

Lubrication properties of dodecanedioate esters-based bio-lubricant

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ABSTRACT

Interest in the synthesis of new bio-lubricants with improved lubricity properties and higher quality is increasing. This study aimed to evaluate the bio-lubrication properties of synthesized dodecanedioate esters-based bio-lubricant. Thirteen samples of dodecanedioate esters with different chemical structures were synthesized. The results showed that di-2-methylbutyl dodecanedioate (D2MBD), di-2-ethylbutyl dodecanedioate (D2EBD), and di-2-ethylhexyl dodecanedioate (D2EHD) showed good low-temperature properties with very low pour point (PP) values of -45 °C, -35 °C, and -55 °C, respectively. Di-oleyl dodecanedioate (DOID) showed a remarkable flash point (FP) value of 300 °C; however, it showed poor oxidative stability (OXS) at 177 °C. The results showed increases in flash point (FP), viscosity index (VI), and oxidative stability (OXT) with increasing carbon chain length and branching in the employed alcohol. Furthermore, friction coefficient, Newtonian and non-Newtonian properties were tested. The results showed that the tested dodecanedioate esters, which have high molecular weight had a low friction coefficient, and they were classified as non-Newtonian fluids except DOLD was classified as a Newtonian fluid. In general, based on the results, the branched dodecanedioate esters can be used as lubricant without additives.

Keywords: *dodecanedioate esters pour point; friction coefficient; Newtonian fluid; non-Newtonian fluid.*

1. INTRODUCTION

Dicarboxylic acid esters are organic, oxygen-containing compounds, which result from the reaction of an alcohol with an organic diacid. The various well-known diesters differ from one another in their alcohol or acid components. The most commonly dicarboxylic acids used are adipic acid, sebacic acid, and azelaic acid. The molecular weight of these common dicarboxylic acids is sufficient to eliminate volatility problems. Branching in the dicarboxylate esters fragments leads to excellent low-temperature performance (low pour point) [1]. Natural and synthetic esters are essential materials in the chemical industry, most commonly applied in the manufacture of lubricating oils, solvents, plasticizers, paints, food, pharmaceuticals, cosmetics, and liquid fuels [2]. Among esters, dicarboxylic acid esters are of particular interest due to their excellent chemical properties, such as low volatility, high flash point, good thermal stability, and low toxicity [3]. Long-chain carbons of esters with branching have been used in a range of commercial products such as biodiesel and other alternative diesel fuels derived from vegetable oils or animal fats [4]. Branched esters, such as isopropyl or isobutyl esters, have been applied to improve the pour point of their respective lubricants at low temperatures [5]. The pour point of a bio-lubricant is a good indicator of its low-temperature fluidity. At low temperatures, plant oils tend to form macro-crystalline structures through uniform stacking of the “bent” triacylglycerol backbone. This macro-crystalline structure restricts the free flow of the system due to the loss of kinetic energy induced by the self-stacking of molecules. Branching of the fatty acid chains may disrupt this stacking process

and result in improved low-temperature properties [6]. It may be assumed that the presence of a large branching-group at the mid-point of a fatty acid chain creates a steric barrier around the molecule, inhibiting crystallization and resulting in lower pour and cloud points [7]. The position of the branching is also critical; branching in the center decreases the pour point to a greater degree than branching at the end of the molecule. Branching decreases the internal symmetry of the molecule, thereby resulting in a decreased pour point [8]. Branched esters offer improvements to the low-temperature properties of biodiesel and conventional diesel fuel. In general, the hydrocarbon chain length is reflected in the material kinematic viscosity, viscosity index, and flashpoint. In contrast, the pour point and oxidation are affected primarily by the extent of branching [9]. The presence of an ester group indicates a degree of molecular polarity, which is reflected in the material vapor pressure, lubricity, and solubility [1].

In comparison to mineral oils, many esters have a series of technical advantages. These advantages include natural high viscosity index, enhanced low-temperature properties, low evaporation losses, and good thermal stability properties, such as excellent high-temperature performances, hydrolytic stabilities, anti-friction capabilities, anti-wear characteristics, and high flash points [10]. However, there have been no comprehensive studies on dodecanedioic acid esters, and the need for work in this area has been recognized by many researchers. As such, the aims of this study were designed to synthesis dodecanedioate esters-based lubricants and to evaluate their lubrication properties.

2. MATERIALS AND METHODS

2.1. Chemicals.

Analytical grade dodecanedioic acid (99%) was obtained from Fisher Scientific. Other chemicals and reagents such as oleyl alcohol, 2-butyl-1-octanol, 2-ethyl-1-hexanol, and 2-ethyl-1-butanol were obtained from Aldrich Chemical and were used directly without further purification.

2.2. Ester synthesis.

An esterification method within a Dean Stark distillation setup was used. A mixture of dodecanedioic acid (DA) and alcohol (mole ratio 1:2), respectively, was initially placed in a three-necked round-bottom flask. Toluene (40-50 ml) was added as a reaction medium. The reaction mixture was heated with stirring in an oil bath to the desired reaction temperature (120-130 °C). A catalytic amount of concentrated H₂SO₄ (2% of DA) was slowly introduced into the reaction vessel. The reaction was carried out for approximately 4 h. Water formed during the reaction was continuously distilled out of the system. The progress of the reaction was monitored by measuring the quantity of water collected in a dropping funnel. The reaction was stopped when the distillation of water was observed to have ceased.

2.3. Purification of dodecanedioate esters.

The crude reaction product was transferred into a round-bottom flask. The toluene was removed, and the crude product was allowed to cool to room temperature and was then transferred into a separating funnel. Diethyl ether (50 ml) was added to the funnel followed by washing three times with 10 ml of saturated sodium bicarbonate solution in order to neutralize the catalytic inorganic acid and to remove unreacted dodecanedioic acid. A saturated sodium chloride solution was added to prevent emulsion formation. The aqueous layer was decanted, and the diethyl ether layer was dried over anhydrous sodium sulfate, which was subsequently filtered off. The dried product was passed through a column packed with silica gel 60 to remove any decomposed materials formed during the reaction and to reduce the black color from the sulfuric acid. The column-treated product was rotary-evaporated to remove the solvent. Trace solvent was further removed under nitrogen gas, and excess alcohol was removed by distillation followed by further drying in a BUCHI Glass Oven B-585. The yield (%) of the diester product was determined. The final diester product was identified by IR, ¹H-NMR, and ¹³C NMR spectral analyses.

