ENHANCING TRIMETHYLOLPROPANE TRIOLEATE BIOLUBRICANT WITH METHYL LAURATE ADDITIVE

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ABSTRACT

Vegetable oil derived biolubricant often suffer from low oxidative and thermal oxidative stability, limiting their effectiveness as lubricants. Chemical modification through the addition of additive offers a solution to enhance their physicochemical and tribological properties. This study aims to analyse the impact of incorporating Methyl Laurate (ML) as an additive to Trimethylolpropane (TMP) Trioleate biolubricant and determine the optimal ML concentration. Three types of ML provided by Wilmar Oleochemicals & Biofuels were tested, with ML concentrations ranging up to 15 wt% in TMP trioleate. The double bond content, evaluated through the iodine value (IV), influenced the oxidative stability of the biolubricant. Wettability was assessed using Image J software following ASTM D733, and viscosity-temperature relations were analysed to determine the viscosity index (VI) according to ASTM D445. Results showed that 100% ME1299 ML type exhibited the lowest IV, better wettability, and higher VI. Therefore, adding 15 wt% of 100% ME1299 ML to TMP trioleate yielded the most desirable combination, resulting in improved viscosity-temperature relations compared to the base oil.

KEYWORDS

Iodine value (IV); Oxidative; Wettability; Viscosity index (VI)

INTRODUCTION

Biodegradability relates directly to a biolubricant's tendency to become chemically degraded via naturally existing microorganisms in soil and water within a decent amount of time [1]. The base oil and additive largely determine lubricant's biodegradability and depend on organic component chemical structures [2]. A lubricant is termed biodegradable when organisms or its enzymes can decompose enzymes in renewable sources formed via anaerobic or aerobic mechanisms [3]. The presence of decomposing bacteria in a bio-lubricant's base oils or additives consumes hydrocarbon to enable them to biodegrade. The characteristics of lubricants are improved by adding special chemical additives to the base fluids. The ratio is mostly 90% base oil and 10% additives [4]. The existence of double bonds does have a great influence on the oxidative stability of a compound [5].

A formulated lubricant will still require additives to enhance its physicochemical and tribological properties. However, conventional additives used in existing bio-lubricants, even at small concentrations, could still contaminate the environment because they contain sulfur and phosphorus [6]. Thus, having a biodegradable base oil is not sufficient. TMP ester as a replacement for current base oils is still not widely used due to a lack of focus on additives to improve TMP ester formulation. It is also essential that the additive package is biodegradable and green, typically derived from vegetable oil. All vegetable oils contain different fatty acid compositions, which affect the characteristics and properties of the bio-lubricants since different fatty acids have their benefits. A biodegradable additive type must be investigated to maximize the possibility of employing TMP ester as a fully biodegradable lubricant.

In the present work, three types of Methyl Laurate (ML) with different families were evaluated to be additive in Trimethylolpropane (TMP) trioleate bio-lubricant where up to 15 %wt of ML was added to TMP. The Iodine Value (IV), wettability, and viscosity index (VI) of all these samples were to be determined.

METHODOLOGY

Materials

The following tests were carried out using a variety of fatty acid families as additives. These potential additive samples, 100% ME12, 5% ME12, and 100% ME1299 were obtained from Wilmar Oleochemicals & Biofuels. The parameters of these samples are shown in Table 1 and Table 2.

Table 1: Physical Properties of ME12

Parameter	Value	Unit	Test Method
Acid value	0.10	mg KOH/g	AOCS Te 2a-64 2017
Saponification value	263	mg KOH/g	AOCS Tl 1a-64 2017
Iodine value	117.2	gI_2/100g	AOCS Tg 1-64 2017

Trimethylolpropane (TMP) Trioleate was used as a bio-lubricant supplied by Wilmar Oleochemicals & Biofuels. The properties of TMP trioleate are shown in Table 3.

