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Synthesis of TMP Ester via Esterification of Corn Oil Fatty Acids and Trimethylolpropane as a Potential Biolubricant Base Stock

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Mineral oils are widely used in the manufacture of biolubricant. However, mineral oils are toxic, non-biodegradable and limited in supply. Therefore, there is a need to find another alternative source to replace mineral oils. Plant oils have been identified as an alternative source to replace mineral oils because they are renewable and environmentally friendly due to their biodegradable and non-toxic properties. However, plant oils also have several drawbacks which cannot be directly used due to the presence of β-hydrogen in the glycerol backbone of the triacylglycerol structure which makes plant oils unstable at higher temperatures and tend to be easily damaged. This limitation can be overcome by chemical modification through the esterification of corn oil fatty acids with trimethylolpropane to produce corn oil trimethylolpropane (COTMP) ester. The esterification was carried out in a mole ratio of 3.5:1 (COFAs: TMP), 2.9% sulfuric acid as a catalyst at 128 °C for 3.9 hours. The characterization of COTMP ester has been done using Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance (^{1}H NMR and ^{13}C NMR) spectroscopy. Next, the evaluation test of COTMP ester has been carried out to evaluate the physicochemical properties of COTMP ester. The result showed that COTMP ester was successfully synthesized with a 97.93% yield. The existence of the ester functional group is evidenced by FTIR at 1743 cm^{-1}, the chemical shift of ^{1}H NMR at 2.29 – 2.37 ppm and ^{13}C NMR at 173.44 ppm. The physicochemical properties analysis showed that COTMP ester has a pour point value of -20 °C, a flash point value of 300 °C, viscosity at 40 °C (48.92 cSt) and viscosity at 100 °C (9.60 cSt), which made COTMP ester suitable to be used as biolubricant base stock.

Keywords: Biolubricant; corn oil fatty acids; trimethylolpropane; polyol ester

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Currently, there are many different types of base oils used in lubricant production including mineral oils, re-refined oils, synthetic oils and plant oils. Among them, mineral oil is the most commonly used. The extensive use of mineral oil has raised concerns and worries in big development industry fields over the use of petroleum-based products which cause progressive reduction of fossil fuels and the impact on the environment as it requires a longer time to break down [1]. Plant oils have been identified as an alternative source to replace mineral oil because they are renewable raw materials, biodegradable and non-toxic compared to conventional mineral-based oils [2, 3]. They are good substitutes for mineral oil because of their physicochemical properties, which include good lubricating properties and are safer for the environment as they are less toxic and will not cause pollution to the environment.

However, most plant oils have several disadvantages that limit their application in the lubricant industry due to the presence of β-hydrogen in the glycerol backbone in triacylglycerol structure, which makes plant oils become unstable at higher temperatures and tend to easily degrade. This results in low oxidative and thermal stability of the plant oils [4]. The β-hydrogen is easily removed from the triacylglycerol structure, resulting in the formation of acid and olefins, which are unsaturated compounds that will polymerize, resulting in the formation of a precipitate that will increase the viscosity of plant oil [5].

Chemical modification of plant oils via esterification with polyhydric alcohol is one of the best ways to solve this problem. There are a few types of polyhydric alcohols which include neopentyl glycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE) that can be used to replace glycerol backbone in the structure of the plant oil. Among these polyhydric alcohols, TMP with the three hydroxyl groups in its structure is the best and most well-known polyhydric

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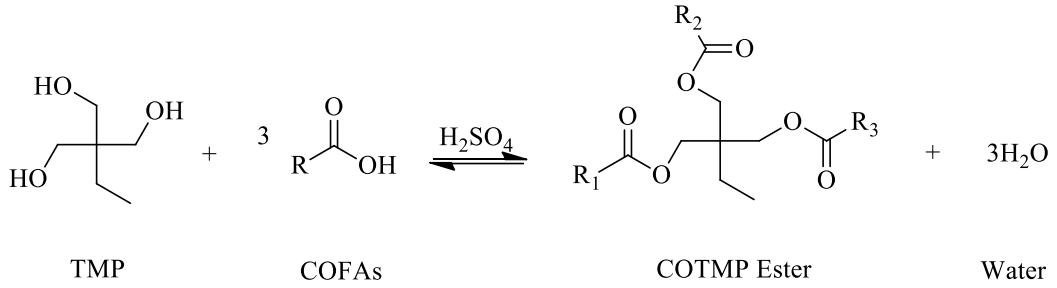

