molar ratio of alcohol to oil was 6:1. The weight of 1 mol oil was 847.3 g (determined from the calculated average molecular weight of palm oil based on the known fatty acid composition of the oil). Different molar ratios of methanol/ethanol, i.e. 6:0, 5:1, 4:2, 3:3, 2:4, 1:5 and 0:6, were used for the transesterification reaction.

At the end of the reaction, the mixture was cooled to room temperature, and the product was transferred to a separatory funnel. The two layers were separated out by sedimentation. The ester phase was washed with hot distilled water. In order to avoid the emulsion during the washing step, 0.1 wt % aqueous tannic acid was used as the washing solution. The excess alcohol was removed on a rotary evaporator at atmospheric pressure.

To examine the effect of temperature, reactions at 30°C, 40°C, 50°C, 60°C and 70°C were studied. The effect of catalyst, KOH, loading at different weight percentages of 0.5%, 0.8%, 1% and 1.5% was studied at a constant temperature of 50°C.

Analysis

The composition of the esters were analysed by gas chromatography using an HP 6890 series gas chromatograph system equipped with a flame ionization detector (GC-FID) and automated split injector (Agilent 7683 automatic sampler). The column was a 60 m × 0.248 mm × 0.15 μm DB-23 capillary column (J & W Scientific, USA). The injection volume was 1 μl with a split ratio of 1/50, while the inlet temperature was 250°C.

Viscosities of the esters were measured at 40ºC using a VT550 rotary viscometer (HAAKE, Germany) with a NV sensor. Density and specific gravity measurements were carried out using a DMA 4500 density/specific gravity meter (Anton Paar, Austria) at temperatures of 15ºC, 20ºC and 30ºC. For moisture analysis, a 737 Karl Fischer coulometer equipped with a stirrer (Metrohm, Switzerland) was used. The gross heats of combustion of the alkyl esters were determined using a calorimeter system (IKA-Calorimeter C5000 control, Germany). Flash point measurements were carried out using a HFP 380 flash point tester (Herzog, Germany). Cloud points and pour points were measured using a cloud/pour point tester (Stanhope-Seta, USA).

RESULTS AND DISCUSSION

Biodiesel Production

Figure 1 shows the GC-FID chromatograms of methyl esters, ethyl esters and a mixture of methyl/ethyl esters with a 4:2 methanol/ethanol molar ratio. It was found that the major fatty acid components in all the esters were palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1) and linoleic acid (C18:2), with highest percentages of palmitic and oleic acids.

The influence of the methanol/ethanol molar ratio was studied at a 6:1 molar ratio of alcohol to palm olein and 1 wt % catalyst dose at a reflux of alcohol for 1 hr and at 50ºC temperature. The yield of palm olein alkyl esters biodiesel as a function of methanol/ethanol molar ratio is shown in *Figure 2*.

As can be seen, the methanolysis yield was higher than the ethanolysis yield due to the higher reactivity of methanol. The biodiesel production yield was calculated from the content of fatty acid alkyl esters (FAAE) analysed by GC using the following equation:

