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Synthesis and Characterization of Sunflower Oil Unsaturated Fatty Acid Pentaerythritol Ester as Green Biolubricant Base Stock

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Sunflower oil (SFO) presents itself as a promising renewable resource for biolubricants production, offering a sustainable alternative to traditional lubricants. However, a drawback of SFO is its low oxidative and thermal stability, primarily due to the presence of beta hydrogen on the glycerol backbone. This issue can be effectively addressed through a chemical modification process involving esterification with polyhydric alcohol. In the esterification process, unsaturated fatty acids derived from sunflower oil (SFOUFA) were reacted with pentaerythritol (PE) to produce sunflower oil unsaturated fatty acids pentaerythritol ester (SFOUFAPEE). This reaction was carried out with a mole ratio of 5:1 by employing 1.5% sulfuric acid as the catalyst at a temperature of 160 °C for 6.0 hours. The confirmation of the functional group and chemical structure of SFOUFAPEE was achieved through Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) techniques. Notably, the results indicate the successful synthesis of SFOUFAPEE with a remarkable 60% yield. SFOUFAPEE remains in liquid form at room temperature. Key indicators of its structure include the presence of the C=O (ester) group at 1742.32 cm^{-1} and the absence of the C=O (carboxylic acid) group at 1710.60 cm^{-1}, with OH stretching observed within the range of 2400-3400 cm^{-1} in FTIR spectrum. For NMR, the existence of the ester group was at a chemical shift of ^{1}H NMR at 4.10 to 4.15 ppm (from PE) and ^{13}C NMR at 173.21 ppm for ester. Analysis of the physicochemical properties revealed the thermal stability of SFOUFAPEE was at 354.95 °C, a pour point of -21 °C, a flash point of 302 °C, and a viscosity index of 145. These characteristics render SFOUFAPEE a promising alternative for use as a lubricant base stock.

Keywords: Esterification; sunflower oil unsaturated fatty acids; pentaerythritol; pentaerythritol ester; polyol ester

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The expansion of product manufacturing derived from renewable sources is escalating in response to apprehensions regarding the utilization of petroleum-based products, which contribute to a decline in fossil fuel availability and exert adverse effects on the environment [1-3]. The incorporation of renewable resources in product fabrication holds paramount significance in guaranteeing the attainment of sustainable development. The detrimental effects of fossil fuels, petroleum, and petroleum-based products, including lubricants, have stimulated the scientific community and industries to explore plant oil as a viable alternative for sourcing raw materials. Plant oil has garnered significant attention due to its renewable nature, biodegradability, and lack of adverse environmental impact [2-4].

Considering the escalating concern regarding the environmental impact of petroleum oil-based fluids, ample opportunities are emerging for the transition to bio-based lubricants (biolubricants). Plant oil exhibits lubricating characteristics, high flash points, and high viscosity indices [2]. However, the low oxidative and thermal stability and poor properties at low temperatures of the plant make it unsuitable for direct used as a lubricant. The presence of oxidation-active sites, specifically beta hydrogen (β-hydrogen) in the glycerol backbone structure contributes to the inherent instability of plant oil at higher temperatures [2, 5]. The β-hydrogen is prone to removal from triacylglycerol molecules, resulting in the formation of acid and olefin (unsaturated compounds). These unsaturated compounds subsequently undergo polymerization leading to the formation of precipitates that increase the viscosity of plant oil [4, 6].

To address the oxidative stability limitation associated with plant oil, scientific approaches must

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be pursued. One promising strategy involves the chemical modification of plant oils through molecular structural redesign. A suitable modification technique involves esterification with polyhydric alcohols such as neopentyl glycol, trimethylolpropane (TMP), and pentaerythritol (PE) to replace the glycerol backbone within the plant oil structure. The incorporation of polyhydric alcohols offers the advantage of eliminating β-hydrogen, thereby significantly enhancing the thermal and oxidative stability of the lubricant, particularly at high temperatures [5, 7, 8].

Numerous studies have been conducted on the production of biolubricants using polyhydric alcohols. Among them, the utilization of neopentyl glycol (NPG) and trimethylolpropane (TMP) as polyhydric alcohols in biolubricant production is more prevalent compared to pentaerythritol (PE) [9]. The use of PE as a polyhydric alcohol for biolubricant production remains limited, with only a few studies exploring its application. For instance, Mahmud et al. (2014) [10] successfully synthesized pentaerythritol ester from oleic acid, achieving a yield of 92-94% with a tetraester composition of 95.23%. The reaction conditions involved a molar ratio of fatty acid to PE of 4.9:1, 2% catalyst and a reaction temperature of 180 °C for 6 hours. The resulting pentaerythritol ester exhibited a high viscosity index of 309, a pour point of -42°C, a flash point exceeding 300 °C, and an oxidative stability of 177 °C. Similarly, Maurad et al. (2018) [11] employed a combined esterification and short-path distillation approach to produce highly pure pentaerythritol ester (PEE). The study demonstrated a tetraester composition of 97%, with a flash point ranging from 160 °C to 300 °C, oxidative stability of 34 °C-50 °C, and a pour point of -9 °C to -3 °C. Moreover, the PEE exhibited 100% biodegradability within less than 9 days. According to previous studies, only a mixture of fatty acids was used in the production of biolubricant.