Table 2: Physical Properties of ME1299

Parameter	Value	Unit	Test Method
Acid value	0.04	mg KOH/g	AOCS Te 2a-64 2017
Saponification value	262	mg KOH/g	AOCS Tl 1a-64 2017
Iodine value	0.02	gI_2 absorbed	AOCS Tg 1-64 2017

Table 3: Physical Properties of TMP trioleate

Parameter	Value	Unit	Test Method
Acid value	0.25	mg KOH/g	GB/T 6365
Saponification value	184.17	mg KOH/g	HG/T 3505
Iodine value	82.21	gI_2/100g	GB/T 5532
Hydroxyl value	8.44	mg KOH/g	AOCS Cd 13-60

Mixing the sample is performed between TMP and Methyl Laurate through the volumetric proportion mixing [7, 8] at room temperature and left for at least one day to ensure homogeneous mixing among the TMPO and ML before undergoing physicochemical properties. Table 4 shows the weight percentage of the sample, limiting the additive component of Methyl Laurate at 15 % wt.

Table 4: Mixing of TMP Trioleate and Methyl Laurate

Methyl Laurate (%wt)	Trimethylolpropane Trioleate (%wt)
5	95
10	90
15	85

Instrumentation

Wettability was determined using a Goniometer, and ImageJ software was used to measure the contact angle. Kinematic viscosity was evaluated by using a digital rotary viscometer. Cooking oil was used as a liquid bath, and a hot plate stirrer was used to blend the samples during the heating process for uniform temperature distribution.

Methods

Iodine Value

The iodine value, represented relative to the number of cg of iodine absorbed per g of test material, was measured according to AOCS Official Method Tg 1-64 2009 [9].

A completely dry sample was melted and filtered using filter paper to remove solid impurities at a temperature not more than the sample's melting point by 10°C. Then, the sample was placed in a 500 mL flask with 20 mL of carbon tetrachloride. 25 mL Wijs solution was pipet into the flask and then swirled. At least two blank determinations were conducted continuously for each sample. The flask was stored for 30 minutes in a dark area at 25 ± 5°C. The flask was removed from storage, and then 20 mL of KI and 100 mL of distilled water were added. 0.1 M of sodium thiosulfate solution

was titrated into it until the yellow colour disappeared. About 1-2 mL of the starch indicator was added, and the titration was continued until the blue colour was gone.

Wettability

This experiment was performed by referring to the ASTM D7334 standard and following the method of Lee et al. [10]. A goniometer used in this experiment is a tool that can measure the angle or rotate an object to a precise angular position. The ImageJ software calculates and displays the tangent to the triple line contact, providing the contact angle value with sharp accuracy on the measurement. A camera software "HAYEAR" was used in this experiment.

With samples placed on the stage and syringe onto the syringe holder, the x-axis, y-axis, and z-axis were adjusted until the tip of the syringe needle touched the sample's surface, and the distance from tip to sample was kept at 3 mm. The sample was extracted using a syringe with no air bubble presence, and the drop deposited must not exceed 20 µL. The image of the droplet was captured within 30 seconds after it was dropped, as shown in Figure 1. Measurement was repeated six times for each sample to measure the average reading.

Figure 1: Contact angle measurement by using ImageJ software

In the ImageJ software, five points were selected, and then the theta E of the left and right sides were calculated by the software. Measurements were repeated when left theta E and right theta E had huge differences. Next, the average theta E after six measurements was calculated, and the value was subtracted with 180 to obtain the final contact angle value.

Viscosity-Temperature Relation

The kinematic viscosity of the sample was determined according to ASTM D445 standard. A rotary digital viscometer was used where the sample underwent a temperature-controlled cooking oil bath. The reading of kinematic viscosity for each sample was taken until it reached the temperature of 90℃. The density of each sample was measured according to the ASTM D1217 standard.