$$\text{Yield (\%)} = \frac{(\text{weight of biodiesel produced}) \times \text{total wt\% of FAAE}}{\text{weight of oil}} \times 100 \quad (1)$$
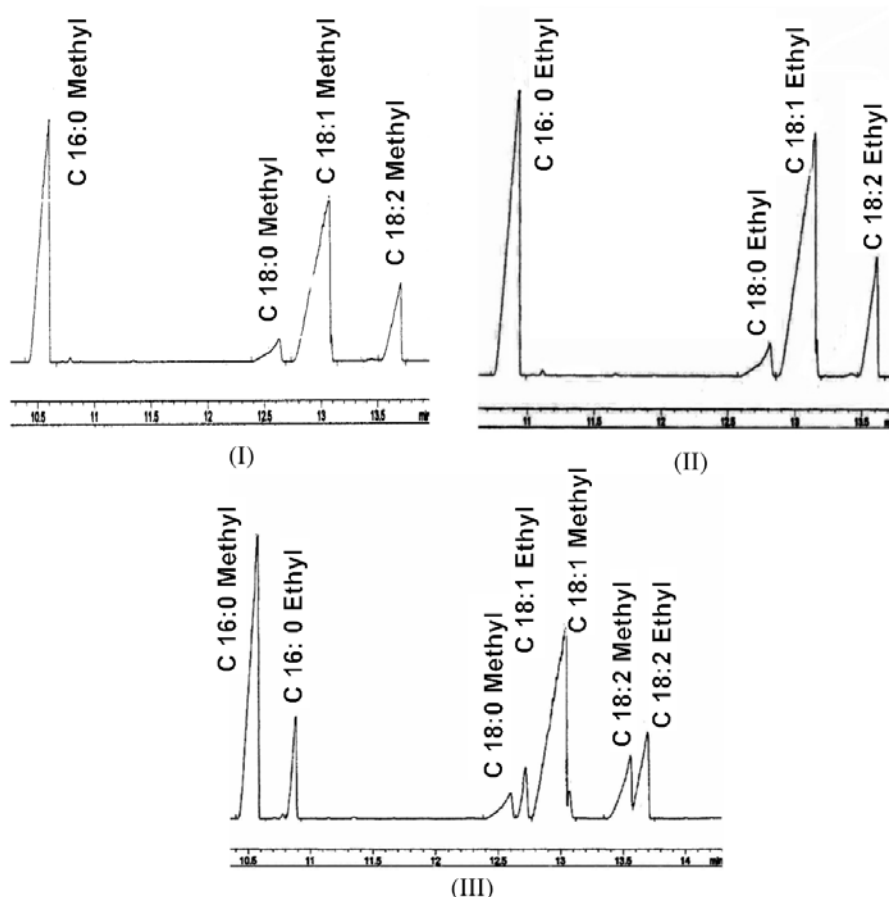

Figure 1. GC-FID chromatograms of methyl esters (I), ethyl esters (II) and a mixture of methyl ethyl esters with 4:2 methanol/ethanol molar ratio (III).
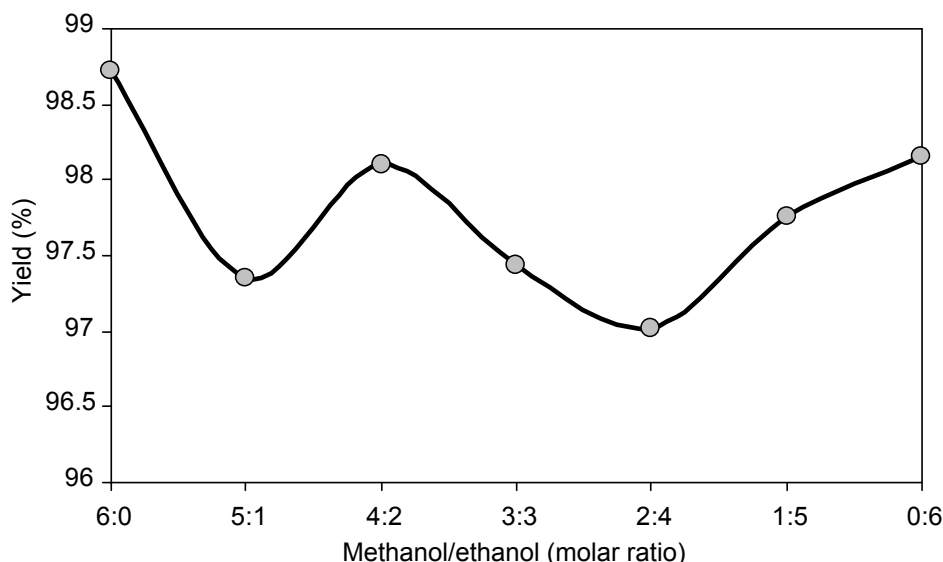
Figure 2. Biodiesel yield as a function of methanol/ethanol molar ratio. Reaction conditions: alcohol to oil molar ratio of 6:1, catalyst dose of 1%, reaction time of 60 min and temperature of 50°C.

For example, 500 g palm olein reacted with 129.93 g alcohol (1:6 molar ratio) comprising 75.61 g methanol and 54.32 g ethanol (4:2 molar ratio) in the presence of 1 wt % KOH. After separation and purification of the ester phase, 561.53 g biodiesel was obtained with an alkyl esters content of 87.35 wt %. Therefore, the calculated yield of that production using equation (1) was 98.10%.