This study focuses on the use of unsaturated fatty acids from sunflower oil compared to previous studies that used oleic acid and a mixture of saturated and unsaturated fatty acids. Additionally, this paper reports on the esterification process of sunflower oil unsaturated fatty acids (SFOUFA) with pentaerythritol (PE) to produce sunflower oil unsaturated fatty acids pentaerythritol ester (SFOUFAPEE), intended for use as a base stock in biolubricants. The study also includes an evaluation of its physicochemical properties, such as pour point, flash point, kinetic viscosity, viscosity index, and thermal stability.

EXPERIMENTAL

Chemicals and Materials

Sunflower oil (SFO) was obtained from Melbelle Natural, Selangor, Malaysia. Pentaerythritol (98%) was purchased from Sigma Aldrich. Sulfuric acid (98%), toluene, ethyl acetate, sodium bicarbonate, sodium chloride, anhydrous sodium sulphate, hydrochloric acid (37%), n-hexane, potassium hydroxide, methanol and ethanol were purchased from Systerm.

Esterification of SFOUFA with PE

SFO was first hydrolyzed to produce sunflower oil fatty acids (SFOFA) according to Murad et al. (2020) [12]. Subsequently, SFOFA was separated into saturated fatty acids (SFOSFA) and unsaturated fatty acids (SFOUFA) according to the technique from Japir *et al.* (2018) [13]. The SFOUFA was then subjected to esterification with pentaerythritol (PE) to produce sunflower oil unsaturated fatty acids pentaerythritol ester (SFOUFAPEE) biolubricant base stock according to the method from Murad et al. (2022) [9] with some modification. The esterification process was carried out using a Dean-Stark three-neck round-bottom flask equipped with a reflux condenser, a magnetic stirrer, and a thermometer. The reaction involved the mixing of SFOUFA and PE in a mole ratio of 5:1, with excess SFOUFA utilized to ensure complete esterification with PE. A 1.5% sulfuric acid (based on the weight of SFOUFA) and 100 mL of toluene as an azeotropic agent were periodically added to the mixture until the reaction reached completion. The reaction mixture was heated at 160 °C for 6 hours. The resulting product, namely sunflower oil unsaturated fatty acids pentaerythritol ester (SFOUFAPEE), was neutralized using sodium hydrogen carbonate solution, followed by washing with sodium chloride solution and ethyl acetate. Anhydrous sodium sulfate was added to the product, which was then left overnight. The product was subsequently filtered using Whatman No. 1 filter paper and the solvent was removed using a rotary evaporator. The SFOUFAPEE was analyzed using FTIR and NMR.

Characterization of SFOUFAPEE

Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) techniques were employed to determine and identify the functional group and chemical structure of SFOUFAPEE. The FTIR analysis was conducted using a Perkin Elmer infrared spectrometer, covering a range of 650 to 4000 cm^{-1}. For NMR analysis, a JOEL-ECP 400 spectrometer operating at 400 MHz (for ^{1}H NMR) and 100.61 MHz (for ^{13}C NMR) was utilized with deuterated chloroform ($CDCl_3$) serving as the solvent.

Evaluation of Lubrication Properties of SFOUFAPEE

The lubrication properties of the SFOUFAPEE biolubricant were determined using the standard methods established by the American Society for Testing and Materials (ASTM). The flash point, pour point, and viscosity of the biolubricant were measured following the ASTM D-92, ASTM D-97, and ASTM D-2270 standards, respectively [14]. The thermal stability was assessed using a thermogravimetric analyzer-differential scanning calorimeter (TGA-DSC), while the viscosity index was determined using the rheometer MCR series from Anton Paar.

RESULTS AND DISCUSSION

Sunflower oil (SFO) is characterized by its light-yellow color and its liquid state at room temperature, predominantly due to its high concentration of unsaturated fatty acids. The hydrolysis process was employed to obtain sunflower oil fatty acids (SFOFA) by separating them from the glycerol backbone, resulting in a 96% yield of SFOFA. Subsequently, the separation between saturated fatty acids (SFOSFA) and unsaturated fatty acids (SFOUFA) was carried out using the methanol crystallization method, yielding 82% of unsaturated fatty acids. The SFOUFA primarily consisted of oleic, linoleic, linolenic and paullinic acids, which underwent esterification with pentaerythritol (PE) to produce the polyol ester known as sunflower oil unsaturated fatty acids pentaerythritol ester (SFOUFAPEE) with percentage yield of 60%. The overall reaction is shown in Figure 1. The structure of SFOUFAPEE was confirmed through the application of FTIR and NMR spectroscopy.

