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Research paper

Optimisation of trimethylolpropane ester synthesis from waste cooking oil methyl ester by response surface methodology, and its physicochemical properties and tribological characteristics

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ABSTRACT

This study is focused on optimising the process variables of trimethylolpropane (TMP) ester synthesis from waste cooking oil methyl ester (WCOME) using response surface methodology with Box–Behnken experimental design in order to maximise the TMP ester (TWCOE biolubricant) yield. The following process variables were optimised: (1) reaction time, (2) TMP-to-WCOME ratio, and (3) sodium methoxide catalyst concentration. The predicted TWCOE biolubricant yield was 97.06 %, which conformed well with the experimental TWCOE biolubricant yield of 96.12 %. The quadratic response surface model demonstrated a robust fit with the experimental data (R^2 = 0.9888).The physicochemical properties and tribological characteristics of the TWCOE biolubricant were assessed and compared with those of commercial lubricants. The TWCOE biolubricant had a kinematic viscosity of 41.55 mm^2/s at 40 °C and 6.93 mm^2/s at 100 °C. The TWCOE biolubricant had an acid value of 0.4 mg KOH/g, flash point of 222.2 °C, and viscosity index of 125.30. The coefficient of friction of the TWCOE biolubricant (0.045) was lower than those of the SAE15W40, SAE0W30, and ATF9 lubricants (0.062, 0.088, and 0.089, respectively). However, the average wear scar diameter for the TWCOE lubricant (0.632 mm) was higher than those of commercial lubricants. The favourable lubricating characteristics suggest that the TWCOE biolubricant has the potential for use as an effective lubricant or additive in industrial machinery.

1. Introduction

The growing worldwide population raises concerns over consumption, especially in terms of energy utilisation and the resultant waste generation. These issues have been the focus of researchers worldwide. The depletion of energy requirements, coupled with the detrimental effects of waste oils on the environment, have spurred researchers to undertake more investigations with the objective of developing cleaner and more ecologically sustainable products. Waste cooking oils (WCOs) undergo both physical and chemical transformations through a range of chemical processes. Fast food establishments, food service establishments, hospitality establishments, and confectionery companies may be considered as the significant contributors of WCOs [1]. According to the United States Department of Agriculture (USDA), the use of cooking oils in Australia has increased steadily alongside the population expansion. The domestic production of canola cooking oils has also increased, amounting to ~1.1–1.2 million metric tonnes (MMT) per year. The projected canola output for 2022/2023 was 4.7 MMT, while the estimated export was 3.6 MMT [2]. In addition, Australia produced 2136 thousand tonnes of canola. According to the Australian Bureau of Statistics (ABS) [3], Western Australia accounted for 48 % of Australian canola production, which amounted to 1022 thousand tonnes in 2019–2020, as shown in Fig. 1.

Global estimates predict that the supply of WCOs will increase from 3.7 billion gallons in 2022 to 5–10 billion gallons in 2030. The consumption of vegetable oil per capita and the collection rate of WCOs in 2022 are shown in Fig. 2 [4]. Fig. 3 shows the worldwide consumption of vegetable oils from 2013/2014 to 2023/2024. The projections indicate

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that global consumption of sunflower seed oil will exceed 20.27 MMT in 2023/2024. During that specific time frame, the total global production of vegetable oils reached over 222 MMT. There is potential for further volume increases. Based on these data, it can be concluded that the supply of WCO feedstocks for biolubricants has great potential for use in several sectors, including the biolubricant sector.

Transesterification is a highly effective technique to produce methyl ester, with a relatively simple method and shorter reaction time. The production of glycerol and fatty acid methyl ester (FAME) can be achieved by conducting transesterification reaction using a catalyst and alcohol [6]. In order to achieve high-quality FAME production, it is crucial to take into account various factors that can affect the transesterification reaction. These factors include free fatty acid content, humidity level, alcohol-to-oil molar ratio, catalyst concentration, reaction time, reaction temperature, and stirring speed [7].

Reducing the environmental impact and searching for alternative resources for biolubricant production have become significant areas of focus for numerous researchers [1,8,9]. WCO is a highly valuable resource for synthesising a wide range of products among waste-based materials. When frying food with vegetable oils, the WCOs need to be refined because they contain toxic components. The WCOs can be reused to produce biolubricants, offering a sustainable alternative to mineral-based lubricants and providing a safe solution for recycling WCOs [10,11].

At present, there is a substantial number of studies on biolubricants derived from WCOs [9]. Angulo et al. [12] synthesised biolubricant from fish oil via transesterification using trimethylolpropane (TMP) and sodium ethoxide catalyst, where the reaction was carried out at a temperature of 100–400 °C under vacuum conditions. They demonstrated that their method was more efficient than enzymatic transesterification using commercially available lipase. The conversion of ethyl ester was 84 %, with TMP triester enriched to 96 %. The biolubricant had kinematic viscosities between those of ISO VG 32 and ISO VG 46 lubricant standards, indicating its potential applicability as a hydraulic oil [12]. Fernández-Silva et al. [13] investigated the viability of using WCO as an eco-friendly lubricant by assessing its complete chemical properties (fatty acid composition, polar components, and acidity). They subjected the WCO to molecular distillation at 220 and 40 °C, yielding heavier and lighter fractions. The test results indicated that the lubricant had a high viscosity index with elevated total polar compounds and low acidity levels, emphasising the advantages of acidity on fluidity at low temperatures and lubricity. The results showed that the lubricant with heavier fraction had enhanced thermal stability. Both fractions demonstrated enhanced friction reduction properties relative to their parent WCO. The light percentage of unseparated oil, fast food restaurant oil, and cooking restaurant oil reduced frictional wear by 11.7, 44.4, and 36.8 %, respectively. This study demonstrated that molecular distillation is a viable technology for producing efficient, eco-friendly lubricants [13]. Negi et al. [14] employed WCO for biolubricant production via transesterification, using 2-ethylhexanol in the presence of p-toluenesulfonic acid to formulate eco-friendly grease. The experimental results revealed a considerable effect on the tribological and rheological performance of the biolubricant. The coefficient of friction of the WCO-based grease was 30.6 % lower than that of mineral oil grease (MAK150) [14].

Recently, Nuruilita et al. [15] synthesised biolubricant from a mixture of WCO and *Callophyllum inophyllum* oil (UCOCI) through an infrared heating process. They optimised polyesterification using response surface methodology (RSM) by varying the reaction time and the ratio of ethylene glycol to the UCOCI methyl ester. The optimum biolubricant yield was 94.03 %, which conformed well with the predicted biolubricant yield of 94.30 %. The biolubricant had a viscosity of 83.46 cSt at 40 °C and 13.2 cSt at 100 °C, and a viscosity index of 216.32. Moreover, the coefficient of friction of the biolubricant–commercial lubricant mixtures were 0.1091–0.071, which were significantly lower than that of the SAE15W40 commercial lubricant. The wear scar diameters resulting from the biolubricant–commercial lubricant mixtures were also significantly smaller (0.100–0.140 mm) compared with the wear scar diameter of the SAE15W40 lubricant (0.549 mm). The test results indicated the possibility of using biolubricants in heavy-duty engines or as natural additives [15]. Patel et al. [16] employed machine learning to evaluate the tribological performance of graphene oxide-reinforced polymer (PEEK) nanocomposites. The wear rate and coefficient of friction were assessed using a pin-on-disk apparatus at ambient temperature with a load of 20, 30, and 60 kg. Increasing the graphene oxide concentration reduced the wear rate when the load and track diameter decreased. Nonetheless, the track diameter, load, and graphene oxide concentration reduced the

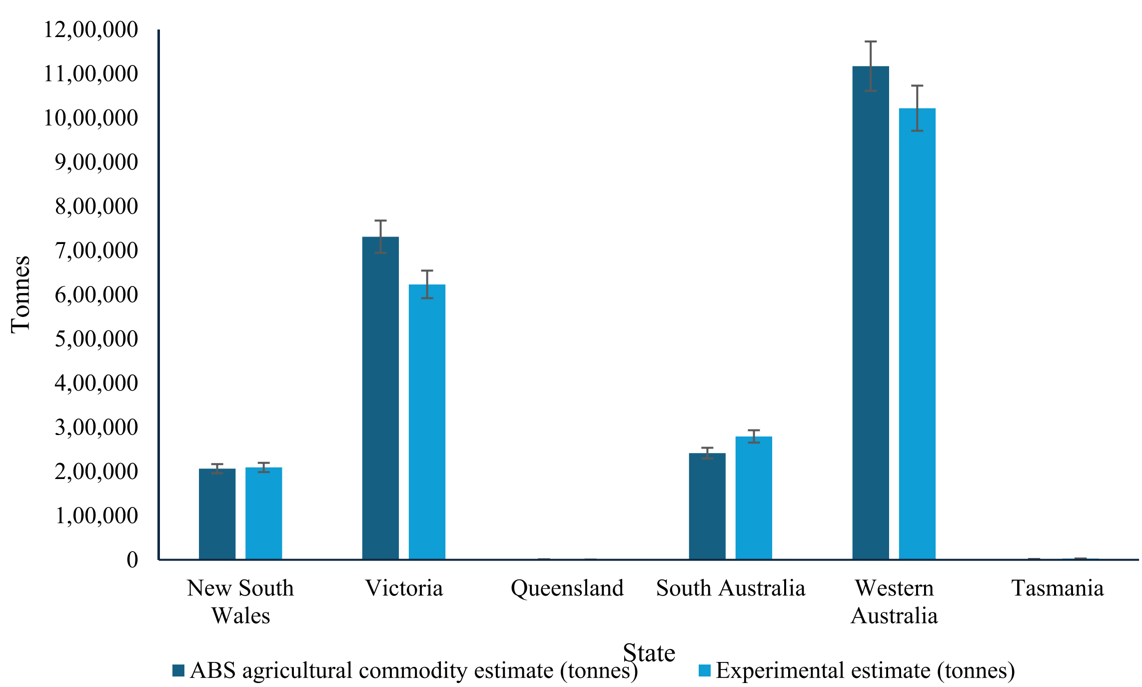

Fig. 1. Estimated calculations of canola production in Australia for 2019–2020 [3].

coefficient of friction. The significant predictive capability of the model indicated that feature selection enhanced the accuracy of the model [16].