R= Aliphatic chains of corn oil fatty acids

Figure 1. Esterification of corn oil fatty acids (COFAs) with trimethylolpropane (TMP).

alcohol since it has a low melting point due to its branching structure [6]. The use of polyhydric alcohol will enhance the thermal stability of plant oils making it suitable for application as a lubricant and enhancing its ability to stand at higher temperatures since polyhydric alcohol does not contain β-hydrogen [7, 8].

Many studies used TMP for esterification reactions with various types of plant oils. This is due to its ability to improve the oxidative stability of plant oils. A previous study that involved the esterification of palm oil fatty acids (POFAs) with TMP in a mole ratio of 3.5:1 with the presence of 1.34% sulfuric acid as a catalyst at 154 °C for 5.97 hours was successfully performed by Nor et al. [9]. The results showed 92% yield of palm oil TMP (POTMP) ester was successfully synthesized with improvements in the physicochemical properties. POTMP ester had oxidative stability at 183 °C, a pour point at 8 °C, a flash point at 290 °C and a 158-viscosity index.

Many research studies have utilized palm oil as the starting material for esterification with TMP. There are fewer studies on the esterification of corn oil fatty acids with TMP. Therefore, this study aimed to focus on corn oil fatty acids derived from the *Zea mays* plant. According to research and statistical data from the World Data Atlas, Malaysia's maize production was 60 thousand metric tons in 2020. The corn plant production in Malaysia climbed from 5 thousand tons in 1971 to 60 thousand tons, expanding at a 14.03% annual rate [10]. This indicates that the production of corn plants is in high volume, which simultaneously proves that corn oil is much easier to get as it can be extracted easily.

The esterification of corn oil fatty acids (COFAs) with TMP to produce corn oil TMP (COTMP) ester is shown in Figure 1. The fatty acid composition of COFAs was analyzed by GC-FID, while FTIR and NMR were used for the structural determination of COTMP ester. Several tests such as pour point, flash point, and viscosity were conducted to analyze the physicochemical properties of COTMP ester.

EXPERIMENTAL

Chemicals and Materials

Corn Oil (Daisy brand) was obtained from a domestic store. All chemicals including ethanol (95%), potassium hydroxide, hydrochloric acid (37%), n-hexane, sodium sulphate, trimethylolpropane (97%), sulfuric acid (98%), toluene, sodium hydrogen carbonate, sodium chloride, ethyl acetate, acetone, acetonitrile, sodium methoxide, sodium hydroxide, and methanol were purchased from Sigma-Aldrich and were used without further purification.

Hydrolysis of Corn Oil

The hydrolysis process which involves two stages including saponification and acidification was carried out to separate the corn oil fatty acids from the glycerol backbone. In saponification, 50 grams of corn oil were mixed with alkaline ethanol and the mixture was heated at 60 °C for 2 hours followed by an acidification process in which 6N hydrochloric acid was added to neutralize the alkaline solution [11]. 6N hydrochloric acid provided a sufficient level of acidity to effectively acidify the solution after hydrolysis. Higher concentrations may not offer significant advantages in terms of reaction efficiency, while lower concentrations may not achieve complete acidification. The washing process was continued using distilled water and hexane as solvent. Anhydrous sodium sulphate was added to the product which is corn oil fatty acids (COFAs) and left overnight to remove the water content. The product was filtered by Whatman No. 1 filter paper and isolated by a rotary evaporator at 70 °C to remove the solvent. The percentage yield of COFAs was calculated using the formula below:

$$\% \text{ Yield of COFAs} = (\text{COFAs}/\text{CO}) \times 100$$

Esterification of COFAs and TMP

The product of hydrolysis (COFAs) was used for esterification with TMP. The esterification process was conducted according to the method from Nor et al. [4] with some modifications. Nor et al. [4] have reported the synthesis of TMP ester via esterification of TMP with different plant oil fatty acids which were palm oil fatty acids. The esterification process was carried out by mixing corn oil fatty acids (COFAs) with TMP in a mole ratio of 3.5:1. 2.9% of sulfuric acid and 100 mL of toluene (azeotropic agent) were added to the mixture. The mixture was heated at 128 °C for 3.9 hours. The product COTMP ester was neutralized with sodium hydrogen carbonate solution and ethyl acetate was added to the mixture product. Then, sodium chloride solution and distilled water were added to avoid any formation of emulsion. Anhydrous sodium sulphate was added and the product was kept overnight. The product was filtered by Whatman No. 1 filter paper and the solvent used was isolated by a rotary evaporator at 70 °C [12]. The percentage yield of COTMP ester was calculated using the formula below:

% Yield of COTMP ester = COTMP ester/ (COFAs + TMP) x 100

Fatty Acid Composition Analysis

GC-FID (HP-5 column) was used to analyze the fatty acid compositions in corn oil and COFAs. In GC-FID analysis, both corn oil and COFAs need to be converted to fatty acid methyl esters (FAME). FAME was prepared using two methods, which are base-catalyzed for corn oil and acid-catalyzed for COFAs. For base-catalyzed, FAME was prepared by blending 0.1 mL of corn oil with 1 mL of hexane. 1 mL of sodium methoxide solution (1.55 g NaOH in 50 mL of methanol) was added to the oil solution and the solution was stirred vigorously using Vortex stirrer for 10 seconds. The solution was allowed to stand for 10 minutes to separate the clear solution of FAME from the cloudy aqueous layer. The upper FAME layer was slowly collected and injected into GC for analysis. For acid-catalyzed, 1 gram of COFAs was mixed with 3.75 mL methanol and 0.75 mL reagent mixture (5 mL methanol and 1.25 mL concentrated hydrochloric acid) was added, followed by 0.75 mL of toluene. The mixture was allowed to be separated into two layers. The upper layer was slowly collected and dried using anhydrous sodium sulphate overnight. Then, the sample was filtered and injected into GC for analysis.

Structure Analysis

Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) were used to identify the ester functional groups and chemical structure of COFAs and COTMP ester. The FTIR analysis was done using a Perkin Elmer infrared spectrometer, scanning from 650 to 4000 cm^{-1}. NMR analysis was performed with a JOEL-ECP 400 spectrometer operating at 400 MHz (for ^{1}H NMR) and 100.61 MHz (for ^{13}C NMR), using deuterated chloroform ($CDCl_3$) as the solvent.

RESULTS AND DISCUSSION

A hydrolysis process was carried out to separate fatty acid from the glycerol backbone. The percentage yield of hydrolysis was 91.43%. The fatty acid composition in corn oil (before hydrolysis) and COFAs (after hydrolysis) has been simplified in Table 1.

Table 1. Percentage comparison of fatty acid composition before (corn oil) and after hydrolysis (COFAs).

Fatty acid composition	Corn Oil (%)	COFAs (%)
Palmitic acid (C16)	14.92	24.88
Linolenic acid (C18:3)	2.15	0.16
Linoleic acid (C18:2)	57.60	67.55
Oleic acid (C18:1)	15.84	5.80
Stearic acid (C18:0)	7.52	0.66
Arachidic acid (C20:0)	1.97	0.95

From the results, the major fatty acids composition in COFAs are linoleic acid with 67.55%, followed by palmitic acid (24.88%), oleic acid (5.80%), arachidic acid (0.95%), stearic acid (0.66%), and linolenic acid (0.16%).

FTIR Analysis

The esterification process was carried out between COFAs and TMP in the presence of sulfuric acid as a catalyst to produce COTMP ester. The percentage yield of COTMP ester was 97.93%. The formation of COTMP ester was confirmed by FTIR analysis. Figure 2 depicts the comparison between the FTIR spectra of COFAs (before esterification) and COTMP ester (after esterification) and Table 2 shows the functional groups that exist in the FTIR spectra of COFAs and COTMP ester.