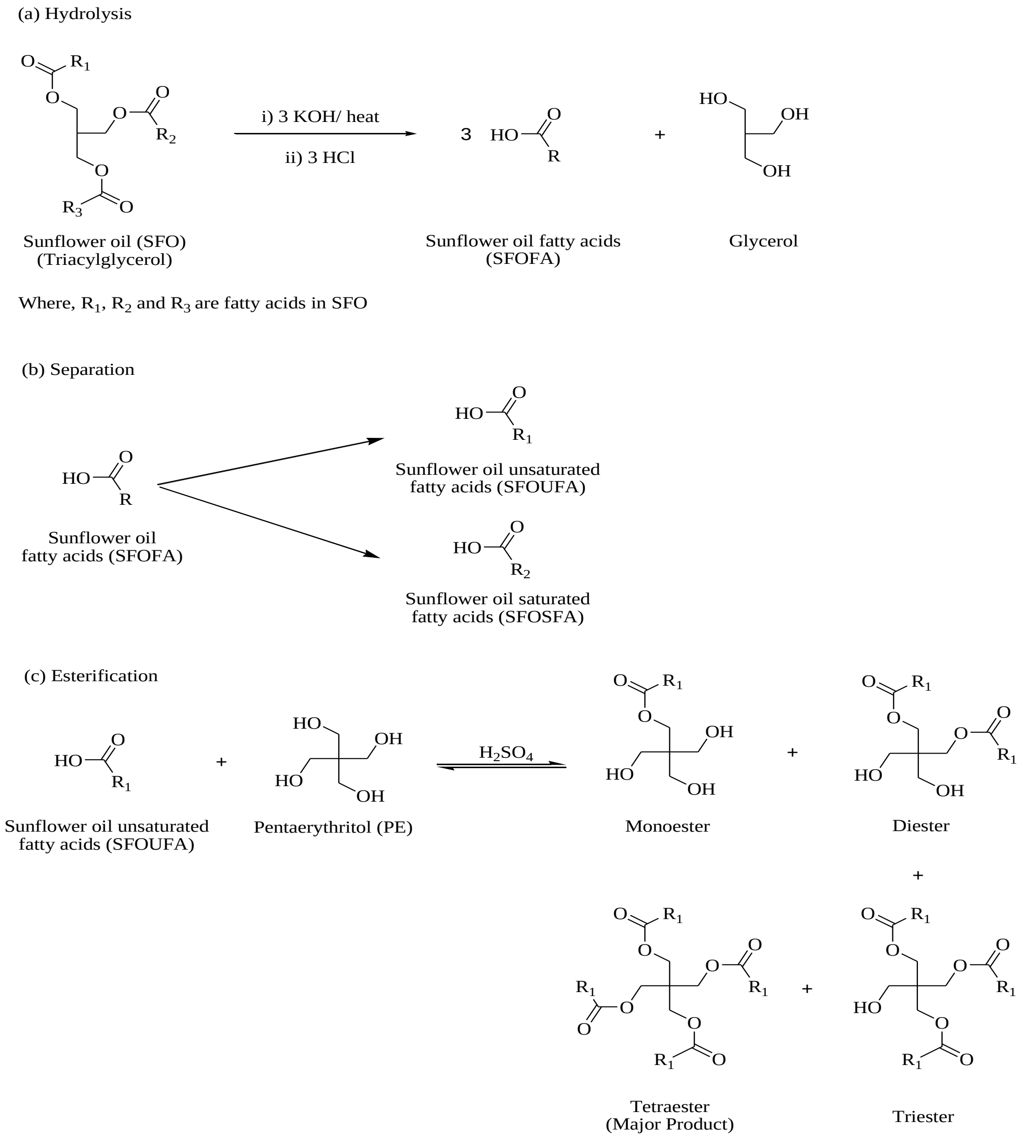

Figure 1. Schematics representation for (a) hydrolysis of SFO, (b) separation of SFOFA and (c) esterification of SFOUFA with PE to form SFOUFAPEE.

