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SYNTHESIS AND CHARACTERIZATION OF PALM OIL PENTAERYTHRITOL ESTER-BASED BIOLUBRICANT FROM MALAYSIA PALM OIL

(Sintesis dan Pencirian Biopelincir Berasaskan Ester Pentaeritritol Minyak Sawit daripada Minyak Sawit Malaysia)

Nurazira Mohd Nor[1,2*], and Jumat Salimon[3]

[1] *School of Chemistry and Environment, Faculty of Applied Sciences, Universiti Teknologi MARA, Cawangan Negeri Sembilan Kampus Kuala Pilah, 72000 Kuala Pilah, Negeri Sembilan, Malaysia*
[2] *Material, Inorganic and Oleochemistry (MaterOleo) Research Group, Faculty of Applied Sciences, Universiti Teknologi MARA, Cawangan Negeri Sembilan Kampus Kuala Pilah, 72000 Kuala Pilah, Negeri Sembilan, Malaysia*
[3] *Department of Chemical Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia*

[*] *Corresponding author: nurazira@uitm.edu.my*

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Abstract

Palm oil is one of the potential renewable resources in biolubricant production. However, the direct application of palm oil as biolubricant is restricted because of its low oxidative stability. It is due to the presence of oxidation active sites β- hydrogen in a glycerol backbone structure. This oxidative drawback can be overcome by molecule structural redesign through a chemical modification process such as esterification with polyhydric alcohol. The esterification of palm oil fatty acids (POFAs) with pentaerythritol (PE) was carried out in a mole ratio of 4.5:1, 1% of sulphuric acid, reaction temperature of 165 °C and reaction time of 7.2 hours. Gas Chromatography equipped with a Flame Ionization Detector (GC-FID) was used to determine the percentage of ester composition in palm oil pentaerythritol (POPE) ester. The structure of the POPE ester was confirmed by Fourier Transformation Infra-Red (FTIR) and proton and carbon Nuclear Magnetic Resonance (^{1}H-NMR and ^{13}C-NMR) spectroscopy. Results showed that POPE ester has been successfully synthesized with 85% of yield and 97.4% composition of tetraesters. The existence of the ester functional group is evidenced by FTIR at 1740 cm^{-1}, the chemical shift of ^{1}H NMR at 2.29-2.33 ppm and ^{13}C NMR at 173.24 ppm. Physicochemical properties analysis showed that POPE ester has oxidative stability at 189 °C, pour point at 17 °C, flash point at 300 °C and 147 viscosity index which makes POPE ester suitable to be used in many industrial lubrication applications.

Keywords: Esterification, oxidative stability, palm oil fatty acid, pentaerythritol

Abstrak

Minyak sawit merupakan salah satu sumber boleh diperbaharui yang berpotensi dalam penghasilan biopelincir. Walau bagaimanapun, penggunaan minyak sawit secara terus sebagai biopelincir adalah terhad kerana kestabilan oksidatifnya yang rendah. Ini disebabkan oleh kehadiran tapak aktif pengoksidaan β- hidrogen dalam struktur tulang belakang gliserol. Kelemahan oksidatif ini boleh diatasi dengan reka bentuk semula struktur molekul melalui proses pengubahsuaian kimia seperti pengesteran dengan alkohol polihidrik. Pengesteran asid lemak minyak sawit (POFAs) dengan pentaeritritol (PE) dijalankan dalam nisbah mol 4.5:1, 1% asid sulfurik, suhu tindak balas 165 °C dan masa tindak balas 7.2 jam. Kromatografi Gas yang dilengkapi dengan Pengesan Pengionan Nyala (GC-FID) digunakan untuk menentukan peratus komposisi ester dalam ester pentaeritritol minyak sawit (POPE). Struktur ester POPE telah disahkan oleh spektroskopi transformasi Fourier infra-merah (FTIR) dan spektroskopi resonan magnetik nukleus proton dan karbon (NMR) (^{1}H-NMR dan ^{13}C-NMR). Keputusan menunjukkan bahawa ester POPE telah berjaya disintesis dengan 85% hasil dan 97.4% komposisi tetraester. Kewujudan kumpulan berfungsi ester dibuktikan melalui FTIR pada 1740 cm^{-1}, anjakan kimia ^{1}H NMR pada 2.29-2.33 ppm dan ^{13}C NMR pada 173.24 ppm. Analisis sifat fizikokimia menunjukkan bahawa ester POPE mempunyai kestabilan oksidatif pada 189 °C, takat tuang pada 17 °C, takat kilat pada 300 °C dan indeks kelikatan 147 yang menjadikan ester POPE sesuai digunakan dalam pelbagai kegunaan pelinciran industri.

Kata kunci: Pengesteran, kestabilan oksidatif, asid lemak minyak sawit, pentaeritritol

Introduction

In recent years, the development of renewable resources-based lubricants has increased due to the increasing cost of petrochemicals and rising concern for environmental pollution [1]. Rapidly depleting crude oil reserves and crude oil production also initiated high demand for industrial biolubricants. In the European region, subsidies, tax breaks and labeling programs are triggering high demand for biolubricants, especially for hydraulic fluid applications. It transmits the power to hydraulic machinery that is mostly used in the mining, industrial, agricultural and marine sectors. In this region alone the market is expected to reach US$884.6 million by 2026 [2].

