SYNTHESIS OF PALMITIC ACID-BASED ESTERS AND THEIR EFFECT ON THE POUR POINT OF PALM OIL METHYL ESTERS

CHEAH HAN SERN*; CHOO YUEN MAY; ZURIATI ZAKARIA* and RUSLI DAIK***

ABSTRACT

The objectives of this research were to synthesis palmitic acid-based esters and to study their effects on the pour point of palm oil methyl esters. Palmitic acid was esterified with six different branched-chain alcohols, namely 2-propanol, 2-butanol, 2-ethyl-1-hexanol, 2-methyl-1-butanol, 2-methyl-1-propanol and 2,2-dimethylpropane-1,3-diol. The purified products were characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR. The effect of the six synthesized palmitic acid-based esters on palm oil methyl esters (biodiesel) was later evaluated. The compounds under study were isopropyl palmitate ***(1)****,* sec*-butyl palmitate* **(2)**, *2-ethylhexyl palmitate* ***(3)****, 2-methylbutyl palmitate* ***(4)****, isobutyl palmitate* ***(5)*** *and 2,2-dimethylpropane-1,3-diyl daipalmitate* ***(6)****. All of the synthesized compounds were miscible in palm oil methyl esters due to similar polarity of the solute and the biodiesel. The blends of the resultant six ester compounds in palm oil methyl esters were evaluated respectively for their effect on pour point property. The 2,2-dimethylpropane-1,3-diyl dipalmitate was able to improve the pour point of palm oil methyl esters from 12°C to 9°C when 5 wt % was added.*

Keywords: palm oil methyl esters, palm oil biodiesel, pour point depressant, palmitic acid, pour point.

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INTRODUCTION

Fatty acid methyl ester (FAME) is an alternative diesel fuel derived from transesterification of vegetable oils or animal fats with methanol. There has been considerable interest in developing biodiesel as an alternative fuel in recent years due to its environmental benefits and also because it is derived from renewable resources such as vegetable oils or animal fats. Most common raw materials for the production of biodiesel include palm oil in Malaysia, rapeseed oil and sunflowerseed oil in Europe and soyabean oil in the US (Korbitz, 1999; Kalam and Masjuki, 2002).

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While most of the fuel properties of biodiesel are comparable to petroleum-based diesel fuel, one of the major problems associated with the use of biodiesel is its poor properties under low temperatures, indicated by relatively high cloud point (CP) and pour point (PP). The CP, which usually occurs at a higher temperature than the PP, is the temperature at which a liquid fatty material becomes cloudy due to the formation of crystals and solidification of the saturates. The PP is the lowest temperature at which the fatty material can still flow under gravity (Gerhard, 2005). Saturated fatty compounds have significantly higher melting points than unsaturated fatty compounds, and in a mixture they crystallize at higher temperatures than the unsaturated (Gerhard, 2005). Crystallization of the saturated FAME components of biodiesel during the cold season causes fuel starvation and operability problems such as the clogging of fuel lines and filters. Thus, biodiesel fuels derived from fats or oils with significant amounts of saturated fatty compounds will display higher CPs and PPs. As palm oil biodiesel (methyl esters) contains around 50% of saturated fatty compounds, palm oil biodiesel has a higher PP and CP at 12°C and 12.9°C, respectively.

Winterization has been employed to reduce the PP of biodiesel (Dunn *et al.*, 1996; Gomez *et al.*, 2002) by lowering its saturated FAME components. To achieve a significant reduction in PP, several winterization steps are required resulting in a yield as low as 25%-26% (Lee *et al.*, 1996), making winterization less acceptable.

Treatment with chemical additives is the most convenient and economical way of improving the low temperature properties of conventional diesel fuel (Zhang *et al.*, 2003). This technology is also very attractive in the biodiesel industry considering the problems encountered when using other methods. The chemical additives are synonymously referred to as PP depressants, flow improvers, paraffin inhibitors and wax modifiers. Most additives function by crystal modification, *i.e.* reducing the size and modifying the shape of the wax crystals (El-Gamal *et al.*, 1997; Chanda *et al.*, 1998; Chiu *et al.*, 2004; Yuping *et al.*, 2005), but do not alter the initial formation of the crystals. Hence, they do not generally affect the CP. They inhibit the crystals from growing to a size large enough to plug filters, and provide a barrier to crystal agglomeration. Chiu *et al.* (2004) evaluated the performance of commercial additives, namely Bio Flow-875, Bio Flow-870 and Diesel fuel anti-gel, for improving the cold flow properties of neat soyabean biodiesel, its blends with kerosene (B80, B90, B100) and low sulphur diesel fuel. The lowest PP achieved for neat soyabean diesel was only -18.0°C when treated with 0.1% of Bio Flow-870. However, 0.1% of Bio Flow-875 was more effective in the B90 and B80 blends than in the B100, with PP of -20.0°C and -33.0°C being attainable in the B90 and B80 blends.