In the case of esters formed by the reaction of RBD palm olein with a mixture of methanol and ethanol, ethyl esters were also formed along with methyl esters. It is obvious that the transesterification yields using a mixed alcohol system are less than methanolysis or ethanolysis. The optimum methanol/ethanol molar ratio was found to be 4:2, giving a biodiesel production yield of 98.10%. The high production yield at the 4:2 ratio can be attributed to a combination of high reactivity of methoxide ions and better solubility of non-polar palm oil in ethanol.

The relationship between KOH catalyst dose and production of palm oil biodiesel using a mixture of methanol and ethanol was studied at a 6:1 molar ratio of alcohol to palm oil and 4:2 methanol/ethanol molar ratio at a reflux of methanol for 1 hr and at 50°C temperature. The catalyst dose represents the mass ratio of KOH catalyst and the reactants. The results are shown in *Figure 3*. The biodiesel production yield was increased from 95.3% to 98.2% with an increase in catalyst dose from 0.5% to 1.5%. It can be concluded that the optimum KOH catalyst dose for the transesterification of palm oil in this mixed alcohol system is 1%.
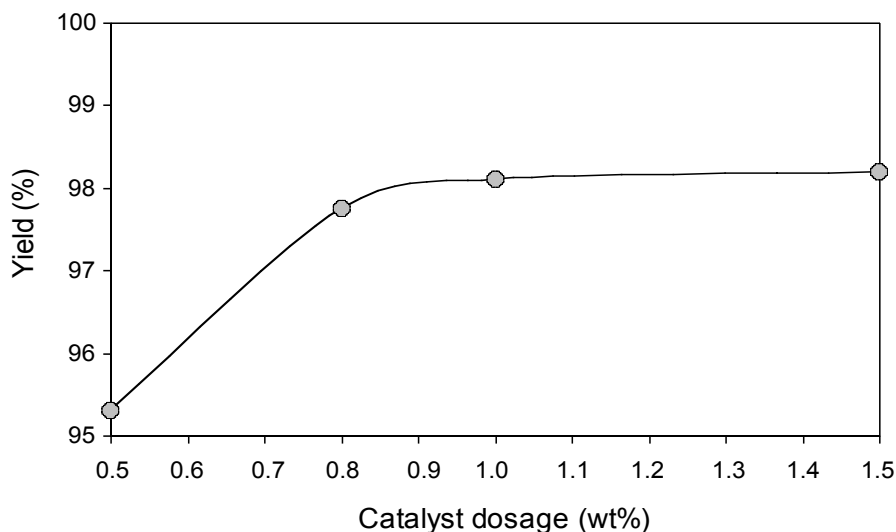

Figure 3. Biodiesel yield as a function of catalyst dose. Reaction conditions: alcohol to oil molar ratio of 6:1, methanol/ethanol molar ratio of 4:2, reaction time of 60 min and temperature of 50°C.

The influence of temperature on transesterification of palm oil using a mixed alcohol system with a 4:2 molar ratio of methanol to ethanol is shown in *Figure 4*. As can be seen that the optimum reaction temperature for the transesterification of palm oil in this mixed alcohol system was 50°C.

Physical Characteristics

The viscosity of palm oil is 37.3 mm²s⁻¹ (Suwarno *et al.*, 2003). After transesterification, the esters showed a substantial reduction in viscosity in the range of 4.6-4.9 mm²s⁻¹ at 40°C, which meets the EN-14214 standard of 3.5-5.0 mm²s⁻¹. The viscosity of the esters was slightly higher than for petroleum diesel fuel which is 4.0 mm²s⁻¹ (Choo *et al.*, 2005). However, they were still in an acceptable range and were able to flow under warm weather conditions. The kinematics viscosities of the esters are shown in *Table 1*. There was not much difference in the viscosities of methyl, ethyl and the various mixtures of methyl and ethyl esters. Ethyl esters are more viscous than methyl esters but the viscosities of mixtures of esters were closer to that of methyl esters.

The density of an ester depends on its molecular weight, free fatty acid content, water content and temperature. The densities of methyl, ethyl and the mixtures of methyl and ethyl esters were measured at 15°C, 20°C and 30°C (*Table 1*). By comparison, methyl ester had a higher density than ethyl. The density of the esters at 15°C was in the range of 0.87 g cm⁻³ which meets with the EN 14214 standard of 0.86-0.90 g cm⁻³.

The density of esters was slightly higher than that of petroleum diesel, which slightly exceeds 0.820 g cm⁻³ (Choo *et al.*, 2005). This, however, is not important, as it will only cause a slight increase of fuel consumption.