FTIR spectrum of COTMP ester showed the appearance of C=O ester stretch at a wavenumber of 1743 cm^{-1} and C-O ester stretch at a wavenumber of 1165 cm^{-1} and 1241 cm^{-1}. This differed from the FTIR spectrum of COFAs in which there was a presence of C=O carboxylic acid stretch that appeared at a wavenumber of 1710 cm^{-1} and C-O carboxylic acid stretch that existed at a wavenumber of 1078 cm^{-1} and 1285 cm^{-1}. Besides that, it was observed that there was no longer any existence of the O-H carboxylic acid stretch in the COTMP ester spectrum. which was initially present at a wavenumber of 2400-3400 cm^{-1} in the FTIR spectrum of COFAs. This proved that COFAs had fully reacted with TMP forming COTMP ester.

COTMP ester also contains an alkane and alkene group. The existence of the functional group of alkanes can be seen through the existence of methyl (CH_3) bend and methylene (CH_2) bend and also the C-H stretch. In the FTIR spectrum of COTMP ester, the peak for the CH_3 bend appeared at a wavenumber of 1373 cm^{-1}, and the CH_2 bend at a wavenumber of 1465 cm^{-1}. Next, the peak for the C-H stretch appeared at a wavenumber of 2855 cm^{-1} and 2927 cm^{-1}. The existence of unsaturated fatty acids could be proved by the presence of sp^2 CH stretch (=C-H) for the alkene group that appeared at a wavenumber of 3007 cm^{-1}.

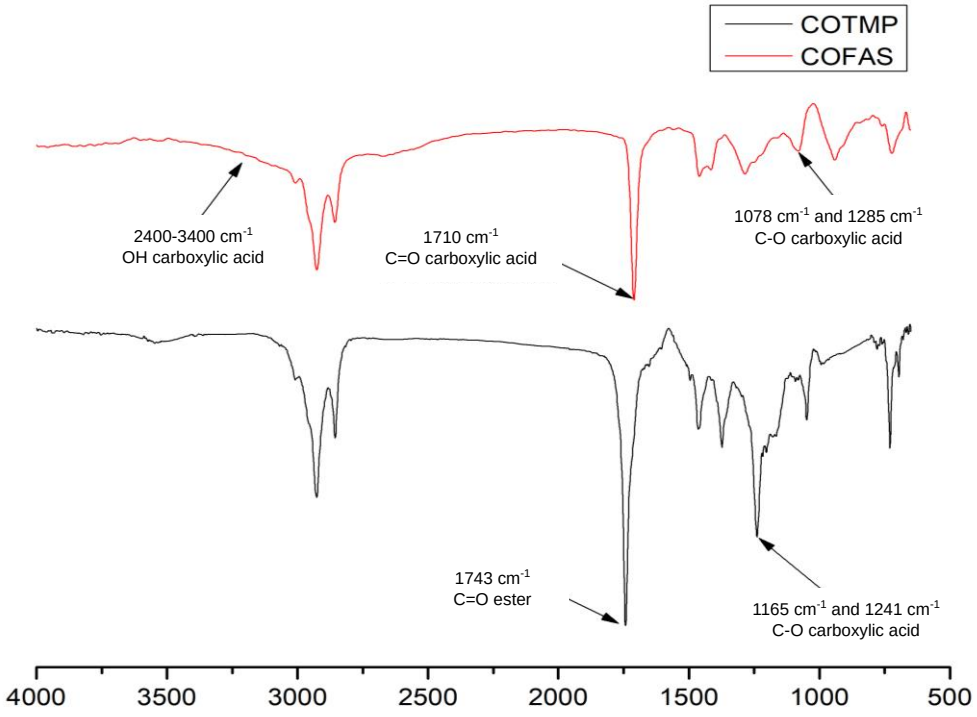

Figure 2. FTIR spectra of COFAs and COTMP ester

Table 2. The functional groups in the FTIR spectra of COFAs and COTMP ester.