Other approaches include blending with petroleum diesel and branched-chain esters. Blending the biodiesel with petroleum diesel will reduce the fraction of saturated long-chain methyl esters in the mixture, lowering both CP and PP (Dunn and Bagby, 1995). The use of branched esters such as *iso*-propyl, *iso*-butyl, and 2-butyl instead of straight-chain methyl esters is another approach for improving the low temperature properties of biodiesel (Inmok *et al.*, 1995). When branched esters are used, intramolecular associations will be attenuated and crystallization temperatures reduced. Thus, the crystallization temperature of biodiesel should be improved by replacing the methyl or ethyl esters with a branched moiety.

The purpose of this study was to evaluate the effect of palmitic acid-based branched esters on the PP property of palm oil methyl ester.

EXPERIMENTAL

Materials

Palm oil methyl ester was obtained from local palm oil refineries in Johor, Malaysia. *Table 1* summarizes the properties of the palm oil methyl esters used in the study. The following alcohols were selected for esterification: 2-butanol (99%), 2,2-dimethyl-1,3-propanediol (99%) and 2-methyl-1-butanol (99+%) purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany; 2-propanol (99.8 %) purchased from Merck KGaA, Darmstadt, Germany; 2-methyl-1-propanol (99%) purchased from Acros Organics, New Jersey, USA; and 2-ethyl-1-hexanol (99%) purchased from Fluka Chemie GmbH, Germany. The palmitic acid was purchased from Cognis Oleochemicals, Selangor, Malaysia.

TABLE 1. PROPERTIES OF PALM OIL METHYL ESTERS USED IN THE STUDY

Analysis		Value
Moisture (%)		0.07
Acid value (mg KOH g^{-1})		0.29
Iodine value		57.8
Carbon chain length distribution (%)		
	C8:0	0.30
	C10:0	0.25
	C12:0	2.32
	C14:0	1.72
	C16:0	39.04
	C16:1	0.20
	C18:0	2.88
	C18:1	41.87
	C18:2	10.94
	C18:3	0.29
	C20:0	0.18

Synthesis

The esterification of palmitic acid with the different branched-chain alcohols yielded palmitic acid- based esters (1)-(6). The synthesis was carried out following the same general route exemplified below by the esterification of palmitic acid with 2-propanol. *Figure 1* illustrates the structures of palmitic acid-based esters **(1)-(6)**.

Synthesis of Isopropyl Palmitate (1)

Palmitic acid (51.3 g, 0.2 mol) was mixed with 2-propanol (36.0 g, 0.6 mol), and concentrated

