



Synthesis, Characterization, Tribological and Rheological Properties of Oleyl Oleate Based Biolubricant

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Abstract

Oleyl oleate (liquid wax ester) is a principal component of sperm whale blubber oil has an important industrial application such as cosmetic, pharmaceutical and biolubricant. In this work, synthesis of oleyl oleate was carried out through esterification between oleyl alcohol and oleic acid using acidic heterogeneous catalyst, sodium hydrogen sulfate. About 95% of oleyl oleate was produced at the optimal condition. The molecular structure of oleyl oleate has been confirmed by using FTIR, NMR and ESI-MS spectroscopies. The physicochemical properties of oleyl oleate were investigated. The results showed that the ester has pour point at $-31 \pm 1^\circ\text{C}$, flash point at $320 \pm 2^\circ\text{C}$, viscosity index of 197.51 ± 1.4 and oxidative stability at $186.9^\circ\text{C} \pm 1.8$. Furthermore, tribological and rheological analysis of oleyl oleate were performed. Oleyl oleate can be classified as a Newtonian fluid with having friction coefficient of 0.53 ± 0.08 at 100°C operation condition. The presence of both ester functional group and long chain carbon moiety in oleyl oleate structure has a positive impact on wear protection thus plausible to be used as general purpose industrial biolubricant.

Keywords: oleyl oleate; acidic heterogeneous catalysts; biolubricant; tribology; rheology

1. Introduction

Plant oils and their derivatives are seeing increased interest as base stocks for biolubricants and functional fluids due to their excellent lubricant properties and biodegradability [1]. They have a very low volatility because of the high molecular weight of the triacylglycerol molecule and have a cramped range of viscosity changes with temperature. Polar ester groups are capable of adhering to metal surfaces and therefore, possess good boundary lubrication properties. Furthermore, plant oils have high solubilizing power for polar contaminants and additives molecules. Low-

temperature behavior studies have explained that most plant oils showed cloudiness, precipitation, poor flow, and solidification at -10°C upon long-term exposure to cold temperature in sharp contrast to mineral oil-based fluids. Plant oils also exhibit poor corrosion protection [2-3].

On the other hand, plant oils show lower oxidative stability and higher melting points [4-5]. These are due to the presence of bis allylic protons and are highly susceptible to radical attack and subsequently, undergo oxidative degradation to form polar oxy compounds. This will result in

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insoluble deposits and an increase in oil acidity and viscosity.

Chemical modifications such as epoxidation, estolides formation and transesterification of plant oils with polyols are frequently used to solve these problems. Moreover, the addition of additives is an attractive way to improve plant oil's oxidative stability and pour point [6-8]. Furthermore, most plant oils are good boundary biolubricants because they increase the low friction coefficient (μ). The friction coefficient for plant oils is nearly one-half of refined mineral oils [9]. Many researchers report that even though the friction coefficient is low, the wear rate is high when using plant oils as boundary biolubricants [10].

Synthetic esters derived from plant-based stocks are excellent alternatives for mineral oils due to their low volatility, high flash point, good oxidative stability, low toxicity, and excellent biodegradability [11], which are considered to meet most field biolubricant applications. Moreover, synthetic wax esters have superior viscosity indices and lubricating properties compared to mineral oils. Synthetic wax ester especially oleyl oleate has been reported. Most of the methods used were using enzymatic catalysts which are more tedious and expensive methods [12-16]. On the other hand, chemical synthesis of oleyl oleate wax esters methods are less reported [17, 18]. These methods are more effective with high yields and cost effective. The objective of this work was to synthesize oleyl oleate via chemical methods by using sodium hydrogen sulfate acidic heterogeneous catalyst. The physicochemical characterization, tribological and rheology properties of the wax ester were evaluated.

2. Experimental

2.1. Materials

All analytical grade chemicals used have been purchased from different chemical companies. Oleic acid (90%) and oleyl alcohol (85%) were of Aldrich (Germany), ethyl acetate, ethanol, sodium hydroxide, sodium hydrogen carbonate, sodium hydrogen sulphate, *p*-toluene sulfonic acid, silica gel and sodium sulphate anhydrous were of System (Malaysia), perchloric acid (70%) was of Aserate (Sydney), sulfuric acid (96.7%) was of John Townsend (J.T.) Baker (USA) and phosphoric acid (98%) was of BDH chemical company (UK). All chemicals were used as received without further purification process.

2.2. Instrumentation

Fourier transforms infrared spectroscopy (FTIR) spectrum was carried out using Perkin Elmer Spectrum GX spectrophotometer in the range of 400-4000 cm^{-1} . Nuclear magnetic resonance spectroscopy (NMR) spectra for proton ^1H and ^{13}C were carried out with model Joel FCP 400 MHz with the solvent CDCl_3 and D_2O . The electrospray ionization mass spectroscopy (ESI-MS) spectrum was recorded on Bruker MicroTOF-Q (German) mass spectrometer equipped with a Kd Scientific apparatus syringe pump (USA). The sample solution was prepared in 80% chloroform and 20% methanol. Nitrogen gas was used as nebulizing gas at a pressure of 0.4 bar and a temperature of 180°C . The sample was infused into the ESI source using a Kd Scientific pump at a flow rate of $180 \mu\text{l h}^{-1}$.