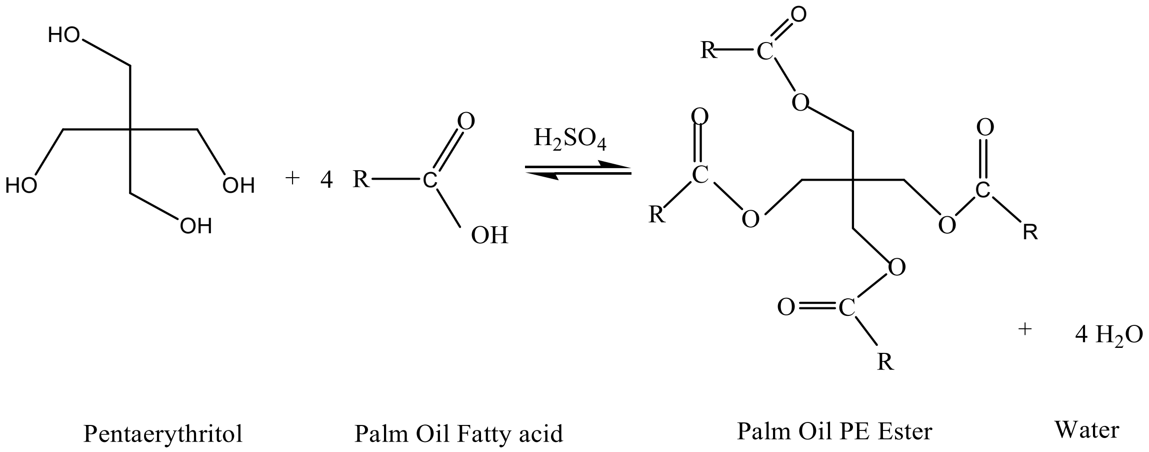
The development of biodegradable and environmentally friendly biolubricants is very much needed nowadays. The world is moving rapidly towards the use of biolubricants, especially in industrial and automotive applications. More than 1700 lubricant manufacturing industries play an important role worldwide [3]. The global biolubricants market is estimated to be worth US$1.9 billion in 2020 and is expected to reach a revised size of US$2.5 billion by 2026 with a Compound Annual Growth Rate (CAGR) of 5.2%. The top market is the U.S. market at US$360.2 million in 2021, while the Chinese market is expected to reach US$230.4 million by 2026. Japan and Canada are forecast to grow at 3.7% and 4.1% CAGR respectively. In Europe, Germany is expected to grow at about 5% CAGR while the rest of the Europe market will reach US$246.8 million by the end of 2026. The driving demand for biolubricants is due to the advances in the development of engine design and operational efficiency and stringent government regulations particularly in North America and Europe, which discourage the use of synthetic and chemical-based lubricants [4].

Plant oils are found to be the best alternative source to replace petrochemical because plant oils are biodegradable, non-toxic and cheaper compared to conventional sources of petrochemicals [5, 6]. Plant oils themselves exhibit good lubricity with high viscosity index [7]. However, plant oil cannot be used directly as a lubricant because of its low oxidative stability [7, 8, 9]. It is due to the presence of oxidation active sites β-hydrogen in the glycerol backbone structure, which will cause plant oil to become unstable at higher temperatures [10]. The β-hydrogen is easily removed from triacylglycerol molecules and it will form acid and olefin (unsaturated compounds). The resulting unsaturated compounds will undergo polymerization and will cause the formation of a precipitate that will increase the viscosity of plant oil [11]. The oxidative stability drawback that incurs in plant oil can be overcome by molecule structural redesign through chemical modifications.

Chemical modification processes such as transesterification and esterification are among important industrial processes due to their simplicity, viability, achievability and low-cost processes [4]. One modification that can be used is esterification with a polyhydric alcohol such as neopentylglycol (NPG) [12], trimethylolpropane (TMP) [13] and pentaerythritol (PE) [14], which will replace the glycerol backbone in plant oil structure. The advantage of using polyhydric alcohol is the absence of hydrogen in the beta position (β-hydrogen), which enhances the thermal and oxidative stability of the lubricant at high temperatures [15,16]. The esterification of plant oil-based fatty acids with various polyhydric alcohols has been reported to successfully achieve high yields percentage and high esters selectivity [4].

Recently, palm oil which is abundantly available all over Malaysia become one of the potential plant oils that can be used as biolubricant base stock [17,18]. There are many studies reported on the production of biolubricant from palm oil and polyhydric alcohols. The production of biolubricant via transesterification of palm oil methyl ester (POME) with trimethylolpropane (TMP) was reported by Yunus et al. [19]. TMP is polyhydric alcohol that has three hydroxyl groups. The transesterification of POME and TMP that was carried out in a mole ratio of 3.9:1, a reaction temperature of 120 °C, a reaction time of 1 hour, 20 mbar of pressure, and 0.8% sodium methoxide catalyst has successfully produced 98% palm oil TMP triesters. Sulaiman et al. [20] also reported the optimization of the transesterification of POME and TMP. The optimum conditions were obtained at 3.8:1 mole ratio, a reaction temperature of 120 °C, a reaction time of 2 hours, 20 mbar of pressure and 0.9% sodium methoxide catalyst. At these optimum conditions, 86% of palm oil TMP triesters were successfully synthesized. In 2013, Salih et al. [21] reported the esterification between palm kernel oil fatty acids (PKOFAs) with TMP in a mole ratio of 4:1, reaction temperature of 150 °C, a reaction time of 5 hours and 1% sulphuric acid as catalyst. The results showed that a 68% yield of TMP ester was successfully synthesized with good lubrication properties such as a high flash point (over 300 °C), a pour point at 3 °C and a high viscosity index (157).