Functional Groups	Wavenumber (cm^{-1})	
	COFAs (%)	COTMP ester
Alkene =C-H (stretch)	-	3007
Hydroxyl O-H	2400-3400	-
Alkane C-H (stretch)	2856 and 2926	2855 and 2927
Carbonyl C=O	1710	1743
C-O	1078 and 1285	1165 and 1241
Alkane CH_2, CH_3 (bend)	1413 and 1460	1373 and 1465

NMR Spectroscopy

The structure of the COTMP ester was analyzed using NMR spectroscopy. Figure 3 shows the ^{1}H NMR spectrum of the COTMP ester and the summary of the chemical shift of the ^{1}H NMR spectrum of the COTMP ester is depicted in Table 3. In the ester structure, there are two types of protons: the proton of alcohol ester and the proton of acid ester. The proton of alcohol is located on the carbon atom, which is bound to the oxygen atom (-C**H**$_2$-O-) while the proton of acid is located on the carbon alpha (α) which is bound to the carbonyl group (C**H**$_2$-C=O). The ^{1}H NMR spectrum showed the alcohol proton (-C**H**$_2$-O-) for COTMP ester was detected at a chemical shift of 4.04-4.15 ppm and the acid proton (-C**H**$_2$C=O) was detected at a chemical shift of 2.30-2.37 ppm. These values are in good agreement with the reference that stated the chemical shift of proton (-C**H**$_2$-O-) was at 4.0-4.5 ppm while the chemical shift for proton (-C**H**$_2$-C=O-) was at 2.1- 2.5 ppm [13]. While the presence of alkene groups was detected at the chemical shift 5.33-5.41 ppm for alkene protons (-C**H**=CH-) and 2.00-2.09 ppm (-CH=CH-C**H**$_2$-). The presence of these two peaks proves the existence of unsaturated fatty acids in COTMP ester. This spectrum also showed that there was no peak signal for β-hydrogen detected in the spectrum.

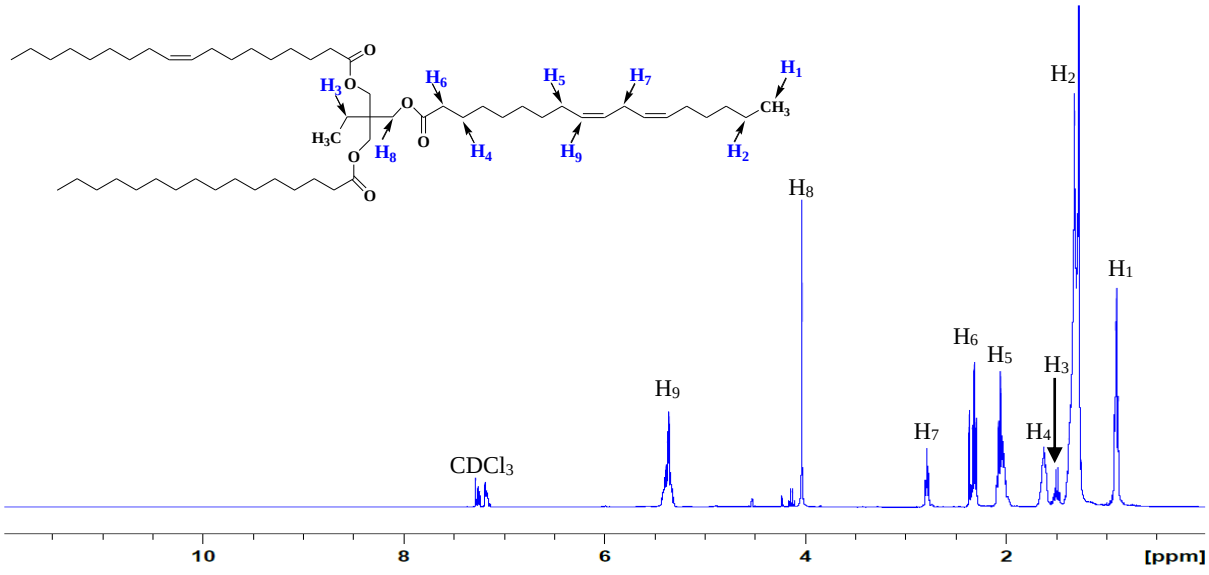

Figure 3. ^{1}H NMR spectrum of COTMP ester.