2.3. Synthesis of oleyl oleate using acidic heterogeneous catalysts

The esterification reaction was carried out according to previous studies [17-18]. Oleic acid (1

mol) was fed into the 100 mL three-neck flask equipped with condenser and magnetic stirrer. The acid was preheated to 100 °C before adding into the mixture of alcohol and sodium hydrogen sulphate (NaHSO₄) acidic heterogeneous catalyst. Once the desirable reaction temperature of 130°C was reached, 9.9 wt% (as percentage of weight of oleic acid) of acidic heterogeneous catalyst, 1mole of oleyl alcohol was placed into the flask and the reaction start to be recorded. After completion of the reaction of 8hours, the flask was allowed to cool to room temperature, and the crude product was dissolved into ethyl acetate 25mL and filtered to remove the acidic heterogeneous catalyst from the product. The product was transferred into a separating funnel and 10 mL of saturated NaHCO₃ solution was then added into the funnel to neutralize the catalytic inorganic acid used in the reaction. Brine solution was then added in order to avoid the formation of any emulsion. Extraction was carried out until a solution with pH 7 was obtained, the aqueous layer was decanted and the product was dried with a sufficient amount of Na₂SO₄. The hydrated Na₂SO₄ was filtered off. Then, the product was rotary-evaporated to remove ethyl acetate at 77°C giving oleyl oleate as a viscous liquid [19].

2.4. Addition of additive to oleyl oleate

Synthesized oleyl oleate (0.02 mol or 10 g) was mixed with 0.5 g methylcellulose as additive. The reaction was proceeded at 100°C with vigorous stirring for 24 hr to provide oleyl oleate as clear oil. After the reaction was complete, the reaction mixture was allowed to cool to room temperature. The physicochemical properties of the product with the additive was characterized for comparison with the pure oleyl oleate.

2.5. Physicochemical analysis

The pour point (PP) was determined by using a U-tube and thermometer ranging from -80 to -20°C according to ASTM method D-97 [20]. For a greater degree of accuracy, PP measurements were done by using thermometer with 1 °C resolution. Flash point (FP) determination was according to the American Standard Test Method (ASTM D-93) [21]. Rheometer with model physical MCR 301 from Anton Paar Instruments Co. (Germany) was used to measure kinematic viscosity. Measurements were run on a hot plate heater set at 40 and 100°C. The viscosity and viscosity index (VI) were calculated using ASTM D 2270-04 (ASTMD-2270) [22]. Pressure Differential Scanning Calorimetry (PDSC) model PDSC822e Mettler Toledo was used to determine the oxidative stability temperature (OST). The OST is the temperature at which a rapid increase in oxidation rate is observed at a constant high pressure. The OST was measured from a plot of heat flow (W/g) versus temperature, which was generated by the sample upon degradation. A 2-μL sample forming a film thickness of less than 1 mm was placed in an aluminium pan. Then it was hermetically sealed with a pinhole lid. The sample was oxidized in the presence of dry air (Gateway Airgas, St. Louis, MO) and was pressurized at a constant pressure of 1378.95 kPa (200 psi). A 10 °C min⁻¹ heating rate from 50 to 350 °C was used during each experiment. The oxidation stability temperature (OST, °C) was calculated from a plot of the heat flow (W/g) versus temperature for each experiment.

2.6. Tribology and rheology determination

The tribological properties of green wax ester were performed according to ASTM method D-

4172 and discussed based on their Stribeck curves at 40 and 100°C [23]. The sliding speed was manipulated between 10^{-1} – 10^3 mm/s at 40 and 100°C. All measurements were run in triplicate and the value was reported as a mean \pm SD of triplicate determinations. The rheological properties of wax ester oil were observed by the rheometer with cone and plate geometry. The cone spindle used was CP 25-2 with a diameter of 0.051 mm. The shear rate was manipulated between 0–100 s^{-1} at 25°C.

3. Results and discussion

3.1. Esterification yields

NaHSO₄ was used as catalyst and desiccant in the esterification reaction of oleic acid with oleyl alcohol. NaHSO₄ has showed high activity and achieved high final percentage yield due to its high

acidity. Optimum conditions of the experiment to obtain high % yield of oleyl oleate were noted at 8 hr of reaction time, 1:1 ratio of oleic acid to oleyl alcohol, 9.9 wt% amount of catalyst and 130°C of reaction temperature. At this optimal condition, the % yield of oleyl oleate was 96.8%. The esterification reaction mechanism is shown in Fig. 1, which involved the protonation of oleic acid carbonyl oxygen by acid catalyst proton donation. This process followed by nucleophilic addition of alcohol molecule to the oleic acid carbonyl carbon to form an active intermediate, then to oxonium ion formation. Removal of water molecules from the oxonium ion followed by deprotonation to produce an ester product.