Other than TMP, there was also a study using pentaerythritol (PE) in the production of biolubricant. PE is polyhydric alcohol with four hydroxyl groups. In 2014, Aziz et al. [22] reported the production of biolubricant through transesterification between POME and PE in a mole ratio of 4.5:1, a reaction temperature of 158 °C, a reaction time of 1 hour and 1.19% sodium methoxide catalyst. The transesterification has produced a 40% yield of PE ester which has a flash point at 302 °C and 12.7 cSt viscosity at 100 °C. However, there is a lack of study reported on the esterification of palm oil fatty acids (POFAs) and PE. Hence, in this study, the esterification of POFAs with PE to produce palm oil pentaerythritol (POPE) ester as shown in Figure 1 is reported. Fatty acid composition of POFAs and POPE ester, as well as ester composition in POPE ester, will be analyzed by GC-FID, while the structure of POPE ester will be confirmed by FTIR and NMR spectroscopy. The physicochemical properties of POPE ester were examined by using several tests such as oxidative stability, pour point, flash point and viscosity index.



R= Mixed palm oil fatty acids (myristic, stearic, palmitic, oleic and linoleic acid)

Figure 1. Esterification of palm oil fatty acids (POFAs) with pentaerythritol (PE)

Materials and Methods

Materials

Palm oil was obtained from Jomalina Refinery, Teluk Panglima Garang, Selangor, Malaysia. Pentaerythritol was purchased from Sigma Aldrich. Sulphuric acid, toluene, ethyl acetate, sodium bicarbonate, sodium chloride, sodium sulphate, hydrochloric acid, n-hexane, potassium hydroxide and ethanol were purchased from Systerm.

Hydrolysis of palm oil

The hydrolysis process involves two stages which are saponification and acidification. In saponification, 50 grams of palm oil was mixed with 300 mL of alkaline ethanol in a 500 mL three-neck round bottom flask equipped with a mechanical stirrer, thermometer and reflux condenser and heated at 60 °C for 2 hours [23]. After the reaction was complete, the mixture underwent an acidification process in which 150 mL of 6N hydrochloric acid was added to neutralize the alkaline solution. The washing was continued using 200 mL of distilled water and 100 mL of hexane as solvent. The product, palm oil fatty acids (POFAs), was kept overnight by adding anhydrous sodium sulphate. The product was filtered by Whatmann No. 1 filter paper and the solvent used was isolated by a rotary evaporator at 70 °C. The product (POFAs) was analyzed using Gas Chromatography equipped with a Flame Ionization Detector (GC-FID).

Esterification of palm oil fatty acids and pentaerythritol

The esterification process was conducted by mixing palm oil fatty acids (POFAs) and pentaerythritol (PE) in a mole ratio of 4.5:1 in a 500 mL three-neck round bottom flask, equipped with a thermometer and Dean-Stark apparatus. 1% sulphuric acid and 100 mL of toluene were added to the mixture. The mixture was heated at 165 °C for 7.2 hours with continuous stirring. The product, palm oil pentaerythritol (POPE) ester, was neutralized with 150 mL of sodium hydrogen carbonate solution (5%), 150 mL of sodium chloride solution (5%) and 100 mL of ethyl acetate. The product was kept overnight by adding anhydrous sodium sulphate. The product was filtered by Whatmann No. 1 filter paper and the solvent used was isolated by a rotary evaporator at 70 °C. The POPE ester was analyzed using GC-FID, Fourier Transformation Infra-Red (FTIR) and proton and carbon Nuclear Magnetic Resonance (^{1}H-NMR and ^{13}C-NMR).

Characterization of palm oil, palm oil fatty acids (POFAs) and palm oil pentaerythritol (POPE) ester

The fatty acid composition of palm oil, POFAs and POPE ester was analyzed using GC-FID (column BPX-70). Fatty acid methyl esters (FAMEs) were prepared using two methods: base-catalyzed for palm oil and POPE ester and acid-catalyzed for POFAs. For base-catalyzed, FAME was prepared by blending 0.1 mL of oil sample with 1 mL of hexane. 1 mL of sodium methoxide solution (1.55 grams of sodium hydroxide and 50 mL of methanol) was added to the oil solution and the solution was stirred vigorously using a Vortex stirrer for 10 seconds. The solution was allowed to stand for 10 minutes to separate the clear solution of FAME from the cloudy aqueous layer. The upper FAME layer was slowly collected and injected into GC for analysis. For acid-catalyzed, 1 gram of POFAs was weighed into a 250 mL three-neck round bottom flask equipped with a mechanical stirrer, a thermometer and a reflux condenser. 3.75 mL of methanol was added with 0.75 mL of reagent mixture (5 mL of methanol and 1.25 mL of concentrated hydrochloric acid (36.5%)), followed by 0.75 mL of toluene. The mixture was heated at 65 °C for 1.5 hours. The mixture was then transferred into a separation funnel. 7.5 mL of hexane and 5 mL of distilled water were added to the mixture. The mixture was allowed to stand to separate two layers. The upper layer was slowly collected and dried using anhydrous sodium sulphate overnight. The sample was filtered and injected into GC for analysis.

The percentage of ester composition in POPE ester was determined using GC-FID (column DB-5HT). The sample was prepared by mixing 0.3 µL of POPE ester with 1mL of ethyl acetate. Subsequently, the structure of the POPE ester was confirmed using Fourier Transformation Infra-Red (FTIR) and proton and carbon Nuclear Magnetic Resonance (^{1}H-NMR and ^{13}C-NMR) spectroscopy. FTIR spectra were recorded on Perkin Elmer Infrared Spectrophotometer in the range of 500-4000cm^{-1}. ^{1}H and ^{13}C NMR were recorded on JEOL-

ECP 400 spectrometer (400 MHz ^{1}H/100.61 MHz ^{13}C) using $CDCl_3$ as a solvent.

