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Synthesis and Tribological Assessment of TMP Ester Bio-Lubricant Derived from Stearic Acid Via Sequential Esterification and Transesterification Reactions

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Abstract

The transition to sustainable lubrication has driven research into bio-lubricants as alternatives to mineral oils. Although mineral lubricants remain dominant in applications, their low biodegradability, toxicity, and reliance on non-renewable resources pose challenges. Fatty acid-derived esters, particularly trimethylolpropane (TMP) esters synthesized from stearic acid, have emerged as promising candidates due to superior lubricity, high viscosity index, and enhanced oxidative stability. However, their physicochemical and tribological performance depends on reactant molar ratio, governing conversion efficiency, molecular structure, and lubricant properties. This study investigates the influence of molar ratios on TMP ester yield and tribological performance. Stearic acid was esterified with methanol, followed by transesterification with TMP. 16 samples with different molar ratios were synthesized within a 3-hour period. Chemical transformation was verified using FTIR spectroscopy, while tribological performance was evaluated using a four-ball tribotester following ASTM D4172, supported by wear scar analysis. The highest conversion (98.26%) was achieved at a 5:1 molar ratio. FTIR analysis confirmed the presence of ester groups on the TMP backbone after transesterification. The 4:1 ratio exhibited the lowest coefficient of friction, achieving an 18.1% reduction compared to TMP, while the 3:1 ratio produced the smallest wear scar diameter, reduced by 11.12%. These findings demonstrate that molar ratio optimization plays a key role in enhancing esterification efficiency and improving tribological performance of TMP ester bio-lubricants.

1 Introduction

Bio-based lubricants have attracted significant attention as sustainable alternatives to conventional mineral-based lubricants due to their renewability, biodegradability, and low environmental impact (Kurre et al., 2023). The presence of long-chain fatty acids in vegetable-derived oils promotes strong adsorption onto metal surfaces, enhancing boundary lubrication performance. In addition, bio-lubricants typically exhibit high viscosity index and good lubricity. However, pure vegetable oils suffer from poor oxidative stability, limited thermal resistance, and inadequate low-temperature properties, which restrict their industrial application under severe operating conditions (Biresaw et al., 2022). To overcome these limitations, chemical modification has been widely applied to tailor molecular structure and improve lubricant performance. Common modification techniques include hydrogenation, epoxidation, esterification, and transesterification (Musik et al., 2021). Among these, esterification and transesterification are particularly effective for producing synthetic esters with improved thermal stability, oxidative resistance, and tribological characteristics. Esterification involves the reaction of fatty acids with alcohols to form esters and water, whereas transesterification replaces the alkoxy group of an ester with another alcohol enabling the formation of polyol esters with enhanced structural stability. Recent studies have demonstrated that polyol esters synthesized via these routes exhibit improved anti-wear and friction-reducing behavior compared to unmodified vegetable oils (Moreira et al., 2025). Trimethylolpropane (TMP) ester is a high-performance polyol ester widely investigated for lubricant applications. Due to its trifunctional hydroxyl structure, TMP can react with long-chain fatty acids to form stable triesters, resulting in high viscosity index, excellent thermal and oxidative stability, low volatility, and superior boundary lubrication performance (Musik et al., 2021; Pawar et al., 2025). These properties make TMP esters promising candidates for environmentally friendly lubricant formulations capable of operating under demanding tribological conditions. Therefore, this study aims to synthesize TMP ester from stearic acid (SA) and TMP via a two-step esterification and transesterification process. The effect of molar ratio on reaction efficiency (conversion rate) is systematically investigated. In addition, the tribological performance of the synthesized TMP esters is evaluated to establish the relationship between synthesis parameters and lubrication behavior.

2 Methodology

2.1 Lubricants and additive

In this study, stearic acid (SA) served as carboxylic acid and trimethylolpropane (TMP) acted as alcohol. The physicochemical properties of stearic acid and TMP are tabulated in Table 1.

