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SYNTHESIS AND CHARACTERIZATION OF NEOPENTYLGLYCOL ESTER AS BIOLUBRICANT BASE STOCK FROM PALM OIL FATTY ACIDS

(Sintesis dan Pencirian Ester Neopentilglikol Sebagai Stok Asas Biopelincir daripada Asid Lemak Minyak Sawit)

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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 a biolubricant base stock is restricted due to some performance limitations such as low oxidative stability. It is due to the presence of oxidation active site 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 neopentylglycol (NPG) was carried out in a mole ratio of 2:1, 1% of sulphuric acid, reaction temperature of 145 °C and reaction time of 4.56 hours. Gas Chromatography equipped with a Flame Ionization Detector (GC-FID) was used to determine the ester composition in Neopentylglycol Diester (NPGDE). The structure of NPGDE was confirmed by Fourier Transformation Infra-Red (FTIR), proton and carbon Nuclear Magnetic Resonance (^{1}H-NMR and ^{13}C-NMR) spectroscopy. Results showed that the percentage yield of NPGDE was 90% and NPGDE existed in liquid form at room temperature. NPGDE was successfully synthesised with 100% composition of diesters. The existence of the ester functional group is evidenced by FTIR at 1738 cm^{-1}, the chemical shift of ^{1}H NMR at 2.29-2.33 ppm and ^{13}C NMR at 173.71 ppm. Physicochemical properties analysis showed that NPGDE has oxidative stability at 184 °C, pour point at 10 °C, flash point at 235 °C and 160-viscosity index which makes NPGDE plausible to be used in lubrication applications.

Keywords: esterification, neopentylglycol, oxidative stability, palm oil fatty acids

Abstrak

Minyak sawit merupakan salah satu sumber boleh diperbaharui yang berpotensi untuk digunakan dalam penghasilan biopelincir. Walau bagaimanapun, penggunaan minyak sawit secara terus sebagai stok asas biopelincir adalah terhad disebabkan oleh had prestasi seperti kestabilan oksidatif yang rendah. Ini disebabkan oleh kehadiran tapak aktif pengoksidaan β-hidrogen dalam struktur tulang belakang gliserol. Kelemahan oksidatif ini boleh diatasi dengan melakukan ubahsuai struktur molekul melalui proses pengubahsuaian kimia seperti pengesteran dengan alkohol polihidrik. Pengesteran asid lemak minyak sawit (POFAs) dengan neopentilglikol (NPG) telah dijalankan pada nisbah mol 2:1, 1% asid sulfurik, suhu tindak balas 145 °C dan masa tindak balas 4.56 jam. Kromatografi gas dengan pengesan nyala pengionan (GC-FID) digunakan untuk menentukan komposisi ester dalam Diester Neopentilglikol (NPGDE). Struktur NPGDE disahkan dengan menggunakan spektroskopi infra-merah transformasi Fourier (FTIR), resonans magnetik nuklear proton dan karbon (^{1}H-NMR dan ^{13}C-NMR). Keputusan menunjukkan bahawa peratusan hasil NPGDE ialah 90% dan NPGDE wujud dalam bentuk cecair pada suhu bilik. NPGDE telah berjaya disintesis dengan 100% komposisi diester. Kehadiran kumpulan berfungsi ester dibuktikan melalui FTIR pada 1738 cm^{-1}, anjakan kimia ^{1}H NMR pada 2.29-2.33 ppm dan ^{13}C NMR pada 173.71 ppm. Analisis sifat fizikokimia menunjukkan bahawa NPGDE mempunyai kestabilan oksidatif pada 184 °C, takat tuang pada 10 °C, takat kilat pada 235 °C dan indeks kelikatan 160 yang menjadikan NPGDE sesuai untuk digunakan dalam aplikasi pelinciran.

Kata kunci: pengesteran, neopentilglikol, kestabilan oksidatif, asid lemak minyak sawit

Introduction

In the field of lubricants, there are wide ranges of lubricant base oils used which include mineral oils, synthetic oils, re-refined oils and plant oils. Among these, mineral oils are the most commonly used [1]. Mineral oil is stable, readily available and exists in a wider range of viscosities [2]. However, they pose a constant threat to ecology and vast groundwater reserves due to their inherent toxicity and non-biodegradable nature [1, 3]. The reduction of petroleum oil resources and increasing greenhouse gas emissions give a clear picture of the importance of the move towards sustainable development [4]. The use of renewable sources in the industry is vital to ensure sustainable development. These include studies on plant oils as feedstock in the manufacture of products for daily use.