Physicochemical properties tests of palm oil pentaerythritol (POPE) ester

The American Society for Testing Materials (ASTM) standards such as ASTM D-6186, ASTM D-5853, ASTM D-92 and ASTM D-2270 were used to measure oxidative stability, pour point, flash point and viscosity index [24]. The oxidative stability test was conducted using Differential Scanning Calorimetry (DSC). 1.5 mg of POPE ester was placed into an aluminum pan with a pinhole cover to allow interaction between the ester product and oxygen gas which acts as a reaction gas. Then, the aluminum pan was put into DSC and heated for 20 minutes up to temperatures of 250 °C by using nitrogen gas. The onset temperature was recorded to determine oxidative stability.

In the pour point test, the POPE ester was filled into a U-shaped glass tube until it reached a height of 4 cm. The thermometer was placed at one end of the U-shaped tube and both ends of the U-shaped tube were covered with parafilm. The U-shaped tube containing the POPE ester was placed in a refrigerator (minimum temperature -80 °C) for 24 hours to ensure that the POPE ester froze completely. After being left overnight, the U tube was removed and flipped upside down. The lowest temperature at which movement of the POPE ester was observed was recorded as the pour point.

For flash point testing, 2 mL of the POPE ester was placed in a crucible and heated on a heating plate. A thermometer with a maximum reading temperature of 360 °C was placed on the POPE ester to measure the temperature. The temperature was rapidly increased at first and then at a slow constant rate as the flash point approached. The lowest temperature at which the vapors above the surface of the liquid ignited was taken as the flash point.

For the viscosity index test, the Rheometer Anton Paar (Physica MCR 301 model) was used to measure the viscosity and viscosity index of the POPE ester. The diameter used for the samples was 0.051 mm. POPE ester was tested at 40 °C and 100 °C. The POPE ester's viscosity index was calculated based on the formula below:

$$\text{Viscosity index} = (L-U)/(L-H) \times 100$$

Where: U= oil's kinematic viscosity at 40 °C, L and H = values based on the oil's kinematic viscosity at 100 °C.

Results and Discussion

Palm oil (PO) is golden yellow and exists in a semi-solid form at room temperature. The liquid fraction contains unsaturated triacylglycerol (TAG) whereas the solid fraction contains more saturated TAG. TAG and fatty acid composition analyses were performed to determine their main composition in palm oil. Table 1 shows that the main TAG in palm oil is POP (39.89%), followed by POO (26.69%), PLP (7.43%), PLO (7.34%) and other TAGs. POP and POO show higher percentages because palmitic acid and oleic acid are the main fatty acid in palm oil. It is evidenced by the fatty acid composition shown in Table 2. The main fatty acid composition of palm oil is oleic acid with 44.8%, followed by palmitic acid (41.9%), linoleic acid (9.1%), stearic acid (3.6%) and myristic acid (0.6%).

The hydrolysis process was carried out to convert triacylglycerols in palm oil into palm oil fatty acids (POFAs), which will be used in the esterification process with pentaerythritol (PE). The percentage yield of POFAs after hydrolysis is 95%. Figure 2 shows a GC-FID (column BPX-70) chromatogram of fatty acid compositions in palm oil (before hydrolysis) and POFAs (after hydrolysis). The percentage composition of each fatty acid has been simplified in Table 2. POFAs also consist of five types of fatty acids. The major fatty acid composition in POFAs is oleic acid at 43.5%, followed by palmitic acid (42.5%), linoleic acid (9.5%), stearic acid (3.7%) and myristic acid (0.8%). The fatty acid composition of palm oil and POFAs is close to the value of the fatty acid composition of palm oil reported by Chowdhury et al. [25].

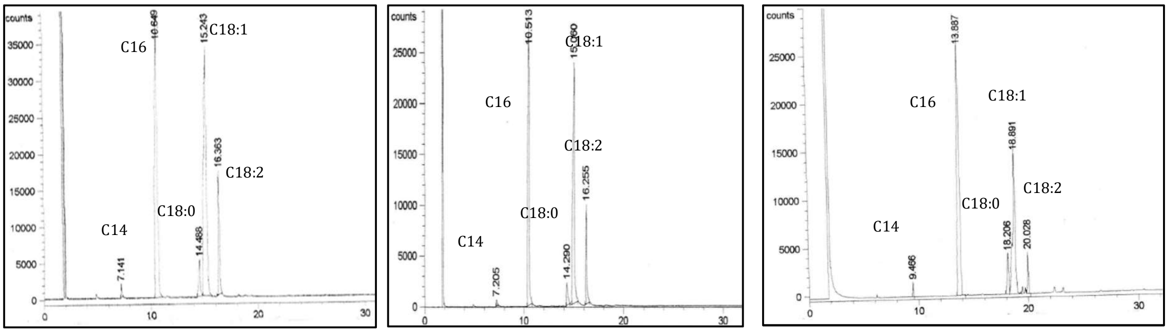
Table 1. Triacylglycerol composition (percentage) of palm oil

Triacylglycerol	Percentage (%)
Free fatty acid	7.03
Monoacylglycerol + Diacylglycerol	2.88
1-oleoyl-2,3-dilinoleoyl-glycerol (OLL)	0.04
1-palmitoyl-2,3-dilinoleoyl-glycerol (PLL)	0.68
1-miristoyl-2-linoleoyl-3-palmitoyl-glycerol (MLP)	0.07
1,3-dioleoyl-2-linoleoyl-glycerol (OLO)	0.45
1-palmitoyl-2-linoleoyl-3-oleoyl-glycerol (PLO)	7.34
1,3-dipalmitoyl-2-linoleoyl-glycerol (PLP)	7.43
1,2,3-tri-oleoyl-glycerol (OOO)	1.55
1-palmitoyl-2,3-dioleoyl-glycerol (POO)	26.69
1,3-dipalmitoyl-2-oleoyl-glycerol (POP)	39.89
1,2,3-tri-palmitoyl-glycerol (PPP)	3.11
1-sterioyl-2,3-dioleoyl-glycerol (SOO)	0.61
1-palmitoyl-2-oleoyl-3-sterioyl-glycerol (POS)	1.99
1,2-dipalmitoyl-3-sterioyl-glycerol (PPS)	0.24