2.2 Chemical modification process

The TMP ester was synthesized through a two-step esterification and transesterification process. In the first step, 50 g of stearic acid was melted at 60–70 °C and reacted with 67.33 g of methanol in a 0.5 L three-necked flask under stirring, using sulfuric acid as a catalyst. The reaction was maintained at 60 °C for 3 h to produce methyl stearate. After completion, the mixture was washed in a separatory funnel to remove residual methanol and by-products, and the organic layer was heated at 100 °C for 1 h to eliminate excess water, yielding purified methyl stearate. In the second step, the methyl stearate was melted and mixed with trimethylolpropane (TMP) at 60 °C to ensure homogeneity. Potassium hydroxide (KOH), dissolved in 5 mL methanol, was added as a catalyst, along with two drops of propanol to reduce foaming. The transesterification reaction was conducted at 140–160 °C for 2 h under continuous stirring and vacuum conditions to remove by-products. The final product was washed to

remove impurities and heated at 100 °C under reduced pressure for 1 h to obtain purified TMP ester for further analysis and tribological evaluation.

Properties	SA	TMP
Molecular weight (g/mol)	284.48	134.17
Density (g/cm3) (20°C)	0.9408	0.916
Melting point (°C)	69.3	NA
Boiling point (°C)	361	>250
Colour	White flake	Yellow to amber
pH	4-5	5-8
Flash point (°C)	196	>200
Auto ignition temperature (°C)	395	>300

Table 1: Physical properties of stearic acid and TMP

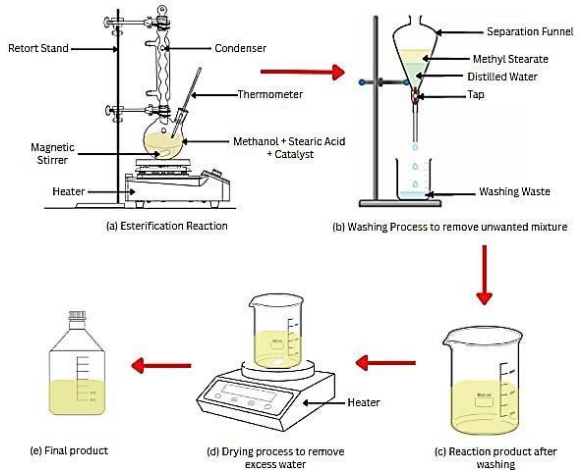

Figure 1: Experimental setup for the esterification stage of TMP ester.

2.3 Tribological test

The tribological performance of the lubricant was evaluated using a four-ball tribotester in accordance with ASTM 4172. The experimental parameters, including rotational speed, applied load, temperature, and test duration, are summarized in Table 2. As illustrated in Figure 3, a rotating steel ball was pressed against three stationary steel balls immersed in the test lubricant under an applied load. The contact configuration allows the assessment of friction and wear performance under controlled sliding conditions.

Properties	Value
Speed (rpm)	1200
Load (N)	392
Temperature (°C)	75
Duration (min)	60
Standard	ASTM 4172

Table 2: Experimental conditions for the four-ball tribological test (ASTM 4172).

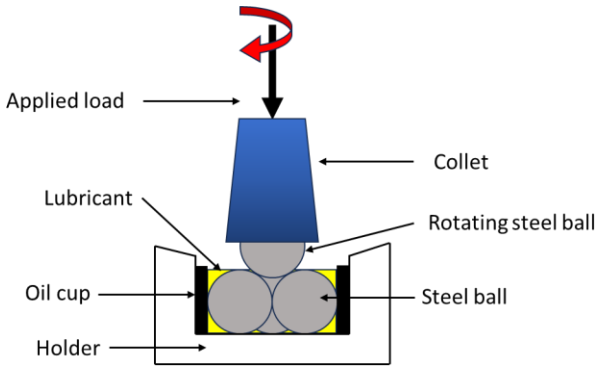

Figure 2: Schematic diagram of the four-ball tribotester configuration.

3 Results and discussion

3.1 Effect of molar ratio to the conversion rate

Figure 4 shows the effect of molar ratio on the conversion rate of TMP ester. The results indicate a clear increasing trend in conversion as the molar ratio increases from 3:1 to 5:1. At a 3:1 molar ratio, the conversion rate is 95.81%. This slightly increases to 96.15% at 4:1 and reaches the highest value of 98.26% at 5:1. From a stoichiometric perspective, the transesterification of trimethylolpropane (TMP) requires three moles of methyl stearate to fully react with one mole of TMP, corresponding to the theoretical stoichiometric ratio of 3:1. However, in practical systems, the reaction is reversible and limited by equilibrium constraints. As a result, using only the stoichiometric ratio may not ensure complete conversion. By increasing the molar ratio beyond the theoretical requirement (4:1 and 5:1), excess methyl stearate shifts the reaction equilibrium toward product formation (Pappu et al., 2011). The additional reactant increases the likelihood of effective molecular collisions and compensates for losses due to side reactions or incomplete mixing. The significant improvement at the 5:1 ratio suggests that excess reactant effectively drives the reaction closer to completion within the fixed reaction time. Therefore, although 3:1 is the theoretical stoichiometric ratio, higher molar ratios enhance conversion efficiency under practical reaction conditions.