Plant oils are not only renewable resources but also cheaper, biodegradable and non-toxic, unlike conventional mineral-based oils [1, 5]. As a lubricant, they also exhibit excellent lubricity and high viscosity index, which are being more closely examined as base stock for lubricants and functional fluids [6-8]. Biolubricants hold great potential for environmental conservation as an alternative lubricant. The global market size for biolubricants was USD 2.20 billion in 2019 and is projected to reach USD 2.46 billion by 2025, at a compound annual growth rate (CAGR) of 4.1% between 2020 and 2025 [9, 10]. Stringent regulations and the growing acceptance among end-users are projected to drive the biolubricants market [9, 10].

However, plant oils have some drawbacks such as poor thermal and oxidative stability which restrict their direct application as a lubricant [2, 8, 11, 12]. It is because of the existence of oxidation active sites β-hydrogen in glycerol backbone structure and double bonds in the unsaturated fatty acid structure that will make palm oil becomes easily damaged at high temperature. 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 precipitate that will increase the viscosity of plant oil [13].

Chemical modification of plant oils becomes one of the attractive ways to solve these problems by replacing glycerol with polyhydric alcohols such as neopentylglycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE) through esterification. The advantage of using polyhydric alcohol is the absence of β-hydrogen which enhances the thermal and oxidative stability of the lubricant at high temperatures [14-16]. 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.

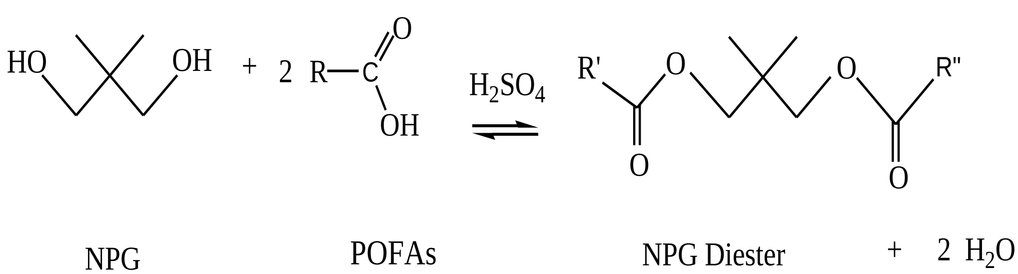
The production of biolubricant via transesterification of palm oil methyl ester (POME) with trimethylolpropane (TMP) was reported by Yunus et al. [19]. TMP is polyhydric alcohol that has three hydroxyl groups. The transesterification of POME and TMP was carried out in a mole ratio of 3.9:1, a reaction temperature of 120 °C, a reaction time of 1 hour, 20 mbar of pressure and 0.8%

of sodium methoxide catalyst has successfully produced 98% palm oil TMP triesters. Sulaiman et al. [20] also reported the optimization of transesterification of POME and TMP. The optimum conditions obtained were a 3.8:1 mole ratio, a reaction temperature of 120 °C, a reaction time of 2 hours, 20 mbar of pressure and 0.9% of sodium methoxide catalyst. At these optimum conditions, 86% of palm oil TMP triesters were successfully synthesised. In 2013, Salih et al. [21] reported the esterification between palm kernel oil fatty acids (PKOs) with TMP in a mole ratio of 4:1, a reaction temperature of 150 °C, a reaction time of 5 hours and 1% of sulphuric acid as catalyst. Results showed that a 68% yield of TMP ester was successfully synthesised with good lubrication properties such as high flash point (over 300 °C), low pour point (3 °C) and high viscosity index (157).

In 2014, Aziz et al. [22] reported the production of biolubricant through transesterification between POME and pentaerythritol (PE). PE is polyhydric alcohol with four hydroxyl groups. The transesterification process was carried out in a mole ratio of 4.5:1, reaction temperature of 158 °C, reaction time of 1 hour and 1.19% of 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.