2.4. Characterization.

Fourier transform infrared spectroscopy (FTIR) was carried out according to reference [11]. The FTIR spectra of the products were recorded on the Perkin-Elmer Spectrum GX spectrophotometer in the range of 700–4000 cm⁻¹. FTIR was used to identify the functional groups present in the diester. A fragile film of the product was coated on a NaCl cell (25 mm id × 4 mm thickness) and was used for the analysis. Nuclear magnetic resonance (NMR) spectroscopy (¹H and ¹³C) was carried out according to reference [11]. Both ¹H and ¹³C NMR experiments were performed using a Joel FCP 400 MHz spectrometer in CDCl₃. A 20 mg portion of each sample was dissolved in 1 ml of CDCl₃ and introduced into an NMR tube. GC-MS analysis was conducted on an Agilent 7890A GC system and an Agilent 5975C inert XL EI/CI MSD with a Triple-Axis detector using a non-polar capillary GC column packed with Agilent HP- 5MS stationary phase (30 m

× 0.25 mm × 0.25 mm film). The sample solutions were prepared in tetrahydrofurane (THF). The GC temperature program was as follows: 1) held at 80 °C for 1 min, 2) increased at a 25 °C/min heating rate to 130 °C and held for 2 min, and 3) increased at a 20 °C/min heating rate to 320 °C and held for 23 min [12].

2.5. Pour point.

The pour point (PP) is defined as the lowest temperature at which a liquid remains pourable, i.e., still behaves as a fluid. The determination of PP is routinely used to determine the low-temperature flow properties of fluids. In this study, the PP values were measured according to ASTM D5949 [12]. Each sample was run in triplicate, and the average values of the measurements were rounded to the nearest whole degree. For a greater degree of accuracy, the pour point measurements were carried out with a resolution of 1 °C instead of the specified increment of 3 °C. Triplicate measurements were made, and the average values were reported with the standard deviation (±SD).

2.6. Flashpoint (FP).

The flashpoint (FP) is the lowest temperature at which a liquid can give off a sufficient quantity of vapor to form an ignitable mixture in the air near the surface of the liquid. In this study, the FP was determined based on the American National Standard Method using a Tag Closed Tester [13]. Each sample was run in triplicate, with the average values rounded to the nearest whole degree and reported with the standard deviation (±SD).

2.7. Viscosity Index (VI).

The viscosity index (VI) is an arbitrary measure of the change of kinematic viscosity (KV) induced by changes in temperature. This index is used by the automotive industry to characterize lubricating oils. In this study, measurements were run using an Anton Paar rheometer (Physica MCR 301 model) set at 40 and 100 °C. The KV and viscosity indices (VIs) were calculated using ASTM methods D445-97 and D 2270-93, respectively [16=13]. Triplicate measurements were performed, with the average values reported with the standard deviation (±SD).

2.8. Oxidative Stability (OXS).

Pressurized differential scanning calorimetry (PDSC) experiments were carried out using a DSC 2910 thermal analyzer from TA Instruments (Newcastle, DE). Three to five milligram of the diester sample was accurately weighed in an open aluminum pan with a pinhole lid for the interaction of the sample with the reactant gas (dry air). A film thickness of less than 1 mm was required to ensure proper oil-air interaction and to eliminate gas-diffusion limitations. Dry air (Gateway Airgas, St Louis, MO) was pressurized in the module and held at 1379 kPa. A 10 °C min⁻¹ heating rate from 50 to 350 °C was used during each experiment. The OXS temperature (°C) as the onset was calculated from the exotherm for each sample as a plot of the heat flow (W/g) versus temperature for each experiment. Each sample was run in triplicate, with the average values reported with the standard deviation (±SD).

2.9. Tribological and Rheological properties.

Tribological properties as a friction coefficient of diesters were performed according to ASTM method D4172-94 (14) and discussed based on their Stribeck curves at 40 °C and 100 °C. The sliding speed was manipulated between 10⁻¹–10³ mm/s at 40 °C and

100 °C (15). Rheological properties (Newtonian and non-Newtonian) of diesters were determined by the rheometer with cone and plate geometry (16). The cone spindle utilized was CP 25-2 and

a diameter of 0.051 mm. The shear rate was manipulated between 0–100 s⁻¹ at 25 °C.

3. RESULTS

3.1. Chemical Reaction.

As an example of the esterification reactions in this study, the procedure of the esterification reaction between dodecanedioic acid and 2-ethyl-1-hexanol to form D2EHD is shown in Figure 1. The water formed through the reaction was removed by the Dean-Stark method, using toluene as an azeotrope. After 4 h, the reaction was stopped and left for 2-3 h to stabilize and cool. Next, the reaction product was put in 50 ml of diethyl ether and loaded into a separating funnel where the mixture was washed with saturated NaHCO₃ (3 × 10 ml) followed by 10 ml of saturated NaCl until pH 7 was achieved.

The synthesized dodecanedioate esters yields (%) are illustrated in Figure 2. The results showed that the efficiency of the reaction depended on the chemical structure and the -OH position of alcohols used. The esterification rate increased with the increase in the long-chain carbon content of the alcohol. On the other hand, the yield percent decreased when secondary and branched alcohols were used. This is due to that the high steric hindrance of the chemical structure of secondary and branched alcohol leads to a low in the rate of esterification reaction and the resultant low yield percentage, as was reported by Remero et al. [17]. Based on Figure 2 DDD had the highest yield percentage of 95 %, while D2EHD had the lowest yield percentage of 83 % among all synthesized dodecanedioate esters.