3.2 FTIR analysis

Figure 6 shows the FTIR spectra of pure TMP and TMP esters. The spectrum for pure TMP exhibits a prominent, wide OH stretching band around 3300-3400 cm^{-1}, which is typical of hydroxyl groups (Yang et al., 2011). Also present are CH stretching vibrations around 2900 cm^{-1} and notable CO stretching peaks in the 1000-1200 cm^{-1} range. The lack of major peaks around 1730 cm^{-1} corroborates that the unreacted TMP lacks any ester carbonyl. The corresponding peak positions in the single bond, double bond, and fingerprint regions are summarized in Table 3.

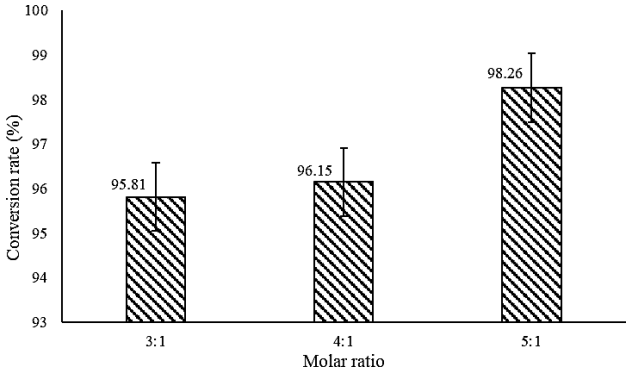

Figure 3: Effect of methyl stearate-to-TMP molar ratio on the conversion rate of TMP ester.

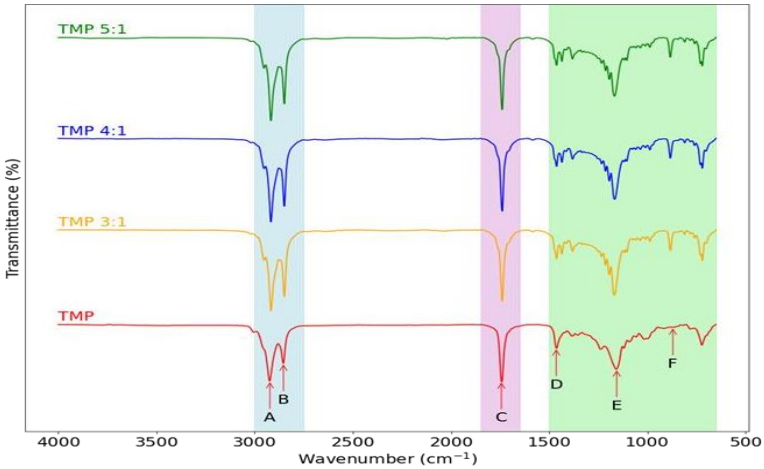

Figure 4: FTIR spectra of pure TMP and TMP esters at different methyl stearate-to-TMP molar ratios.

Region	3:1	4:1	5:1	TMP
Single bond	2916	2917	2917	2923 (A)
	2848	2849	2849	2854 (B)
Double bond	1739	1739	1740	1741 (C)
Fingerprint	1462	1462	1462	1462 (D)
	1169	1167	1167	1158 (E)
	883	883	883	No peak (F)

Table 3: FTIR peak positions of pure TMP and TMP esters at different molar ratios in various regions.

The FTIR spectra show clear changes during esterification as the methyl stearate-to-TMP molar ratio increases from 3:1 to 5:1. In the 3:1 sample, the OH peak decreases compared to pure TMP and a new peak appears around 1730 cm^{-1}, indicating the formation of ester carbonyl (C=O) groups; however, the remaining OH signal suggests incomplete esterification due to insufficient acyl groups. At a 4:1 ratio, the OH peak further decreases while the carbonyl peak becomes more intense, showing improved conversion as more hydroxyl groups are esterified. In the 5:1 sample, the OH peak is almost negligible and the carbonyl peak is strongest, indicating nearly complete esterification. Overall, the gradual reduction of the hydroxyl peak and the increase in the ester carbonyl peak confirm that higher

molar ratios promote more efficient ester formation, with additional minor changes in the C–O and C–H regions reflecting structural modifications during the reaction.