Water is introduced into the biodiesel during the washing process and is removed by distillation. The esters are hygroscopic and can absorb water during storage. This free water promotes biological growth, and the sludge/slime produced may cause blockage of fuel filters and fuel lines. High water content reacts with the FAAE, partly converting them into free fatty acids which are linked to filter blockage. Also, corrosion of zinc and chrome parts within the engine or injection system can occur. *Table 2* shows
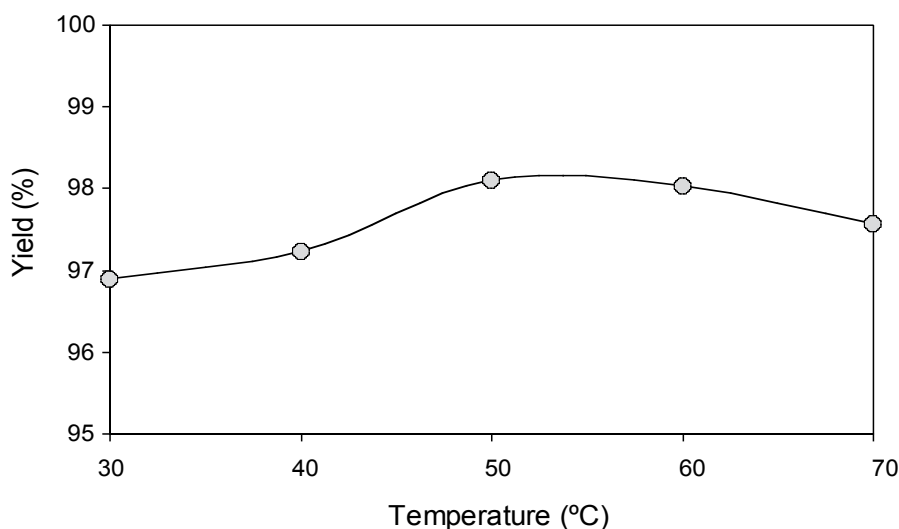

Figure 4. Biodiesel yield as a function of temperature. Reaction conditions: alcohol to oil molar ratio of 6:1, methanol/ethanol molar ratio of 4:2, catalyst dose of 1% and reaction time of 60 min.

TABLE 1. KINEMATICS VISCOSITY AND DENSITY OF ALKYL ESTERS

Methanol/ethanol molar ratio	Viscosity (mm² s⁻¹)	Density (g cm⁻³)		
		15°C	20°C	30°C
6:0	4.6	0.87635	0.87272	0.86537
5:1	4.6	0.87634	0.87267	0.86539
4:2	4.7	0.87738	0.87375	0.86643
3:3	4.9	0.87495	0.87128	0.86403
2:4	4.8	0.87456	0.87094	0.86360
1:5	4.7	0.87281	0.86915	0.86189
0:6	4.9	0.87264	0.86899	0.86173

TABLE 2. FLASH POINT, GROSS HEAT OF COMBUSTION, WATER CONTENT, CLOUD POINT AND POUR POINT OF ALKYL ESTERS

Methanol/ethanol molar ratio	Flash point (°C)	Gross heat of combustion (J g⁻¹)	Water content (mg kg⁻¹)	Cloud point (°C)	Pour point (°C)
6:0	172	40 334	504.3	9.8	6.0
5:1	173	40 174	492.8	9.5	6.0
4:2	174	40 366	414.9	8.7	6.0
3:3	176	40 203	432.8	8.1	6.0
2:4	172	40 281	308.1	7.7	6.0
1:5	174	40 310	503.6	7.4	5.0
0:6	175	40 346	447.3	7.3	5.0

the water content of methyl, ethyl and various mixtures of methyl/ethyl esters. As can be seen, the ester moisture contents were in the range of the EN-14214 standard (maximum 500 mg kg⁻¹).

The flash points of esters are also listed in *Table 2*. The flash points were in the range of 172ºC - 176°C which meet the EN 14214 standard of 120°C (minimum), and were far higher than that of petroleum diesel fuel, *i.e.* 80°C (Choo *et al.*, 2005).