The tribological performance of chemically modified TMP esters derived from vegetable oils, which exhibit enhanced thermo-oxidative stability, is crucial for their application as lubricants. Table 1 presents the tribological performance of various chemically modified TMP esters derived from vegetable oils. Although numerous tribological studies have been conducted on TMP esters derived from WCOs [9,17–19], there is a lack of studies focused on optimising biolubricant synthesis from these oils and characterising their physicochemical properties and tribological characteristics relative to those of commercial lubricants, which forms the motivation of this study. It is believed that this study will assist researchers, automotive professionals, and industries in selecting the most appropriate biolubricant for their application.

Optimisation is essential for attaining optimal outcomes in biolubricant production and this can be achieved using RSM. Moreover, additional examination is required to define the tribological performance of biolubricants. In this study, two-step transesterification was carried out to produce TMP ester (TWCOE biolubricant) from waste cooking oil methyl ester (WCOME). The objective is to generate biolubricants from sustainable resources since WCO is an organic waste. The TWCOE biolubricant synthesis process variables (reaction time, TMP-to-WCOME ratio, and sodium methoxide catalyst concentration) were optimised using RSM in order to maximise the TWCOE biolubricant yield. Fourier transform infrared (FTIR) spectroscopy was performed on the TWCOE biolubricant and LB15W40 (SAE15W40) commercial lubricant to determine their functional groups. The physicochemical properties (kinematic viscosity, viscosity index, and flash point) and tribological characteristics of the TWCOE biolurbicant were assessed and compared with those of commercial lubricants.

2. Materials and methods

2.1. Materials and experimental set-up

The WCO used for this study was collected from local restaurants around Sydney, Australia. The following reagents were used in the synthesis of the TWCOE biolubricant: methanol (Merck, CH_3OH, purity: ≥99 %), sulphuric acid (Merck, H_2SO_4, purity: >96 %), potassium

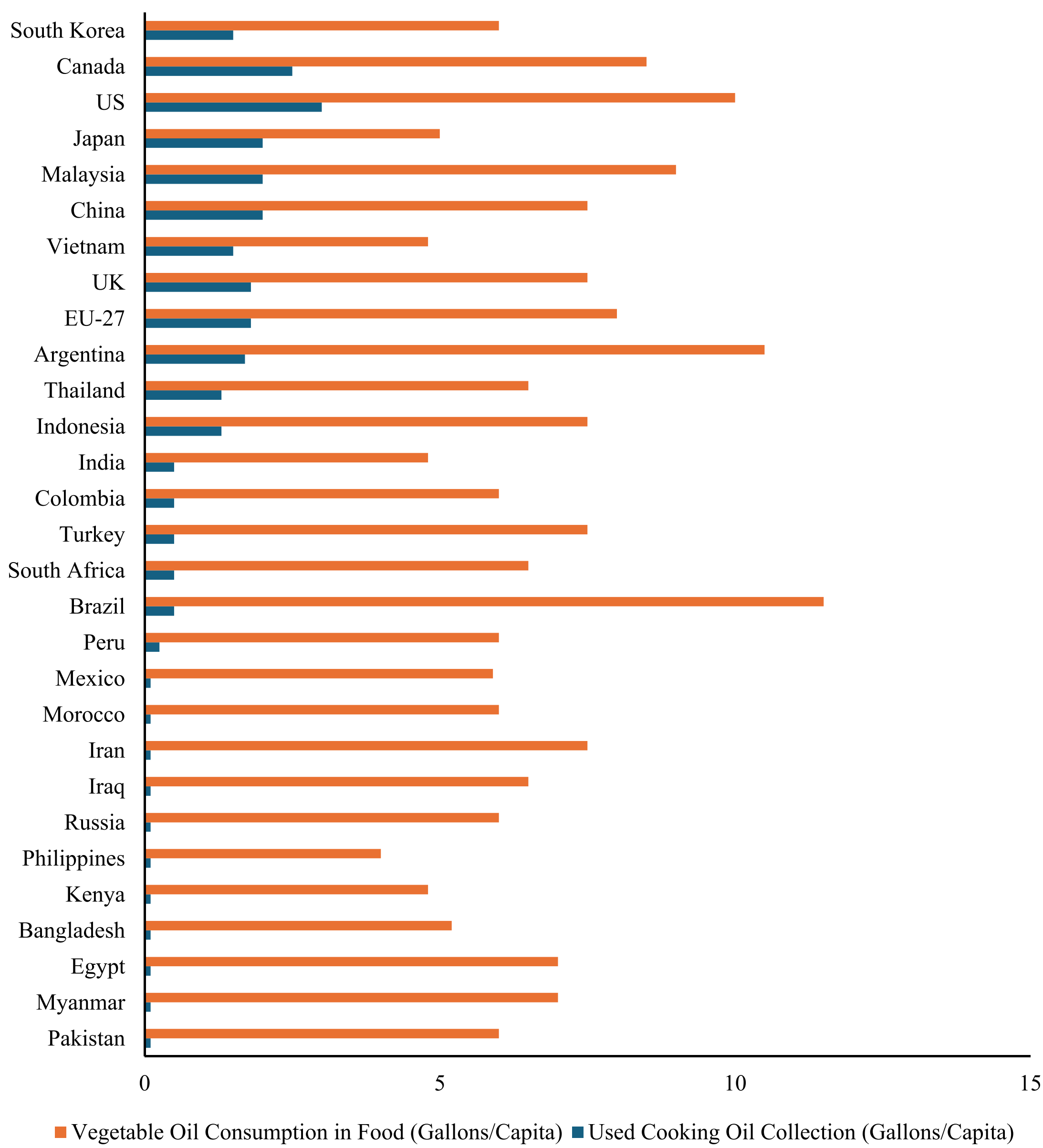

Fig. 2. Vegetable oil consumption per capita and WCO collection rate for year 2022 [4].

hydroxide (KOH, purity: ≥85 %), TMP ($C_6H_{14}O_3$, purity: ≥97 %) and reagent-grade sodium methoxide (CH_3NaO, purity: ≥95 %). These reagents were sourced from a local supplier. The cleaning solvent used was acetone. The rotating and stationary balls of the four-ball wear tester were made of E-52,100 steel, which was a chrome alloy steel. The balls had a diameter of 12.7 mm and Rockwell C hardness of 64–66. They were classified as Grade 25 EP (Extra Polish). A lubricant with SAE15W40 viscosity grade and API SN/CF specifications, containing additives for anti-corrosion, acid neutralisation, anti-wear, anti-foaming, soot reduction, and antioxidant qualities, was acquired from a local petroleum firm.

2.2. Pre-treatment of waste cooking oil (WCO)

First, the WCO was filtered to remove any residues such as food and solid particles present in the oil. Subsequently, the WCO was heated to a temperature of 100–110 °C for 30 min to reduce its water content. Following this, an equivalent quantity of the filtered and heated WCO was transferred into a glass beaker. The glass beaker was heated to a temperature of 100 °C and agitated at a constant speed for 1 h It shall be noted that WCO contains a greater amount of free fatty acids compared with fresh oil. A higher concentration of free fatty acids is undesirable because it can lead to the formation of soap. If the concentration of free fatty acids exceeds 3 %, the use of a homogeneous base catalyst becomes ineffective for the transesterification reaction. To reduce the free fatty acid content of the WCO, the WCO was subjected to pre-treatment (acid-catalysed esterification) prior to transesterification.

In the acid-catalysed esterification, a solution containing 1 % (v/v) of sulphuric acid (H_2SO_4) was added into 1000 mL of WCO with a methanol-to-oil ratio of 20 % (v/v). The mixture was then transferred to a double-jacketed glass reactor equipped with a stirrer operating at an stirring speed of 600 rpm. The temperature was adjusted to 60 °C. The duration of the esterification reaction was 90 min. After the reaction was complete, the product was transferred into a separatory funnel and left for 6 h to facilitate the separation of contaminants from the WCO. Subsequently, the esterified WCO was collected and placed in a rotary evaporator, where it was subjected to vacuum conditions at a temperature of 60 °C for 30 min. This process was carried out to eliminate any remaining traces of methanol present in the esterified WCO.