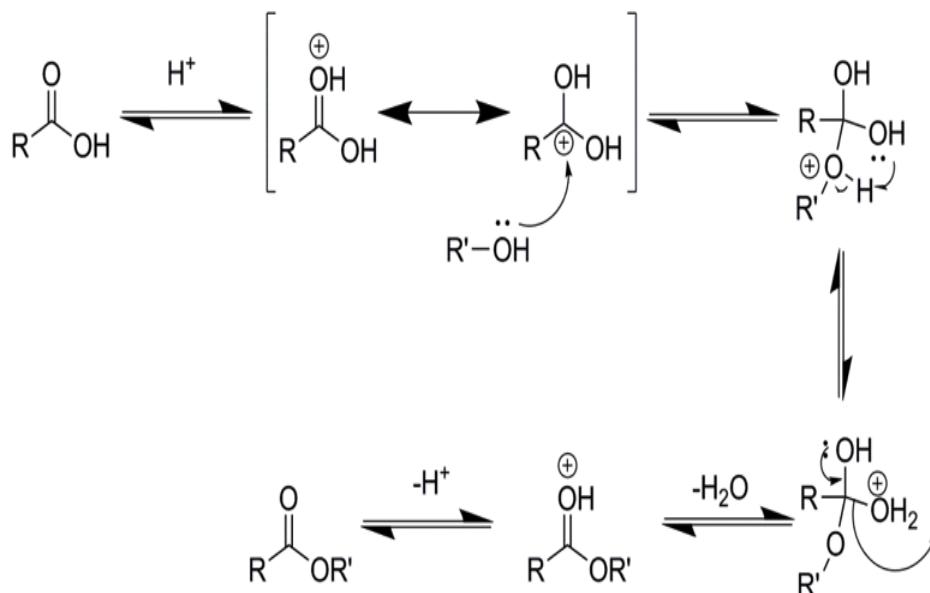


Fig. 1. The general mechanism of the esterification reaction

3.2. Structural characterization analysis

Final product produced from esterification reactions of oleic acid with oleyl alcohol in the presence of NaHSO_4 , was purified and FTIR spectrum was obtained. The presence of $\text{C}=\text{O}$ ester functional group proved that oleyl oleate has been produced. The comparison between oleyl alcohol, oleic acid, and oleyl oleate FTIR spectra are shown in Figure 2. The OH stretching vibration peak of primary alcohol and the stretching vibration peak of methylene carbon, $=\text{CH}$ at 3338 and 3004 cm^{-1} respectively can be observed for oleyl alcohol [24,25]. As the absorption due to OH of hydroxyl group at 2900 cm^{-1} and carbonyl $\text{C}=\text{O}$ group of carboxylic acid at 1709 cm^{-1} are observed for oleic acid. The FTIR spectrum as shown in Fig. 2 shows the stretching vibration peak at wave number of 1739 cm^{-1} , attributed to the stretching frequency of the carbonyl $\text{C}=\text{O}$ group of ester moiety. The bands at 1172 and 1242 cm^{-1} , respectively are due to C-O stretching bands. Moreover, the stretching vibration peak of $=\text{CH}$ at 3004 cm^{-1} can be observed for oleyl oleate. The disappearance of $\text{C}=\text{O}$ functional group of carboxylic acid at 1709 cm^{-1} , and the stretching vibration peak of OH at 2900 cm^{-1} confirmed that the esterification reaction was successfully taking place to produce oleyl oleate.

