

# Synthesis and Characterization of Dicarboxylate Esters as Environmentally Friendly Palm Biodiesel Pour Point Depressants

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**ABSTRACT:** *The alternative renewable energy of Palm BioDiesel (PBD) is gaining eminence to be used in transportation and industrial applications. However, its regular usage in temperate countries has the main issue to be solved due to its poor cold flow properties. The Pour Point Depressant (PPD) is required to enhance the PBD cold flow properties to a certain acceptable range. In this work, environmentally green PPD diesters for PBD were synthesized through the acid catalyst esterification process between selected dicarboxylic acids (succinic, suberic, and dodecanedioic) with branched alcohols (2-butyl-1-octanol and 2-ethyl-1-hexanol) in the presence of sulphuric acid. The resultant synthesized dicarboxylate esters were successfully produced at high yield percentages in the range of 85-98%. The chemical structures of dicarboxylate esters were confirmed by using FT-IR, <sup>1</sup>H, and <sup>13</sup>C NMR. The results showed that green PPDs derived from the dicarboxylic acids with the same carbon chain length of the respective branched alcohol have more capability to reduce PBD pour point. On the other hand, green PPDs derived from the same alcohol of the respective increasing dicarboxylic acids carbon chain length showed a slight reduction in PBD pour point. A selected blending green PPD of di(2-butyloctyl) suberate (D2BOsub) into PBD has produced the lowest PBD pour point down to 3°C. Therefore, properly chosen green PPDs capable of reducing the PBD pour point are to be regularly used as an alternative fuel in tropical countries. It is plausible for the synthesized PPD to be used together with petrol-diesel blends in selected proportions or as a full substitute for diesel engines.*

**KEYWORDS:** *Branched dicarboxylate esters, Green pour point depressant, Biofuel, Low-cost fuel.*

## INTRODUCTION

The drastic change in industrial globalization and modern lifestyle has triggered a high demand for world fuel

energy consumption. The direct impact of these activities has led to drastic impletion of existing non-renewable

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fossil or petroleum fuel [1]. Alternatively, most industries are looking the alternative fuel from renewable and sustainable fuel sources to accommodate the globalization advancement activities [2]. Besides, high market prices and negative impact on the environment also has driven the replacement of fossil fuels with cheaper renewable fuel sources [3]. Biofuels have emerged as the most potential alternative renewable and sustainable fuel for the future [4]. Among the biofuels, biodiesels are among the green alternative fuels for the replacement of fossil fuels due to their naturally abundant resources and environmentally benign benefits.

Green biodiesel has several advantages for future energy compared to conventional petroleum diesel [5, 6]. Biodiesel is produced from naturally renewable and environmentally friendly oils and fats either from plants or animals. Biodiesel is also can be produced from non-edible and waste cooking oils. Biodiesel is simple Fatty Acid Methyl Ester (FAME) produce from the transesterification process of plant oils such as palm, corn, rapeseed, and soybean etc., or from animal fats such as tallow. It has very similar engine combustion energy when compared to conventional petroleum diesel [6]. Biodiesel has greater biodegradability properties, complete combustion, reduced toxicity, and improved lubricity in comparison with fossil fuels diesel [7]. The physicochemical properties of green biodiesel very much depend on the nature of its raw oils and fats materials used. Therefore, most countries have put specified relevant parameters for green biodiesel standards to be used in their own countries [8, 9]. The specific chemicals' characteristic properties from plant oil or animal fat feedstock contribute to their own characteristic performance of biodiesel. In general, plant oil-based biodiesel is less viscus, density, and cetane number compared to animal fat-based biodiesel due to their high unsaturated fatty acids content. Standard green biodiesel should comply with certain country standard parameters such as Pour Point (PP), iodine value (IV), density, viscosity, cetane number, copper strip corrosion, linolenic acid methyl esters content, and phosphorus content [10, 11]. Palm BioDiesel (PBD) is one alternative green energy fuel produced from Crude Palm Oil (CPO) which is obtained from the palm fruit mesocarp fraction. The palm oil tree is a species of monocotyledon flowering plant that belongs to the *Elaeis guineensis* species in the Acaceae family [12, 13]. Palm Oil (PO) trees are mostly cultivated as cash crops or

horticulture plants in tropical and subtropical countries in Southeast Asia (Malaysia and Indonesia) and Africa. Its pinnate leaves could grow 3–5 meters long and economically sustained for about thirty years [9]. Palm oil commodity crops are known as the highest oil-containing fruit (CPO) crops with the lowest cost of production. Malaysia is among the largest palm oil producers in the world besides Indonesia [14]. In Malaysia, CPO is the main feedstock for PBD production. This is due to its major agricultural product export commodities [15]. High-free fatty acid crude palm oil (HFFA-CPO) and palm oil-based Used Frying Oils (UFO) also are among the major PBD feedstock due to their low-quality oil and food safety reasons. Due to its high long chains of saturated fatty acids content and high PP, PBD is restricted to be used in temperate countries. According to the ASTM standard, the PP is the “lowest temperature at which movement of the oil is observed”, whereas the Cloud Point (CP) is the temperature at which crystals are formed within the oil and turn to visible (in the form of cloudiness) [16].