Other than TMP and PE, there was also a study using neopentylglycol (NPG) in the production of biolubricant. NPG is a polyhydric alcohol with two hydroxyl groups. Synthesis of neopentylglycol (NPG) ester was reported by Vanitah et al. [23]. Synthesis of NPG ester was carried out via esterification of NPG and oleic acid in a mole ratio of 1:2, reaction temperature of 130 °C, reaction time of 4 hours and 2% sulphuric acid as catalyst. Results showed that an 80% yield of NPG ester was successfully synthesised with oxidative stability at 177 °C, high flash point (200 °C), low pour point (-44 °C) and high viscosity index (227).

In this study, the esterification of palm oil fatty acids (POFAs) with NPG to produce NPG Diester (NPGDE) as shown in Figure 1 is reported. Fatty acid composition of POFAs and NPGDE, as well as ester composition in NPGDE, were analysed by GC-FID, while the structure of NPGDE was confirmed by FTIR and NMR spectroscopy. Physicochemical properties of NPGDE 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 neopentylglycol

Materials and Methods

Materials

Palm oil was obtained from Jomalina Refinery, Teluk Panglima Garang, Selangor, Malaysia. Neopentylglycol 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 was conducted by mixing 50 g of palm oil with alkaline ethanol and heated at 60 °C for 2 hours [24]. Then, the mixture was washed with 150 mL of 6N hydrochloric acid, 200 mL of distilled water and 100 mL of *n*-hexane. The washing process was continued with 100 mL of hexane followed by 50 mL of distilled water until the pH became neutral. 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 rotary evaporator at 70 °C. The product (POFAs) was analysed using GC-FID.

Esterification of POFAs and NPG

The esterification process was conducted by mixing POFAs and NPG at a 2:1 molar ratio. 1% of sulphuric acid and 100 mL toluene were added to the mixture and then heated at 145 °C for 4.56 hours. The product, NPG Diester (NPGDE) was neutralised with sodium hydrogen carbonate solution, sodium chloride solution and 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 NPGDE was analysed using Gas Chromatography equipped with a Flame Ionization Detector (GC-FID), Fourier Transformation Infra-Red (FTIR), and proton and carbon Nuclear Magnetic Resonance (^{1}H-NMR and ^{13}C-NMR).

Fatty acid composition analysis

Fatty acid composition of palm oil, POFAs and NPGDE were analysed using GC-FID (column BPX-70). Fatty acid methyl esters (FAMEs) were prepared using two methods: acid-catalysed for POFAs and base-catalysed for palm oil and NPGDE. For acid-catalysed, 1 g of POFAs was weighed into a 250 mL three-neck round bottom flask equipped with a mechanical stirrer, thermometer and reflux condenser. 3.75 mL methanol was added with 0.75 mL reagent mixture (5 mL methanol and 1.25 mL 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 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. For base-catalysed, FAME was prepared by mixing 0.1 mL of the palm oil or NPGDE with 1 mL of hexane. 1 mL of sodium methoxide solution (1.55 g NaOH and 50 mL of methanol) was added to the 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 FAMEs from the cloudy aqueous layer. The upper FAMEs layer was slowly collected and injected into GC for analysis.

NPGDE analysis

Ester composition in NPGDE was determined using GC-FID (column DB-5HT). The sample was prepared by mixing 0.3 µL of NPGDE with 1mL of ethyl acetate. The structure of NPGDE was confirmed using FTIR and NMR analysis. FTIR spectra were recorded on a 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 solvent.

Physicochemical properties tests of NPGDE

The American Society for Testing Materials 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 [25]. The oxidative stability test was conducted using Differential Scanning Calorimetry (DSC). 1.5 mg of NPGDE was placed into an aluminium pan with a pinhole cover to allow interaction between ester product and oxygen gas which acted as a reaction gas. Then, the aluminium pan was put into DSC and heated for 20 minutes up to temperatures of 250 °C by using nitrogen gas. Onset temperature was recorded to determine oxidative stability.

In the pour point test, the NPGDE 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 sample was placed in the refrigerator (minimum temperature -80 °C) for 24 hours to ensure that the sample froze completely. After being left overnight, the U tube was removed and flipped upside down. The lowest temperature at which movement of the sample was observed was recorded as the pour point.