3.3 Friction coefficient analysis

Figure 7 shows the relationship between the average coefficient of friction (COF) and the molar ratio of reactants based on the four-ball wear test conducted at 75 °C, 40 kg load, and 1200 rpm. Among all samples, the lubricant produced at a 4:1 molar ratio exhibited the lowest COF (0.0686), indicating the best friction-reducing performance and suggesting an optimal chemical balance at this ratio. In contrast, unmodified TMP showed the highest COF (0.08378), while the 3:1 and 5:1 ratio recorded slightly higher COF values (0.0763 and 0.0741, respectively) than the 4:1 sample, although they still performed better than raw TMP. Similar trends have been reported by Singh et al. (2015), who highlighted the influence of molar ratio on lubrication performance. Since a lower COF reflects better lubrication, smoother motion, and reduced wear (Waqas et al., 2021), it also contributes to lower heat generation and improved lubricant stability during operation (Björling et al., 2014). Overall, the findings suggest that the 4:1 molar ratio is the most optimal condition for producing TMP ester lubricants with superior anti-friction properties.

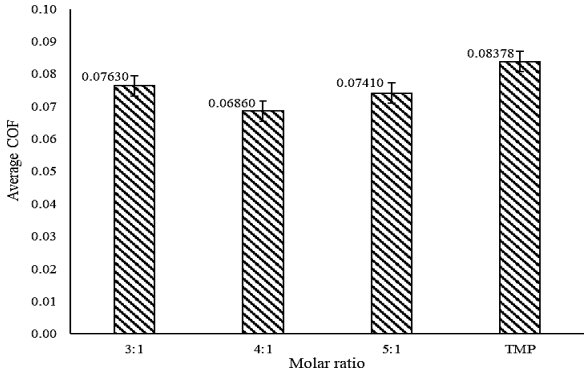

Figure 5: Average COF of TMP ester at different molar ratios and pure TMP under four-ball test.

3.4 Wear scar diameter analysis

The wear scar diameter (WSD) results for the 3:1, 4:1, and 5:1 molar ratios, compared with pure TMP, show that the 3:1 ratio produced the lowest WSD (719.707 μm), indicating the best anti-wear performance. As the molar ratio increased to 4:1 and 5:1, the WSD slightly increased to 742.634 μm and 748.063 μm, respectively, suggesting a gradual reduction in wear protection. The pure TMP sample recorded the highest WSD (809.775 μm), reflecting the poorest wear resistance among all samples. This trend can be attributed to the effect of ester formation and molecular structure on lubrication behaviour, as reported by Wang et al. (2023). At the 3:1 ratio, a balanced ester structure likely enhances lubricating film formation and surface protection, resulting in lower wear. However, higher molar ratios may introduce excess fatty acids or unreacted components that disturb film stability and reduce anti-wear effectiveness. In contrast, pure TMP lacks sufficient ester functionality to form a strong protective film, leading to greater wear. Overall, the results indicate that the 3:1 molar ratio provides the most favorable chemical balance for improving anti-wear.

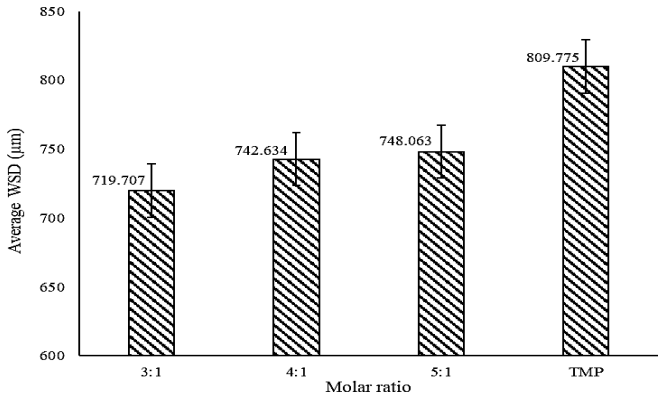

Figure 6: Average WSD of TMP ester at different molar ratios and pure TMP under four-ball test.