The disadvantage of biodiesel has limits to use in cold weather. The CP and PP of biodiesel depend on the nature of plant oil from where the biodiesel is derived [17]. The higher composition of saturated fatty acids increases the CP and PP of biodiesel [17, 18]. For example, the major saturated fatty acid composition in PBD is palmitic acid (63 %) and its PP is 19°C. On the other hand, in soybean biodiesel, the major unsaturated fatty acids compositions are linoleic acid (53 %) and oleic acid (25 %) and its PP is 10°C. Therefore, to diversify the usage of PBD, especially in temperate countries, its PP needs to be improved by the addition of PP depressants (PPD). The use of PPDs which is a conventional method has been established to overcome and improve the PP of petroleum diesel. The PPDs are suitable, economically, and technically available to be used for the improvement of the PP properties of biodiesel [19]. The mechanism of these PPDs molecules to reduce the biodiesel PP is still unclear. Nevertheless, PPDs molecules are proposed to adsorb into the wax crystals, redirect their growth, form smaller and more isotropic crystals, and remain in the liquid fuel. Some PPDs molecules have unique structures and one part is like the paraffin wax crystals. It provides nucleation sites and crystallizes together with the paraffin waxes. At the same time, the other part of the structure dislikes the wax crystals and blocks the extensive growth of the wax nucleation.

This makes the bulk biodiesel stream remain liquid and easily pourable and pumpable [20, 21]. Most PPDs are oil soluble and have the tendency and ability to co-crystallize with the growing wax crystals [20]. PPDs molecules adsorb on the surface of the emergent and growing wax crystals. As the result the growth of the wax crystals is inhibited by insulating surface layer of PPDs. In this condition, PPDs capable to adsorb oil and turn into gels form. The efficiencies of PPDs are varied depending on the types of PPD used. Some PPDs have excellent effect occurring at an optimum concentration level. Typical levels of PPDs application in commercial oils are in the range of 1-5 % [22]. The existing PPDs in the market are petroleum based such as chlorinated paraffins and naphthalene polyacrylates, copolymers of ethylene and vinyl esters, copolymers of  $\alpha$ -olefins and maleates and poly- $\alpha$ -olefin, polymethacrylate, etc. [23-31]. However due to the environmental concern, PPD bio-based derived from plants and animals are interested of the concern for many researchers.

Bio-based polyesters are suitable and environmentally friendly to be used as PPD due to their polar ester functional group. Most branched polyester PPDs such as diisopropyl azelate (DIAZ) is among of them and has showed effectively improved the biodiesel PP of both soybean biodiesel and palm biodiesel at 30 % loading into PP of 5-6°C, respectively [32]. The branched dicarboxylate esters consist of polar (ester functional group) and nonpolar (long chain hydrocarbon) moiety as in biodiesel so they are preferred as PPDs for biodiesel. It is expected that the polar carbonyl groups of the dicarboxylate esters will bond with the carbonyl group of biodiesels by Van der Waals forces, and the non-polar attractions between hydrocarbon atoms and molecules, resulting in the decrease of biodiesel crystallinity [33, 34]. As a result, the wax-like crystals growing of PBD for example is inhibited, thus reducing the PBD PP at the acceptable range that could be used in temperate countries. Plant-based polyesters containing ester monomers of carbon C<sub>16</sub> to C<sub>40</sub>, polyol esters, azelate-based esters, and vegetable oil-based esters have been reported as pour point depressants for biodiesel and diesel engines [35 - 39]. Since then, bio-based pour point depressants, PPDs have been investigated tremendously due to environmental concerns.

The aim of this work is to produce bio-based PPD through the synthesis of branched dicarboxylic based diesters such as di(2-butyloctyl) succinate (D2BOSuc),

di(2-ethylhexyl) succinate (D2EHSuc), di(2-butyloctyl) suberate (D2BOSub), di(2-ethylhexyl) suberate (D2EHSub), di(2-butyloctyl) dodecanedioate (D2BOD) and di(2-ethylhexyl) dodecanedioate (D2EHD). The branched polyester mixture of the present study may be used as pour point depressants for crude oil, mineral oil and/or mineral oil products or plant biodiesel. Preferably selected branched polyester uses as pour point depressant for palm biodiesel by adding at least one of the branched polyesters above to the palm biodiesel. The aspect of the present study is to synthesise the branched polyester between selected bio-based dicarboxylic acids with two type of alcohols (2-butyl octanol and 2-ethyl hexanol) and the use of a branched polyester mixture of the present study as pour point depressant. Thus, another aspect of the present study is a method of reducing the palm biodiesel pour point comprising the step of adding a branched polyester of the present study to palm biodiesel. The resultant pour point or the yield point refers to the lowest temperature at which a sample of palm biodiesel, in the course of cooling, still just flows. These diesters might be helpful for palm biodiesel PPD to reduce palm biodiesel pour point at recommended temperature for suitable alternative green fuel application at tropical countries.