Density measurements of the TMPO and ML mixtures were determined using a precise four-digit sensitivity analytical balance at room temperature and within a range of 50-55℃. Each density measurement was repeated three times to enhance accuracy, and the average density for each mixture was calculated. By utilizing average values, potential experimental errors were minimized, allowing for a reliable analysis of the viscosity-temperature relationship in the studied samples. Then, the two data points were plotted in Excel, and the equation obtained was used to calculate the kinematic viscosity of temperature rising of dynamic viscosity. The formula to calculate kinematic viscosity is represented by Equation (1).

$$\upsilon = \frac{\eta}{\rho} \tag{1}$$

The kinematic viscosity at 40℃ and 100℃ was determined. The VI was calculated following the ASTM D2270-10 (2016) Method. Equation (2) was used to calculate VI if U is greater than H.

$$VI = \left[\frac{(L-U)}{(L-H)}\right] \times 100 \tag{2}$$

Where: L is kinematic viscosity at 40°C of a viscosity index 0 oil of similar kinematic viscosity @ 100°C as the viscosity index to be evaluated (mm^2/s); H is kinematic viscosity at 40°C of a viscosity index 100 oil of similar kinematic viscosity @ 100°C as the viscosity index to be evaluated (mm^2/s); U is kinematic viscosity of the oil to be calculated viscosity index at 40 °C (mm^2/s).

The value of L and H were extracted from Table 1 in ASTM D2270-10 (2016) [11] for kinematic viscosity at 100 °C is less than or equal to 70 mm^2/s while for kinematic viscosity greater than 70 mm^2/s, the value L and H were calculated by using equation (3) and (4).

$$L = 0.8353Y^2 + 14.67Y - 216 \tag{3}$$

$$H = 0.1684Y^2 + 11.85Y - 97 \tag{4}$$

Where: Y- kinematic viscosity at 100 °C of a viscosity index 0 oil of similar kinematic viscosity @ 100 °C as the viscosity index to be evaluated (mm^2/s). The VI was calculated using equation (5) for value U less than H.

$$VI = \left[\frac{\left((anti\ log\ N) - 1\right)}{0.00715}\right] + 100 \qquad (5)$$

Where the value of N was obtained from equation (6) or (7).

$$N = \frac{(log\ H - log\ U)}{log\ Y} \qquad (6)$$

$$Y^N = \frac{H}{U} \qquad (7)$$

RESULTS

Iodine Value

The number of double bonds in the molecules in the sample is represented by the IV, which means the more unsaturated fatty acids present in the sample, the higher the IV. From Table 5, the IV increases from 100% ME12, followed by 5% ME12, and lastly, 100% ME1299. Therefore, 100% ME12 is the most saturated among all three samples, while 100% ME1299 is less unsaturated.

Table 5: Iodine value of Methyl Laurate

Samples	Iodine value
100% ME12	15.22
5% ME12	6.33
100% ME1299	0.05

Wettability

When added to TMP trioleate, the contact angle of 5% ME12 and 100% ME1299 decrease as the concentration increases, while for 100% ME12, the average contact angle increases with the increase of concentration. From Table 6, we can see that 5 %wt of added 5% ME12 to TMP trioleate is the most hydrophobic, indicating less wettability, while 15 %wt of added 100% ME1299 is the most hydrophilic, indicating better wettability [12].

Therefore, adding 15 %wt of 100% ME1299 to TMP trioleate is optimal because it exhibits the highest hydrophilicity property. The sample's friction coefficient will decrease as its hydrophilicity increases [13]. The presence of double bonds in the chain is reducing, which causes the kinematic viscosity to increase [14].

Table 6: Contact Angle of TMP Trioleate when added with Methyl Laurate

Type	Concentration of Methyl Laurate (%wt)	Average Contact Angle
TMP Trioleate	-	31.08
TMP Trioleate + 100% ME12	5	30.57
	10	31.20
	15	31.46
TMP Trioleate + 5% ME12	5	31.98
	10	30.32
	15	28.77
TMP Trioleate + 100% ME1299	5	30.23
	10	29.37
	15	28.20

Viscosity Index

Figure 2 shows the result for dynamic viscosity when TMP trioleate is added to 100% ME1299. The increasing temperature will cause the molecules to move further apart; therefore, friction increases, and hence, fluid density decreases. The viscometer found that TMP trioleate has higher dynamic viscosity than the other samples when added with the different types of Methyl Laurate. The trend indicates a dilution effect when TMP trioleate is added with Methyl Laurate, which possesses a significantly lower viscosity than TMP trioleate. It is also to note that the viscosity values across all tested samples reduce as the temperature increases.