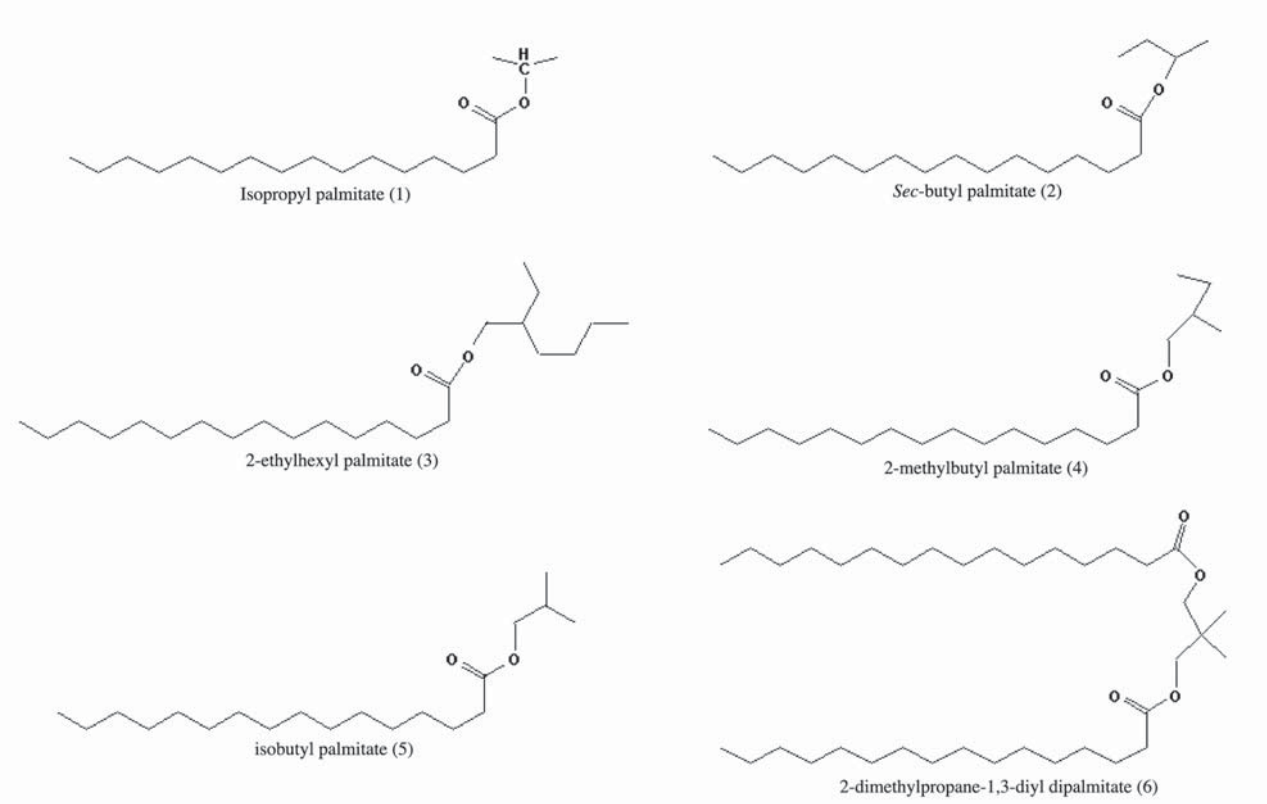

Figure 1. The structures of isopropyl palmitate ***(1)****, sec-butyl palmitate* ***(2)****, 2-ethylhexyl palmitate* ***(3)****, 2-methylbutylpalmitate* ***(4)****, isobutyl palmitate* ***(5)*** *and 2,2-dimethylpropane-1,3-diyl dipalmitate* ***(6).***

sulphuric acid (0.5 wt-% of palmitic acid) was added cautiously to this mixture in a 250-ml round-bottom flask, equipped with a Dean and Stark apparatus with a stopcock at the lower end, and attached to a reflux condenser at its upper end. The Dean and Stark apparatus was filled up with toluene (10 ml), and the remaining of toluene (60 ml) was added into round-bottom flask. The mixture was refluxed using a hotplate unit until water no longer collected in appreciable amount in the Dean and Stark apparatus, showing that the reaction had been completed or reached the point of equilibrium. Once the reaction was complete, the mixture was poured into a separatory funnel and washed with warm distilled water to get rid of the concentrated sulphuric acid from the mixture. The neutralized mixture was dried using anhydrous sodium sulphate. Finally, (1) was purified by vacuum distillation.

FT-IR

Infra red spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer fitted with a universal ATR sampling accessory.

FT-IR (cm^{-1}, ATR): ~2960, ~2923 and ~2854 (sharp CH_2 stretches), ~1738 (sharp carbonyl stretch), ~1464 (CH_2 bending vibration), ~1379 (CH_3 symmetrical bending vibration), ~1172 and ~1116 (ester C-O stretch), ~721 (CH_2 rocking vibration).

^{1}H-NMR (δ, ppm): 0.70 (C**H**$_3$, t, 3), 1.02 (C**H**$_3$, d, 6), 1.09 (C**H**$_2$, single broad peak, 24), 1.42 (C**H**$_2$, quintet, 2), 2.05 (C**H**$_2$, t, 2), 4.80 (-OC**H**, septet, 1); ^{13}C-NMR (δ, ppm): 13.89 (**C**H$_3$), 21.59 (**C**H$_3$), 22.59 (**C**H$_2$), 24.88 (**C**H$_2$), 29.04 (**C**H$_2$), 29.23 (**C**H$_2$), 29.33 (**C**H$_2$), 29.43 (**C**H$_2$), 29.56 (**C**H$_2$), 29.62 (**C**H$_2$), 29.65 (**C**H$_2$), 31.87 (**C**H$_2$), 34.37 (**C**H$_2$), 66.82 (-O**C**H-), 172.61 (**C**=O).

Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) spectra were recorded on a Jeol ECP 400 MHz using acetone-d_6 as the solvent and using the solvent signal as reference.

Isopropyl palmitate **(1)**, ^{1}H-NMR (δ, ppm): 0.70 (C**H**$_3$, t, 3), 1.02 (C**H**$_3$, d, 6), 1.09 (C**H**$_2$, single broad peak, 24), 1.42 (C**H**$_2$, quintet, 2), 2.05 (C**H**$_2$, t, 2), 4.80 (-OC**H**, septet, 1); ^{13}C-NMR (δ, ppm): 13.89 (**C**H$_3$), 21.59 (**C**H$_3$), 22.59 (**C**H$_2$), 24.88 (**C**H$_2$), 29.04 (**C**H$_2$), 29.23 (**C**H$_2$), 29.33 (**C**H$_2$), 29.43 (**C**H$_2$), 29.56 (**C**H$_2$), 29.62 (**C**H$_2$), 29.65 (**C**H$_2$), 31.87 (**C**H$_2$), 34.37 (**C**H$_2$), 66.82 (-O**C**H-), 172.61 (**C**=O).

Sec-butyl palmitate **(2)**, ^{1}H-NMR (δ, ppm): 0.71 (C**H**$_3$, t, 6), 1.00 (C**H**$_3$, d, 3), 1.10 (C**H**$_2$, s, 24), 1.35 (C**H**$_2$, m, 2), 1.44 (C**H**$_2$, m, 2), 2.06 (C**H**$_2$, t, 2), 4.64 (-OC**H**, sextet, 1); ^{13}C-NMR (δ, ppm): 9.47 (**C**H$_3$), 13.89 (**C**H$_3$), 19.26 (**C**H$_3$), 22.59 (**C**H$_2$), 24.95 (**C**H$_2$), 28.72 (**C**H$_2$), 29.07 (**C**H$_2$), 29.24 (**C**H$_2$), 29.33 (**C**H$_2$), 29.44 (**C**H$_2$),

29.56 (**C**H_2), 29.62 (**C**H_2), 29.65 (**C**H_2), 31.88 (**C**H_2), 34.38 (**C**H_2), 71.35 (-O**C**H-), 172.68 (**C**=O).

2-ethylhexyl palmitate **(3)**, ^{1}H-NMR (δ, ppm): 0.76 (C**H**$_3$, t, 9), 1.14 (C**H**$_2$, s, 24), 1.18 (C**H**$_2$, s, 6), 1.24 (C**H**$_2$, sextet, 2), 1.45 (C**H**, m, 1), 1.49 (C**H**$_2$, quintet, 2), 2.15 (C**H**$_2$, t, 2), 3.85 (-OC**H**$_2$, d, 2); ^{13}C-NMR (δ, ppm): 10.85 (**C**H_3), 13.90 (**C**H_3), 13.97 (**C**H_3), 22.68 (**C**H_2), 22.96 (**C**H_2), 23.81 (**C**H_2), 25.00 (**C**H_2), 28.93 (**C**H_2), 29.18 (**C**H_2), 29.33 (**C**H_2), 29.41 (**C**H_2), 29.53 (**C**H_2), 29.65 (**C**H_2), 29.70 (**C**H_2), 29.74 (**C**H_2), 30.46 (**C**H_2), 31.96 (**C**H_2), 34.21 (**C**H_2), 38.81 (**C**H), 66.26 (-O**C**H_2-), 173.37 (**C**=O).

2-methylbutyl palmitate **(4)**, ^{1}H-NMR (δ, ppm): 0.73 (C**H**$_3$, t, 6), 0.76 (C**H**$_3$, d, 3), 1.11 (C**H**$_2$, s, 24), 1.25 (C**H**$_2$, quintet, 2), 1.45 (C**H**$_2$, quintet, 2), 1.55 (C**H**, octet, 1), 2.12 (C**H**$_2$, t, 2), 3.75 (-OC**H**$_2$, d, 2); ^{13}C-NMR (δ, ppm): 10.96 (**C**H_3), 13.86 (**C**H_3), 16.14 (**C**H_3), 22.57 (**C**H_2), 24.87 (**C**H_2), 25.92 (**C**H_2), 29.10 (**C**H_2), 29.20 (**C**H_2), 29.30 (**C**H_2), 29.40 (**C**H_2), 29.54 (**C**H_2), 29.59 (**C**H_2), 29.63 (**C**H_2), 31.85 (**C**H_2), 34.02 (**C**H), 34.06 (**C**H_2), 68.38 (-O**C**H_2-), 172.97 (**C**=O).