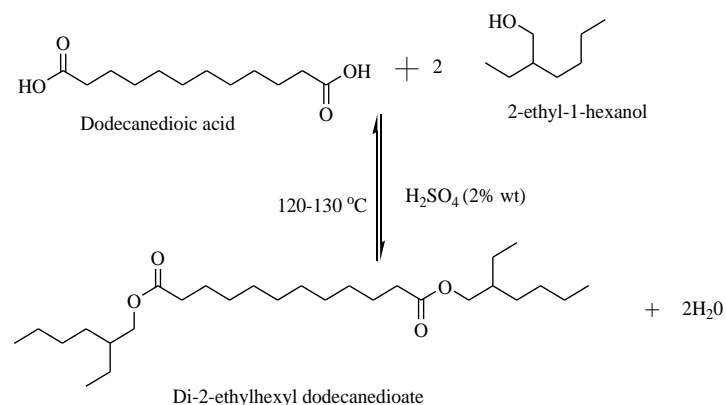


Figure 1. Esterification of dodecanedioic acid with 2-ethyl-1-hexanol to form D2EHD.

3.2. Ester characterization.

The chemical structures of all of the synthesized diesters were verified by FTIR, ¹H, and ¹³C NMR spectroscopy. The FT-IR spectra of all the synthesized diesters showed a significant carbonyl stretching vibration (C=O) indicative of the ester in the range of 1735 cm⁻¹ to 1740 cm⁻¹. Bands representing the -CH₃ groups (2850–2980 cm⁻¹), the C-O stretching vibrations (1244–1171 cm⁻¹) and the C-O-C vibrations (965–1101 cm⁻¹) while, the peaks at 3008 cm⁻¹ of C=C band were attributed to the unsaturated aliphatic carbons atoms of di-oleyl dodecanedioate ester (DOID). The absence of stretching vibrations of the hydroxyl group of alcohol (OH) at 3230–3550 cm⁻¹ and of the carbonyl of saturated acids (COOH) at 1700–1725 cm⁻¹ in the spectra suggests that the final products of diester were free of any unreacted alcohol and acid impurities [18].

The FT-IR spectra of D2EHD, D2EBD and D2MBD are given in Figure 3. The carbonyl stretching vibrations (C=O) of the three diesters appeared at 1737.26 cm⁻¹, 1734.97 cm⁻¹ and 1737.68 cm⁻¹, respectively. Bands representing the -CH₃ groups (2850–2980 cm⁻¹), the C-O stretching vibrations (1244–1171 cm⁻¹) and the C-O-C (965–1101 cm⁻¹) vibrations of synthesized diesters are clearly visible in the spectra.

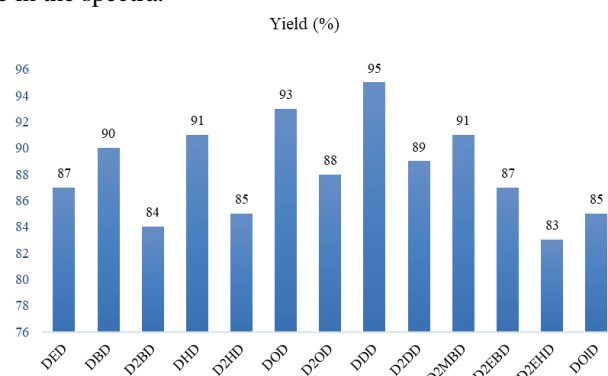


Figure 2. The yield percentage (%) of dodecanedioate esters.

Notes: DED: Diethyl dodecanedioate; DBD: Dibutyl dodecanedioate; D2BD: Di-2-butyl dodecanedioate; DHD: Dihexyl dodecanedioate; D2HD: Di-2-hexyl dodecanedioate; DOD: Dioctyl dodecanedioate; D2OD: Di-2-octyl dodecanedioate; DDD: Didecyl dodecanedioate; D2DD: Di-2-decyl dodecanedioate; D2MBD: Di-2-methyl-1-butyl dodecanedioate; D2EBD: Di-2-ethylbutyl dodecanedioate; D2EHD: Di-2-ethylhexyl dodecanedioate; DOID: Dioleyl dodecanedioate.

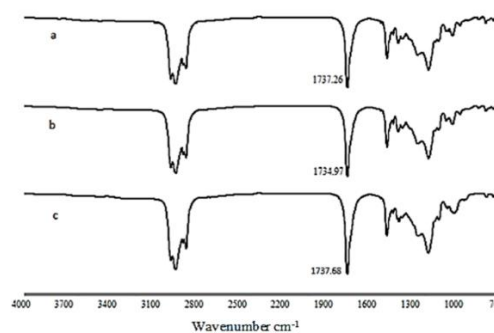


Figure 3. FT-IR spectra: (a) D2EHD, (b) D2EBD and (c) D2MBD.

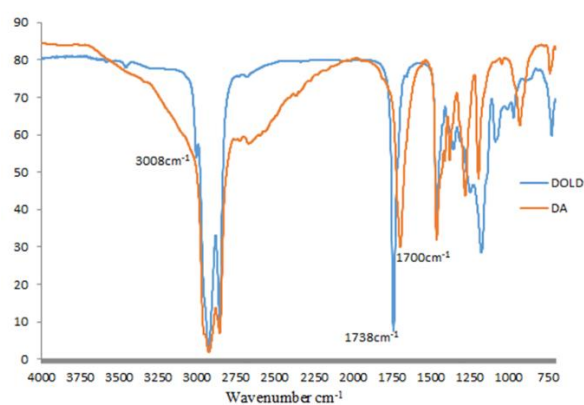


Figure 4. Comparison FTIR spectra of DOID and DA.

Figure 4 shows the FTIR spectra of dioleyl dodecanedioate (DOID) as the final product and dodecanedioic acid (DA) as raw material. The peak of the carbonyl group (C=O) of DA appeared at

1700 cm^{-1} , while it was at 1738 cm^{-1} for DOID. Thus, the DA was completely esterified under the reaction conditions. The peak at 3008 cm^{-1} of C=C band was attributed to the unsaturated carbons atoms (C=C) of DOID.