2.3. Waste cooking oil methyl ester (WCOME)

The WCO, which had been converted into ester form, was quantified and heated to a temperature of 60 °C using a circulating bath reactor. For the alkaline-catalysed transesterification reaction, 1 % (w/w) of potassium hydroxide (KOH) catalyst was first dissolved in methanol and the methanol–catalyst mixture was then added into the heated esterified WCO with a methanol-to-oil molar ratio of 1:4. The reaction proceeded for a maximum duration of 1.5 h During the transesterification process, the oil mixture was continuously stirred at an stirring speed of 500 rpm using an overhead stirrer, while maintaining a constant temperature of 60 °C. After the reaction was complete, the WCOME was transferred into a separatory funnel and left for 6 h to separate glycerol from the WCOME. To achieve a high reaction rate, researchers have found that the ideal stirring speed is within the range of 500–1500 rpm. This range has been found to be effective in the production of FAMEs from different types of feedstocks [26,27].

In the separation phase, the bottom layer formed in the separatory

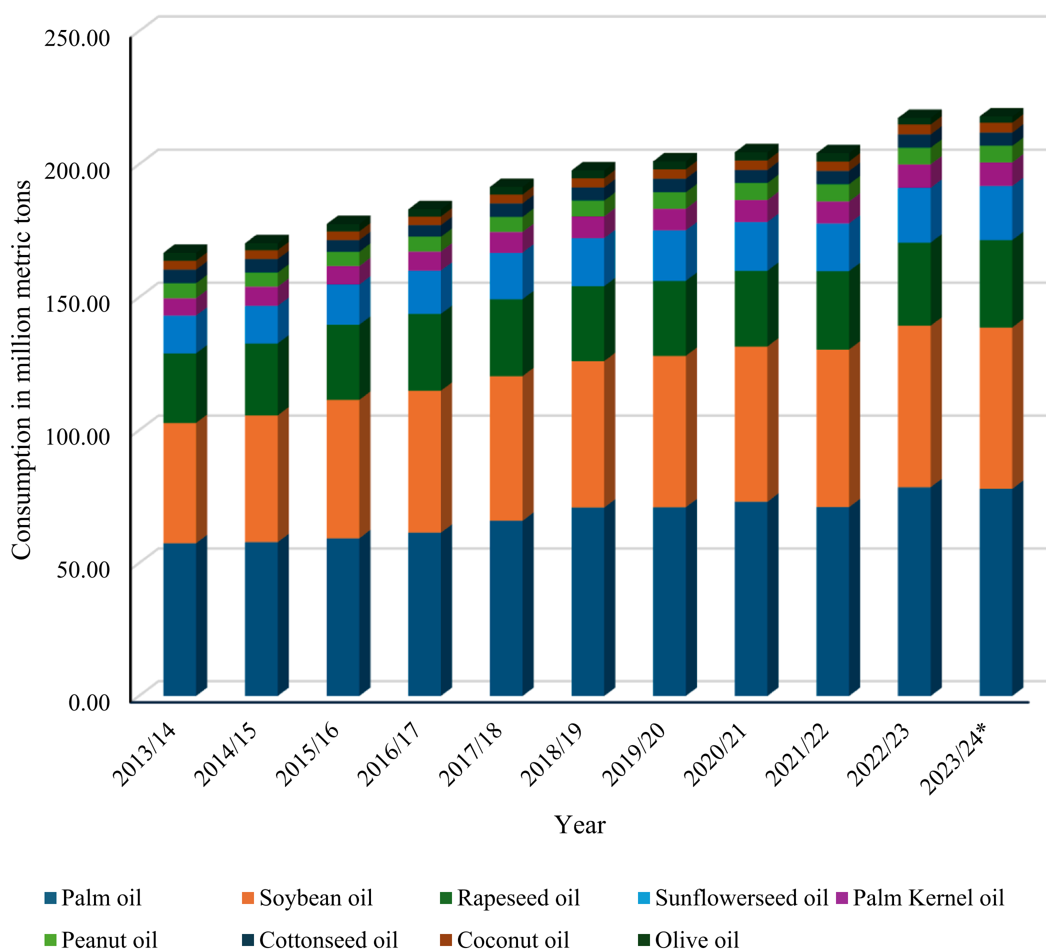

Fig. 3. Projected increase in global vegetable oil consumption from 2013/2014 to 2023/2024 [5].

Table 1
Recent studies on the tribological performance of vegetable oil-derived TMP esters.

Biolubricant	Ref. lubricant	Method and operating conditions	Findings	Ref.
Cottonseed oil-derived TMP ester	Commercial lubricant (SAE40)	High-frequency reciprocating rig (HFRR) tribotester, load: 50 N, frequency: 10 Hz, temperature: 75 °C, duration: 60 min.	Biolubricant derived from cottonseed oil serves as an energy-efficient lubricant additive for automotive engines. A concentration of 10 % resulted in minimal friction and wear compared with SAE40 lubricant. However, higher concentrations could significantly increase wear and friction.	[20]
TMP trioleate ester	Fully synthetic engine oil (5W40) and mineral oil (15W40)	Four-ball wear tester, load: 392 N, speed: 400–1200 rpm, temperature: 75 °C, duration: 60 min.	TMP esters outperformed alternatives due to their heat stability and film-forming capabilities. The modest viscosity and inadequate molecular structure of mineral oils enhanced friction. The high viscosities of synthetic oils render them better lubricants; however, the reduction of friction for these oils was not as marked as TMP esters.	[21]
Sunflower oil- and palm olein oil-derived TMP ester	–	TR-30 L tribometer, load 40 kgf, speed: 1200 rpm, temperature: 75 °C, duration: 60 min.	Sunflower oil-derived TMP ester exhibited superior tribological performance compared with palm olein-derived TMP ester, and demonstrated comparable tribological performance to petroleum-based lubricants.	[22]
Canola oil-derived TMP ester	Commercial lubricant oil (synthetic polymeric ester)	Four-ball wear tester, load: 392 N, speed: 1200 rpm, temperature: 75 °C, duration: 60 min.	The canola oil-derived TMP ester demonstrated exceptional cooling performance, with its rheological and tribological properties surpassing those of commercial lubricating oils. Furthermore, incorporating a 2 % additive led to outstanding wear prevention, achieving a wear scar diameter of 0.42 mm.	[23]
Pelargonic acid TMP ester	Mineral oil (polyalphaolefin)	High-frequency reciprocating rig (HFRR), load 600 g, temperature: 60 °C, duration: 75 min.	Comparison was made between the performance of biolubricant and mineral oil of equivalent viscosity. The results from the friction test showed that the biolubricant had outstanding performance, achieving a minimum coefficient of friction of 0.099 and an average wear scar diameter of 221.5 μm.	[24]
Cotton oil-derived TMP triester	Commercial lubricant SAE-40	Four-ball wear tester, load: 392 N, speed: 1200 rpm, temperature: 75 °C, duration: 60 min.	The cotton oil-derived biolubricant exhibited superior viscosity, viscosity index, and tribological properties, comparable to those of SAE40 commercial lubricant. The microscopic image revealed a small wear scar area accompanied by shallow grooves. The wear scar diameter and coefficient of friction were 0.849 mm and 0.074, respectively.	[25]

funnel, which consisted of glycerol, methanol, and other contaminants, was extracted from the separatory funnel. Next, the WCOME was repeatedly rinsed with distilled water to eliminate any remaining glycerol and contaminants present in the WCOME. In this procedure, 50 % (v/v) of warm distilled water with a temperature of 50–60 °C was evenly distributed over the surface of the WCOME. Subsequently, the WCOME was placed in the rotary evaporator under vacuum conditions at a temperature of 60 °C for 15 min to eliminate any remaining methanol and water. Finally, the product was filtered using filter paper. The WCOME samples are shown Fig. 4.

2.4. Biolubricant synthesis from WCOMEs

The TWCOE biolubricant was synthesised using the TMP method, which involved the use of TMP and sodium methoxide (as heterogeneous catalyst), along with the previously obtained WCOME. The WCOME was poured into a 500-mL two-neck flask that had a heating and stirring mantle. The experimental set-up included a thermometer and condenser. First, the WCOME was poured into a three-neck flask reactor and heated to a temperature of 120 °C. Once it reached the desired temperature, the experiment continued with TMP and sodium methoxide according to the process variables (reaction time, TMP-to-WCOME ratio, and sodium methoxide catalyst concentration) set in the Box–Behnken experimental design, which consisted of 17 experimental runs. The TMP esters (TWCOE biolubricants) are shown in Fig. 5.

2.4.1. Optimisation of TWCOE biolubricant synthesis using RSM

RSM with Box–Behnken experimental design was used in this study in order to maximise the TWCOE biolubricant yield. Design-Expert® version 11.0.1.0 software was used for this purpose. The factors, namely, reaction time (A), TMP-to-WCOME ratio (B), and sodium methoxide catalyst concentration (C), were varied in order to optimise the TWCOE biolubricant yield (y). Table 2 shows the values of the factors and their coded levels.