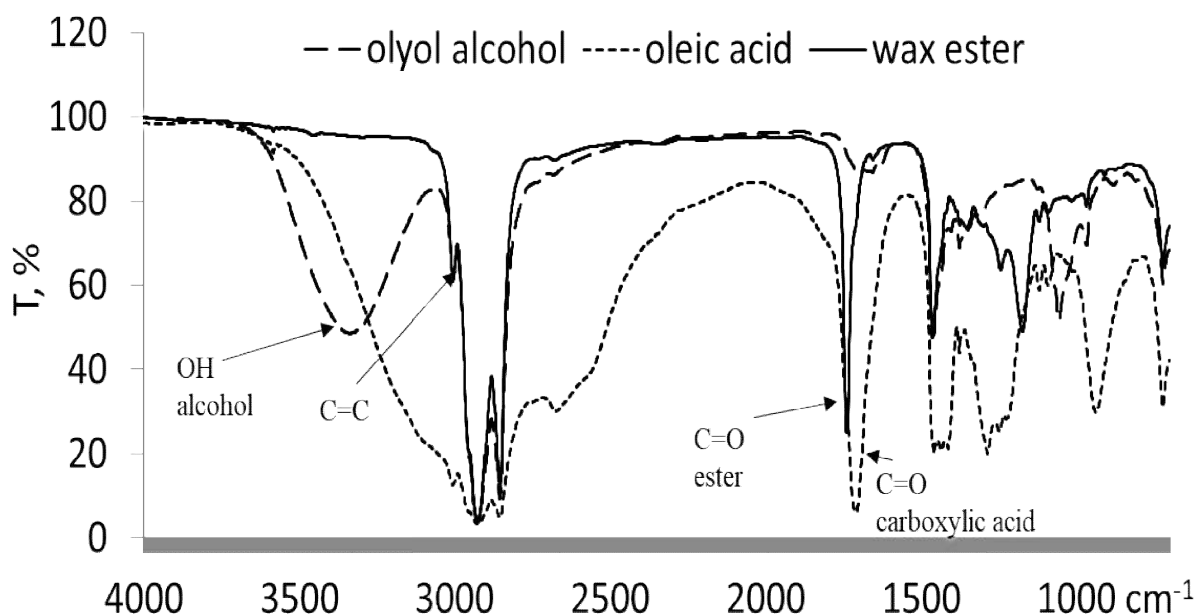


Fig. 2. FTIR spectra of oleyl alcohol, oleic acid, oleyl oleate

Fig. 3 (a), (b), and (c) indicate the ^1H NMR spectra of oleic acid, oleyl alcohol, and oleyl oleate, respectively. Fig. 3 (c) shows the chemical signal for proton's decreasing for the carboxylic acid group, which appeared at 11.17 ppm as a broad peak in the ^1H NMR spectrum of oleic acid in Fig. 3 (a), and shifting signal $\text{CH}_2\text{-COO-H}$ at 2.35 ppm to 2.22 ppm for ester $\text{CH}_2\text{-COO-R}$. Another distinctive feature come together with previous peak is the two protons of the $\text{CH}_2\text{-O-C=O}$ for ester group appeared at about 3.99 ppm, which confirmed the success of the esterification reaction. These signals were not observed in the ^1H NMR spectra of oleic acid (Fig. 3 a) and oleyl alcohol (Fig. 3 b), respectively. Furthermore, ^1H NMR spectrum of oleyl alcohol (Fig. 3 b) shows both signals at

about 4 ppm and 3.5 ppm due to the R-OH(D₂O exchangeable) and -CH₂-OH groups, respectively, which were disappeared for the prepared ester compound. The ¹³C NMR spectra show the main chemical signals of oleic acid, oleyl alcohol and oleyl oleate (Fig. 4). The distinguishable peak appeared at about 64.24 ppm corresponds to carbon of CH₂-O-C=O group (Fig. 4 c) which are not observed in the ¹³C NMR spectra of oleic acid and oleyl alcohol Fig. 4 (a) and (b), respectively. The ¹³C chemical signal shift ranges for unsaturated C=C bond was observed at 129-131 ppm, while for C-O was observed at 64-65 ppm. Whereas the ¹³C chemical shift value for C=O ester was observed at 173 ppm. These observations were in agreement with the values from literatures [26-28].

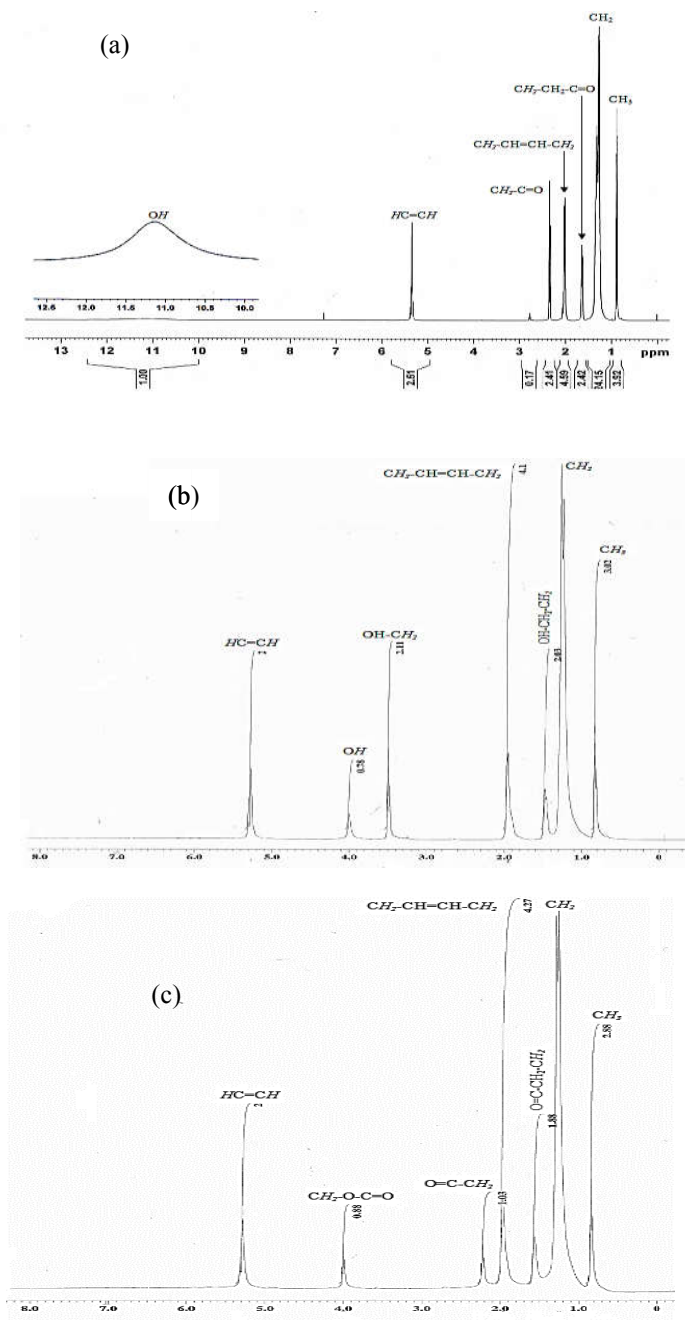


Fig. 3. ¹H NMR spectrum of (a) oleic acid, (b) oleyl alcohol and (c) oleyl oleate