For flash point testing, 2 mL of NPGDE 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 sample to measure the sample's temperature. The temperature was rapidly increased at first and then at a slow constant rate as the flash point was approached. The lowest temperature at which the vapours 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 NPGDE. The diameter used was 0.051 mm. The viscosity of NPGDE was tested at 40 °C and 100 °C. The NPGDE viscosity index was calculated based on the formula below:

$$\text{Viscosity index} = (L-U)/(L-H)\times 100 \qquad (1)$$

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 is golden yellow and exists in the semi-solid form at room temperature. The hydrolysis process has successfully separated 95% of the fatty acids from the glycerol backbone. Figure 2 shows a GC-FID chromatogram of fatty acid compositions in palm oil (a-before hydrolysis) and POFAs (b-after hydrolysis). The percentage composition of fatty acids has been simplified in Table 1. The major fatty acids in POFAs were oleic acid with 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 both samples is approximately close to the value of the fatty acid composition of palm oil reported by Chowdhury et al. [26].

The esterification process between POFAs and NPG has successfully produced a 90% yield of NPGDE. Fatty acid compositions in NPGDE are shown in Figure 2(c) and the percentage composition of fatty acids also has been simplified in Table 1. The GC result showed that NPGDE contains 54.2% of saturated fatty acid and 45.8% unsaturated fatty acid. It means that saturated fatty acid which has a straight-chain structure has a higher tendency to react with NPG compared to the bent structure of unsaturated fatty acid due to less steric hindrance.

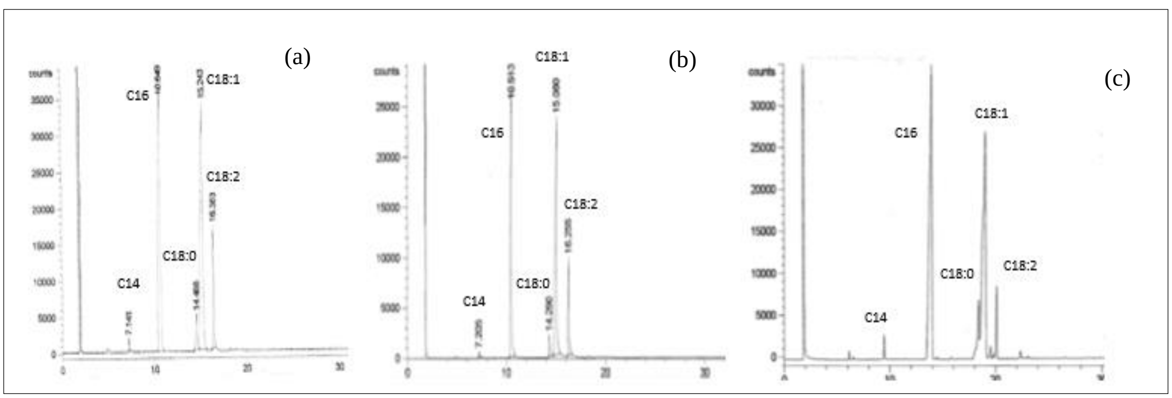


Figure 2. GC-FID chromatogram a) palm oil; b) POFAs; c) NPGDE

Table 1. Fatty acid composition (percentage) of palm oil, POFAs and NPGDE

Fatty Acid Composition	Palm Oil	POFAs	NPGDE	Reference [26]
Myristic acid (C14)	0.6	0.8	1	1.23
Palmitic acid (C16)	41.9	42.5	47	41.78
Stearic acid (C18)	3.6	3.7	6.2	3.39
Oleic acid (C18:1)	44.8	43.5	41.4	41.9
Linoleic acid (C18:2)	9.1	9.5	4.4	11.03

The percentage of ester composition was also determined by GC-FID as shown in Figure 3. In esterification, two types of esters will be produced which are monoesters and diesters. Monoesters will be formed as intermediate products towards the completion of the reaction producing NPGDE diesters. Figure 3 shows that 100% of diesters were produced in NPGDE. It means all hydroxyl groups in NPG were successfully esterified with POFAs. This result was supported by the low hydroxyl value of NPGDE which was 24.68 mgKOH/g compared to the hydroxyl value of NPG which was 1075 mgKOH/g.