The Box–Behnken experimental design facilitated the assessment of the influence of each factor (reaction time, TMP-to-WCOME ratio, and sodium methoxide catalyst concentration) and the relationship between these factors on the response variable (TWCOE biolubricant yield). The experimental data were analysed using response surface regression, which is represented by the following polynomial:

$$Y = b_o + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i_{>j}}^{k} . \sum_{j}^{k} b_{ij} X_i + e \quad (1)$$

Eq. (1) defines the variables used in the model. Y represents the response variable (TWCOE biolubricant yield), X_i represents the independent variables (factors), b_o represents the intercept, b_i represents the first-order coefficient, b_{ii} represents the quadratic coefficient of the ith factor, b_{ij} represents the linear coefficient for the interaction between the ith and jth factors, k represents the number of factors studied and optimised in the experiment, and e represents the experimental error associated with Y. Eq. (1) represents the quadratic response surface model for the TWCOE biolubricant yield. Here, factor X_1 represents the reaction time in minutes (min), factor X_2 represents the TMP-to-WCOME ratio in weight per cent (% (w/w)), and factor X_3 represents the sodium methoxide catalyst concentration in weight per cent (% (w/w)). Eq. (2) was used to determine the TWCOE biolubricant yield, which is expressed as the weight of the TWCOE biolubricant obtained in grammes (g) divided by the WCOME used in grammes (g) and multiplied by 100:

$$\text{TWCOE biolubricant yield } (\% \text{ (w/w)}) = \frac{\text{Weight of TWCOE biolubricant obtained (g)}}{\text{Weight of WCOME used (g)}} \times 100 \quad (2)$$

Fig. 4. Waste cooking oil methyl esters (WCOMEs).

2.5. Physicochemical properties and FTIR spectroscopy of the TWCOE biolubricant

The physicochemical properties of the TWCOE biolubricant, consisting of the flash point, oxidation stability, acid value, dynamic viscosity, kinematic viscosities at 40 and 100 °C, and viscosity index, were assessed and compared with those of commercial lubricants. The TWCOE biolubricant was also examined using an FTIR spectrometer at a wavenumber range of 450–4000 1/cm and a scanning rate of 2 mm/s to determine its functional groups and confirm that the biolubricant synthesis was complete [9,17].

2.6. Four-ball wear tests

The steel balls in the lubricant test cup were cleaned thoroughly using acetone. The chuck assembly was also cleaned meticulously with acetone to eliminate dirt or oil stains. Afterwards, the equipment was carefully wiped with clean tissues to ensure it was moisture-free. Three steel balls were carefully positioned in the lubricant test cup and securely fastened with nuts, ensuring a precise distance of 68±μm using a torque wrench. The steel ball was inserted into the ball chuck, and the chuck was secured to the chuck holder to ensure that the steel ball remained in place during the four-ball wear test. The TWCOE biolubricant (or commercial lubricant) was poured carefully into the lubricant test cup, ensuring that the three stationary balls were fully immersed in the lubricant (±10 mL), as shown in Fig. 6. Following this, the test cup was connected to the test tool until it reached the fourth ball, which was located on the clamp holder. The four-ball wear test was conducted to analyse the wear prevention properties of the lubricant using the four-ball wear tester (FBT-3, Ducom Instruments, Inc., United States of America) according to the ASTM D4172–94 standard test method. The wear tests were conducted using the parameters listed in Table 3. The specifications of the steel balls are tabulated in Table 4. The schematic diagram of the four-ball wear tester is shown in Fig. 7.

Fig. 5. TMP esters (TWCOE biolubricants).

Table 2
Selected factors for the TWCOE biolubricant synthesis and their coded levels.

Symbol	Factor (independent variable)	Unit	Coded level		
			−1	0	+1
X_1	Reaction time (A)	min	120	180	240
X_2	TMP-to-WCOME ratio (B)	% (w/w)	15	25	35
X_3	Sodium methoxide catalyst concentration (C)	% (w/w)	0.5	1	1.5

3. Results and discussion

3.1. Optimisation of TWCOE biolubricant synthesis using RSM

The purpose of the Box–Behnken experimental design is to optimise the process variables (reaction time, TMP-to-WCOME ratio, and sodium methoxide catalyst concentration) of the TWCOE biolubricant synthesis in order to maximise the TWCOE biolubricant yield. The experimental design consisted of three factors, with three levels for each factor, resulting in a total of 17 experimental runs. The TWCOE biolubricants were synthesised using the TMP method based on the process variables presented in Table 5.

It can be seen from Table 5 that the TWCOE biolubricant yield ranged from 61.80 % to 96.12 %. The TWCOE biolubricant yield (Y_{TWCOE}) can be predicted based on the reaction time (A), TMP-to-WCOME ratio (B), and sodium methoxide catalyst concentration (C) using the following quadratic equation:

$$Y_{TWCOE} = 95.52 + 1.29A + 12.26B + 0.4250C + 0.8750AB + 1.40AC - 0.5500BC + 0.6225A^2 - 16.25B^2 - 2.22C^2 \quad (3)$$

The quadratic response surface model presented in Eq. (3) predicts the TWCOE biolubricant yield as a function of the biolubricant synthesis process variables, which are represented as uncoded independent variables. The TWCOE biolubricant yields predicted using Eq. (3) are presented in Table 5. It is evident that the TWCOE biolubricant yields obtained from experiments conformed well with those predicted by the quadratic response surface model.

Analysis of variance (ANOVA) was performed to assess the statistical significance and appropriateness of the quadratic response surface model. ANOVA was employed to evaluate the validity of the quadratic response surface model and the results are summarised in Table 6. The quadratic response surface model had an F-value of 68.57 and p-value of <0.0001 at a 99 % confidence interval, indicating that the model was statistically significant. Based on the results, factors B and B^2 were significant model terms (p-value < 0.0500), whereas factors A, C, AB, AC, BC, A^2, and C^2 were not significant model terms. If the p-value of the model term exceeds 0.0500, this indicates that the model term is not statistically significant. The F-value for the lack of fit (10.06) indicated that the lack of fit was significant, where there was only a 2.46 % chance that a lack of fit F-value this large could occur due to noise.

Fig. 8 shows the normal probability plot of the externally studentized residuals. The residuals exhibited favourable behaviour, as demonstrated by their proximity to the diagonal line, signifying the validity of the model. The residual is the discrepancy between the observed and predicted values. Hence, there is a residual for each observation in the dataset. If the experimental error is random, the estimated residuals follow a Gaussian distribution. Firstly, it is crucial to evaluate the adequacy of the quadratic response surface model to determine if the

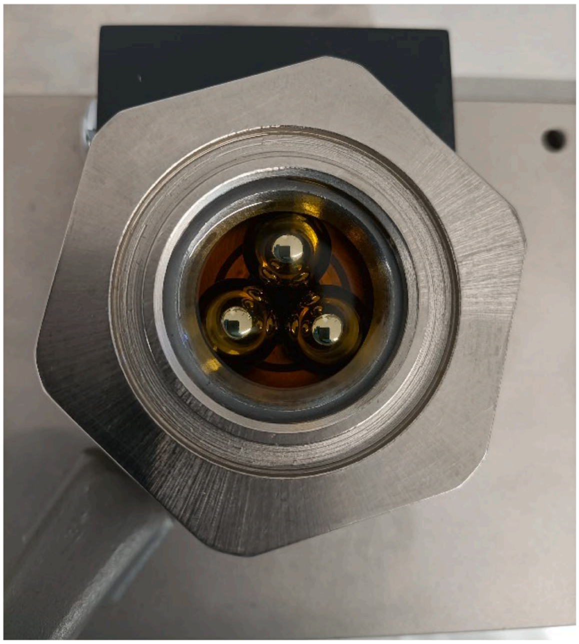

Fig. 6. Three stationary steel balls immersed in the lubricant in the four-ball test cup.

Table 3
Parameters of the four-ball wear tests.

Parameter	Value	Unit
Duration	3600	s
Sample temperature	75	°C
Rotational speed	1200	rpm
Applied load	40	kg

Table 4
Specifications of the steel balls used in the four-ball wear tester.

Steel ball	Description	Unit
Material	E-52,100 carbon steel balls, Grade 25 EP (Extra Polish)	—
Composition	C: 1.1 %, Cr: 1.6 %, Fe: 96.50 %, Mn: 0.45 %, P: 0.025 %, Si: 0.30 %, S: 0.025 %	%
Diameter	12.7	mm
Hardness	62	HRc

residuals conform to a normal distribution. As a result, the residuals are normalised and divided by their estimated standard deviation, yielding the residuals that are being examined. The residuals that have been examined are subsequently modelled using a normal distribution function [7,28].

Fig. 9 shows a comparison of the predicted and experimental TWCOE biolubricant yields, and it can be observed that there was a strong correlation between the values. The coefficient of determination (R^2) of the model was >90 %, indicating a high significance of each model term. The R^2 value is a statistical metric that reflects the degree of agreement between the values predicted by the model and those obtained from experiments [29,30]. The R^2 value of the model was 0.9888, indicating that 98.88 % of the variability in the TWCOE biolubricant yield was explained by the variability of the reaction time, TMP-to- WCOME ratio, and sodium methoxide catalyst concentration, as shown in Table 6. The high R^2 value suggests that the model adequately accounts for the majority of the variability in the TWCOE biolubricant yield. The TWCOE biolubricant yields predicted by the model closely aligned with the experimental TWCOE biolubricant yields, and therefore, the R^2 value was close to 1 [25]. The high R^2 value demonstrates the reliability of the RSM adopted in this study, suggesting that the model is consistent with the data and can be trusted to predict the TWCOE biolubricant yield under optimal conditions [15,31].

The coefficient of variation (CV) is calculated by dividing the standard deviation by the mean. A low CV signifies good dependability and precision in the experiment, whereas a higher CV suggests greater dispersion around the mean value [32]. The CV in this study was 2.25 %, indicating a high level of reliability and precision in the experimental results [33,34]. Adequate precision is a quantification of the ratio between the signal and noise. The adequate precision was determined to be 22.06, which was greater than 4, as shown in Table 6. This suggests that the model is capable of effectively exploring the design space and accurately predicting the TWCOE biolubricant yield. The predicted and experimental TWCOE biolubricant yields are shown in Fig. 9. The difference between the predicted R^2 value (0.8395) and adjusted R^2 value (0.9744) was <0.2, suggesting a satisfactory level of accuracy in the regression polynomial [33].