The ^1H and ^{13}C NMR are perhaps the most valuable techniques used for chemical structure analysis. The ^1H and ^{13}C NMR spectra of the synthesized dodecanedioate esters showed appropriate ^1H and ^{13}C chemical shifts. The ^1H chemical shift of the $\text{RCOO}-\text{CH}_2$ (ester) protons is clearly present between 3.83 and 3.92 ppm. The ^1H chemical shift of $-\text{COOH}$ of acid and OH of alcohol are not evident, suggesting complete esterification of the dodecanedioic acid. The ^{13}C chemical shift of the (C=O) of each ester appeared at 174 ppm. With regard to DOID, the ^1H chemical shift of the unsaturated (C=C) group appeared at 5.32 ppm, while the ^{13}C chemical shift for the unit appeared at 129.9 ppm. In general, due to the large similarity in the chemical composition of the synthesized dodecanedioate esters, therefore their spectra were similar with a slight difference in values of the ^1H and ^{13}C NMR chemical shifts.

The ^1H and ^{13}C NMR chemical shifts of DOID, D2EHD, D2EBD, and D2MBD are presented here in detail.

The ^1H chemical shifts (Figure 6) have appeared at 4.02 ppm for $\text{RCOO}-\text{CH}_2$ (e), 5.31 ppm $\text{HC}=\text{CH}$ (d), 2.25 ppm for $\text{H}_2\text{C}-\text{C}=\text{O}$ (f), 2.23 ppm for $-\text{H}_2\text{C}-\text{HC}=\text{CH}-\text{CH}_2-$ (g), 1.97 for $-\text{CH}_2-$ (c), 1.58 -1.27 ppm for $-\text{CH}_2-$ (b) and 0.85 ppm for the terminal $-\text{CH}_3$ (a).

The ^{13}C chemical shifts (Figure 7) were appeared at 173.9 ppm for (C=O) of ester, 129.8 ppm for (C=C), 64.4 ppm for O- C (e), 34.39 for $\text{H}_2\text{C}-\text{C}=\text{O}$ (f), 31.97, 29.39, 28.72, 29.83 ppm for $-\text{CH}_2-$ (b), 25.9 ppm for $-\text{CH}_2-$ (c), 25.0 ppm for $-\text{CH}_2-$ (g) and 14.15 ppm for the terminal $-\text{CH}_3$ methyl.

Di-oleyl dodecanedioate (DOID):

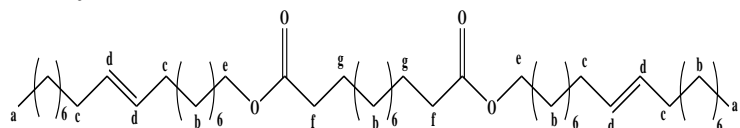


Figure 5. Chemical structure of di-oleyl dodecanedioate (DOID).

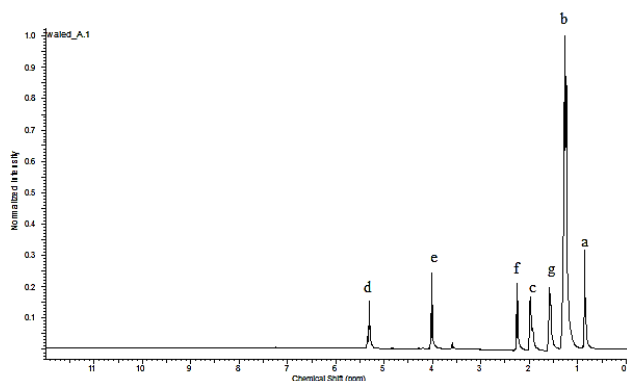


Figure 6. The ^1H NMR spectrum of DOID.

The ^1H and ^{13}C NMR spectra (Figures 9 and 10) showed peaks with appropriate chemical shifts for the proposed structures of D2EHD. The ^1H chemical shift appeared at 3.90 and 3.92 ppm for $\text{RCOO}-\text{CH}_2$ (d), 2.25 ppm for $\text{H}_2\text{C}-\text{COOR}$ (e), 2.14 ppm for a $-\text{CH}-$ branch point (c), 1.57 ppm for $-\text{CH}_2-$ (f) 1.21 - 1.34 ppm for the $-\text{CH}_2-$ methylene of the saturated alkyl chain (b) and 0.83 ppm for $-\text{CH}_3$ (a) and (a^1). The ^{13}C chemical shifts appeared at 174 ppm for

the (C=O) carbon of the ester, 66.63 ppm for (O-C) carbon of the ester (d), 34.42 ppm for $-\text{CH}_2-\text{C}=\text{O}$ (e), 38.79 ppm for the $-\text{CH}-$ branch point (c), 24.04 for $-\text{CH}_2$ (f), 30.46, 29.13, 28.96, 23.83 and 23.01 ppm for the methylene $-\text{CH}_2-$ group (b) and 14.08 ppm and 11.015 ppm for the terminal $-\text{CH}_3$ methyl at (a^1) and (a).

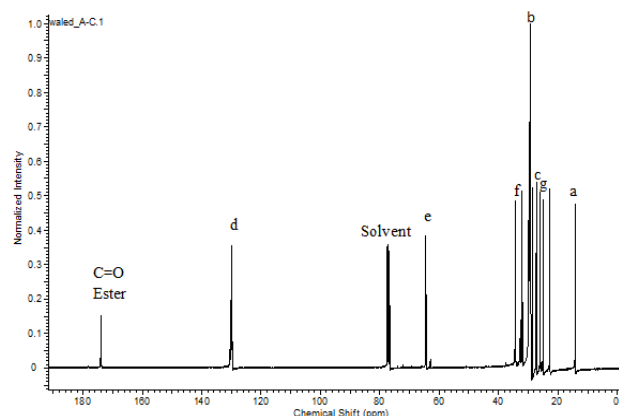


Figure 7. The ^{13}C NMR spectrum of DOID.

Di-2-ethylhexyl dodecanedioate (D2EHD):

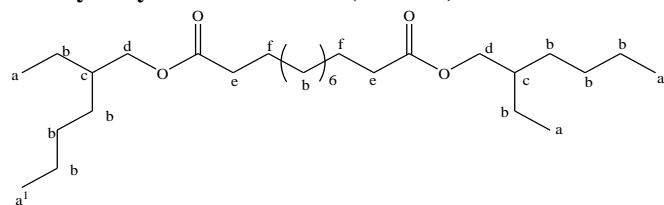


Figure 8. Chemical structure of di-2-ethylhexyl dodecanedioate (D2EHD).