Table 3. Chemical shift of the ^{1}H NMR spectrum of COTMP ester.

	Type of proton group	Chemical shift δ, ppm	Chemical shift δ, ppm (Reference)
H_1	R-C**H**$_3$	0.88-0.92	0.7-1.3
H_2	R-C**H**$_2$-R	1.38-1.49	1.2-1.5
H_3	CH_3-C**H**$_2$-C-	1.50-1.52	1.5-1.6
H_4	O=C-CH_2-C**H**$_2$-	1.60-1.64	1.5-2.0
H_5	-CH=CH-C**H**$_2$-	2.00-2.09	1.6-2.6
H_6	-C**H**$_2$-C= O	2.30-2.37	2.1-2.5
H_7	=CH-C**H**$_2$-CH=	2.78-2.80	2.5-3.0
H_8	-C**H**$_2$-O	4.04-4.15	4.0-4.5
H_9	-C**H**=CH-	5.33-5.41	4.5-6.5

Figure 4 depicts the ^{13}C NMR spectrum of COTMP ester that shows the presence of carbonyl ester carbon (**C**OOR) in COTMP ester at a chemical shift of 173.44 ppm. This value is aligned with Pavia *et al.* [13] which stated that the chemical shift for carbon carbonyl ester (**C**OOR) was in the range of 155-185 ppm. The peak signal for the -**C**H_2-O carbon that bound the fatty acid to TMP was detected at the chemical shift of 63.71 ppm. The presence of both C=O and -**C**H_2-O peaks indicated the presence of an ester bond between COFAs and TMP forming COTMP ester. The summary of the chemical shift of the ^{13}C NMR spectrum of the COTMP ester is depicted in Table 4.

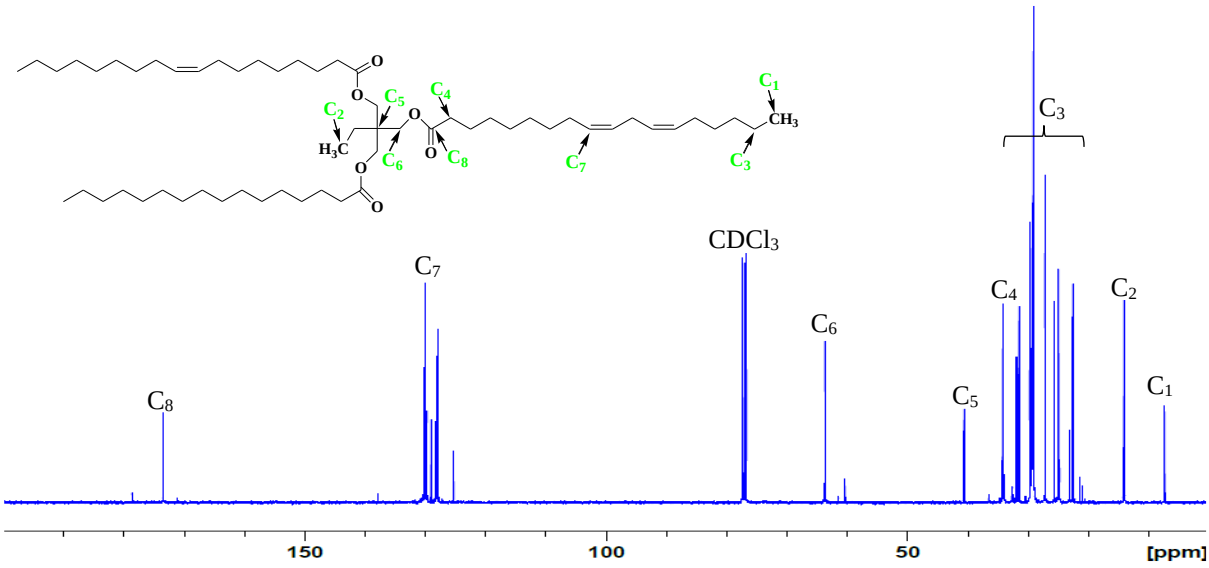

Figure 4. ^{13}C NMR spectrum of COTMP ester

Table 4. The chemical shift of the ^{13}C NMR spectrum of COTMP ester.