Fig. 10 shows the externally studentized residuals versus the experimental runs of the TWCOE biolubricant production. It can be observed that there were significant differences in the externally studentized residuals from one experimental run to another. It is worth noting that the outlier, denoted as *t*, quantifies the extent of difference between the experimental and predicted values. Fig. 10 shows that all of the examined residuals fall within the range of ±4.81, suggesting that there is good fitting between the model and response surface.

3.2. Effects of the TWCOE biolubricant synthesis process variables

Three-dimensional response surface plots were plotted to examine the effects of the reaction time, TMP-to-WCOME ratio, and sodium methoxide catalyst concentration on the TWCOE biolubricant yield. The plots in the following sub-sections effectively illustrate the process variables that significantly affect the TWCOE biolubricant yield.

3.3. Effect of TMP-to-WCOME ratio and reaction time

RSM was employed to optimise the process variables of the sodium methoxide-catalysed TWCOE biolubricant synthesis, as elaborated in the preceding section. The optimum reaction time, TMP-to-WCOME ratio, and sodium methoxide catalyst concentration were 227 min, 31.04 % (w/w), and 0.7 % (w/w), respectively. The TWCOE biolubricant yield predicted using Eq. (2) and the optimum process variables was 97.47. Numerous studies have documented the transesterification of triesters with TMP, ethyl hexanol, neopentyl glycol, and ethylene glycol as polyols for biolubricant synthesis, employing conventional reactors with a reaction time of 4–6 h [23,25,35,36]. In this study, the effect of varying the TMP-to-WCOME ratio (15–35 % (w/w)) and reaction time (120–240 min) on the TWCOE biolubricant yield was investigated.

Fig. 11 shows the three-dimensional response surface plot illustrating the effect of both TMP-to-WCOME ratio and reaction time on the TWCOE biolubricant yield. Overall, it is evident that increasing the TMP-to-WCOME ratio had a substantial effect on the TWCOE biolubricant yield when the reaction time was kept constant. The biolubricant production was enhanced by increasing the TMP-to-WCOME ratio to 25–30 % (w/w). Furthermore, incorporating TMP at higher concentrations (>30 % (w/w)) reduced the TWCOE biolubricant yield. The results suggest that the separation of FAME and TMP ester becomes more challenging due to soap formation. This aligns with the findings of Kamyab et al. [23], who synthesised TMP ester from canola oil via two-stage transesterification, achieving a yield of 95.7 % (w/w). The reversibility of the transesterification reaction necessitates the use of excess reactants to enhance the forward reaction rate [23]. This has also been noted in earlier studies involving the synthesis of TMP ester from WCO. The presence of three hydroxyl groups in the molecular structure of TMP indicates that the addition of excess methyl ester will drive the

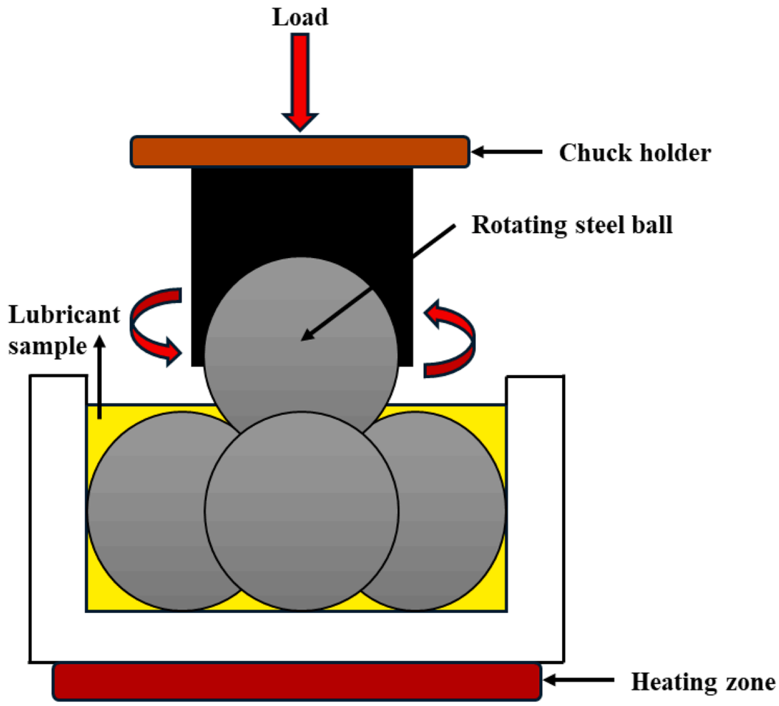

Fig. 7. Schematic of the four-ball wear tester.

Table 5
Box–Behnken experimental design used to optimise the TWCOE biolubricant yield.

Experimental run	A: Reaction time (min)	B: TMP-to- WCOME ratio (% (w/w))	C: Sodium methoxide catalyst concentration (% (w/w))	Experimental TWCOE biolubricant yield (% w/w))	Predicted TWCOE biolubricant yield (% (w/w))
1	240	35	1.0	94.40	94.35
2	240	15	1.0	68.90	68.08
3	180	25	1.0	95.74	95.52
4	120	25	0.5	95.70	93.64
5	180	15	0.5	61.80	63.81
6	180	15	1.5	67.00	65.76
7	180	35	1.5	91.20	89.19
8	180	25	1.0	96.12	95.52
9	240	25	1.5	95.00	97.06
10	180	25	1.0	93.95	95.52
11	120	15	1.0	67.20	67.25
12	120	35	1.0	89.20	90.03
13	180	25	1.0	95.95	95.52
14	180	35	0.5	88.20	89.44
15	120	25	1.5	90.50	91.69
16	240	25	0.5	94.60	93.41
17	180	25	1.0	95.84	95.52

reaction equilibrium in the forward direction. The reduction in biolubricant yield may result from the restricted surface area of the catalyst and the dilution effect caused by the addition of excessive reagents, as noted by Wang et al. [37].

3.4. Effect of sodium methoxide catalyst concentration and reaction time

Fig. 12 shows the effect of sodium methoxide catalyst concentration and reaction time on the TWCOE biolubricant yield. The sodium methoxide catalyst concentration ranged from 0.5 % (w/w) to 1.5 % (w/w). It can be observed that the sodium methoxide catalyst concentration had a negligible effect on the TWCOE biolubricant yield. The sodium methoxide catalyst had limited effectiveness in the production of TWCOE biolubricant, even with an extended reaction time of 240 min compared with 120 min. Increasing the sodium methoxide catalyst concentration decreased the TWCOE biolubricant yield, while simultaneously increased soap formation. According to Gul et al. [25], the sodium methoxide catalyst concentration is the least effective factor, resulting in low biolubricant yields. Sodium methoxide enhances the conversion rate of methyl ester into TMP triester (biolubricant); however, it also increases soap formation, which requires optimisation [25, 38].

3.4.1. Effect of TMP-to-WCOME ratio and sodium methoxide catalyst concentration

Fig. 13 shows the three-dimensional response surface plot illustrating the effect of TMP-to-WCOME ratio (15–35 % (w/w)) and sodium methoxide catalyst concentration (0.5–1.5 % (w/w)) on the TWCOE biolubricant yield. It is apparent that increasing the TMP-to-WCOME ratio increased he TWCOME biolubricant yield when the sodium methoxide catalyst concentration was kept constant. Fig. 13 also shows that the maximum TWCOE biolubricant yield was achieved when the TMP-to-WCOME ratio was 30 % (w/w). The TWCOE biolubricant yield decreased when the TMP-to-WCOME ratio exceeded 30 % (w/w).

Table 6
ANOVA results.

Source	Sum of squares	df[a]	Mean square	*F*-value	*p*-value	
Model	2381.85	9	264.65	68.57	< 0.0001	Significant
A-Reaction time	13.26	1	13.26	3.44	0.1062	
B-TMP-to-WCOME	1202.95	1	1202.95	311.67	< 0.0001	
C-Sodium methoxide catalyst concentration	1.44	1	1.44	0.3744	0.56	
AB	3.06	1	3.06	0.7934	0.4026	
AC	7.84	1	7.84	2.03	0.1971	
BC	1.21	1	1.21	0.3135	0.593	
A^2	1.79	1	1.79	0.4645	0.5175	
B^2	1111.5	1	1111.5	287.97	< 0.0001	
C^2	20.8	1	20.8	5.39	0.0533	
Residual	27.02	7	3.86			
Lack of fit	23.86	3	7.95	10.06	0.0246	significant
Pure error	3.16	4	0.7902			
Cor Total[b]	2408.87	16				
R^2[c]	0.9888		Adj R^2[e]	0.9744		
Mean	87.14		Pred R^2[f]	0.8395		
CV %[d]	2.25		AdeqPrecision[g]	22.0667		

[a] Degree of freedom.
[b] Corrected total sum of squares.
[c] Coefficient of determination.
[d] Coefficient of variation.
[e] Adjusted R^2.
[f] Predicted R^2.
[g] Adequate precision.