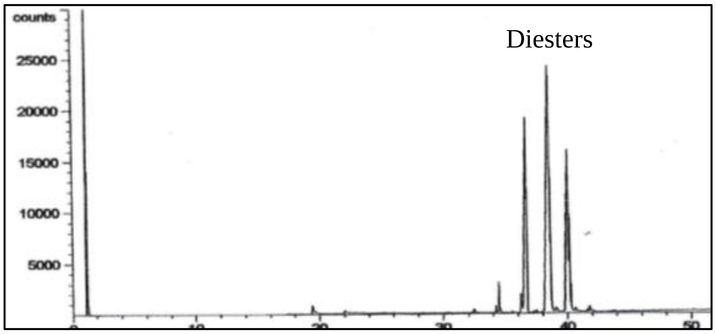


Figure 3. GC-FID chromatogram of NPGDE

FTIR analysis

The formation of ester was confirmed by FTIR analysis. The comparison between FTIR spectra of POFAs (before esterification) and NPGDE (after esterification) is shown in Figure 4. In the FTIR spectrum of NPGDE, there are appearances of the stretching of the C=O ester peak at 1738 cm^{-1} and the stretching of the C-O ester peak 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 at 1696 cm^{-1} and the stretching of C-O carboxylic acid at 1291 cm^{-1} and 1247 cm^{-1}. The shift in wavenumbers for both spectra showed that POFAs have been successfully esterified with NPG to form NPGDE. In addition, the -OH peak which initially exists in the POFAs spectrum (2400-3400 cm^{-1}) is no longer visible in the NPGDE spectrum.

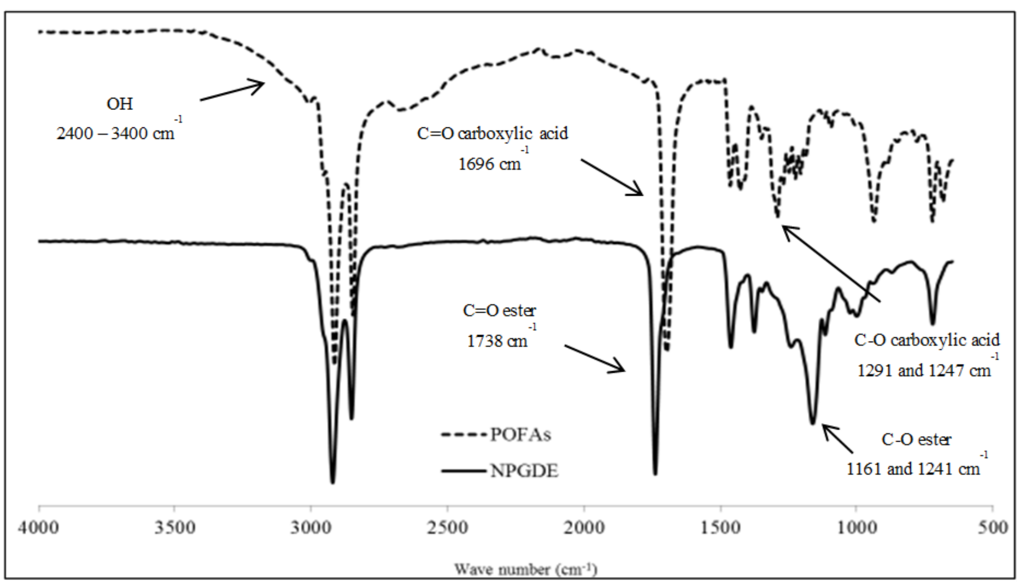


Figure 4. FTIR spectra of POFAs and NPGDE

NMR spectroscopy

NPGDE structure was also analysed using NMR spectroscopy. Figure 5 shows the ^{1}H NMR spectrum of NPGDE. In the ester structure, there are two types of protons which are the proton of C**H**$_2$-O and the proton of C**H**$_2$-C=O. The proton of C**H**$_2$-O for NPGDE was detected at 3.88 ppm and the proton of C**H**$_2$C=O was detected at 2.29-2.33 ppm. These values are in agreement with the reference which is a chemical shift for proton C**H**$_2$-O is 3.5- 4.8 ppm, while the chemical shift for proton C**H**$_2$C=O is at 2.1- 2.5 [27]. NPGDE 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 4.5-6.5 ppm and proton of methylene group which bound to double bond (-C=C-C-**H**) at chemical shift 1.6-2.6 ppm [25]. Figure 5 shows the existence of both protons at chemical shifts 5.32-5.37 ppm (-C=C-**H**) and 1.95-2.03 ppm (-C=C-C-**H**). This spectrum also shows there is no signal detected for the hydroxyl group which means all hydroxyl groups have reacted with fatty acids.