The gross heat of combustion affects fuel consumption at a given power output. The gross heat of combustion of the palm olein alkyl esters was well below that of petroleum diesel, being around 40 174-40 366 J g⁻¹ compared to 45 800 J g⁻¹ for Malaysian petroleum diesel (*Table 2*). The small change in carbon number of the alkyl group of the esters from methyl (CH_3-) to ethyl (CH_3CH_2-) esters did not change the gross heat of combustion significantly.

The cloud point of biodiesel is defined as the temperature at which a cloud of crystals first appears when it is cooled at a specific rate. The pour point is the lowest temperature at which the biodiesel can still be moved. The cloud points and pour points of the methyl/ethyl esters are presented in *Table 2*.

Some physical properties of the palm olein methyl/ethyl esters (from this work) including density, viscosity and gross heat of combustion were compared with methyl/ethyl esters of canola oil and waste fryer grease (Issariyakul *et al.*, 2007; Kulkarni *et al.*, 2007). The comparisons are shown in *Figures 5*, *6* and *7*. The densities of the palm olein methyl/ethyl esters were less than the methyl/ethyl esters of canola and waste fryer grease (*Figure 5*). Viscosities of the palm olein methyl/ethyl esters were higher than the methyl/ethyl esters of canola oil, but lower than the methyl/ethyl esters of waste fryer grease (*Figure 6*). The gross heat of combustion of the methyl/ethyl esters of palm olein was slightly higher but comparable to those of the canola oil and waste fryer grease methyl/ethyl esters (*Figure 7*).
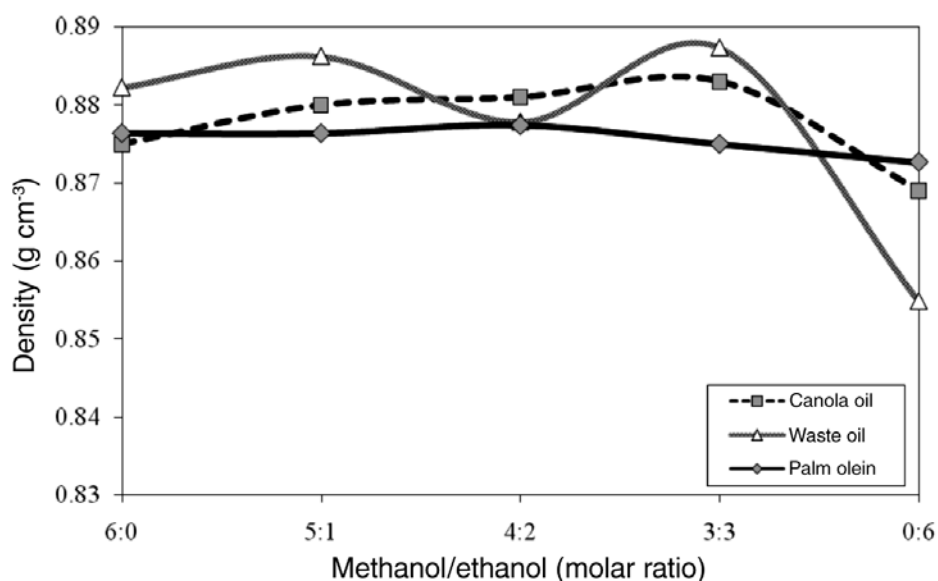