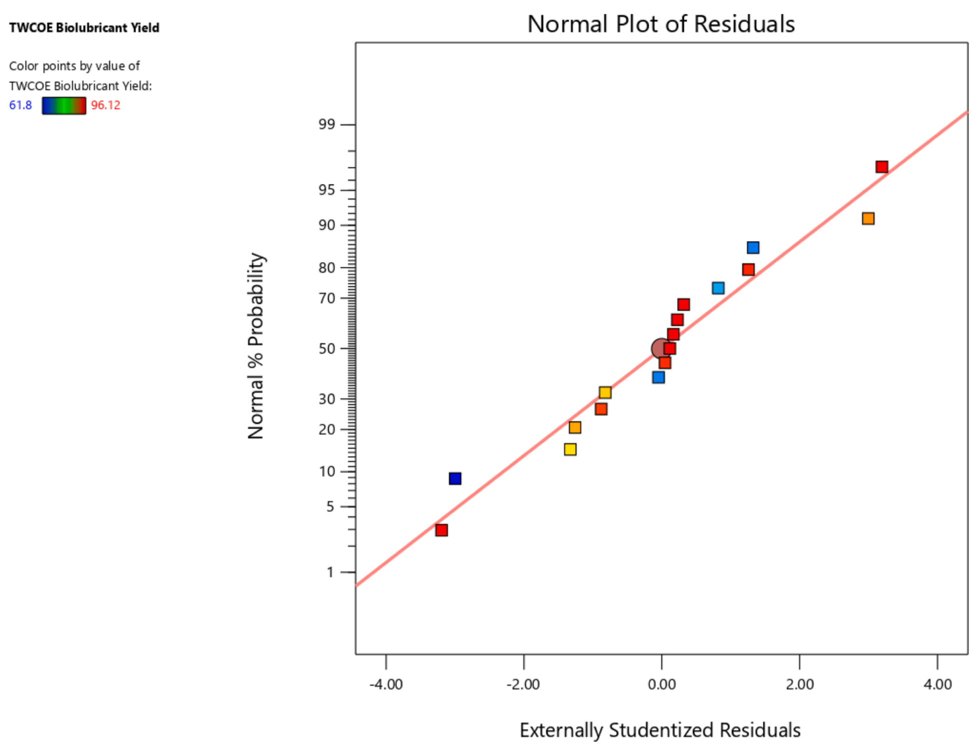

Fig. 8. Normal probability plot of externally studentized residuals.

Table 5 shows that the TWCOE biolubricant yield was within a range of 67.00–95.00 % (w/w) when the sodium methoxide catalyst concentration was 1.5 % (w/w). On the other hand, when the sodium methoxide catalyst concentration decreased, the TWCOE biolubricant yield increased. Specifically, when the sodium methoxide catalyst concentration was 1 % (w/w), the TWCOE biolubricant yield was within a range of 68.90–96.12 % (w/w). Furthermore, the use of the minimum sodium methoxide catalyst concentration (0.5 % (w/w)) and the lowest TMP-to-WCOME ratio (15 % (w/w)) reduced TWCOE biolubricant yield to 61.80 % (w/w). The TWCOE biolubricant yield was maximum (96.12 %) under the following conditions: (1) TMP-to-WCOME ratio: 25 % (w/w), (2) sodium methoxide catalyst concentration: 1 % (w/w), and (3) reaction time: 180 min. These values were the optimal conditions for TWCOE biolubricant production by two-step transesterification. Increasing the catalyst concentration in the reaction leads to a higher yield of fatty acids. The presence of metal catalyst can facilitate saponification, leading to the formation of soap [39]. Aziz et al. [40] found that increasing the catalyst concentration can improve the production of fatty acids. In the presence of a metal catalyst, water or moisture in the oil reacts with methyl ester to produce fatty acids, leading to the formation of soap. This subsequently affects the formation of esters. Vacuum filtration effectively eliminates solid substances, such as soap, from

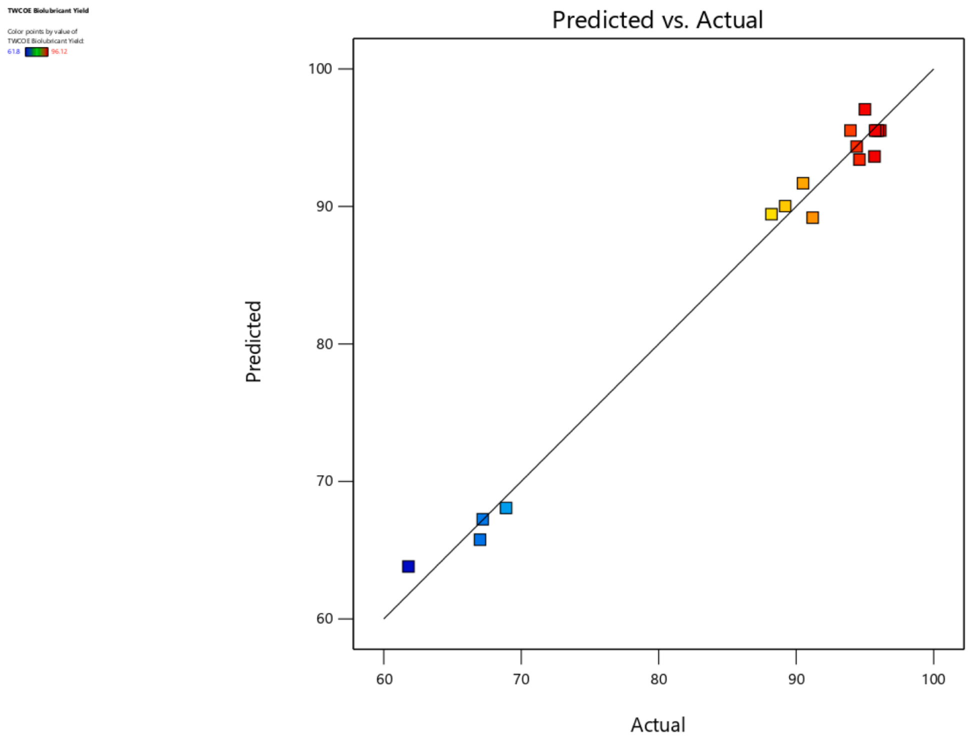

Fig. 9. Correlation between the experimental and predicted TWCOE biolubricant yields.

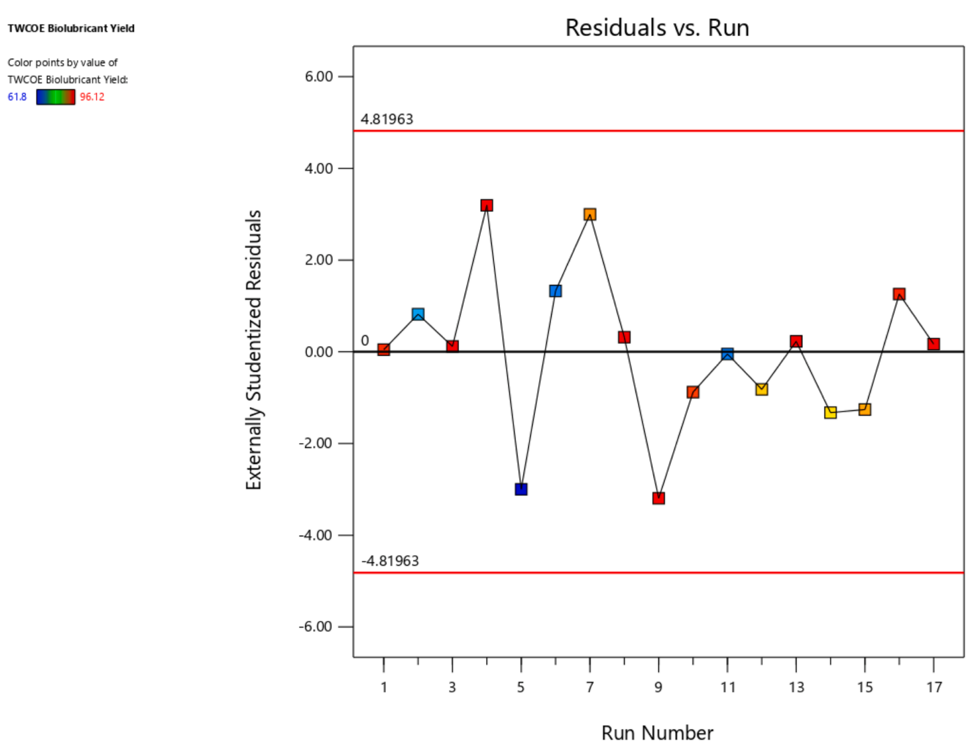

Fig. 10. Plot of the externally studentized residuals versus experimental runs.

the final product [39,41].