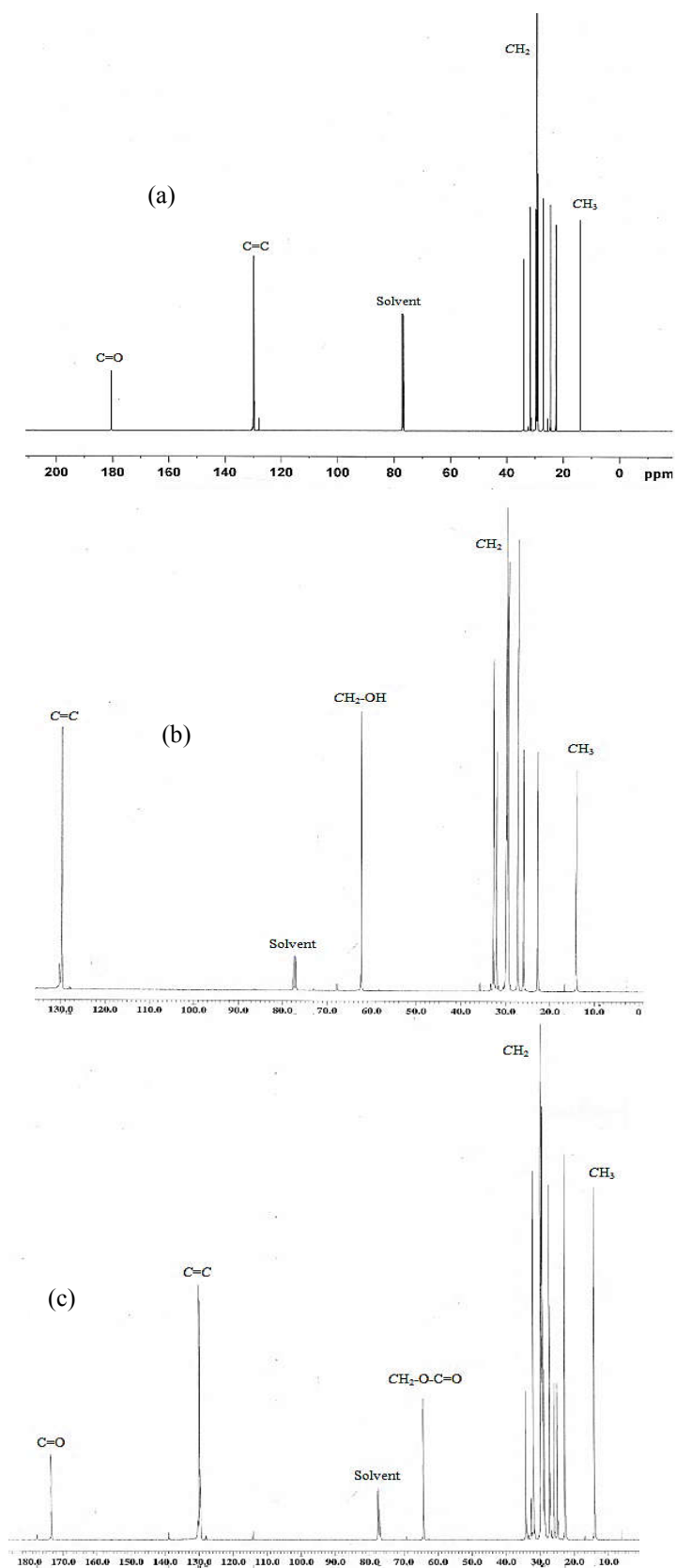


Fig. 4. ^{13}C NMR spectrum of (a) oleic acid, (b) oleyl alcohol, and (c) oleyl oleate

Generally, ESI-MS results in protonated molecules, $[M+H]^+$, in the positive-ion mode. However, for some molecules the formation of alkali metal ion adducts, like $[M+Na]^+$ or $[M+K]^+$, instead of proton addition are often observed [29]. Fig. 5 shows the spectrum of ESI-MS analysis of the oleyl oleate. The fragmentation pattern of the end product showed its intensity as a function of the mass over charge (m/z) ratio. The peak appearing at an m/z of 555 was present corresponds to the sodium adducts ($[M+Na]^+$ of oleyl oleate. Overall, the ESI-MS results confirmed that the end product obtained by the esterification reaction of oleic acid and oleyl alcohol was the oleyl oleate wax ester with a molecular weight of 532.