Figure 5. Densities of palm olein (this work), canola and waste oil biodiesel produced using the mixed methanol/ethanol system (Issariyakul et al., *2007; Kulkarni* et al., *2007).*
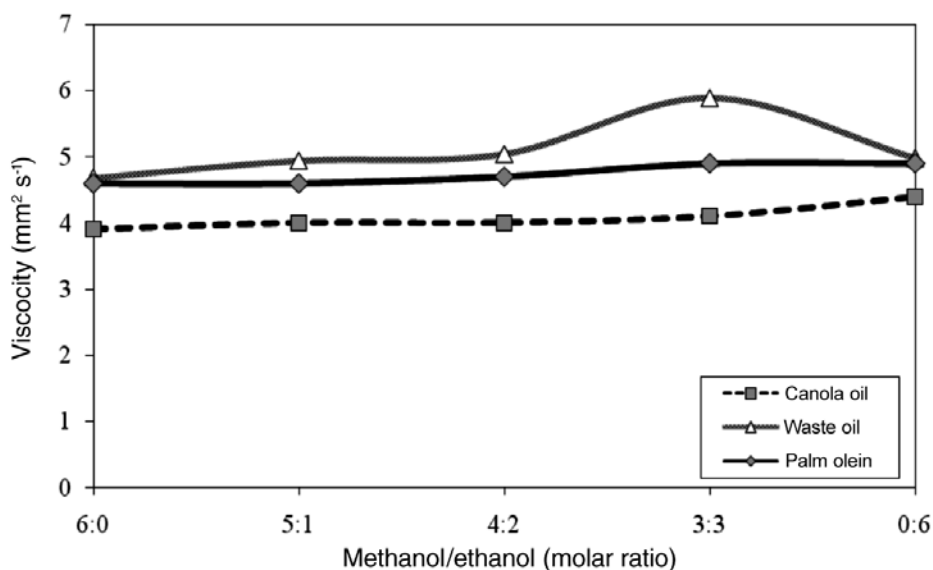
Figure 6. Viscosities of palm olein (this work), canola and waste oil biodiesel produced using the mixed methanol/ethanol system (Issariyakul et al., 2007; Kulkarni et al., 2007).
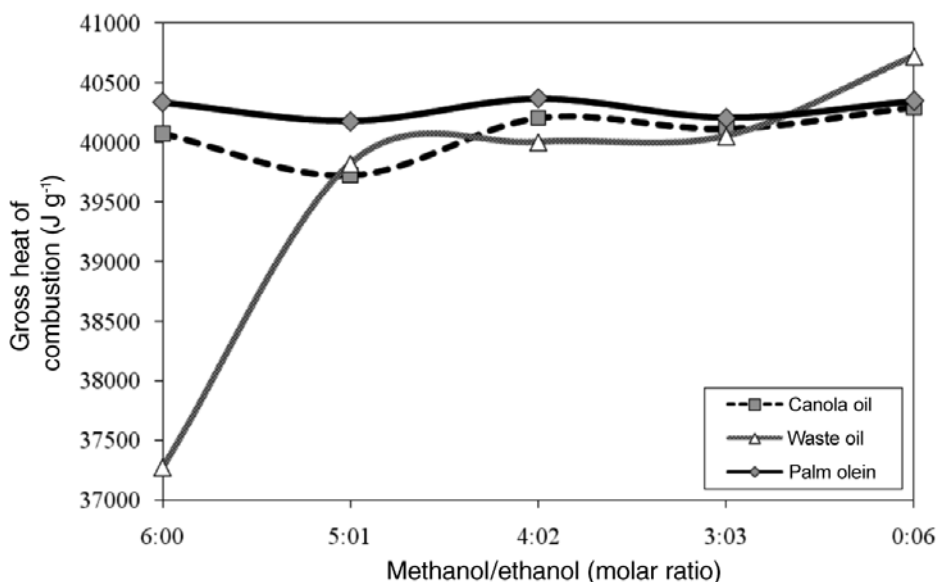

Figure 7. Gross heats of combustion of palm olein (this work), canola and waste oil biodiesel produced using the mixed methanol/ethanol system (Issariyakul et al., 2007; Kulkarni et al., 2007).

CONCLUSION

Palm olein was transesterified successfully with methanol, ethanol and a mixture of methanol and ethanol in a batch reactor using potassium hydroxide as a catalyst. When the mixed methyl-ethyl alcohol was used in the transesterification process, ethyl ester was also formed. The optimum biodiesel production yield was 98.10% when using a methanol/ethanol molar ratio of 4:2 and an alcohol to oil molar ratio of 6:1, a reaction time of 1 hr and a reaction temperature of 50ºC. There were not many differences in the physical properties (kinematics viscosity, density, specific gravity, flash point, cloud point, pour point and gross heat of combustion) of the esters with different methanol/ethanol molar ratios. Physical characteristics of the palm oil biodiesel obtained from the mixed alcohol system were within the limits of the EN 14214 standards and were also comparable with those of Malaysian petroleum diesel.

Methyl/ethyl biodiesel produced from palm oil showed a lower density and a higher heat of combustion compared to canola oil and waste fryer grease methyl/ethyl esters. Palm methyl/ethyl esters were more viscous than canola esters, but their viscosities were less than waste fryer grease esters. If a mixture of methanol and ethanol is used for the transesterification reaction then this will have

some advantages like better lubricity, faster reaction and less dependency on the synthetic sources for methanol. However, methyl esters may be the preferred choice in terms of cost.

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