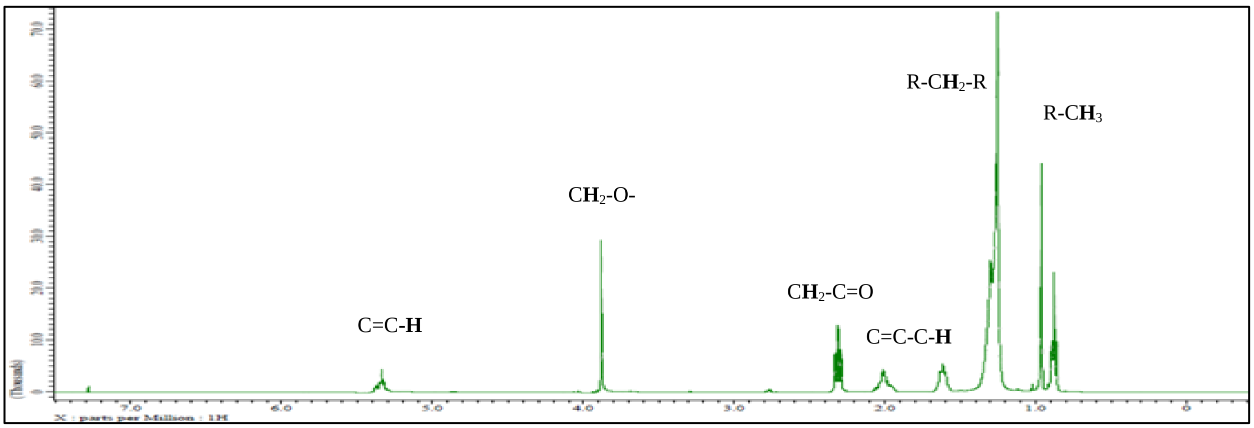


Figure 5. ^{1}H NMR spectrum of NPGDE

Figure 6 shows the ^{13}C NMR spectrum of NPGDE. The existence of ester carbon carbonyl (**C**=O) in NPGDE was detected at a chemical shift of 173.71 ppm. This value was in agreement with Pavia et al. [27] 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 bound fatty acid to NPG was detected at a chemical shift of 68.96 ppm. The presence of both carbons indicates the presence of an ester bond between POFAs and NPG which forms NPGDE. The quaternary carbon for NPGDE $(CH_3)_2$-**C**-$(CH_2OCOR)_2$ was detected at 34.59 ppm and this value was in agreement with the reference which was 20-60 ppm [27]. The alkene group (**C**=**C**) in NPGDE was detected at chemical shift 127.87-130.51ppm and this value was in agreement with the reference which was 100-150 ppm [27]. This spectrum also shows there is no signal detected for the hydroxyl group.