	Type of proton group	Chemical shift δ, ppm	Chemical shift δ, ppm (Reference)
C_1	-**C**H_3	8.36	8 - 30
C_2	-**C**H_3	14.04-14.17	8 - 30
C_3	-**C**H_2-	21.42-29.76	15 - 55
C_4	**C**H_2-C=O	31.90-33.89	20 - 60
C_5	-**C**-	40.61	20 - 60
C_6	-**C**H_2-O-	63.71	40 - 80
C_7	**C**=C	125.28-130.18	100 -150
C_8	**C**OOR	173.44	155 -185

Table 5. Physicochemical properties of corn oil and COTMP ester.

Physicochemical properties	CO	COTMP ester
Pour point (°C)	-16	- 20
Flash point (°C)	280	300
Kinematic viscosity index at 40 °C (cSt)	31.04	48.92
Kinematic viscosity index at 100 °C (cSt)	6.97	9.60
Rheology	-	Dilatant

Physicochemical Properties of COTMP Ester

COTMP ester was tested with several tests to evaluate the physicochemical properties as biolubricant base stock. The results of the physicochemical properties obtained are shown in Table 5.

The pour point is the lowest temperature of oil that the liquid can flow only under gravitational forces [14]. This is also an important parameter for analysing the flow properties of the oils at low temperatures. The -20 ℃ pour point value of COTMP ester indicates that the ester product begins to flow at a lower temperature compared to corn oil, which is one of the good characteristics for an application as a biolubricant. In comparison, the pour point standard for commercial lubricants derived from paraffin distillates typically falls within the range of -7 °C to -18 °C internationally [15]. COTMP ester has a lower pour point due to branching in the carbon chain and bent structure that disrupts the stacking process and creates a steric barrier around the individual molecules which form microcrystalline structures rather than macrocrystalline structures, resulting in better flow of the fluid [16].

Another important factor in evaluating the performance of biolubricant is the flash point. The flash point of oil is referred to as the lowest temperature at which a liquid gives off vapor to ignite in the air when exposed to an ignition source [17]. COTMP ester has a higher flash point value at 300 ℃ compared to corn oil at 280 ℃. This is due to the increasing carbon chain and molecular weight of the COTMP ester with the presence of the ethyl group, which indicates that the ester needs more energy to be burned. In the application of biolubricant, a high flash point is important to ensure that the biolubricant is not burned in the engine during its operations [16, 18].

Viscosity is also an important factor that influences the efficiency of the biolubricant in reducing friction during its operations. The presence of an ethyl group (CH_3CH_2) in the structure of TMP has contributed to the increase in the COTMP ester molecular weight, further increasing its viscosity. The viscosity of COTMP ester was in a medium range: 48.92 cSt at 40 ℃ and decreasing to 9.60 cSt at 100 ℃. This shows that the viscosity of COTMP ester decreases as temperature increases. Since the viscosity of COTMP ester is in the medium range and not too viscous or too thin, the ester has a good property as a biolubricant. A good biolubricant does not drastically change as temperature changes and therefore works well. This is a good indicator and suitable for use in large temperature ranges. Overall, an effective biolubricant is a lubricant that has a low pour point, a high flash point and a high viscosity index.

The rheological test showed that the shear stress of the COTMP ester is almost directly

proportional to the increase in shear rate and produces a slightly linear line. This shows that COTMP ester is a dilatant fluid where the viscosity of COTMP ester increases as the shear stress is applied.

CONCLUSION

The high demand for renewable and biodegradable biolubricants from plant oils will offer sustainable development and a green-environmental approach. Hence, COTMP ester was successfully synthesized via esterification of corn oil fatty acids and TMP with a percentage yield of 97.93%. Evaluation of COTMP ester showed that there was an improvement in the physiochemical properties of COTMP ester in terms of low pour point, high flash point, and medium value of viscosity. A good biolubricant is a lubricant that has a low pour point and a high flash point. It makes it suitable for use as a biolubricant base stock, for example for engine operation and machining purposes.

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