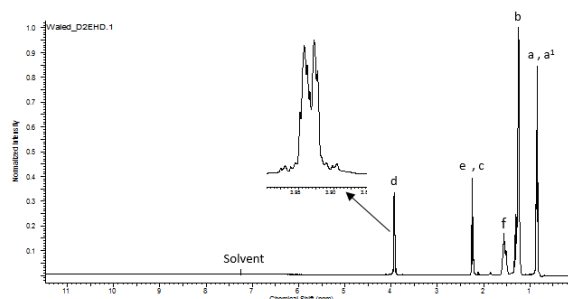


Figure 9. The ^1H NMR spectrum of D2EHD.

The ^1H chemical shifts (Figure 12) appeared at 3.92 ppm for the $\text{RCOO}-\text{CH}_2$ group (d), 2.24 ppm for $\text{H}_2\text{C}-\text{COOR}$ (e), 2.12 ppm for the $-\text{CH}-$ branch point (c), 1.57 ppm for $-\text{CH}_2-$ (f) 1.21 - 1.34 ppm for the $-\text{CH}_2-$ methylene of the saturated alkyl chain (b) and 0.83 ppm for the terminal $-\text{CH}_3$ methyl of the alkyl chain (a).

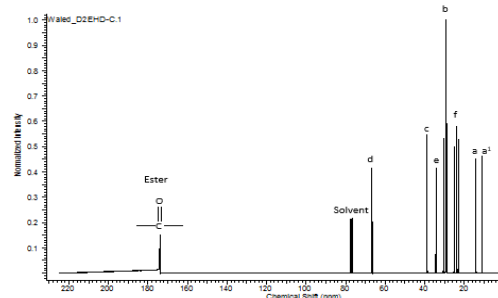


Figure 10. The ^{13}C NMR spectrum of D2EHD.

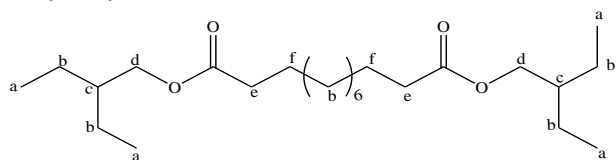
Di-2-ethylbutyl dodecanedioate (D2EBD)


Figure 11. Chemical structure of di-2-ethylbutyl dodecanedioate (D2EBD).

The ^{13}C chemical shifts (Figure 13) appeared at 174 ppm for the (C=O) of the ester, 66.54 ppm for (O- C) of the ester (d), 34.39 ppm for the $-\text{CH}_2-\text{C}=\text{O}$ carbon (e), 40.33 ppm for the $-\text{CH}-$ branch point (c), 25.03 for $-\text{CH}_2-$ (f), 29.38, 29.23, 29.15, and 23.33 ppm for the $-\text{CH}_2-$ methylene units of the saturated alkyl chain (b) and 11.31 ppm for the terminal $-\text{CH}_3$ methyl groups (a).

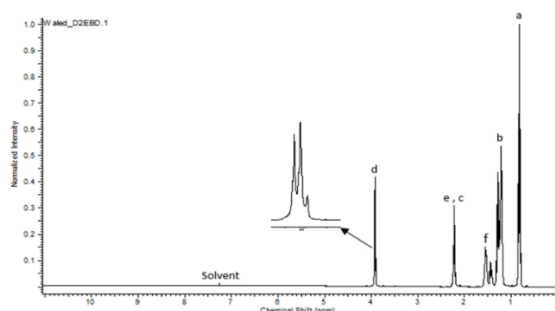


Figure 12. The ^1H NMR spectrum of D2EBD.

The ^1H chemical shifts appeared at 3.92 and 3.83 ppm for $\text{RCOO}-\text{CH}_2$ (d), 2.10 ppm for the $-\text{CH}-$ branch point (c), 2.26 ppm for the $\text{H}_2\text{C}-\text{COOR}$ protons (e), 1.55 ppm for $-\text{CH}_2-$ (f), 1.22-1.35 ppm for the methylene $-\text{CH}_2-$ units of the saturated alkyl chain (b) and 0.83 ppm for the terminal $-\text{CH}_3$ methyl groups on the alkyl chain (a and a^1). The ^{13}C chemical shifts appeared at 174 ppm for the (C=O) carbon of the ester, 69.22 ppm for (O- C) carbon of the ester (d), 34.16 ppm for the $-\text{CH}_2-\text{C}=\text{O}$ carbon (e), 34.39 ppm for the $-\text{CH}-$ branch point (c), 25.05 for $-\text{CH}_2-$ (f), 29.40, 29.25, 29.16, 29.08, 26.06, and 24.77 ppm the $-\text{CH}_2-$ methylene groups of the saturated alkyl chain (b) and 16.40 and 11.23 ppm for terminal $-\text{CH}_3$ methyl groups at (a^1) and (a), respectively.

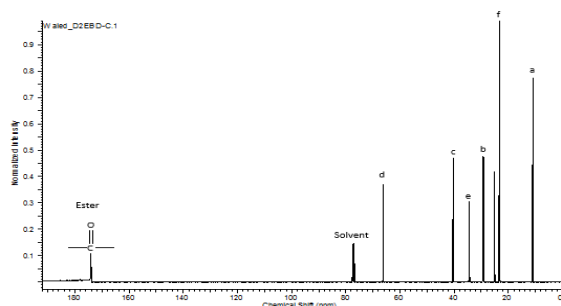


Figure 13. The ^{13}C NMR spectrum of D2EBD.

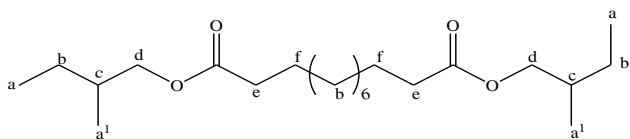
Di-2-methylbutyl dodecanedioate (D2MBD):


Figure 14. Chemical structure of di-2-methylbutyl dodecanedioate (D2MBD).