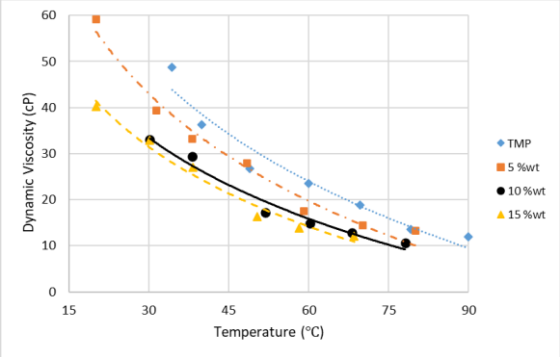

Figure 2: Graph of dynamic viscosity vs temperature for TMP trioleate when added with 100% ME1299

The greater the viscosity index (VI), the lesser the viscosity change to temperature [15, 16]. By analysing Table 7, we can see that TMP trioleate added with 100% ME1299 has the highest VI among all three different samples with different concentrations, while adding 100% ME12 achieves the lowest VI. Among all the samples with different concentrations, adding 15 %wt 5% ME12 has the highest VI at 270.

The results obtained from the study indicate that adding different percentages of ML resulted from kinematic viscosity ranging from 24cSt to 43cSt. These viscosity values are equivalent to the international standard grades of ISO VG22 to ISO VG46, commonly used for hydraulic oil applications [17, 18]. For example, ISO VG22 grade lubricant is often utilized in airline applications [19] for air tools due to its appropriate flow characteristics and lubrication properties. On the other hand, high-powered machine tools that require a slightly higher viscosity for optimal lubrication and protection require lubricants that meet ISO VG46 [20].

These findings highlight the potential versatility of the formulated TMPO with ML mixtures, as the formulated TMPO can cover a range of viscosity grades commonly needed in various industrial applications. The ability to tailor the mixture's viscosity to specific requirements could offer significant advantages in terms of performance and efficiency for different types of machinery and equipment. Additionally, the environmentally friendly nature of the ML additive adds further appeal to these formulations, making them a promising option for industries seeking more sustainable hydraulic oil solutions.

Table 7: Viscosity Index of TMP Trioleate when added with Methyl Laurate

Samples	%wt	Kinematic Viscosity		VI
		40°C	100°C	
TMP trioleate	-	43.137	8.153	166
TMP trioleate + 100% ME12	5	38.026	6.669	132
	10	32.274	6.695	171
	15	24.110	6.578	252
TMP trioleate + 5% ME12	5	36.534	7.372	173
	10	28.537	7.213	234
	15	27.172	7.564	270
TMP trioleate + 100% ME1299	5	35.880	8.493	226
	10	29.543	6.988	211
	15	26.609	7.229	258

CONCLUSION

The IV represents the number of double bonds in the molecules in the sample; hence, the higher the concentration of unsaturated fatty acids in the sample, the higher the IV. The oil will become more viscous when IV is high because it will oxidize more quickly. As indicated by the IV measurement, the amount of unsaturated fatty acids affects kinematic viscosity. It has been discovered that 100% ME12 has the greatest IV value. Additionally, when TMP trioleate is added with 5 %wt, 5% ME12 is the most hydrophobic, while TMP trioleate, when added with 15 %wt 100% ME1299, is the most hydrophilic.

According to the viscosity-temperature relationship, only the mixture of TMP trioleate and 5 %wt 100% ME12 has a lower VI than the neat TMP trioleate, demonstrating that nearly all of the samples can increase the VI of the TMP trioleate bio-lubricant. Moreover, adding 15 %wt of 5% ME12 of all the evaluated samples results in the highest VI. High VI lubricants are preferred, especially in hot weather when a sudden change in viscosity due to temperature might cause an engine to overheat since the bio-lubricant does not work effectively. In particular, high VI offers extra advantages because it requires less oil and experiences less wear at high temperatures. Similarly, boundary lubrication will happen when the bio-lubricant's viscosity is low. Overall, adding

TMP trioleate to the 100% ME1299 Methyl Laurate, which has the lowest IV, can be an excellent mixture in which the viscosity-temperature relation can be optimized.

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