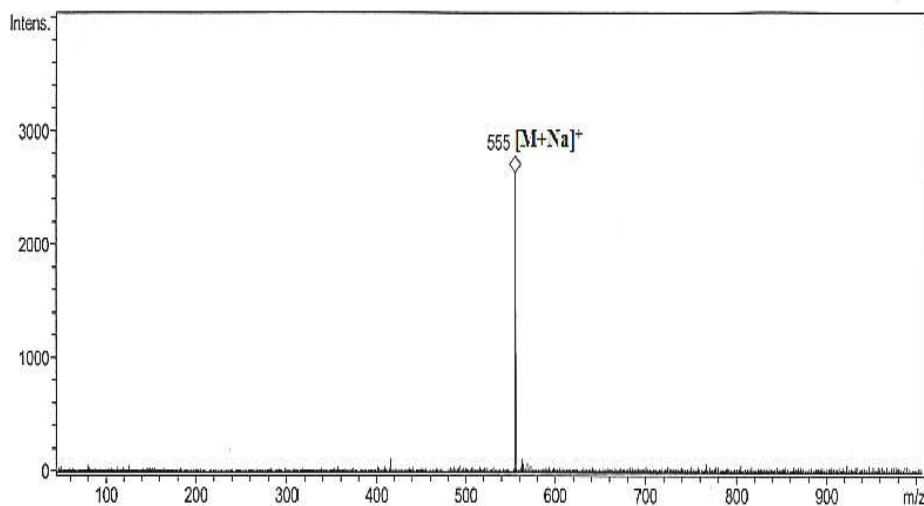


Fig. 5. ESI-MS spectrum of oleyl oleate

3.3 Physicochemical and tribological properties analysis

3.3.1 Pour and flash points

The ability of a compound to remain liquid at low temperatures is an important property for a number of industrial supplies such as biolubricants, surfactant and fuels. As biolubricants to have low pour point (PP) is an important and crucial parameter to ensure safe and efficient lubrication process for moving metals surface protection. A compound with lower PP exhibit improved fluidity at low temperatures than those with higher PP. In this work, the PP of oleyl oleate with and without the addition of additive (methylcellulose) and commercial biolubricant have been carried out for comparison. The results revealed an improvement in the cold flow behavior of oleyl oleate with additive (-40 ± 2 °C) over commercial biolubricant (-39 ± 2 °C) and oleyl oleate (-31 ± 1 °C). This observation may be due to the methylcellulose additive reacts as the pour point depressants (PPD). It inhibits the formation of interlocking crystal networks by creating a steric barrier around the individual molecules. This result is in agreement with other studies on the effect of PPD additive on the PP of plant oils (VO), epoxidized VO, ring-opened products from epoxidized VO, estolides, and polyol esters [30].

Another important parameter in determining how well oil will behave as a potential biolubricant is to evaluate the flash point [31]. The flash point is often used as a descriptive feature of fuel oil and also used to describe as nonfuel oil. The international standards agree that oil with a flash point of less than 43 °C is flammable and a flash point above this temperature are combustible [32]. Table-1 also shows the improvement in flash point of oleyl oleate, which increased to $320^{\circ}\text{C} \pm 2$ compared to 189°C for oleic acid. In general, the flash point increases with the increasing molecular weight of the compound. However, the flash point value remained unchanged at $320^{\circ}\text{C} \pm 1$ when methylcellulose was added to the oleyl oleate. This may be due to the addition in a small amount (5%) of the additive into the wax ester.

Table 1
Pour and flash points comparison

Compounds	Pour point (°C)	Flash point (°C)
Oleyl oleate	-31 ± 1	320 ± 2
Oleyl oleate with additive	-40 ± 2	320 ± 1
Commercial biolubricant	-39 ± 2	222 ± 1

3.3.2. Viscosity and viscosity index

The viscosity index (VI) highlights how a biolubricant's viscosity changes with a variation in temperature. A low viscosity index signifies a relatively large change of viscosity with temperature. In other words, the biolubricant becomes too viscous at low temperature and too thin at high temperatures. On the other hand, the best biolubricants (with the highest VI) will not change much in viscosity over such mechanical operational at those temperatures range. Therefore, the biolubricant will perform well throughout. The VI data of compounds oleyl oleate, oleyl oleate with additive and commercial biolubricant are shown in Table-2.

The results indicate that the viscosity index (VI) of the prepared product with the additive increase (204.52 ± 2.2) as compared to its pure wax ester (197.51 ± 2.4). This may be due to its total molar weight increase. Furthermore, an additional molecule of the additive could alter the overall molecule structure packing arrangement. The more polar molecule the higher the viscosity index compared to oleyl oleate. In addition, high polymer molecular weight (methylcellulose) could create better condition and balance between the thickening efficiency and shear stability of the polymer at two different temperatures thus shows good viscosity index value. In general, polymers with high molecular weight make better thickeners. However, it tends to break down when exposed to high temperature and mechanical shear. On the other hand, low molecular weight polymer is more shear and heat resistant, but do not improve viscosity as effectively at higher temperatures. Therefore, large quantities of this polymer need to be used to act as a good viscosity additive [11].