## EXPERIMENTAL SECTION

### Materials

Succinic, suberic, and dodecanedioic acids at 98 % purity were purchased from Merck. Palm biodiesel with a pour point of 9.50 °C was obtained from Malaysian Palm Oil Broad (MPOB). 2-Ethyl-1-hexanol and 2-butyl-1-octanol were purchased from Sigma-Aldrich. All other chemicals such as sulphuric acid, toluene, sodium sulfate, sodium chloride, and sodium bicarbonate were supplied by Fisher Scientific (Pittsburgh, PA, USA). All the chemicals used in this study were analytical or high-performance liquid chromatography (HPLC) grade and used without further purification.

### Instrumentation

Fourier Transforms InfraRed (FT-IR) spectroscopy was carried out using Spectrum GX spectrophotometer (Perkin Elmer) in the range of 400-4000 cm<sup>-1</sup>. JEOL-ECP 400 spectrometer (400 MHz <sup>1</sup>H/100.61 MHz <sup>13</sup>C) Nuclear magnetic resonance spectroscopy (NMR) was used for proton <sup>1</sup>H and <sup>13</sup>C analyses using CDCl<sub>3</sub> solvent.

Shimadzu GC-17A Gas Chromatography (GC) equipped with a flame ionization detector (FID) and capillary column (30 m × 0.25 mm × 0.25 μm film) was used to identify the fatty acid composition of Palm BioDiesel (PBD). PBD (1.0 μL) was injected into GC for analysis. The peaks were identified through retention times compared to genuine standards determined under the same conditions.

#### **Synthesis of dicarboxylate esters as pour point depressant**

The potential of palm biodiesel pour pint depressant of dicarboxylate esters (PPD) was synthesized through the esterification process between selected dicarboxylic acids (succinic, suberic, and dodecanedioic acids) with two branched carbon chain alcohols (2-butyl-1-octanol and 2-ethyl-1-hexanol), in a three-necked flask equipped with a reflux condenser. One mole of dicarboxylic acid (1.77 g; 0.015 mole of succinic acid or 2.16 g; 0.015 mole of suberic acid or 3.45 g; 0.015 mole of dodecanoic acid) was mixed with two moles of alcohol (5.589 g; 0.03 mole of 2-butyl-1-octanol or 3.906 g; 0.03 mole of 2-ethyl-1-hexanol) in 20-30 mL of toluene as a medium for the reaction. Dean Stark distillation method equipped with a mild vacuum system (76 kPa) was used to carry out the esterification reaction. The reaction mixture was heated at a suitable experimental temperature of 120-130°C in a magnetic heater oil bath and stirred. Concentrated H<sub>2</sub>SO<sub>4</sub> of 2% (as a percentage of the weight of dicarboxylic acid) was added to the mixture before the reaction. After completion of 4 hours of reaction time, the heating was turned off and the reaction product was left to cool at room temperature. The reaction product was dissolved with 25 mL of diethyl ether and transferred into a 100 mL separation funnel. 10 mL of saturated sodium bicarbonate (NaHCO<sub>3</sub>) was added to the separation funnel and vigorously shaken before left to stand until two layers were formed. The aqueous layer at the bottom was removed, leaving the organic layer. Subsequently, the organic layer was washed with 10 mL of saturated sodium chloride (NaCl) and 10 mL of distilled water twice, to avoid any formation of emulsion. Once the two layers were formed, the aqueous bottom layer was removed. The washing was repeated until a solution with pH 7 was obtained. The washed organic layer was poured into a round flask of a rotary evaporator apparatus to remove solvent and any excess alcohol through evaporation at a temperature of 90-100 °C. Any colored or decomposed materials formed during

the reaction was removed by column-packed filtration with silica gel. The column-filtered ester product possesses a viscous yellowish liquid. The synthesized ester products were placed in a small beaker and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) was added to absorb the remaining moisture in the sample for overnight. The hydrated Na<sub>2</sub>SO<sub>4</sub> was filtered off.

#### **Fatty acids composition**

Fatty acid composition of PO and PBD was determined by using GC-FID (Shimadzu, Series GC-17A) equipped with BPX 70 polarized capillary column (30m × 0.25 mm × 0.25 μm thinning thickness; SGE) according to Bahadi, et al. (2021) [14]. Fatty Acid Methyl Ester (FAME) was first prepared from PO using base-catalyzed transesterification. The injector and detector temperatures were set at 250 and 280°C respectively. The column temperature was maintained at 120°C for 1 min and then increased to 250°C at a rate of 3°C / min and maintained at the final temperature for 15 min. Nitrogen gas was used as carrier gas at a flow rate of 0.40 mL/min with a total flow rate of 13 mL/min. The samples (PO FAME) or PBD in the solvent were injected using a split injector mode with a separation ratio of 29: 1. The fatty acid composition was identified based on the retention time of Merck authentic standards FAME solution analyzed under the same condition.