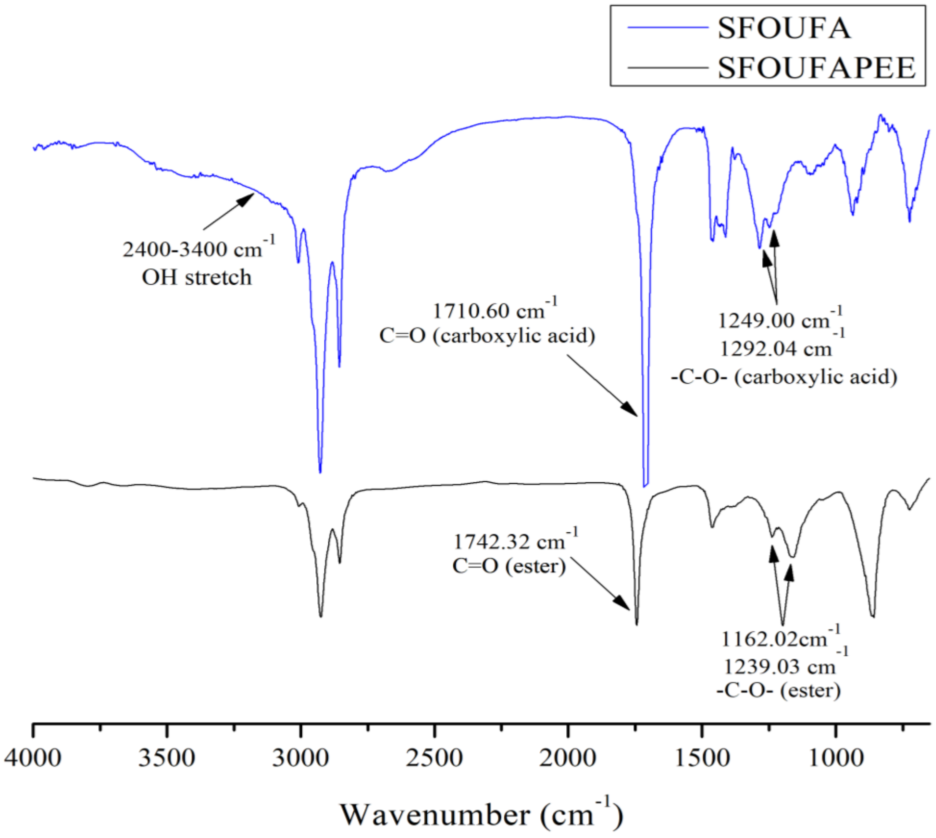

Figure 2. FTIR spectra of SFOUFA and SFOUFAPEE.

Table 1. Functional group and wavenumber of SFOUFA and SFOUFAPEE.

Functional group	Wavenumber (cm^{-1})	
	SFOUFA	SFOUFAPEE
OH stretching (carboxylic acid)	2400-3400	-
C=C bending vibration (aliphatic)	3010.11	3008.48
C-H stretching vibration (aliphatic)	2926.93 and 2856.16	2925.96 and 2854.51
C=O stretching vibration (ester)	-	1742.32
C=O stretching vibration (carboxylic acid)	1710.60	-
-C-O stretching vibration (ester)	-	1239.03, 1162.02
-C-O stretching vibration (carboxylic acid)	1292.04 and 1249.00	-

FTIR Analysis

Figure 2 shows a comparison of the FTIR spectra before (SFOUFA) and after (SFOUFAPEE) the esterification. The FTIR spectrum of SFOUFAPEE demonstrates the emergence of a C=O ester stretching peak at 1742.32 cm^{-1}. In contrast, the FTIR spectrum of SFOUFA revealed the stretching of the C=O group of carboxylic acid, observed at 1710.60 cm^{-1} has disappeared. Notably, the FTIR spectrum of SFOUFAPEE exhibited the presence of C-O ester group stretching at 1239.03 cm^{-1} and 1162.02 cm^{-1}, attributed to the combination of sp^2 and sp^3 C-O stretching vibrations in the ester. Conversely, the sp^2 C-O stretching of carboxylic acid appeared at 1292.04 cm^{-1} and 1249.00 cm^{-1} in the SFOUFA spectrum. The observed shifted wavenumbers in both spectra confirmed the successful esterification of SFOUFA with PE, resulting in the formation of SFOUFAPEE. Furthermore, the OH stretching peak, originally present in the SFOUFA spectrum within the range of 2400 to 3400 cm^{-1}, was no longer visible in the FTIR spectrum of SFOUFAPEE. The disparity in intensity between SFOUFA and SFOUFAPEE spectra arose from the presence of hydrogen bonding facilitated by the carboxylic acid in SFOUFA, resulting in higher intensity. Conversely, in SFOUFAPEE, the conversion of the carboxylic acid to an ester has led to a reduction in intensity due to the elimination of hydrogen bonding interactions [15]. Table 1 provides a summary of the functional groups and their corresponding wavenumbers for both spectra.

NMR Analysis

The success of the esterification reaction was assessed through the analysis of ^{1}H and ^{13}C-NMR spectra, as depicted in Figures 3 and Figure 4, respectively. In the ^{1}H-NMR spectrum, characteristic peaks were observed at specific chemical shifts, indicating the presence of various proton environments. The peaks observed for SFOUFA and SFOUFAPEE were as follows: 0.89-0.93 ppm for $\text{-C}\mathbf{H}_3$, 1.28-1.39 and 1.26-1.39 ppm for $\text{-C}\mathbf{H}_2\text{-}$, 1.62-1.67 and 1.60-1.62 ppm for $\text{O=C-CH}_2\text{-C}\mathbf{H}_2\text{-}$, 2.03-2.10 and 2.00-2.09 ppm for $\text{-CH=CH-C}\mathbf{H}_2\text{-}$, 2.34-2.38 and 2.29-2.37 ppm for $\text{O=C-C}\mathbf{H}_2\text{-}$, 2.78-2.81 and 2.77-2.80 ppm for $\text{=CH-C}\mathbf{H}_2\text{-CH=}$, 5.33-5.41 and 5.31-5.34 ppm for $\text{-C}\mathbf{H}\text{=CH-}$, and 7.28 ppm for $CDCl_3$ (solvent). The appearance of a peak at 4.10-4.15 ppm ($\text{C}\mathbf{H}_2\text{-O}$) confirmed the presence of pentaerythritol in the chemical structure of SFOUFAPEE. Notably, the absence of a peak at the chemical shift 11.35 ppm indicated the successful conversion of SFOUFA to SFOUFAPEE, as the $\text{-O}\mathbf{H}$ group from SFOUFA was no longer present. Table 2 shows the chemical shift of ^{1}H NMR spectra for SFOUFA and SFOUFAPEE.