Table 2
Viscosity and viscosity index comparison

Compounds	Kinematic viscosity@ 40 °C (cSt)	Kinematic viscosity@ 100 °C (cSt)	Viscosity index
Oleyl oleate	17.80 ± 0.4	5.35 ± 0.4	197.51 ± 1.4
Oleyl oleate with additive	20.81 ± 0.5	9.31 ± 0.4	204.52 ± 1.2
Commercial biolubricant	49.12 ± 0.6	8.41 ± 0.6	135.61 ± 1.5

3.3.3. Oxidative stability

The ability of substance to resist oxidative degradation is another important property for biolubricants. The present work shows that the addition of the additive gave a side effect on the oxidative stability. The OST of

oleyl oleate was observed at $186.9\text{ }^{\circ}\text{C} \pm 1.8$ while OST of oleyl oleate with additive methylcellulose lead a decrease in OST at $183.8\text{ }^{\circ}\text{C} \pm 1.19$ (Fig. 6). This observation may be due to the additive molecule undergoes thermal and oxidative degradation faster than the wax ester.

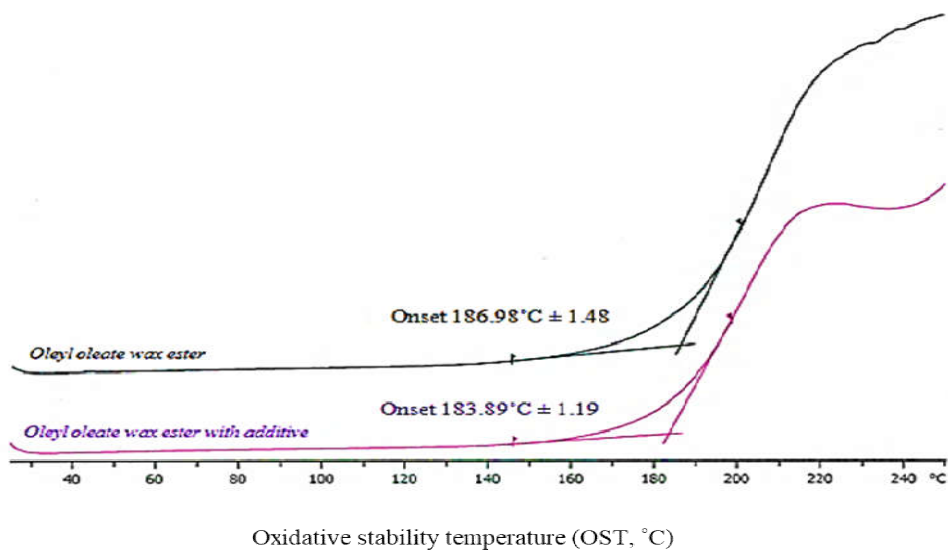


Fig. 6. PDSC of oleyl oleate and oleyl oleate with additive

3.3.4. Tribological and rheological determinations analysis

The classification of rheological property of fluids depends on the relation between the shear stress (τ) and shear rate ($\dot{\gamma}$). Fluids can be classified as a Newtonian fluid whenever the relation is linear as the shear rate increases. However, when the relationship is curved as the shear rate increases, the fluids are classified as non-Newtonian fluid. Fig. 7 shows this relationship for the wax ester studied and selected commercial biolubricant. For all samples tested, they show linear relation between the shear stress (τ) against the shear rate ($\dot{\gamma}$). This observation indicated that under such conditions, oleyl oleate, with or without additive and the selected biolubricant can be classified as a Newtonian fluid model.

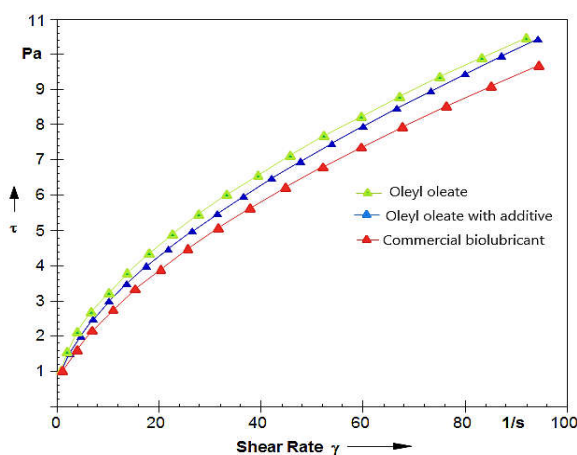
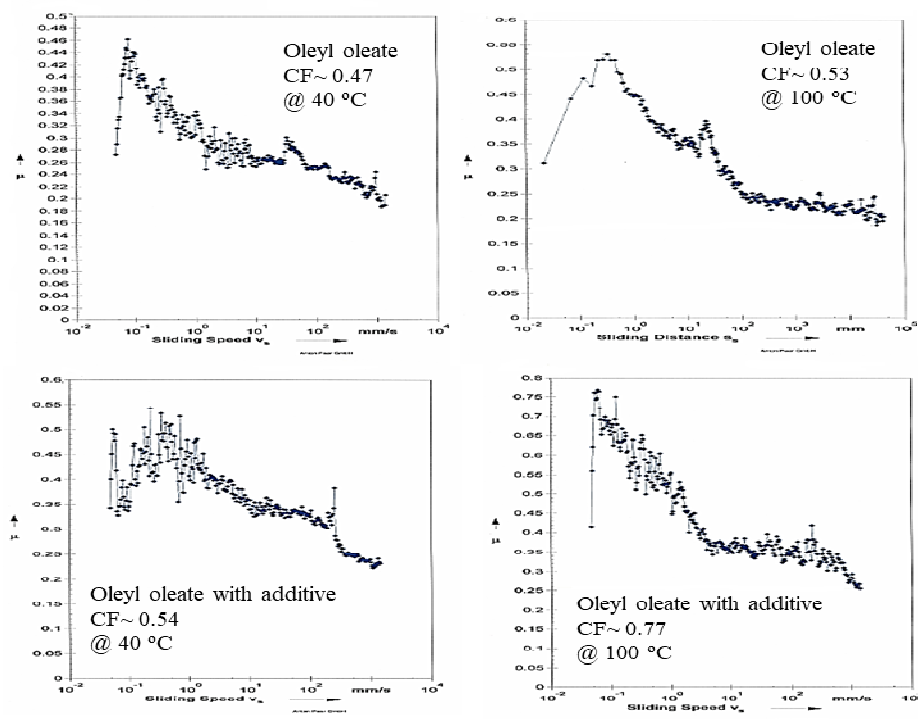