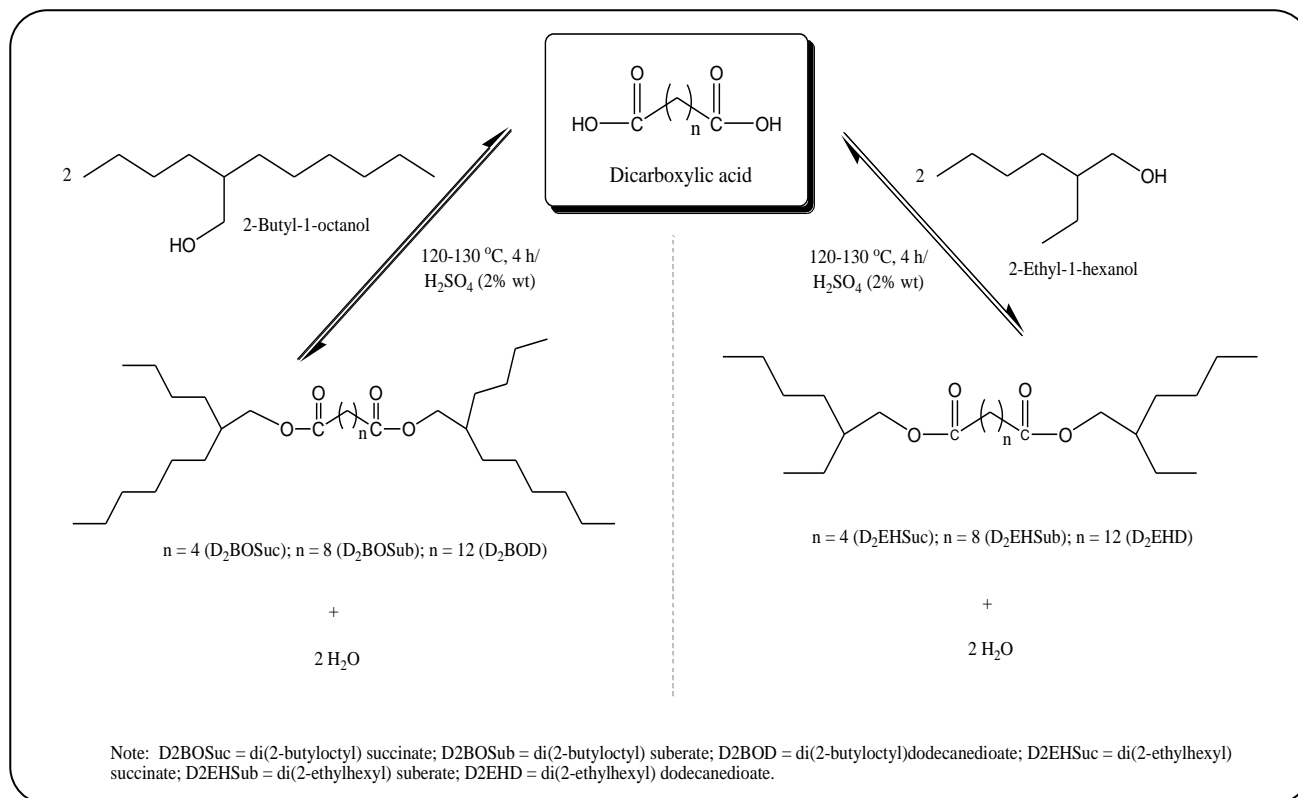
#### **Pour point measurement**

Palm biodiesel, PBD were blended separately and thoroughly with each pour point depressant, PPD of D2BOD, D2EHD, D2BOSub, D2EHSub, D2BOSuc, or D2EHSuc at various concentrations of 2, 4, 6, 8, 10 and 12 wt%. Then, the pour points of the PBD without PPD and with PPD mixtures were measured according to the ASTM D97-05 method (accuracy of ± 0.1°C). [40]. The synthesized dicarboxylate ester solution in xylene (5 mL) at different concentrations (% wt of PBD) was added to 50 mL of palm biodiesel sample and heated in a thermostatic bath maintained at 50 °C prior to the pour point measurement. The pour points of PBD were measured in triplicates for each sample.

## **RESULTS AND DISCUSSION**

### **Synthesis and characterization of dicarboxylate esters (PPDs)**

An esterification reaction was performed between selected dicarboxylic acids (C<sub>4</sub>, C<sub>8</sub> and C<sub>12</sub>) and branched alcohols (2-butyl-1-octanol and 2-ethyl-1-hexanol)



**Fig. 1: Esterification reaction of selected dicarboxylic acids with 2-butyl-1-octanol or 2-ethyl-1-hexanol to form dicarboxylate esters.**

at mole ratio 1:2 in the presence of 2 % (wt) of concentrated H<sub>2</sub>SO<sub>4</sub> as a catalyst. The six resultants of dicarboxylate ester products for palm biodiesel Pour Point Depressants (PPDs) were evaluated. The final esterification reaction to produce the products is illustrated in Fig. 1.