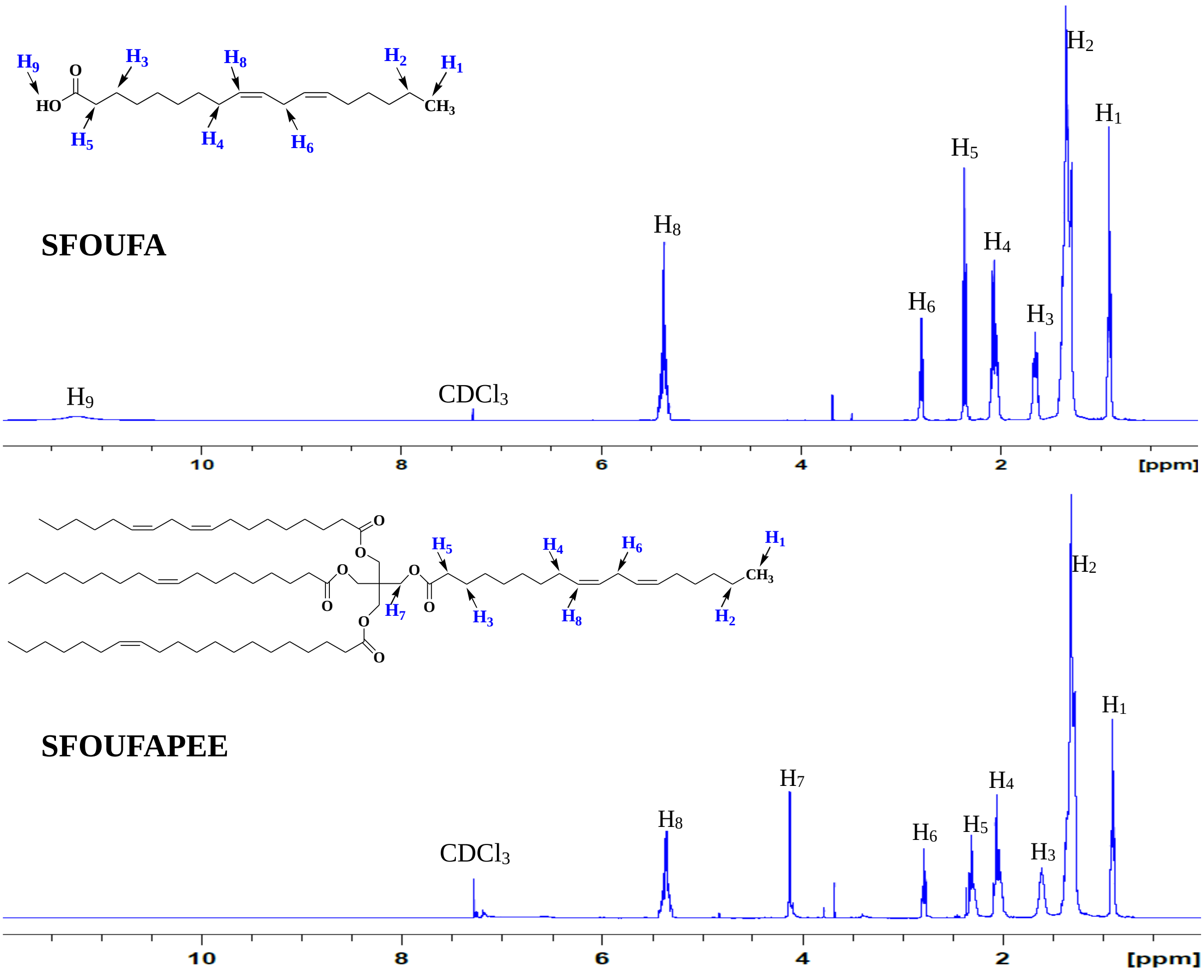

Figure 3. ^{1}H NMR spectra of SFOUFA and SFOUFAPEE.

Table 2. The chemical shift of ^{1}H NMR spectra for SFOUFA and SFOUFAPEE.