3.5. Physicochemical properties of the TWCOE biolubricant and other commercial lubricants

The physicochemical properties of the TWCOE biolubricant are presented in Table 7 [42–44]. The physicochemical properties of the ISO VG 32, ISO VG 46, ISO VG 68, and ISO VG 100 lubricant standards are also included for comparison. The physicochemical properties play a vital role in assessing the compatibility of biolubricants for use in automotive or industrial applications. The viscosity index was determined by assessing the variation in viscosity at temperatures of 40 °C and 100 °C. A low viscosity index indicates a notable variation in viscosity across this temperature range. A higher viscosity index is

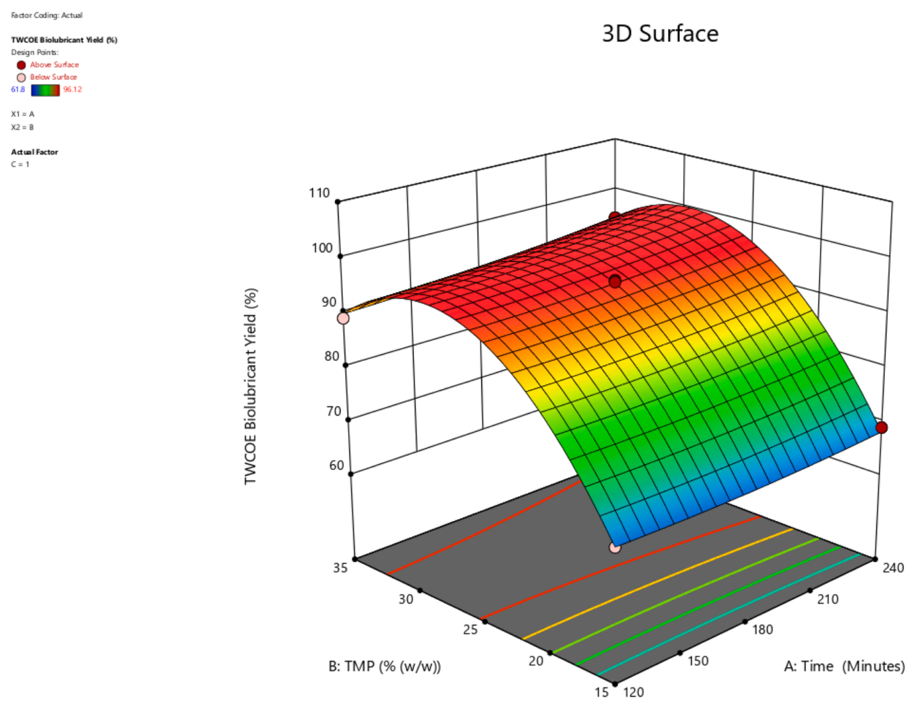

Fig. 11. Three-dimensional response surface plot illustrating the effect of TMP-to-WCOME ratio and reaction time on the TWCOE biolubricant yield.

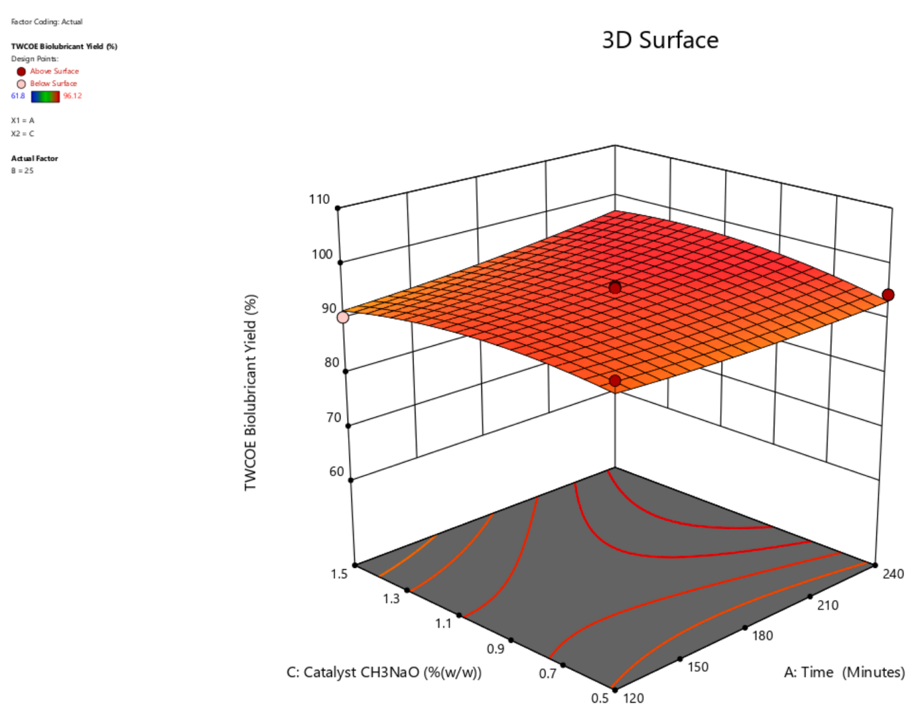

Fig. 12. Three-dimensional response surface plot illustrating the effect of sodium methoxide catalyst concentration and reaction time on the TWCOE biolubricant yield.

advantageous as it signifies that the viscosity remains relatively stable despite temperature variations, rendering the lubricant suitable for automotive lubricants. The viscosity indexes for the SAE15W40, SAE0W20, and ATF9 commercial lubricants were 137, 166, and 154, respectively. These values were higher than the viscosity index of the TWCOE biolubricant produced in this study. However, the viscosity index can be improved by exploring the addition of additives in future research.

As shown in Table 7, the TWCOE biolubricant had higher kinematic viscosities at 40 and 100 °C, and a high viscosity index, with a value of 41.55 mm^2/s, 6.93 mm^2/s, and 125.30, respectively. However, the values were slightly lower than those specified for ISO VG 68, ISO VG 100, and SAE15W40 lubricants. The acid value of the TWCOE biolubricant was found to be 0.4 mg KOH/g. The flash point of the TWCOE biolubricant was slightly higher than those of ISO VG 46 and SAE0W20 commercial lubricants. Compared with the work of Joshi et al. [18], the transesterification process produced biolubricants that possessed favourable tribological characteristics. The kinematic viscosities of the

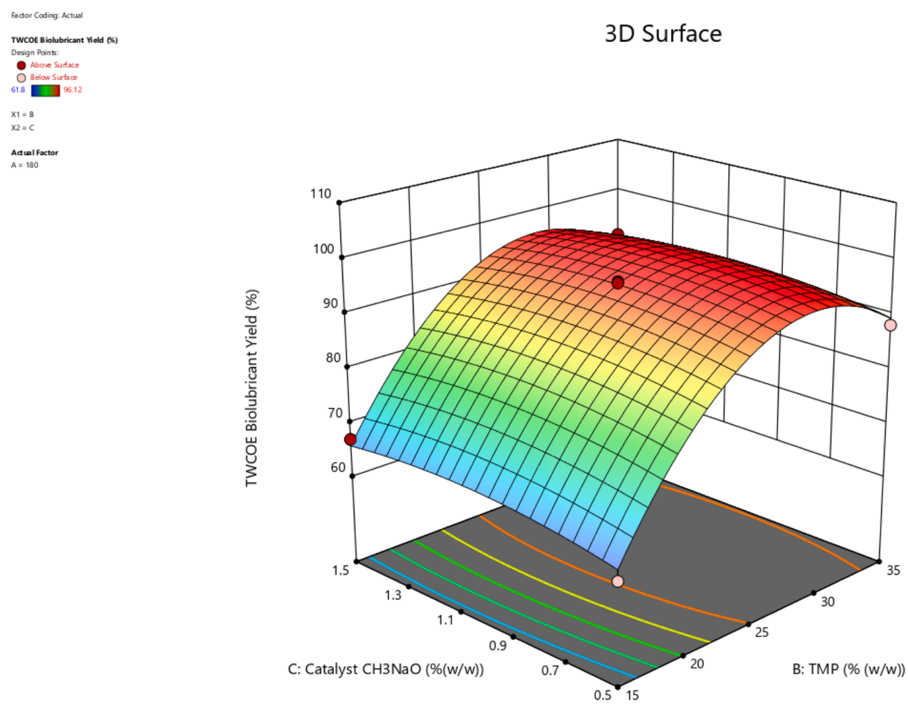

Fig. 13. Three-dimensional response surface plot illustrating the effect of TMP-to-WCOME and sodium methoxide catalyst concentration on the TWCOE biolubricant yield.

ethyl hexyl ester generated from WCO were measured at 40 and 100 °C. The kinematic viscosities at 40 and 100 °C and viscosity index obtained were 34.91 mm^2/s, 6.09 mm^2/s, and 121.59, respectively [18]. The viscosity and flash point will significantly affect the flow characteristics and atomisation of the lubricant. The presence of contaminants in biolubricants (such as free glycerol and glycerides) as well as temperature can affect both the viscosity and flash point. Based on the physicochemical properties summarised in Table 7, the TWCOE biolubricant is a suitable lubricant, with physicochemical properties comparable to commercial lubricants such as ISO VG 46 and SAE0W20 for hybrid engine vehicles.

3.5.1. FTIR spectra of the TWCOE biolubricant and LB15W40 commercial lubricant

FTIR spectroscopy is a characterisation technique used to analyse chemical compounds through the generation of infrared absorption spectra. In this study, FTIR spectroscopy was employed to analyse the functional groups in the TWCOE biolubricant and LB15W40 (SAE15W40) commercial lubricant, and the FTIR spectra are shown in Fig. 14. The FTIR spectrum of the TWCOE biolubricant closely aligned with the FTIR spectrum obtained by Kamyab et al. [23], who synthesised TMP ester from canola oil via a two-stage transesterification process. The FTIR spectrum of the TWCOE biolubricant also aligned with that of the LB15W40 (SAE15W40) commercial lubricant [23]. The absorption peaks at 3736, 2924, 2860, 1730, 1448, 1176, 1041, and 711 1/cm indicate the functional groups present in the TWCOE biolubricant. The peak at 3736 1/cm corresponds to the stretching vibration of O–H bonds in the TWCOE biolubricant. The pronounced absorption peaks at ~2924 and ~1730 1/cm indicate the presence of C = O ester groups and C–H stretching vibrations in the TWCOE biolubricant. The moderate absorption peaks between 1448 and 1041 1/cm indicate the presence of C–H and C–O bonds characterised by stretching vibrations. A prominent peak near 711 1/cm signifies the presence of C = C double bonds in the TWCOE biolubricant. This aligns with the findings of Kamyab et al. [23]. They identified significant peaks at ~1736 and ~1165 1/cm, indicating the presence of C = O ester groups. Hussein et al. [9] and Mohamed et al.