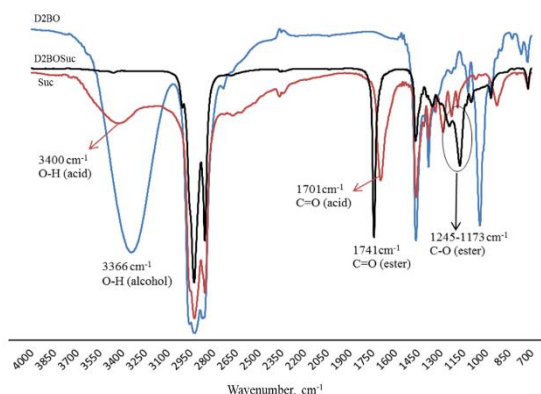
In this study, the esterification reactions have produced a high yield percentage of dicarboxylate ester product as a yellowish-liquids. However, the purification process may have affected the yield percentage by losing a small number of diester products that were stuck on the wall of the silica gel column. The isolated final products, dicarboxylate esters, were verified by using FT-IR and NMR spectroscopy. The isolated esters product yield percentages are given in Table 1. Di(2-butyloctyl) succinate (D<sub>2</sub>BOSuc) has the highest yield percentage of 98 %, while di(2-ethylhexyl) dodecanedioate (D<sub>2</sub>EHD) has the lowest yield percentage of 85 % among other diesters. The ester yields are comparable with other findings and higher conversion percentage as compared to 91% of polyol ester in the presence of SnO<sub>2</sub> at longer 19 h and nano-SnO<sub>2</sub> with 92% conversion during 15 h [41]. This is due to the bigger structure cause more steric hinderance and hinder the esterification reaction take

place. In general, the FT-IR spectra of D<sub>2</sub>BOD, D<sub>2</sub>EHD, D<sub>2</sub>BOSub, D<sub>2</sub>EHSub, D<sub>2</sub>BOSuc, and D<sub>2</sub>EHSuc were similar. Strong intensity bands were observed corresponding to C=O and C-O of ester. The absorption band peaks of C=O ester, C-O ester stretching vibrations, and C-O-C ester bands appeared in the ranges of 1732-1740 cm<sup>-1</sup>, 1244-1166 cm<sup>-1</sup>, and 968-1109 cm<sup>-1</sup>, respectively. Fig. 2 shows the FT-IR spectra of di(2-butyloctyl) succinate (D<sub>2</sub>BOSuc). The results showed that the absence of important bands for OH alcohol at 3366 and 3400 cm<sup>-1</sup> for OH acid carbonyl, the disappearance of C=O and C-O-C acid stretching vibrations bands, and the appearance of C=O and C-O-C ester stretching vibrations bands proof that the esters have been successfully synthesized.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of D<sub>2</sub>BOSuc are illustrated in Fig. 3 and Fig. 4, respectively. The <sup>1</sup>H chemical shifts (Fig. 3) appeared at 3.91-4.01 ppm for RCOO-CH<sub>2</sub> (d); 2.22-2.32 ppm for H<sub>2</sub>C-COOR (e); 1.65-1.72 ppm for -CH- 3° aliphatic (c); 1.24-1.35 ppm for -CH<sub>2</sub>- (b); and 0.80-0.89 ppm for -CH<sub>3</sub> (a). The <sup>13</sup>C NMR spectrum of D<sub>2</sub>BOSuc (Fig. 4), shows the <sup>13</sup>C chemical

**Table 1: Yield (%) of selected synthesized dicarboxylate esters product.**

Dicarboxylic acid	Alcohol	Diester	Yield, %
Succinic acid	2-Butyl-1-octanol	di(2-butyloctyl) succinate (D2BOSuc)	98
Succinic acid	2-Ethyl-1-hexanol	di(2-ethylhexyl) succinate (D2EHSuc)	96
Suberic acid	2-Butyl-1-octanol	di(2-butyloctyl) suberate (D2BOSub)	92
Suberic acid	2-Ethyl-1-hexanol	di(2-ethylhexyl) suberate (D2EHSub)	90
Dodecanedioic acid	2-Butyl-1-octanol	di(2-butyloctyl) dodecanedioate (D2BOD)	88
Dodecanedioic acid	2-Ethyl-1-hexanol	di(2-ethylhexyl) dodecanedioate (D2EHD)	85

**Fig. 2: FT-IR spectra of 2-Butyl-1-octanol (D2BO), Succinic acid (Suc) and di(2-butyloctyl) succinate (D2BOSuc).**

shifts at: 172.5 ppm for C=O ester; 67.57 ppm for O-C- (d) ester; 40.71 ppm for -CH- 3° aliphatic (c); 36.83 (-COO-CH<sub>2</sub>), 31.87, 31.27, 29.67, 28.95, 26.71, 24.91 ppm for -CH<sub>2</sub>- (b); 23.03, 22.71 for -CH<sub>2</sub>- (b\*); and 14.12 ppm for -CH<sub>3</sub> (a). The spectra confirmed the existence of the D2BOSuc ester compound as the synthesized product. The same trends were shown for the other resultant esters products.