As noted, the ^1H and ^{13}C chemical shifts of D2EHD, D2EBD, and D2MBD very similar due to the similarities of the

chemical environments in their respective in their chemical structures. The only major difference was the ^1H chemical shift arising from the $\text{RCOO}-\text{CH}_2$ group of the ester (d), which appeared as a multiplet in the D2EHD and D2MBD spectra, but a duplet in the spectrum of D2EBD. The existence of the multiplet peak for (d) in D2EHD (Figure 9) was the result of splitting by the magnetic fields of the protons at (c) and (b), while the protons at (d) for D2MBD were split by the protons at (c), (b) and (a^1). The duplet peak at 3.92 ppm in the spectrum of D2EBD (Figure 12) resulted from the protons at (d) being coupled to only the proton at (c). There are characteristic differences in the ^{13}C chemical shifts, most notably for the carbon atoms at (c), the ($-\text{CH}-$) branch point for the three diesters, where the shifts were found at 38.79 ppm for D2EHD, 40.33 ppm for D2EBD and 34.39 ppm for D2MBD. These differences result from the different environments of the respective carbon atoms. They are attached to a different group of alkyl, which affect the magnetic field and shift of carbon resonances. The $-\text{CH}_3$ (terminal methyl) at (a) and (a^1) of D2EHD (Figure 8) resonated at 11.02 ppm and 14.08 ppm, respectively (Figure 10). The two peaks are a result of the different external magnetic fields required to bring them into resonance at a particular radio frequency [18]. The same was also noted for D2MBD (Figure 14), where the peaks of terminal carbon atoms at (a^1) and (a) resonated at 16.40 ppm and 11.23 ppm, respectively. The $-\text{CH}_3$ (terminal methyl) carbon (a) of D2EBD (Figure 11) gave only one peak (Figure 13) due to the chemical equivalence of the two carbon atoms, a condition known to result in resonance at a single peak [19]. GC MS analyses of tested esters (D2EHD, D2EBD and D2MBD) were performed using non-polar capillary GC columns and an electron impact ionization (EI) technique for chromatographic separation and detection, respectively. The D2EHD, D2EBD and D2MBD eluted at 19.10, 17.27 and 16.27 min, respectively, as a result of the GC method employed. The molecular masses (m/z) constituting the predominant peaks (%) were as follows: D2EHD (454.4) at 213.3 (52.5 %), 112.1 (40 %), 72.0 (56 %), 57.1 (100 %) and 56.3 (30%); D2EBD (398.34) at 213.3 (75%), 100.0 (46%), 84.1 (100 %), and 57.1 (32.5 %); D2MBD (370.6) at 213.3 (67.5 %), 100.0 (58 %), and 57.0 (100 %). The calculated of masses of D2EHD, D2EBD and D2MBD, as determined by the largest peaks, were 454.2, 396.4 and 370.4, respectively.

3.3. Lubrication Properties.

The lubrication properties, such as PP, FP, KV, VI and oxidation stability (OXS) of dodecanedioate esters, are presented in **Table 1**. The branched dodecanedioate esters showed significantly improved low-temperature characteristics as compared to the long-chain dodecanedioate esters. The efficiency of the lubricant in reducing friction and wear is greatly influenced by its KV. The KV decreases as temperature increases [20]. For instance, the requirements for kinematic viscosities (KV's) at 100 °C range from 3.8 to 20 cSt for engine oils, from 4.1 to 40 cSt for automotive gear lubricants, and from 35.2 to 3520 cSt for industrial gear lubricants [8].

The dynamic viscosities of the synthesized dodecanedioate esters were measured in a rotational controlled strain rheometer. At least three replicates of each test were performed on fresh samples. KV values were obtained as the ratio of dynamic viscosity to density. The KV at 100 °C was used to find the L and H values

directly from an ASTM reference table [21]. The VI of esters was then obtained on the basis of the L and H values using the following equation [22].

$$VI = \frac{L-U}{L-H} \times 100$$

Where U is the kinematic viscosity of ester at 40 °C, the values of L and H that correspond to the viscosity at 100 °C were read from the reference table [21]. Substituting the obtained values of U, L, and H into the above equation yields the VI. The VI is an indication of the effect of temperature on the KV of the oil. A low VI represents relatively large changes of KV induced by changes in temperature. On the other hand, a high VI indicates that KV is constant mainly over a wide temperature range. The importance of the VI can be easily illustrated by considering the case of automotive lubricants. Esters having a high VI resist excessive thickening when the engine is cold, and consequently promote rapid starting and prompt circulation. These materials with high VIs resist excessive thinning when the motor is hot, providing full lubrication and preventing excessive oil consumption. The results (Table 1) showed that the KV values of the dodecanedioate esters were found to be in the range of 10.8 to 44.7 cSt at 40 °C, making them suitable for use as hydraulic fluids. However, these values are too low for some other applications, such as engine oil and grease oil. KV modifiers are clearly needed to expand the potential applications of diester lubricants [23]. The KV of the dodecanedioate esters increased with increasing molecular weight, chain length, and degree of branching present in the alcohol (Table 1). The VI of the lubricant was primarily dependent on the degree of linearity and the length of the alcohol chain. The VI values of the long-chain dodecanedioate esters were in the range of 169 to 190, while the VI values of branched dodecanedioate esters were in the range of 140 to 191. Generally, the least viscous lubricant that still separates two moving pieces is the most desirable. If the lubricant is too viscous, it will require a large amount of energy to move. However, when the lubricant is too thin, the surfaces will rub, creating friction. The VI highlights how the lubricant KV changes with the variations in the temperature. Many lubricant applications require performance across a wide range of conditions (e.g., in an engine). Automotive lubricants must reduce friction between engine components regardless of whether it is being started in a cold climate or running at temperatures of up to 200 °C [24]. Esters with good VI values can be obtained by selecting suitable starting materials, which are those that have linear structures [25]. The results (Table 1) showed that the KV values were affected by branching and this effect was notable in D2EHD of (18.95 cSt (40°C) and 5.4 cSt (100 °C)) as compared to the equivalent DOD of (21.52 cSt (40°C) and 6.4 cSt (100 °C)).