Table 2. Fatty acid composition (percentage) of palm oil, POFAs and POPE ester

Fatty Acid Composition	Palm oil	POFAs	POPE Ester	Reference[25]
Myristic acid (C14)	0.6	0.8	1.0	1.2
Palmitic acid (C16)	41.9	42.5	53.5	41.8
Stearic acid (C18)	3.6	3.7	6.5	3.4
Oleic acid (C18:1)	44.8	43.5	35.1	41.9
Linoleic acid (C18:2)	9.1	9.5	3.9	11

The esterification process was carried out between POFAs and PE in the presence of sulphuric acid as a catalyst to produce POPE ester. The percentage yield of POPE ester was 85% and obtained in the semi-solid form at room temperature. Figure 2(c) shows the fatty acid compositions in POPE ester and it has been simplified in Table 2. The GC result showed that POPE ester contains 61% of saturated fatty acids and 39% unsaturated fatty acids. It means saturated fatty acids which have a straight-chain structure have a higher tendency to react with PE compared to the bent structure of unsaturated fatty acids due to less steric hindrance.



(a) (b) (c)

Figure 2. GC-FID (column BPX-70) chromatogram a) Palm oil; b) POFAs; c) POPE ester

POPE ester identification and characterization

The percentage of ester composition in POPE ester was determined by GC-FID (column DB-5HT) analysis as shown in Figure 3. Four types of esters will be produced from the esterification process, which are monoesters, diesters, triesters and tetraesters. In the esterification process, monoesters, diesters and triesters were formed as intermediate products towards the completion of the reaction producing POPE tetraesters. Figure 3 shows that 97.4% of tetraesters and 2.6% of triesters were produced in the POPE ester. Almost all hydroxyl groups in PE were successfully esterified with POFAs. This result was supported by the low hydroxyl value of POPE ester, which was 33.42 mgKOH/g compared to the hydroxyl value of PE, which was 1645 mgKOH/g. However, there were still hydroxyl groups that unsuccessfully reacted in this esterification. It can be seen by the presence of trace triester which has a hydroxyl group in its structure.

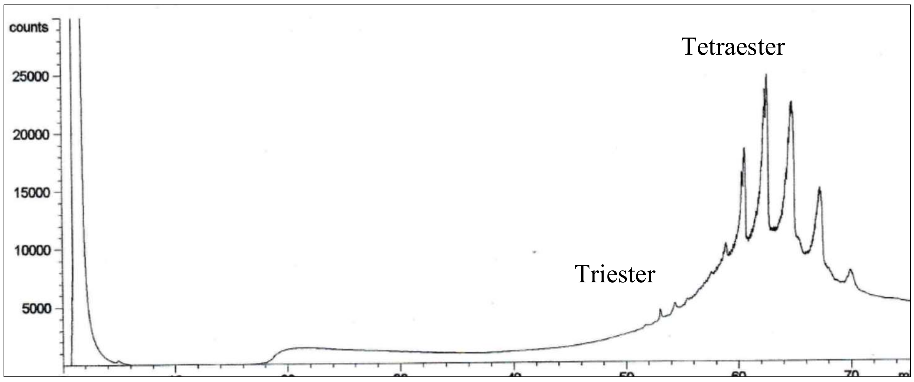


Figure 3. GC-FID (column DB-5HT) chromatogram of POPE Ester

Identification of the functional group present in the POPE ester was confirmed by FTIR analysis. The comparison between FTIR spectra of POFAs (before esterification) and POPE ester (after esterification) is shown in Figure 4. FTIR spectrum of the POPE ester shows the appearance of a C=O ester peak at 1740 cm^{-1} and the stretching of the C-O ester group exists at 1154 cm^{-1} and 1234 cm^{-1}. These values are supported by the study conducted by Nor et al. [4], which states the appearance of the stretching of the C=O ester peak is at 1738 cm^{-1} and the stretching of the C-O ester peak is at 1161 cm^{-1} and 1241 cm^{-1}. On the other hand, the FTIR spectrum of POFAs shows the stretching of the C=O group of carboxylic acid appeared at 1696 cm^{-1} and the stretching of the C-O carboxylic acid exists at 1291 cm^{-1} and 1247 cm^{-1}. According to Nor et al. [4], the stretching of the C=O group of carboxylic acid is at 1696 cm^{-1} and the stretching of C-O carboxylic acid is at 1291 cm^{-1} and 1247 cm^{-1}. The shift in wavenumbers for both spectra showed that POFAs have been successfully esterified with PE to form POPE ester.

Figure 5 shows the ^{1}H NMR spectrum of the POPE ester. In the ester structure, there are two types of protons, which are the proton of $C\mathbf{H}_2$-O and the proton of $C\mathbf{H}_2$-C=O. The proton of $C\mathbf{H}_2$-O for the POPE ester was detected at 4.05-4.11 ppm and the proton of $C\mathbf{H}_2$C=O was detected at 2.29-2.33 ppm. These values agree with the reference that exhibits a chemical shift for proton $C\mathbf{H}_2$-O at 3.5- 4.8 ppm and a chemical shift for proton $C\mathbf{H}_2$C=O at 2.1- 2.5 ppm [26]. POPE ester consists of a mixture of acyl groups such as myristate, palmitate, stearate, oleate and linoleate. The presence of unsaturated fatty acids was determined by the identification of the alkene group. In the alkene group, there are two types of protons, which are protons of double bond (-C=C-**H**) at chemical shift of 4.5-6.5 ppm and protons of methylene group, which are bound to double bond (-C=C-C-**H**) at chemical shift of 1.6-2.6 ppm [26]. Figure 5 shows the existence of both protons at chemical shifts of 5.33-5.39 ppm (-C=C-**H**) and 2.02-2.29 ppm (-C=C-C-**H**).