NMR spectra multiplet report for D2BOSuc is shown as follows:

D2BOSuc - <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ ppm 0.80 - 0.89 (m, 6 H), 1.24-1.35 (d, *J*=13.73 Hz, 16 H), 1.65 - 1.72 (s, 1 H), 2.22 - 2.32 (m, 2 H), 2.60-2.62 (m, 2H), 3.94 - 4.01 (m, 2 H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ ppm 14.12 (s, 1 C), 22.71 (s, 1 C), 23.03 (s, 1 C), 24.91 (s, 1 C), 26.71 (s, 1 C), 28.95 (s, 1 C), 29.67 (s, 1 C), 31.27 (s, 1 C), 31.87 (s, 1 C), 36.83 (s, 1 C), 40.71 (s, 1 C), 67.57 (s, 1 C), 172.5 (s, 1 C).

#### Fatty acids composition

The fatty acids composition of palm oil, PO, and PBD were determined for a better understanding of the chemical composition of palm biodiesel and its relationship

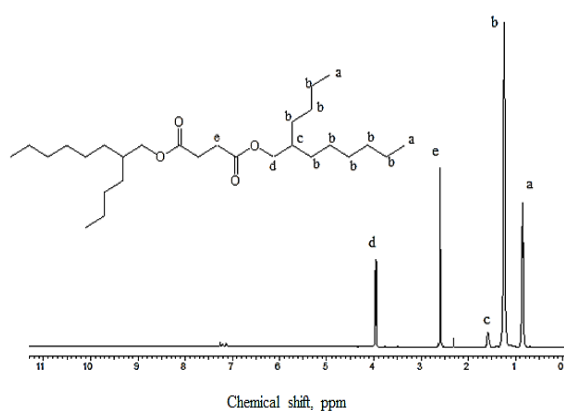
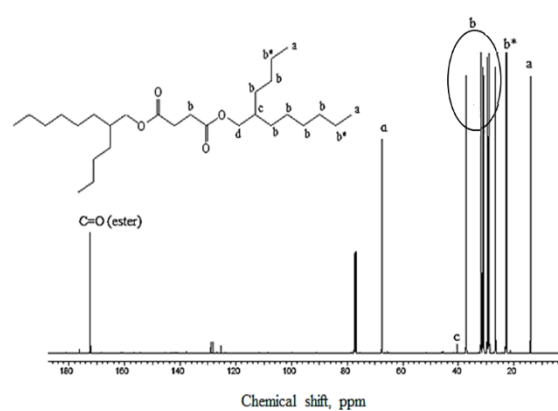
with the raw material used. The results revealed that the major fatty acids for both PO and PBD were palmitic acid (43.9 and 46.3 %), oleic acid (39.9 and 38.9 %), and linoleic acid (10.7 and 9.5 %), respectively as shown in Table 2. In general, the fatty acid composition of PBD is greatly contributed by nearly equal saturated and unsaturated fatty acids as composed by its raw material of PO. In a relationship, the higher the saturated fatty acids composition, the higher the Pour Point (PP) of the corresponding biodiesel. The high PP of the studied PBD (9.50 °C) is suitable for usage in tropical countries and limits the benefits of biodiesel utilization in cold climates [42, 43]. This is due to the predominance of a palmitic acid composition in PO and as well as in PBD.

#### Pour point improvement

The PP of biodiesel indicates the importance of cold flow properties at certain temperatures. The PP is the main issue for PBD to regularly use as a potential alternative fuel to petroleum diesel. At low temperatures below the PP, PBD forms gum and crystallizes the fuel particles. This winterization can be hindered and improved by blending or addition of PP improvers or PP depressants, PPDs. In this study, the synthesized dicarboxylate esters were used to improve the PP property of PBD. As mentioned earlier, the hypothesis is that compounds with bulky or branched-chain moieties polar head group and nonpolar hydrocarbon tail group might be effective in hindering nucleation at additive level concentrations through the reducing the rate of molecules co-crystallization process. The synthesized PPDs were separately blended in different percentages (wt%) with PBD and the PBD PPs were evaluated. Table 3 shows the average of PBD PP after the blending process. The results in general, showed the reduction of BPD PP after the blended process. The results showed that the synthesized PPDs

**Table 2: Fatty acids composition (%) and pour point of palm oil, PO and palm biodiesel, PBD.**

Fatty acids	Composition (%)	
	PO	PBD
Lauric acid (C <sub>12:0</sub> )	0.2	0.2
Myristic acid (C <sub>14:0</sub> )	1.1	1.0
Palmitic acid (C <sub>16:0</sub> )	43.9	46.3
Stearic acid (C <sub>18:0</sub> )	4.2	4.2
Oleic acid (C <sub>18:1</sub> )	39.9	38.9
Linoleic acid (C <sub>18:2</sub> )	10.7	9.5
Σ Saturated fatty acids	49.4	51.7
Σ Unsaturated fatty acids	50.6	48.3
	PP (19.7 °C)	PP (9.5 °C)

**Fig. 3: <sup>1</sup>H NMR spectrum of di(2-butyloctyl) succinate (D2BOSuc).****Fig. 4: <sup>13</sup>C NMR spectrum of di(2-butyloctyl) succinate (D2BOSuc).**

have shown an effect on the reduction of PBD PP at certain levels according to their respective dicarboxylate ester. It indicates that dicarboxylate ester with the bulky moiety of polar headgroup and nonpolar tail group can be used as PBD PPDs. However, the degree of effectiveness in reducing the PBD PP is dependent on the type of carboxylate ester.