Isobutyl palmitate **(5)**, ^{1}H-NMR (δ, ppm): 0.73 (C**H**$_3$, t, 3), 0.78 (C**H**$_3$, d, 6), 1.12 (C**H**$_2$, s, 24), 1.47 (C**H**$_2$, quintet, 2), 1.76 (C**H**, nonet, 1), 2.13 (C**H**$_2$, t, 2), 3.68 (-OC**H**$_2$, d, 2); ^{13}C-NMR (δ, ppm): 13.93 (**C**H_3), 18.92 (**C**H_3), 22.63 (**C**H_2), 24.94 (**C**H_2), 27.67 (**C**H), 29.13 (**C**H_2), 29.27 (**C**H_2), 29.36 (**C**H_2), 29.47 (**C**H_2), 29.59 (**C**H_2), 29.66 (**C**H_2), 29.69 (**C**H_2), 31.91 (**C**H_2), 34.08 (**C**H_2), 69.99 (-O**C**H_2), 173.08 (**C**=O).

2,2-dimethylpropane-1,3-diyl dipalmitate **(6)**, ^{1}H-NMR (δ, ppm): 0.83 (C**H**$_3$, t, 6), 0.91 (C**H**$_3$, s, 6), 1.21 (C**H**$_2$, s, 48), 1.57 (C**H**$_2$, m, 4), 2.25 (C**H**$_2$, t, 4), 3.83 (-OC**H**$_2$, s, 4); ^{13}C-NMR (δ, ppm): 14.10 (**C**H_3), 21.74 (**C**H_3), 22.73 (**C**H_2), 25.01 (**C**H_2), 29.20 (**C**H_2), 29.35 (**C**H_2), 29.43 (**C**H_2), 29.54 (**C**H_2), 29.67 (**C**H_2), 29.76 (**C**H_2), 31.99 (**C**H_2), 34.22 (**C**H_2), 34.63 (-**C**-), 68.88 (-O**C**H_2), 173.39 (**C**=O).

Miscibility

Palmitic acid-based esters (0.2 g) were weighed into glass flasks and palm oil methyl esters (20 g) were added to each flask. Each mixture was stirred for 24 hr by using a magnetic stirrer. These mixtures were checked periodically to evaluate the miscibility of palmitic acid-based esters in palm oil methyl esters.

Pour Point

Pour point (PP) measurement for palm oil methyl esters were carried out following the ASTM standard D-97 (2002). Soluble palmitic acid-based esters (0, 0.4, 1.2 and 2 g) were weighed into separate flasks. Palm oil methyl esters (40 g) were added to each flask (Chiu *et al.*, 2004). The mixtures were mixed thoroughly. Each sample was tested using the ISL CPP 97-2 analyser purchased from Instrumentation Scientifique de Laboratoire, Carpiquet Cedex, France.

PP are expressed in integers that are positive or negative multiples of 3°C. The observation of the samples starts at a temperature that is at least 9°C above the expected PP. The sample was immersed into a 0°C cooling bath. Readings were taken for every 3°C decrease, until the sample totally ceased to flow (tested by holding the sample in a horizontal position for 5 s). If the sample had not ceased to flow when its temperature had cooled to +9°C, the sample was then transferred to a -18°C cooling bath. Readings of the test thermometer were taken, and 3°C was added to the temperature recorded as the result of the ASTM D-97 PP.

RESULTS AND DISCUSSION

Synthesis

Esterification between a carboxylic acid and an alcohol is a reversible process and proceeds very slowly (Vogel, 1978). Equilibrium is only obtained after refluxing for several days. However, if a catalyst was used, *e.g.* concentrated sulphuric acid, the same point of equilibrium can be reached after a few hours. As esterification is a reversible reaction, when equimolecular quantities of the acid and alcohol are employed, only about two-thirds of the theoretically possible yield of ester is obtained. Thus, an excess of one of the components is required to drive the reaction to the right according to LeChatlier's Principle.