Fig. 7. Shear stress (τ) vs. shear rate ($\dot{\gamma}$) plots of oleyl oleate, oleyl oleate with additive and commercial biolubricant

Tribological properties are useful tools to identify the type of biolubricant. The polarity section at the biolubricant oil molecule increases its lubrication efficiency by reducing wear [33-35]. Due to polarity properties, oleyl oleate fluids have a high affinity for metal surfaces. This makes it act as a boundary biolubricants with low friction coefficient (μ) at both low and high temperature. From the friction coefficient value which are shown in Table-3, it can be seen that increasing the sliding speed velocity decreases the friction. The results indicate that the oleyl oleate has a natural tendency to have good lubrication property. This is reflected by its low friction coefficient and even lower compared to the commercial biolubricant. The presence of polar ester functional group in oleyl oleate structure increased the strength of the tribological film at the metal contact zone, thereby increasing its efficiency to reduce wear [36-37]. In general, increasing pressure causes the viscosity to rise and increasing temperatures causes the viscosity to fall (Table-2). Further, as the viscosity increases, the friction coefficient decreases. As the speed increases, the rate of work imparted to the samples and the biolubricant increases. This causes the temperature of the biolubricant to rise, which, in turn, causes the viscosity to drop, causing an increase in the friction coefficient [38-41]. Fig. 8 shows the sliding speed's effect on the friction coefficient at 40 and 100 °C of oleyl oleate, oleyl oleate with additive and commercial biolubricant.

Table 3
Friction coefficients (μ) comparison

Characteristics	Oleyl oleate	Oleyoleate with additive	Commercial biolubricant
Viscosity index	197.5 \pm 1.3	169.4 \pm 1.4	135.6 \pm 1.5
Friction coefficient			
40°C	0.47 \pm 0.05	0.54 \pm 0.06	0.76 \pm 0.04
100°C	0.53 \pm 0.08	0.77 \pm 0.07	1.08 \pm 0.04



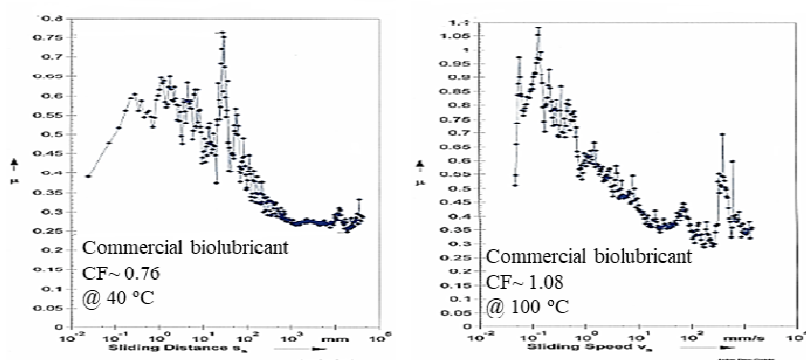


Fig. 8. Friction coefficient of oleyl oleate, oleyl oleate with additive and commercial biolubricant

4. Conclusion

Sodium hydrogen sulphate acidic heterogeneous catalyst was successfully performed the esterification reaction between oleic acid with oleyl alcohol to form wax ester oleyl oleate at high percentage yield (97 %). This low-cost catalyst, easy separation from the product, its ability to absorb water, easy elimination of the catalyst preparation step and produce high yield % of oleyl oleate are the advantages of this process. The pour point at low-temperature properties of oleyl oleate ester can be improved by adding an additive of methylcellulose which act as pour point depressant. The molar weight and the changing in the molecular structure arrangement in the present of an additive in oleyl oleate results an increase viscosity index to 197.5 ± 1.29 , oxidative stability to 186.98 ± 1.48 , and flash point to 260 ± 5 values. However, additive addition to prepared wax ester decreased the oxidative stability to 183.89 ± 1.19 . Furthermore, the presence of the ester group in oleic acid based wax ester structure has a positive impact on wear protection resulting in stronger absorption potential on metal

surfaces makes it good candidate for the general uses of a biolubricant.

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6. Conflict of interest

The authors have no conflict of interest.

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