Type of proton		Chemical shift (ppm)		Theoretical*
		SFOUFA	SFOUFAPEE	
H_1	-C**H**$_3$	0.89-0.93	0.88-0.93	0.70-1.3
H_2	-C**H**$_2$-	1.28-1.39	1.26-1.39	1.2-1.4
H_3	O=C-CH$_2$-C**H**$_2$-	1.62-1.67	1.60-1.62	1.5-2.0
H_4	-CH=CH-C**H**$_2$-	2.03-2.10	2.00-2.09	1.6-2.6
H_5	O=C-C**H**$_2$-	2.34-2.38	2.29-2.37	2.1-2.5
H_6	=CH-C**H**$_2$-CH=	2.78-2.81	2.77-2.80	2.5-3.0
H_7	-C**H**$_2$-O- (pentaerythritol)	-	4.10-4.15	4.0-4.5
H_8	-C**H**=CH-	5.33-5.41	5.31-5.34	4.5-6.5
H_9	-COO**H**	11.35	-	10-12

*[16]

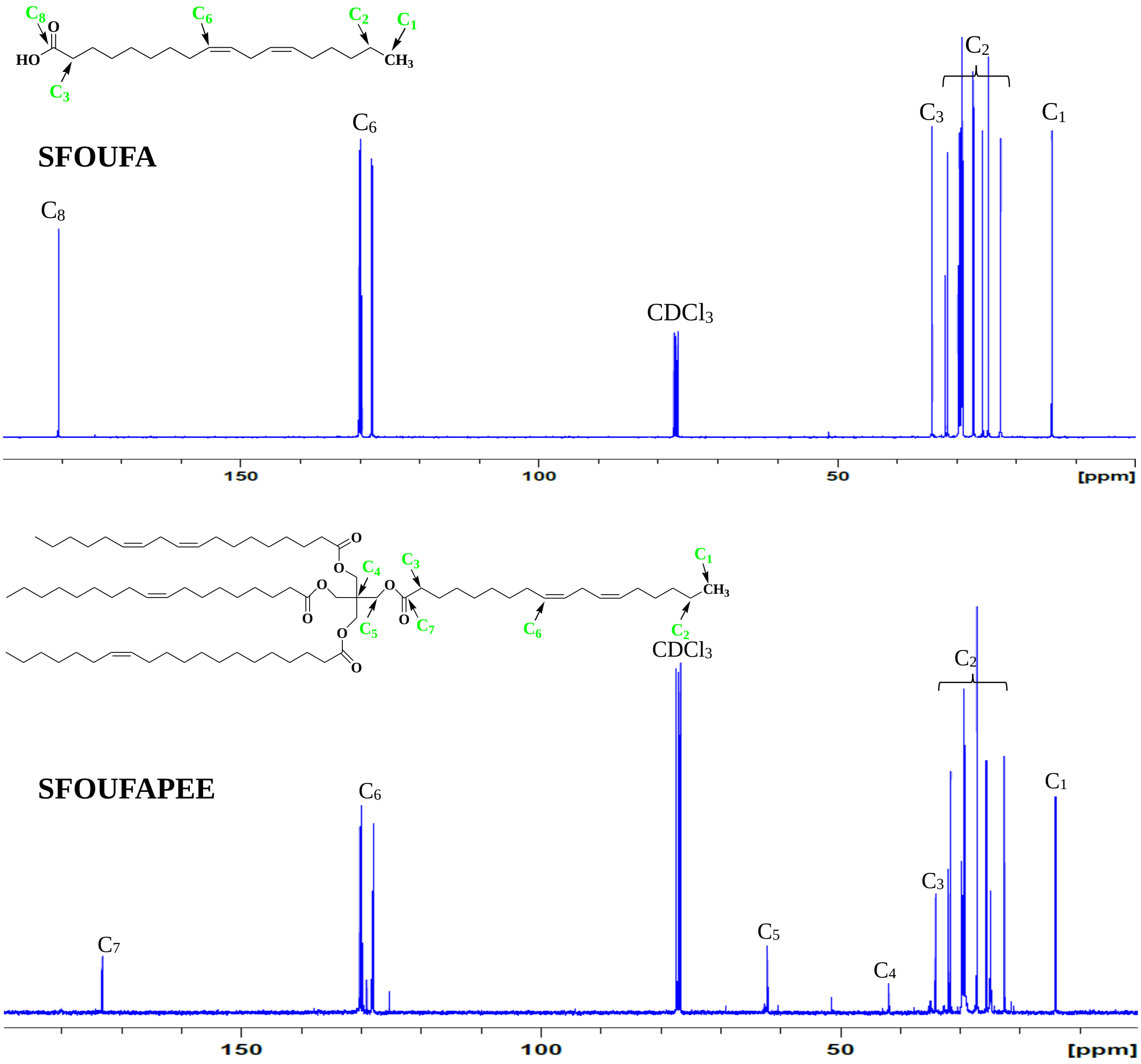

Figure 4. ^{13}C NMR spectra of SFOUFA and SFOUFAPEE.

Table 3. The chemical shift of ^{13}C NMR spectra for SFOUFA and SFOUFAPEE.