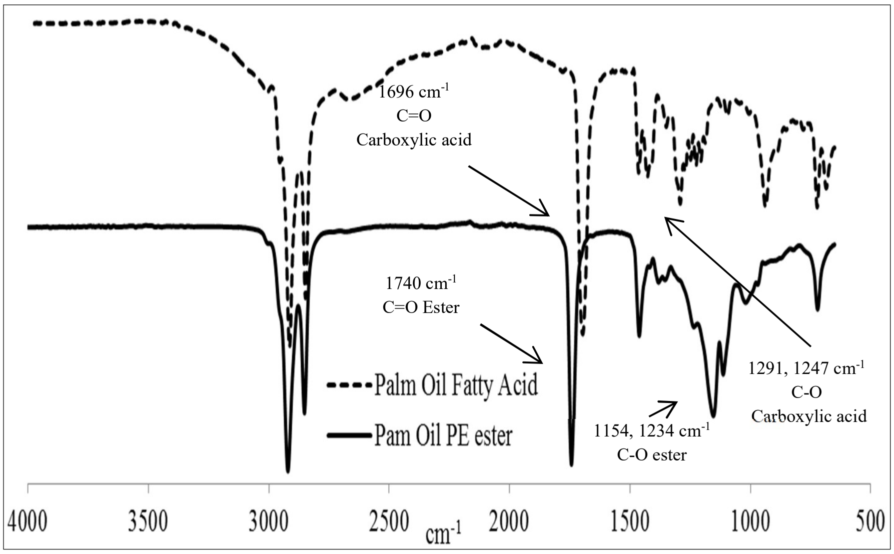


Figure 4. FTIR Spectra of POFAs and POPE ester

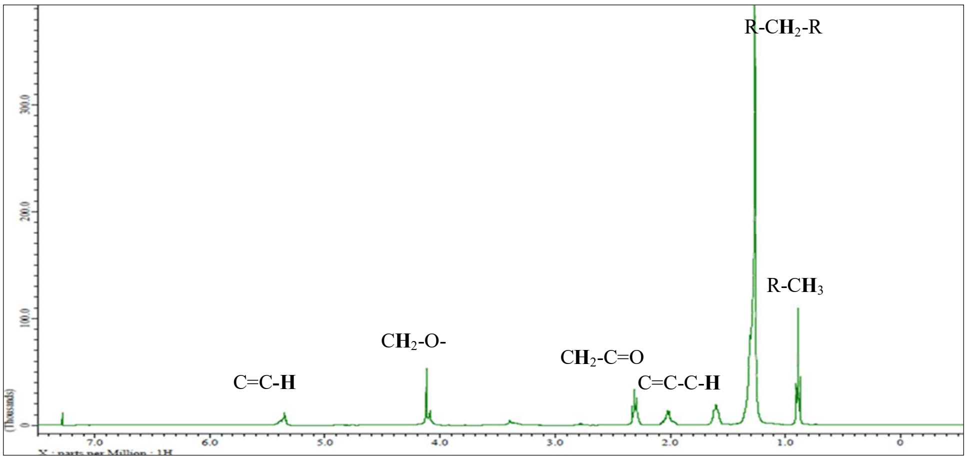


Figure 5. ^{1}H NMR Spectrum of POPE ester

Figure 6 shows the ^{13}C NMR spectrum of the POPE ester. The existence of carbon carbonyl ester (**C**=O) in the POPE ester was detected at a chemical shift of 173.24 ppm. This value is in agreement with Pavia et al. [26], who showed that the chemical shift for carbon carbonyl ester (**C**=O) was in the range of 155-185 ppm. The signal peak for carbon **C**-O, which bind fatty acid to PE was detected at chemical shift of 62.12-62.51 ppm. The presence of both carbons indicates the presence of an ester bond between POFAs and PE, which form POPE ester. The quaternary carbon for POPE ester **C**-$(CH_2OCOR)_4$ was detected at 41.78 ppm and this value is in agreement with the reference, which shows a chemical shift for quaternary carbon at 20-60 ppm [20]. The presence of unsaturated acyl groups was determined by the identification of the alkene group (**C**=C) at a chemical shift of 100-150 ppm [26]. The alkene group (**C**=C) in the POPE ester was detected at a chemical shift of 127.88-130.55 ppm.