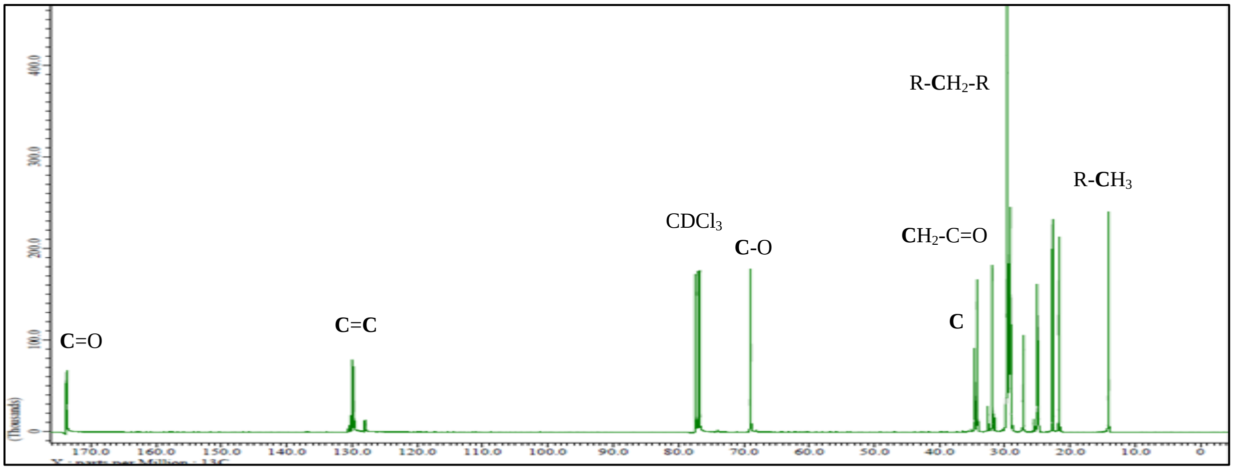


Figure 6. ^{13}C NMR spectrum of NPGDE

Physicochemical properties of NPGDE

The quality of biolubricant depends on various physicochemical properties such as oxidative stability, pour point, flash point, viscosity and viscosity index. Modification of the oil structure has influenced the properties of biolubricant. The physicochemical properties results obtained are shown in Table 2.

The ability of a substance to resist oxidative degradation is an important property of biolubricant. NPGDE was analysed using Differential Scanning Calorimetry (DSC) to measure its oxidative stability by determination of onset temperature (OT). A higher onset temperature indicates that the lubricant has high oxidation stability [2]. In this study, NPGDE possesses good oxidative stability with a high onset temperature at 184 °C. It is due to its high percentage of saturated fatty acid (54.2%). Reduction of unsaturated fatty acid will reduce oxidation active site; thus it will make NPGDE more stable in high temperatures.

Pour point is one of the important quality parameters to determine the cold flow properties of the lubricant. NPGDE has a high pour point (10 °C) due to the high saturated fatty acid content. High saturated fatty acids content has caused lubricant tends to form macrocrystalline structures through uniform precipitation at low temperatures. 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. NPGDE ester showed a high flash point at 235 °C. A high flash point value is important to ensure that the biolubricant is not burned in the engine during its operation [2].

Viscosity has also become one of the most important quality parameters for lubricating oils. The efficiency of the 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 each other and friction will increase [2]. The viscosity of NPGDE was in the medium range which was 50.07 centistokes (cSt) at 40 °C and decreased to 11.47 cSt at 100 °C. The viscosity of oils decreases as temperature increases [2]. The viscosity index highlights how the viscosity of biolubricant changes with variations in temperature [2]. NPGDE has high viscosity index which is 160 compared to palm oil (130). It shows the viscosity of NPGDE is less affected by temperature changes and does not drastically change when the temperature varies. This is a good indicator and suggests its suitability for use in a large temperature range.

Table 2 also shows a comparison of lubrication properties between the biolubricant base stock produced (NPGDE) 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, NPGDE has a higher viscosity index compared to 100A and 100B lubricants.

Table 2. Physicochemical properties of palm oil and NPGDE.

Physicochemical properties	**Palm oil**	**NPGDE**	**100A[a]**	**100B[b]**
Oxidative stability (°C)	181	184	n/a	n/a
Pour point (°C)	7	10	-19	-27
Flash point (°C)	240	235	276	254
Kinematic viscosity at 40 °C	56.97	50.07	96	96.7
Kinematic viscosity at 100 °C	9.24	11.47	10.9	11
Viscosity index (VI)	130	160	97	100
ISO viscosity grade	46	46	100	100

a: 100A: Denicol Compressor Oil ISO VG 100 [28], b: SubsTech Hydraulic Oil ISO 100 [29]

Conclusion

Neopentylglycol Diester (NPGDE) was successfully synthesised from palm oil fatty acids and neopentylglycol with 90% of yield and 100% of diesters composition. NPGDE showed good lubrication properties which are having high oxidative stability and high viscosity index compared to palm oil. The removal of β-hydrogen in palm oil and replacing polyhydric alcohol in NPGDE has successfully increased the lubricity properties. This makes NPGDE plausible to be used as a biolubricant.

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