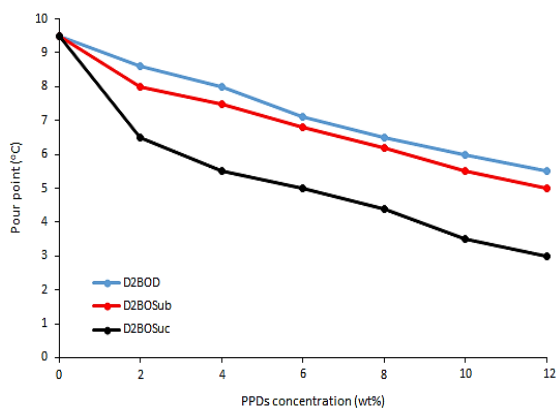
Fig. 5 shows the reduction in PP of PBD when blended with various concentrations (wt%) of D2BOD, D2BOSub, and D2BOSuc. At 2 wt% of D2BOD, D2BOSub and D2BOSuc, the PP of PBD is reduced by 0.9 °C, 1.5°C and 3°C, respectively. The reduction in PBD PP was increased with a higher concentration of dicarboxylate esters used in blended. At the highest concentration (12 wt%) of D2BOD, D2BOSub, and D2BOSuc, the PBD PP is reduced by 4, 4.5, and 6.5°C, respectively. The results showed that the synthesized esters were comparatively as good as other PPD such as terpolymer<sup>a</sup> [44], terpolymers<sup>b</sup> [45], and MEL-A<sup>c</sup> [38].

D2BOSuc produced the highest effect on the reduction of PBD PP that was attributed to the highly bulky branched moieties of the short-chain alkyl head group of D2BOSuc as compared to D2BOSub and D2BOD. The alignment of the molecules head-to-head bilayers in the crystal lattice was disturbed by the bulky moiety of polar headgroups and the short chain PPD of D2BOSuc. Therefore, the rate of co-crystallization molecules was insignificant. In general, the branched configuration structure of D2BOD, D2BOSub and D2BOSuc leads to a good reduction in the PP of PBD. This is a potential mechanism for the reduction of biodiesel PP with the use of bulky moieties that disrupt the orderly stacking of ester molecules during crystal nucleation [46]. It is well known that the branched-chain esters such as isopropyl and 2-butyl esters of fatty acids have better PP compared to their corresponding straight-chain isomers [47-49]. For example, the neat esters of the short-chain alkyl group (head group)

**Table 3: Effect of PPDs at different wt% blended towards PBD pour point values**

PPDs	PP of PPDs (°C)	PP (°C) of blended PBD with PPDs (wt%)						
		0 %	2 %	4 %	6 %	8 %	10 %	12 %
D2BOD	-65±0.1	9.5±0.1	8.6±0.1	8.0±0.1	7.0±0.1	6.5±0.1	6.0±0.1	5.5±0.1
D2BOSub	>-70±0.1	9.5±0.1	8.0±0.1	7.5±0.1	6.8±0.1	6.3±0.1	5.5±0.1	5.0±0.1
D2BOSuc	>-70±0.1	9.5±0.1	6.5±0.1	5.5±0.1	5.0±0.1	4.4±0.1	3.5±0.1	3.0±0.1
D2EHD	-55±0.1	9.5±0.1	9.0±0.1	8.4±0.1	8.0±0.1	7.4±0.1	6.9±0.1	6.2±0.1
D2EHSub	-62±0.1	9.5±0.1	8.7±0.1	8.4±0.1	7.5±0.1	7.0±0.1	6.4±0.1	5.7±0.1
D2EHSuc	-70±0.1	9.5±0.1	8.1±0.1	7.7±0.1	6.9±0.1	6.4±0.1	5.7±0.1	5.3±0.1
Terpolymers <sup>a</sup>	B20 blend	9	n/a	n/a	n/a	n/a	3	n/a
Terpolymers <sup>b</sup>	WCOB	10	n/a	n/a	n/a	n/a	5	n/a
MEL-A <sup>c</sup>	PBE-B30-A2	-5	n/a	0	n/a	n/a	n/a	n/a

<sup>a</sup>Terpolymers poly(alkyl acrylates), alkyl methacrylates, methyl methacrylate (75:25:10); <sup>b</sup>Terpolymers alkyl methacrylates, Benzyl methacrylate, N-Vinylpyrrolidone (20:1:1); <sup>c</sup>PBE-B30-A2 (Palm butyl ester-butanol-PPD MEL-A); Source: a = [44]; b = [45]; c = [38].