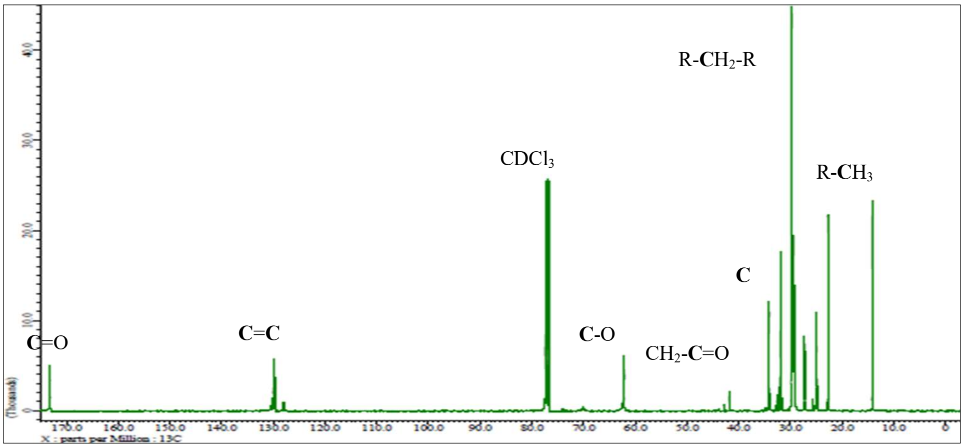


Figure 6. ^{13}C NMR Spectrum of POPE ester

Physicochemical properties of POPE Ester

POPE ester was characterized for physicochemical properties such as oxidative stability, pour point, flash point, viscosity and viscosity index. The physicochemical properties results obtained are shown in Table 3. The ability of a substance to resist oxidative degradation is an important property of biolubricant. Oxidative stability is determined by the onset temperature (OT) using Differential Scanning Calorimetry (DSC). OT is the temperature at which the occurrence of a sharp increase in the rate of oxidation of the sample. A higher onset temperature indicates that the lubricant has high oxidation stability [9]. In this study, POPE ester possesses good oxidative stability with a higher onset temperature of 189 °C compared to palm oil (181°C) due to its high percentage of saturated fatty acid (61%). Reduction of unsaturated fatty acid will reduce oxidation active site; thus, it will make POPE ester more stable at high temperatures.

The ability of a substance to remain liquid at low temperatures is an important attribute for several industrial materials, such as biolubricants, surfactants and fuels [27]. The pour point is a good indicator of its low-temperature fluidity. POPE ester has a higher pour point (17 °C) compared to palm oil (7 °C) due to the high saturated fatty acids content. High saturated fatty acids content has caused lubricant tends to form macro crystalline structures through uniform precipitation at low temperatures.

The efficiency of biolubricant in reducing friction and wear is greatly influenced by its viscosity. The least viscous biolubricant, which still forces the two moving surfaces apart is desired. If the biolubricant is too viscous, it will require a large amount of energy to move and if is too thin, the surfaces will rub and friction will be increased [9]. The viscosity of the POPE ester is in the medium range which is 60.18 cSt at 40 °C and decreased to 11.38 cS at 100 °C. It shows the viscosity of biolubricant decreases as temperature increases. The viscosity index highlights how the viscosity of biolubricant changes with variations in temperature [9]. POPE ester has a higher viscosity index which is 147 compared to palm oil (130). It shows the viscosity of the POPE ester is less affected by temperature changes and does not drastically change when the temperature varies. This is a good indicator and it is suitable for use in a large temperature range.

Flash point is often used as a descriptive characteristic of fuel oil and it is also used to describe oils that are not used as fuels such as a lubricant. The oils with a flash point that is less than 43 °C are flammable, while those having a flash point above this temperature are combustible. POPE ester showed a higher flash point at 300 °C compared to palm oil (240 °C) due to the high molecular weight of the ester and the big branched molecular structure that requires more energy to burn. A high flash point value is important to ensure that the biolubricant is not burned in the engine during its operation. Biolubricant which has a low flash point value is considered to have been contaminated by volatile and usually requires precautions and special care when handling this biolubricant [9].

Table 3 also shows a comparison of lubrication properties between the biolubricant base stock produced (POPE ester) with commercial lubricants in the market. The selected commercial lubricants are ISO VG 100 grade lubricants, namely Denicol Compressor Oil (100A) [28] and SubsTech Hydraulic Oil (100B) [29]. Based on the comparison made, the POPE ester has a higher flash point and a higher viscosity index compared to 100A and 100B lubricants.

Table 3. Physicochemical properties of RBD palm oil and POPE ester

Physicochemical Properties	**Palm Oil**	**POPE Ester**	**100A**[a]	**100B**[b]
Oxidative stability (°C)	181	189	n/a	n/a
Pour point (°C)	7	17	-19	-27
Flash point (°C)	240	300	276	254
Kinematic viscosity at 40°C	56.97	57.47	96	96.7
Kinematic viscosity at 100°C	9.24	10.87	10.9	11
Viscosity index (VI)	130	147	97	100
ISO viscosity grade	46	46	100	100

a: 100A: Denicol Compressor Oil ISO VG 100 [22], b: SubsTech Hydraulic Oil ISO 100 [23].

Conclusion

POPE ester has been successfully synthesized from palm oil fatty acids and pentaerythritol with 85% of yield and 97.4% of tetraesters compositions. POPE ester showed good lubrication properties such as having higher oxidative stability, higher flash point and higher viscosity index compared to palm oil. The removal of β-hydrogen in palm oil and replacing pentaerythritol in POPE ester has successfully increased the lubricity properties. This makes POPE ester suitable to be used as biolubricant.

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References

1. Hoang, T. T. K. and Kim, Il. (2015). Epoxidation and ring-opening of palm oil to produce high functionality polyols. *Australian Journal of Basic and Applied Sciences*, 9(8): 89-93.
2. Global biolubricants markets report 2022-2026: Increasing focus on biodegradable, non-toxic, and eco-friendly products (2022). Markets Report 2022-2026. https://www.globenewswire.com/en/news-release/2022/04/06/2417401/28124/en/Global-Biolubricants-Markets-Report-2022-2026-Increasing-Focus-on-Biodegradable-Non-toxic-and-Eco-Friendly-Products.html. [Accessed online 1 June 2022].
3. Kurre, S. K. and Yadav, J. (2023). A review on bio-based feedstock, synthesis, and chemical modification to enhance tribological properties of biolubricants. *Industrial Crops and Products*, 193: 116122.
4. Nor, N. M., Salih, N. and Salimon, J. (2022). Optimization and lubrication properties of Malaysia crude palm oil fatty acids based neopentyl glycol diester green biolubricant. *Renewable Energy*, 200: 942-956.
5. Cerretani, L., Bendini, A., Estrada, M. T. R., Vittadini, E. and Chiavaro, E. (2009). Microwave heating of different commercial categories of olive oil: Part I. Effect on chemical oxidative stability indices and phenolic compounds. *Food Chemistry*, 115:1381-1388.
6. Salimon, J. and Salih, N. (2009). Oleic acid diesters: Synthesis, characterization and low temperature properties. *European Journal of Scientific Research*, 32(2): 216-222.