3.5 Physical wear observation

Figure 9 shows the worn surface morphologies lubricated with TMP ester synthesized at different molar ratios (3:1, 4:1, and 5:1) compared with neat TMP. The 3:1 sample exhibits severe abrasive wear, with deep and continuous grooves, pronounced ploughing, and localized craters, indicating strong asperity contact and material removal. This suggests weak boundary film formation, possibly due to incomplete esterification and the presence of residual or partially reacted components that reduce film stability. At the 4:1 ratio, grooves and ploughing are still visible but appear more uniform and less severe, reflecting improved surface protection and better ester conversion that enhances adsorption and boundary film formation. In contrast, the 5:1 sample shows a smoother morphology dominated by smearing and fewer deep grooves, indicating improved plastic flow and the formation of a more stable protective tribofilm. Compared to neat TMP, which displays evident abrasive features, the transesterified samples, particularly at 5:1, provide better surface coverage and reduced direct asperity contact due to the presence of long-chain fatty structures. Overall, the wear mechanism shifts from severe abrasive wear at lower ratios to a more stable boundary lubrication regime at higher TMP content, highlighting the importance of optimizing the molar ratio to enhance tribological performance.

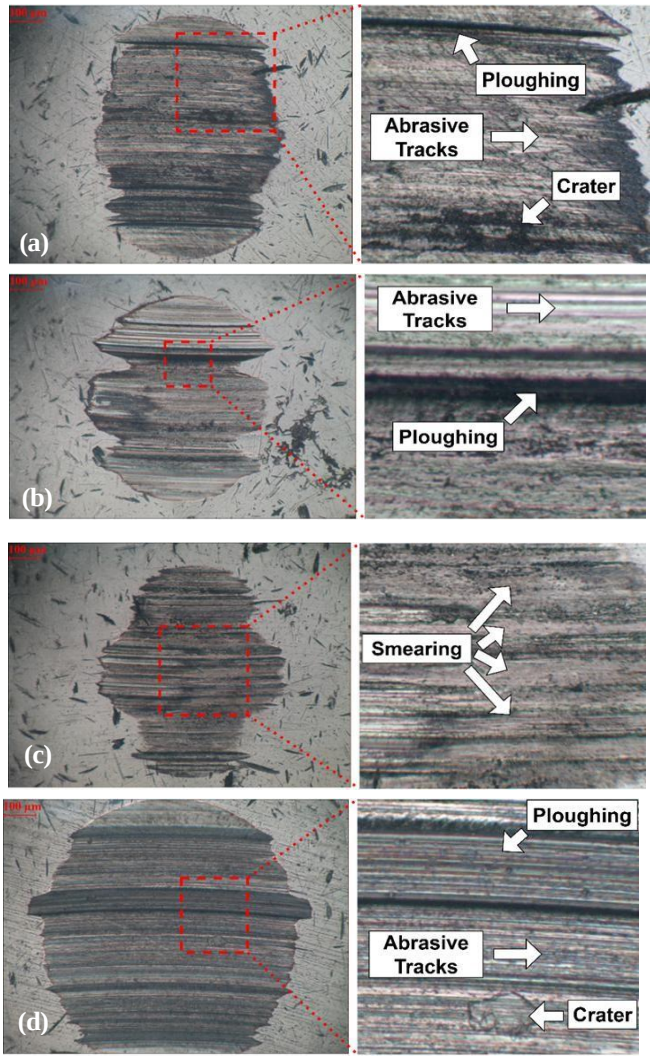

Figure 9: Worn surface morphologies for (a) 3:1, (b) 4:1, (c) 5:1 and (d) neat TMP

Conclusion

It can be concluded that all molar ratio achieved conversion yield greater than 80%. FTIR confirmed the existence of ester group in TMP. The 4:1 ratio outperformed neat TMP in the tribological performance, with the lowest friction (0.0686, 18.14% reduction vs. TMP), and significant wear reduction (WSD 8.29% lower than TMP). Worn-surface micrographs showed a persistent, compact boundary coating compatible with the suggested polar ester headgroup adsorption and chemisorption process and saturation C18-chain packing. These findings demonstrate that stearic-acid/TMP esters, particularly the 4:1 formulation, provide a high-performance, and environmentally aligned bio-lubricant base oil, addressing the need for next-generation green lubricants that reduce frictional energy losses and improve equipment durability

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