The PP is the most important low-temperature property of any oil used as a lubricant. It is defined as the lowest temperature at which a liquid remains pourable (i.e., the liquid still behaves as a fluid). The PPs were measured in accordance with ASTM D97 and are summarized in Table 1. The flow properties of dodecanedioate esters constructed from long-chain alcohols were inferior. However, the branched alcohols were more effective in giving materials with low PPs (-45 °C, -35 °C, and -55 °C for D2MBD, D2EBD, and D2EHD, respectively) in agreement with prior work by Nagendramma and Savita [1]. The linear, long-chain DBD, DHD, DOD, and DDD diesters showed high PPs, with values above

10 °C. This variation of PPs indicates that the branching of the alkyl chains within the esters plays a significant role in decreasing PPs. Cermak et al. [26] stated that branched esters show lower PPs as compared to their linear chain analogs. It can be assumed that the presence of a large branching point on the diester creates a steric barrier around the individual molecule, inhibiting crystallization, and decreasing the PP [27]. Rizvi [28] reported that the PPs of esters depends on the chemical structure and weight of alcohol used. The PPs of the dodecanedioate esters in this study increased with the increasing length of carbon chain in the alcohol, as was expected due to the presence of saturation and the high molecular weights of the larger molecules. All the dodecanedioate esters were liquids at room temperature except DDD, which was solid. Recently, such solid diesters have been used as a new organic phase for thermal energy storage applications [12]. The effect of the use of unsaturated alcohol was clear in the performance of DOID at 18 °C. Despite the high molecular weight and long organic chain, the PP was lower than might have been expected, which might be attributed to the unsaturation of the DOID. These results were in agreement with results obtained by Rizvi [28], indicating that unsaturation in the diester causes a decrease in PP. The low-temperature fluidity properties of di-2-butyl dodecanedioate (D2BD) at -15 °C, di-2-hexyl dodecanedioate (D2HD) at -10 °C, and D2OD at -8 °C were lower than the compounds with same carbon number (i.e., DBD at 14 °C, DHD at 18 °C, and DOD at 22 °C), as a result of the presence of the branching. The effect of the position of branching on the PP was evidenced by the PPs of D2BD at -15 °C and D2MBD at -45 °C. Moreover, our result showed that the decrease in PP caused by branching was magnified when the branch was distant from the carbonyl group, while the effect of long of branching was clear in D2EBD at -35 °C and D2EHD at -55 °C. Despite the high molecular weight of D2EHD, it gave a lower PP compared to D2EBD due to its length of the branching. A material's FP is useful in determining the volatility and fire resistance of a lubricant, as well as in determining the transportation and storage temperature requirements of the lubricants. The FP should be high enough to ensure safe operation and minimum volatilization at the maximum operating temperature. For demanding applications such as in aviation jet engines, an effective flash of greater than 300 °C may be required [29]. FP is important for both flammable oils and combustible oils. There are various international standards for defining the FP for each flammable and combustible oil, but the most convenient standard labels oils with a FP of less than 43 °C as flammable, while those having a FP above this temperature are combustible [20]. An anomalously low FP indicates the possible presence of highly volatile and flammable material in a relatively nonvolatile or nonflammable material. A mixture can be ignited only if the concentration of fuel vapor in the air is greater than approximately 1 % by volume [30]. The FPs of the dodecanedioate esters were as high for materials constructed of long-chain alcohols due to their high molecular weights, while FPs as low was observed for short-chain alcohol materials (Table 1). The highest FP belonged to DOID (300 °C), due to its high molecular weight, and the lowest value (160 °C) was recorded for di 2-butyl dodecanedioate (D2BD), which is constructed with short-chain alcohol. In general, the low volatilities of some dodecanedioate esters were a result of their uniform or close to uniform

compositions. In this study, the results showed that the FPs were slightly affected by the branching. For instance, the D2EHD, D2OD, and DOD with identical molecular weight showed FPs of 200 °C, 205 °C, and 210 °C, respectively. The FPs of some dodecanedioate esters (e.g., DOID at 300 °C, DHD at 200 °C, DOD at 215 °C, and D2OD at 205 °C), in addition to other properties such as low PP and high VI, made them suitable as lubricants in high-temperature applications as their FPs exceeded 200 °C. All of the FPs data for the dodecanedioate esters are presented in Table 1. Diacid esters with low volatilities are desired to eliminate the need for replenishing lost oil, the increase in KV during use, and the negative impact of the evaporated oil on the environment [23], [31]. In addition, low volatility diacid esters have lower flash and fire points.

OXS is the resistance of a lubricant to molecular breakdown or rearrangement at elevated temperatures in an ordinary air environment and is an essential oil characteristic for lubricants undergoing long-term use (e.g., turbines, transformers, hydraulic, and heat transfer units). Esters differ in their rates of oxidation depending upon the structure and branching of their hydrocarbon chains [32]. In this study, the synthesized dodecanedioate esters were screened to measure their OXS temperature using PDSC, which are defined as the temperature at which a rapid increase in the rate of oxidation is observed. OXS indicates more excellent stability against oxidation [33]. The results from each scan were analyzed to determine the OXS. Replicate scans were conducted at least three times on fresh samples. The effects of evaporation, indicated by tailing, split peaks, and changes in the baseline, resulted from a loss of sample mass; however, these effects were generally apparent at temperatures higher than the initial oxidation peak. Moreover, these effects did not interfere with the measurement of the OXS values due to the extrapolation of peak onset temperatures. The OXS was calculated from a plot of heat flow (W/g) versus temperature for each tested material. The OXS was affected by branching. For example, DOD long-chain diester showed a higher OXS (206 °C) than the branched isomer D2EHD (199 °C). In general, the results showed that the long-chain dodecanedioate esters [e.g., DBD (OXS 185 °C), DHD (OXS 201 °C), and DOD (OXS 206 °C)] were more stable to oxidation than the branched dodecanedioate esters isomers, such as D2BD (179 °C), D2HD (199 °C) and D2OD (197 °C). Murrenhoff and Rimmelmann [32] state that diesters differ in their rates of oxidation depending on the structure and branching of their hydrocarbon chains. Kubouchi et al. [34] also state that OXS increases with the increase in chain length of the esterified acid and constitutive alcohol. In this study, despite the low molecular weight of D2EBD (216 °C), it had a higher OXS than D2EHD (199 °C) due to the low in the degree of branching. In the case of DOID (183 °C), the OXS was low because of the presence of unsaturation (C=C).