**Fig. 5: Pour point of PBD with various concentrations of D2BOSuc, D2BOSub and D2BOD.**

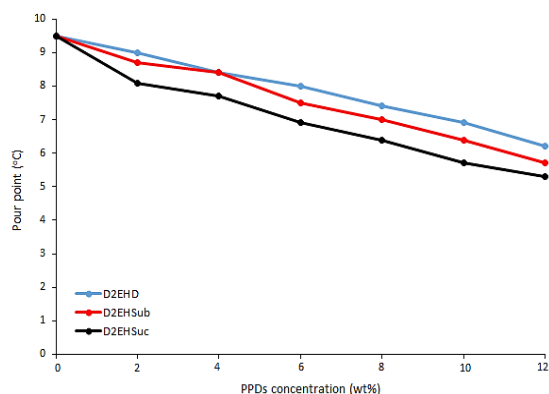
with bulky moieties had better reduction PBD PP. Subsequent alignment of nonpolar saturated short-chain fatty methyl esters would not occur among the ester tail nonpolar groups. The rate of co-crystallization molecules was insignificant and the crystalline growth habit was hindered. Wax crystal growth habit was affected by the presence of the bulky moieties head groups by interfering with the formation of clusters of molecules that precede nucleation in a bulk liquid solution, thus reducing the PBD PP. On the other hand, esters with long straight-chain head groups have less affected on the biodiesel PP. In the presence of long-chain PPD such as D2BOSub and D2BOD, the effect of the co-crystallization molecules and subsequent alignment of nonpolar saturated long-chain fatty methyl esters will occur among the ester tail nonpolar groups were significant [50]. Thus, having little or no alteration in the rate of crystal growth and subsequently reduce slightly

in biodiesel PP.

However, PBD PP improvement depends directly proportional to the PPDs blend level. Fig. 6 shows the reduction in the PP of PBD blended with various concentrations of D2EHD, D2EHSub, and D2EHSuc. The figure displays a reduction of 0.5°C when PBD was blended with 2 % D2EHD and 0.8°C with 2 % D2EHSub. The highest reduction is 1.4°C, obtained by blending PBD with 2 % D2EHSuc. This PP reduction was increased with a raised level of dicarboxylate esters concentration (wt %). The reduction increases up to 3.3, 3.8, and 4.2°C when blended with 12 % of D2EHD, D2EHSub, and D2EHSuc respectively. This is due to the increase in the concentration of PPD propel more interaction between the PPD and the PBD, thus decreasing the PP. The effect of D2EHSuc on the reduction of PP is proven to be higher compared to D2EHSub and D2EHD. The high degree of reduction refers to the low molecular weight of D2EHSuc. All three diesters were derived from the same branched alcohol as 2-ethyl-1-hexanol, but with different chain lengths of the dicarboxylic acid (C<sub>4</sub>, C<sub>8</sub>, and C<sub>12</sub>).

The effect of dicarboxylate esters branching on the PBD PP was also noted. By keeping the mid-chain length of the dicarboxylate esters constant, increasing the side chain branching caused a high reduction of PP. Therefore D2BOD, D2BOSub, and D2BOSuc, gave higher PP reduction than D2EHD, D2EHSub and D2EHSuc. This is due to the ethyl-based PPDs having less bulky moiety polar head groups as compared to the bulkier moiety of butyl-based PPDs. This study also reveals that among the PPDs derived from the same di-carboxylic acid, an increase in chain





**Fig. 6:** Pour point of PBD with various concentrations of D2EHSuc, D2EHSub and D2EHD.

length of the branched alcohol involved in the esterification reaction leads to better effect towards the PP reduction. Contrariwise, when the side chain branching of the alcohol is kept constant, increasing the dicarboxylic acid mid-chain length slightly effect on the PP reduction. Therefore, the slopes of all the graphs tend to be similar at high concentrations even though all PPDs have different functional groups. Blending PBD with D2BOsub has produced the lowest PP of 3°C (12 wt %). The lowest PP of 3 °C is within the range of the standard by ASTM D 6751 of -15 to 10°C. However, it is far from the desired and recommended PP of -6°C for two-stroke engine total lost lubricant as stated by the standard IS14234 and -15°C min by IS 15607 [51].

## CONCLUSIONS

Series of dicarboxylate esters (C<sub>4</sub>, C<sub>8</sub> and C<sub>12</sub>) with two types of alcohols of 2-ethyl-1-hexanol and 2-butyl-1-octanol for palm biodiesel, PBD pour point depressant, PPD were successfully synthesized. The resulting esters were produced in high yields. The effectiveness of the synthesized esters as PBD PPD was evaluated by individually blending with PBD. The dicarboxylate esters derived from the 2-butyl-1-octanol provide higher PP reduction as compared to those derived from 2-ethyl-1-hexanol. The bulky moiety of the polar group head of the esters and the nonpolar carbon chain length of the tail group have played an important role in the reduction of PBD PP. Blending PBD with D2BOsub (12 wt%) has produced the lowest PBD PP from 9.5 to 3°C. This low PP PBD is plausible to be used as an alternative green fuel in tropical countries. However, further reduction of PBD PP

up to -6 °C with other suitable PPDs or additives to make it suitable to be used in two-stroke engine in temperate countries.

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