In this study, esterifications were carried out by using concentrated sulphuric acid (0.5 wt-% of palmitic acid) as the catalyst, and excess alcohols were used (ratio of palmitic acid to alcohols is 1:3) except for the reaction involving 2,2-dimethylpropane-1,3-diol, in which case the ratio of palmitic acid to 2,2-dimethylpropane-1,3-diol was 1:1. For the reaction between palmitic acid and 2,2-dimethylpropane-1,3-diol, a longer reaction time was required to achieve higher yield due to the equimolecular quantities of the acid and alcohol employed. *Table 2* shows the reaction temperature, reaction time, yield and PP of palmitic acid-based esters.

Besides that, the reaction mixture was subjected to reflux under a Dean and Stark water separation unit. This allows the separation and removal of water from the azeotrope, with the organic phase being returned continuously to the reaction flask. According to LeChatlier's Principle, removal of water from the reaction mixture enables a good yield of the required esters. The esters were purified by vacuum distillation, whereby the pure fractions were collected at constant boiling point.

TABLE 2. REACTION TEMPERATURE, REACTION TIME, YIELD AND POUR POINT (PP) OF PALMITIC ACID-BASED ESTERS

Ester	Reaction temperature (°C)	Reaction time (hr)	Yield (%)	PP (°C)
Isopropyl palmitate **(1)**	91	8	94	+12
Sec-butyl palmitate **(2)**	103	7	93	+12
2-ethylhexyl palmitate **(3)**	127	5	95	-3
2-methylbutyl palmitate **(4)**	115	5	97	+9
Isobutyl palmitate **(5)**	104	5.5	96	+12
2,2-dimethylpropane-1, 3-diyl dipalmitate **(6)**	115	6	97	+12

The purified esters were characterized by using FT-IR, ^{1}H-NMR and ^{13}C-NMR. FT-IR showed no remaining carboxylic acid (~1720 cm^{-1}, carbonyl) and only ester (~1735 cm^{-1}, carbonyl). The proton and carbon-13 NMR spectra results further confirmed these purified esters only consisted of ester. The yield percentages of the final products **(1)** – **(6)** after distillation were 94%, 93%, 95%, 97%, 96% and 97%, respectively.

Miscibility

A total of six synthesized palmitic acid-based esters were evaluated for their miscibility in palm oil methyl esters. All the six compounds were found to be miscible.

The six synthesized palmitic acid-based esters and palm oil methyl esters are categorized in the same homologous series. Thus, the similar polarity of these six compounds with palm oil methyl esters might result in miscibility of these compounds in biodiesel. The structures of the miscible compounds are shown in *Figure 1*.

Pour Point

The effects of the soluble compounds on the PP of palm oil methyl esters are summarized in *Table 3*.

Almost all the compounds essentially had no effect on the PP except for 2,2-dimethylpropane-1,3-diyl dipalmitate **(6)** which showed a lowering of 3°C when 3 wt-% was added. Originally, palm oil methyl esters have high PP and CP due to high contents of the saturated fatty ester, methyl palmitate. Thus, palmitic acid-based esters were synthesized by using different branched-chain alcohols. However, from the results shown in *Table 3*, it can be concluded that the palmitic acid-based esters with different ester head groups had not effectively disrupted macrocrystalline formation at reduced temperatures.

TABLE 3. POUR POINTS OF PALM OIL METHYL ESTERS BLENDED WITH PALMITIC ACID-BASED ESTERS

Additive	Amount of additive (wt % of methyl esters)	Pour point (°C)
Isopropyl palmitate **(1)**	1	12
	3	12
	5	12
Sec-butyl palmitate **(2)**	1	12
	3	12
	5	12
2-ethylhexyl palmitate **(3)**	1	12
	3	12
	5	12
2-methylbutyl palmitate **(4)**	1	12
	3	12
	5	12
Isobutyl palmitate **(5)**	1	12
	3	12
	5	12
2,2-dimethylpropane-1, 3-diyl dipalmitate **(6)**	1	12
	3	9
	5	9

CONCLUSION

A total of six different palmitic acid-based esters **(1)** – **(6)** were synthesized. FTIR spectra of all the synthesized compounds showed no remaining carboxylic acid (~1720 cm^{-1}, carbonyl) but only ester (~1735 cm^{-1}, carbonyl). Proton and carbon-13 NMR spectra further confirmed the purified esters consisted of only branched esters. All the six synthesized compounds were miscible with palm oil methyl esters due to similar polarity of the solute and the biodiesel. The blends of the resultant six ester compounds in palm oil methyl esters were evaluated for their effect on the PP property. The 2,2-dimethylpropane-1,3-diyl dipalmitate was able to improve the PP of palm oil methyl esters from 12°C to 9°C when 5 wt-% was added.

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