	Type of proton	Chemical shift (ppm)		Theoretical*
		SFOUFA	SFOUFAPEE	
C_1	-**C**H_3	14.03-14.07	14.05	8-30
C_2	-**C**H_2-	22.39-29.77	25.09-31.91	15-55
C_3	O=C-CH_2	34.10-34.36	34.07	15-55
C_4	-C- (pentaerythritol)	-	41.86	20-60
C_5	-**C**H_2-O (pentaerythritol)	-	62.14	40-80
C_6	-**C**=C-	127.90-130.54	127.91-130.20	100-150
C_7	O=**C**-OR (ester)	-	173.21	155-185
C_8	O=**C**-OH (carboxylic acid)	180.33	-	155-185

*[16]

In the ^{13}C-NMR spectrum, carbon peaks appeared at specific chemical shifts, revealing different carbon environments. The peaks observed for SFOUFA and SFOUFAPEE were as follows:14.03-14.07 and 14.05 ppm for -**C**H_3, 22.39-29.77 and 25.09-31.91 ppm for -CH_2-, 34.10-34.36 and 34.07 ppm for O=C-**C**H_2, 76.71-77.35 ppm for $CDCl_3$ (solvent), and 127.90-130.54 and 127.91-130.20 ppm for -**C**H=CH-. The disappearance of the peak corresponding to the carboxylic acid carbonyl group (COOH) at 180.33 ppm and the presence of a peak at a chemical shift of 173.21 ppm, indicative of the ester carbonyl group (COOR), has confirmed the successful conversion of SFOUFA to the SFOUFAPEE. The appearance of peaks in SFOUFAPEE at chemical shifts of 41.86 ppm and 62.14 ppm indicated the presence of -C- and -CH_2-O moieties of pentaerythritol as a backbone. Table 3 shows the chemical shift of ^{13}C NMR spectra for SFOUFA and SFOUFAPEE. The chemical shifts of the peaks obtained from both ^{1}H and ^{13}C-NMR spectra were found to be consistent with the theoretical values, further supporting the successful formation of the desired SFOUFAPEE. These findings from the NMR analysis provide valuable evidence of the completion of the esterification reaction.

Lubrication Properties of SFOUFAPEE

The lubrication properties of SFOUFAPEE were assessed to determine its potential as a biolubricant base stock and its compatibility for market use as a lubricant. Key lubrication tests, including pour point, flash point, kinetic viscosity, viscosity index, and thermal stability, were conducted on the SFOUFAPEE.

The pour point, which signifies the lowest temperature at which the liquid remains flowable under standard test conditions [17], was considered to evaluate the biolubricant potential of SFOUFAPEE. A low pour point is indicative of favorable low-temperature flow behavior in lubricants [18]. Biolubricants with short-chain saturated fatty acids (C4-C12) and a higher proportion of unsaturated fatty acids generally exhibit low pour points [19]. The synthesized SFOUFAPEE demonstrated a pour point of -21 °C, indicating its suitability for use in regions with colder climates. Comparatively, the international standard for pour point in commercial lubricants based on paraffin distillates ranged from -18 °C to -7 °C [20]. Thus, the pour point of SFOUFAPEE was found to be comparable to that of established commercial lubricants. The results suggest that SFOUFAPEE exhibits promising biolubricant potential and qualifies as a viable alternative to conventional commercial lubricants, particularly in regions with colder environmental conditions.

The flash point of a biolubricant serves as a crucial indicator of its flammability and volatility [17]. It represents the lowest temperature at which the biolubricant can ignite and produce a flame when exposed to an external ignition source. In the present study, the flash point of the SFOUFAPEE was determined to be 302 °C. Comparison with international lubricating standards reveals that petroleum-based lubricants are typically required to have a high flash point of around 290 °C, whereas ester-based lubricants are expected to possess a flash point of approximately 250 °C [4]. Remarkably, the SFOUFAPEE demonstrated a flash point exceeding these values, further reinforcing its potential as a biolubricant. The flash point of the SFOUFAPEE was influenced by its carbon composition, specifically, carbon atoms ranging from 16 to 18 in length. This composition contributed to the higher flash point observed, enhancing the safety and applicability of the biolubricant in various scenarios. The SFOUFAPEE exhibited a notable flash point, highlighting its reduced flammability and enhanced stability as a biolubricant, thus making it a favorable option for potential industrial applications [4].

The viscosity of SFOUFAPEE was found to be higher than that of SFO at both 40°C and 100°C. This disparity could be attributed to the greater molecular weight and polarity exhibited by SFOUFAPEE in comparison to SFO. Specifically, the elongated carbon chain within the structure of SFOUFAPEE contributed significantly to this viscosity increase. Additionally, the presence of a greater number of ester groups in SFOUFAPEE enhanced its polarity, leading to stronger intermolecular interaction forces and a consequent viscosity rise in the lubricant. The viscosity of SFOUFAPEE decreased from 80.49 cSt to 14.25 cSt as the temperature increased from 40 °C to 100 °C. SFOUFAPEE demonstrated a lower viscosity index when compared to SFO, with values of 145 and 163, respectively. This discrepancy was attributed to the increased number of double bonds in SFOUFAPEE, rendering it more susceptible to oxidation, which impacted its viscosity and viscosity index.