3.4. Tribological and rheological properties.

Boundary lubrication is defined as a condition where the solid surfaces are so close together that surface interaction between

single or multimolecular films of lubricants and the solid asperities dominates the contact [35]. T

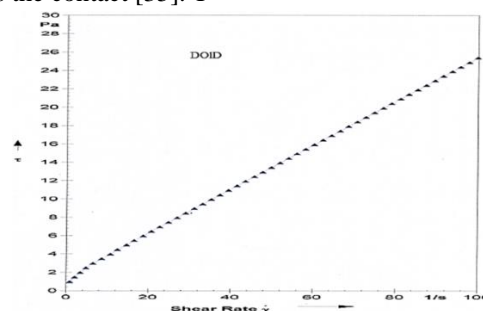


Figure 15. Shear stress vs shear rate plots of DOID at 25 °C

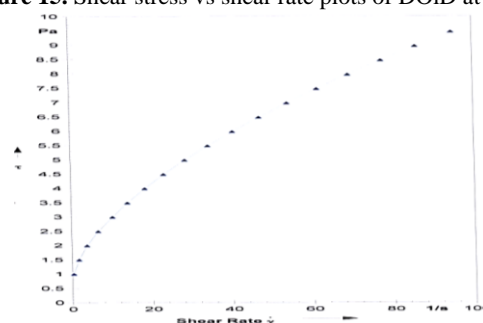


Figure 16. Shear stress vs shear rate plots of D2EHD at 25 °C.

The polar structures of synthesized diesters are able to form an effective boundary layer and the resultant low friction. Durak et al. [36] state that the polar in the end groups of long-chain carbon oil can be adsorbed on a metallic surface, which decreases or suppresses the surface energy and causes a reduction of the friction coefficient (FC). Salimon et al. [37] also state that the long fatty acid chain and presence of polar groups in the structure of plant oil make it amphiphilic in nature, therefore allows it to be used as both boundary and hydrodynamic biolubricants. The results of the FC for the synthesized dodecanedioate esters with the varying chemical structure are presented in Table 2.

The low value of FC of DOID was attributed to its high in the molecular weight and viscosity. The results (Table 2) showed that the FC increased with the low in the molecular weight and the viscosity, and vice versa. Generally, all of the tested dodecanedioate esters recorded low FC below than 0.45 at 40 °C and 100 °C as shown in Table 2; therefore, the tested dodecanedioate esters were classified as boundary lubricants.

Figure 15 and Figure 16 show the plot of shear stress vs. shear rate of DOID and D2EHD, respectively. From the plot, fluids can be classified as Newtonian or non-Newtonian fluids. Classification of fluids as Newtonian and non-Newtonian depends on their viscosity by increasing shear rate, where the constant viscosity is Newtonian, while non-constant viscosity is non-Newtonian [35]. Therefore, and based on Figure 15 DOID was identified as a Newtonian fluid, whereas, based on Figure 16 D2EHD was identified as non-Newtonian fluid. Other tested diesters were identified as a non-Newtonian fluid.

Table 1. Lubrication properties of dodecanedioate esters.

Diesters	KV(cSt) at 40 °C	KV (cSt) at 100 °C	VI	PP (°C)	FP (°C)	OXS(°C)
DBD	13.4 ± 0.1	3.6 ± 0.1	169 ± 5	10±1	170±3	185±2
D2BD	10.8 ± 0.1	3.0 ± 0.0	140 ± 3	-15±3	160±2	179±3
DHD	14.8 ± 0.2	4.0 ± 0.1	181 ± 3	18±3	200±5	201±3

Diesters	KV(cSt) at 40 °C	KV (cSt) at 100 °C	VI	PP (°C)	FP (°C)	OXS(°C)
D2HD	12.7 ± 0.2	3.4 ± 0.1	157 ± 5	-10±2	190±5	190±4
DOD	21.5 ± 0.1	6.4 ± 0.2	189 ± 1	22±2	215±4	206±3
D2OD	19.7 ± 0.1	5.2 ± 0.2	179 ± 7	-8±3	205±3	197±3
DDD	22.2 ± 0.3	6.9 ± 0.1	190 ±1	32±1	230±5	208±4
D2DD	20.8 ± 0.1	5.9 ± 0.1	187 ± 1	20±3	220±5	199±2
D2MBD	11.3±0.2	3.2±0.1	159±7	-45±2	175 ±3	198±2
D2EBD	14.1±0.1	3.6±0.1	150±2	-35±5	185 ±5	216±3
D2EHD	18.9±0.1	5.4±0.1	191±1	-55±5	200 ±6	199±2
DOID	44.7±0.2	12.5±0.1	169±1	18±2	305 ±5	183±2

Table 2. The friction coefficient (FC) of dodecanedioate esters at 40 and 100 °C

Dodecanedioate esters	FC (μ)	
	40 °C	100 °C
DOID	0.15	0.19
D2DD	0.18	0.23
DOD	0.21	0.28
D2OD	0.22	0.29
D2EHD	0.24	0.31
DHD	0.26	0.32
D2HD	0.28	0.37
D2EBD	0.30	0.40

4. CONCLUSIONS

This study indicated that the lubrication properties of diesters could be modified by altering both the length and degree of branching present in their structures. Some of the synthesized dodecanedioate esters were suitable for use in cold climates without the need for PP depressants. In practice, the usable liquid range is limited by the PP at low temperatures and OXS and FP at high temperatures. The current study indicated that most of the dodecanedioate esters had good lubrication properties (e.g., high FP

and high VI in the absence of additives. The VIs of the dodecanedioate esters showed good values (> 140). Based on the results, the tested dodecanedioate esters, which have high molecular weight, had a low friction coefficient, and they were classified as non-Newtonian fluids except DOLD was classified as a Newtonian fluid. It is thus plausible to use the branched dodecanedioate esters to formulate a suitable lubricant without additives.

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