7. Nirmal, V. P. and Dineshbabu, D. (2015). Performance and emission of *Pongamia pinnata* oil as a lubricant in diesel engine. *International Journal of Innovative Research in Science, Engineering and Technology*, 4(2): 435-441.
8. Masood, H., Yunus, R., Choong, T. S. Y., Rashid, U. and Yap, Y. H. T. (2012). Synthesis and characterization of calcium methoxide as heterogeneous catalyst for trimethylolpropane esters conversion reaction. *Applied Catalyst A: General*, 425-426:184-290.
9. Salimon, J., Salih, N. and Yousif, E. (2011). Chemically modified biolubricant basestocks from epoxidized oleic acid: improved low temperature properties and oxidative stability. *Journal of Saudi Chemical Society*, 15:195-201.
10. Resul, M. F. M. G., Ghazi, T. I. M. and Idris, A. (2012). Kinetic study of *Jatropha* biolubricant from transesterification of *Jatropha curcas* oil with trimethylolpropone: Effect of temperature. *Industrial Crops and Products*, 38: 87-92.
11. Fox, N. J. and Stachowiak, G. W. (2007). Vegetable oil-based lubricants-a review of oxidation. *Journal of Tribology International*, 40:1035-1046.
12. Arbain, N. H., Salimon, J., Salih, N. and Ahmed, W. A. (2022). Optimization of epoxidation of Malaysian *Jatropha curcas* oil-based trimethylolpropane ester biolubricant. *Applied Science and Engineering Progress*, 15 (3): 5552.
13. Salih, N. and Salimon, J. (2021). A review on eco-friendly green biolubricants from renewable and sustainable plant oil sources. *Biointerface Research in Applied Chemistry,* 11(5): 13303-13327.
14. Salih, N. and Salimon, J. (2022). A review on new trends, challenges and prospects of ecofriendly friendly green food-grade biolubricants. *Biointerface Research in Applied Chemistry*, 12(1):1185-1207.
15. Leung, D. Y. C, Wu, X. and Leung, M. K. M. (2010). A review of biodiesel production using catalyzed transesterification. *Applied Energy*, 87: 1083-1095.
16. Sripada, P. K., Sharma, R. V. and Dalai, A. K. (2013). Comparative study of tribological properties of trimethylolpropane-based biolubricant derived from methyl oleate and canola biodiesel. *Industrial Crops and Products*, 50: 95-103.
17. Nor, N. M., Derawi, D., and Salimon, J. (2017). Chemical modification of epoxidized palm oil for biolubricant application. *Malaysian Journal of Analytical Sciences*, 21(6): 1423-1431.
18. Nor, N. M., Derawi, D., and Salimon, J. (2018). The optimization of RBD palm oil epoxidation process using D-optimal design. *Sains Malaysiana*, 47(7):1359-1367.
19. Yunus, R., FakhrulRazi, T. L., OoiI, S. E., Iyuke, and Idris. A. (2003). Development of optimum synthesis method for transesterification of palm oil methyl esters and trimethylolpropane to environmentally acceptable palm oil-based lubricants. *Journal of Oil Palm Research*, 15: 35-41.
20. Sulaiman, S. Z., Chuah, A. L. and Fakhru`I-Razi, A. (2007). Batch production of trimetylolpropane ester from palm oil as lubricant base stock. *Journal of Applied Sciences*, 7: 2002-2005.
21. Salih, N., Salimon, J. and Jantan, F. N. (2013). Synthesis and characterization of palm kernel oil based trimethylolpropane ester. *Asian Journal of Chemistry*, 25(17): 9751-9754.
22. Aziz, N. A. M., Yunus, R., Rashid, U. and Syam, A. M. (2014). Application of response surface methodology (RSM) for optimizing the palm-based pentaerythritol ester synthesis. *Industrial Crops and Products*, 62: 305-312.
23. Nor, N. M., Derawi, D., and Salimon, J. (2019). Esterification and evaluation of palm oil as biolubricant base stock. *Malaysian Journal of Chemistry*, 21(2): 28-35.
24. Nadkarni, R.A. (2007). Guide to ASTM test methods for the analysis of petroleum products and lubricants. ASTM International, West Conshohocken.
25. Chowdhury, K., Banu, L. A., Khan, S. and Latif, A. (2007). Studies on the fatty acid composition of edible oil. *Bangladesh Journal of Scientific and Industrial Research*, 42(3): 311-316.
26. Pavia, D. L., Lampman, G. M. and Kriz, G. S. (2010). Introduction to spectroscopy. 4th edition. United States: Thomson Learcning, Inc.

27. Salimon, J. and Salih, N. (2010). Modification of epoxidized ricinoleic acid for biolubricant base oil with improved flash and pour points. *Asian Journal of Chemistry*, 22(7): 5468-5476.
28. Denicol Motor Oils (2020). Denicol compressor oil. https://pdf4pro.com/view/compressor-oil-iso-vg-32-46-68-100-150-denicol-5786bc.html. [Accessed online 25 December 2020].
29. SubsTech: Substances and Technologies (2012). SubsTech hydraulic oil. http://www.substech.com/dokuwiki/doku.php?id=hydraulic_oil_iso_100. [Accessed online 25 December 2020].