The thermal stability of sunflower oil (SFO) and SFOUFAPEE were studied by the thermo-gravimetric analyzer-differential scanning calorimeter (TGA-DSC). The graphs of weight loss against temperature are shown in Figure 5. It shows that SFOUFAPEE is thermally stable with temperature onset (T_{onset}) at 354.95 °C compared to SFO at 353.80 °C as shown in Table 4. Table 4 displays the thermal degradation behavior of SFOUFAPEE and SFO, revealing a weight loss of 10 wt.% occurring at 411.56 °C and 397.35 °C, respectively. Moreover, the maximum weight loss, constituting 90 wt.%, was observed at 475.83 °C for SFOUFAPEE and 453.08 °C for SFO, indicative of their respective thermal stability profiles. Hence, it is conclusive that SFOUFAPEE is thermally more stable as compared to SFO which can be due to the absence of β-hydrogen in esters and improves the thermal stability of polyol esters-based biolubricant.

Table 4. Thermal stability and degradation profile of SFO and SFOUFAPEE.

Sample	Temperature (°C)					
	Onset	Endset	10% wt. loss	50% wt. loss	90% wt. loss	DTA
SFO	353.80	492.41	397.35	419.34	453.08	408.37
SFOUFAPEE	354.95	501.42	411.56	458.20	475.83	464.22

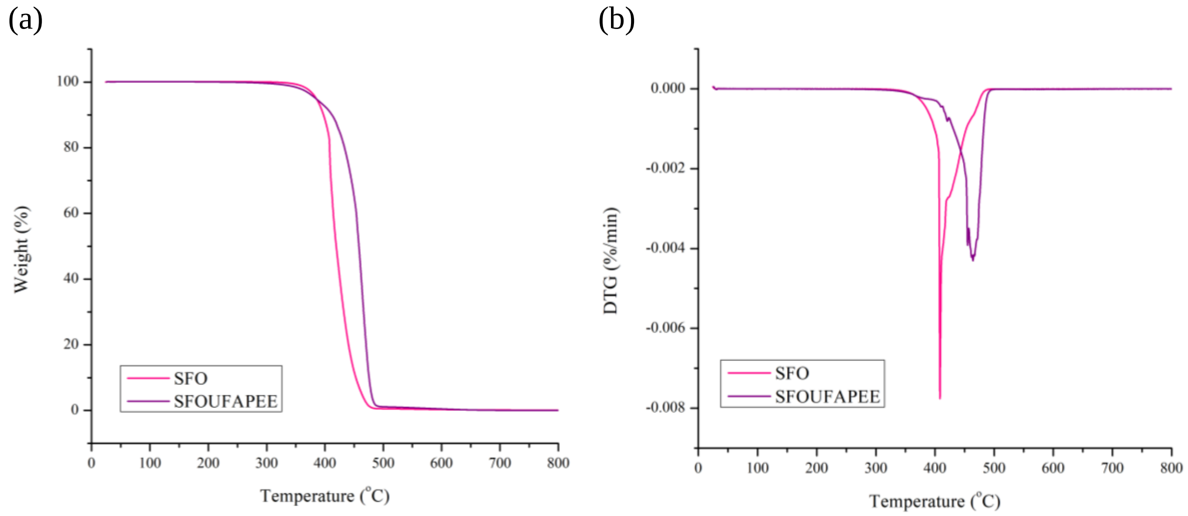

Figure 5. TGA curve of SFO and SFOUFAPEE (a) and DTG curve of SFO and SFOUFAPEE (b).

CONCLUSION

The successful synthesis of SFOUFAPEE was achieved using sunflower oil unsaturated fatty acids (SFOUFA) and polyhydric alcohol (PE) with a notable yield of 60%. The resulting liquid SFOUFAPEE exhibits promising characteristics to serve as a potential biolubricant base stock. SFOUFAPEE displays favorable lubrication properties, as evidenced by its low pour point, high flash point and improved thermal stability in comparison to sunflower oil. These attributes underscore the potential of SFOUFAPEE as an effective lubricant. The improved lubrication properties of SFOUFAPEE can be attributed to the successful removal of beta hydrogen in sunflower oil (SFO) through the replacement with polyhydric alcohol (PE). This modification in the chemical structure contributes significantly to the enhancement of its lubrication capabilities. The synthesis of SFOUFAPEE from sunflower oil unsaturated fatty acids and PE has resulted in a liquid product with desirable lubrication properties, making it a promising choice as a biolubricant base stock. The successful alteration of its chemical composition by eliminating beta hydrogen and incorporating polyhydric alcohol has contributed to the improvement of its lubrication characteristics.

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