Table 7
Comparison of the physicochemical properties of TWCOE biolubricant with SAE15W40, SAE0W40, and ATF9 commercial lubricants and lubricant standards.

Property	Unit	EHE-WCO [18] *	TWCOE[a]	LB15W40 (SAE15W40)	HB0W20 (SAE0W20)	ATF9	Lubricant standards		
							ISO VG 32	ISO VG 46	ISO VG 68
Kinematic viscosity 40 °C	mm^2/s	34.91	41.55	106.00	45.20	29.60	>28.80	>41.10	>61.40
Kinematic viscosity 100 °C	mm^2/s	6.09	6.93	14.27	8.40	6.00	>4.10	>4.10	>4.10
Viscosity index	—	121.59	125.30	137.00	166.00	154.00	>90.00	>90.00	>198.00
Flash point	°C	216.0	222.2	241.0	201.0	199.0	204.0	220.0	226.0
Oxidation stability	min	—	—	—	—	—	—	—	1670.26
Pour point	°C	−1	—			−45			
Acid value	mg KOH/g	—	0.4	—	—	—	—	—	—
Dynamic viscosity at 40 °C	mPa.s	—	37.52	—	—	—	—	—	—
Dynamic viscosity at 100 °C	mPa.s	—	5.97	—	—	—	—	—	—
Density at 40 °C	g/cm^3	—	0.90	—	—	—	—	—	—
Density at 100 °C	g/cm^3	—	0.86	—	—	—	—	—	—

* Ethyl hexyl ester of waste cooking oil (EHE-WCO).
[a] This study.

[27] identified significant peaks in the spectra at 2923 and 2853 1/cm, which was ascribed to C–H bond stretching. The peaks corresponded to methylene and methyl groups, respectively. The TWCOE biolubricant had an ester structure, as indicated by the absorption band at 1741 1/cm, corresponding to carbonyl ester stretching [9,27]. The results of this study showed good agreement with those of other studies. Minor discrepancies arise from the employed methodologies or different reaction catalysts, which also yield distinct spectral waves.

3.6. Tribological characteristics of the TWCOE biolubricant

3.6.1. Coefficient of friction of the TWCOE biolubricant and other commercial lubricants

Fig. 15 shows the variations of the coefficient of friction of the TWCOE biolubricant, LB15W40 (SAE15W40) and HB0W30 (SAE0W30) commercial lubricants, and automatic transmission fluid for electric vehicles (ATF9) with respect to time. The coefficient of friction, denoted as μ, is a scalar variable without dimensions that expresses the ratio of the frictional force acting between two objects to the normal force applied to them. It can be seen that the TWCOE biolubricant had a higher coefficient of friction (0.00833) for the first 10 min compared with the LB15W40 lubricant. However, at 12 min, the coefficient of friction of the LB15W40 lubricant increased to 0.08661, then decreased to a value between 0.06633 and 0.06597 up to 60 min of testing. The TWCOE biolubricant exhibited very good results in this friction test. In the first 10 min, the coefficient of friction of the TWCOE biolubricant increased until it reached its maximum value at 8 min (0.07378). The coefficient of friction of the TWCOE biolubricant decreased to 0.03191 thereafter until the end of the test.

Fig. 15 and Table 8 show that the average coefficient of friction of the TWCOE biolubricant (0.045) was lower than that of the LB15W40 lubricant (0.062) obtained from the four-ball wear tests. The average coefficients of friction for the HB0W30 and ATF9 commercial lubricants were higher than those of the TWCOE biolubricant and LB15W40 lubricant, with a value of 0.088 and 0.089, respectively. The difference in the coefficient of friction between the TWCOE biolubricant and LB15W40 lubricant was 0.017, indicating the potential of the TWCOE biolubricant as a commercial lubricant and in reducing friction. The conversion of natural materials, particularly waste materials, into value-added products such as lubricants can eliminate various environmental problems and reduce dependence on fossil fuel resources.

The results suggest that the performance of the TWCOE biolubricant is similar to that of commercial lubricants; however, it is worth noting that its actual performance is still slightly inferior to that of commercial lubricants. The results of the study indicate that the TWCOE biolubricant can improve lubrication, with a lower coefficient of friction and wear scar diameter. The TWCOE lubricant had a coefficient of friction that was roughly 27 % lower than those of commercial lubricants, and resulted in a wear scar diameter that was 26 % higher than those of commercial lubricants. The TWCOE biolubricant had a lower coefficient of friction than commercial lubricants, which can be linked to the variations in fatty acid chain lengths, as indicated by its viscosity index (Table 5). The increase in the fatty acid chain length results in higher viscosity, subsequently thickening the adsorbed layer and thereby improving surface protection [19,45].

The TWCOE biolubricant can serve as an effective additive to enhance the performance of commercial lubricants. The majority of vegetable oils, along with WCOs, are composed of triglycerides, which are a type of polar ester molecule found in nature. The carbon chain of triglycerides has the potential to enhance the biolubricant protective film, leading to improved strength on the surface coated with the biolubricant. This effectively reduces friction compared with petroleum-based commercial lubricants. The low oxidation stability of vegetable oils is primarily attributed to the triglyceride components [46,47]. The TWCOE biolubricant minimises friction between sliding surfaces owing to the presence of free fatty acids [15].

3.6.2. Wear scar diameters of the wear scars resulting from the TWCOE biolubricant and other commercial lubricants

Fig. 16 shows the was average wear scar diameters of the steel balls lubricated with the TWCOE biolubricant and other commercial lubricants. Wear is the process of material deformation or removal from a metal surface that occurs when there is relative motion. A larger wear scar diameter suggests that there is a rapid rate of material deformation and removal, leading to significant surface degradation. Compared with the LB15W40 lubricant, the TWCOE biolubricant resulted in a slightly larger wear scar diameter on each stationary steel ball. The LB15W40, HB0W30, and AT9 commercial lubricants resulted in an average wear scar diameter of 0.501, 0.212, and 0.169 mm, respectively. The presence of fatty acids in the TWCOE biolubricant provides an effective lubrication layer between moving components, enhancing their smooth operation. However, higher concentrations of biolubricant may lead to increased wear and surface roughness, as demonstrated by a previous

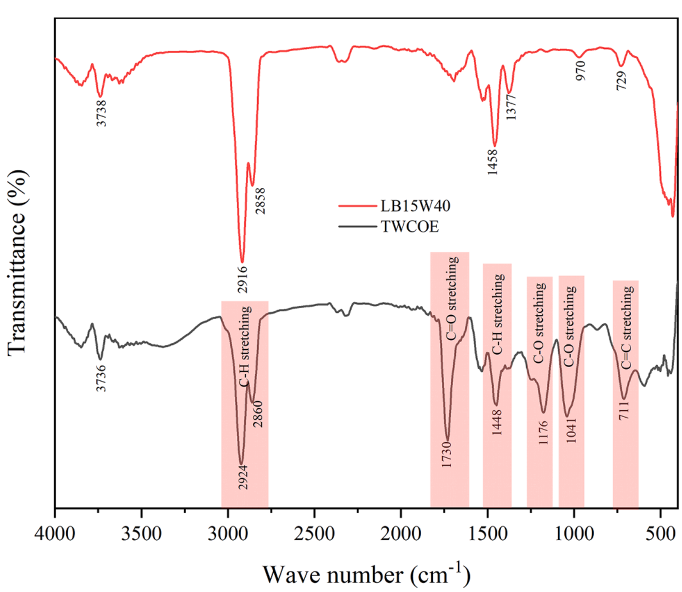

Fig. 14. FTIR spectra of the TWCOE biolubricant and LB15W40 (SAE15W40) commercial lubricant.

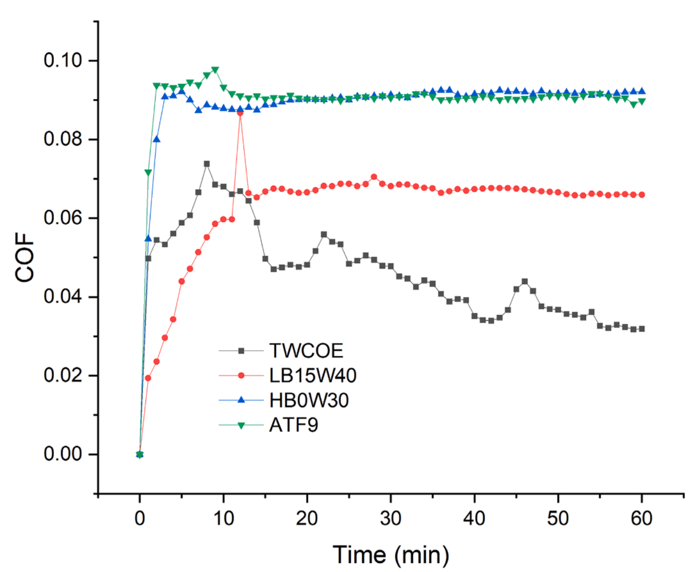

Fig. 15. Variations of the coefficient of friction of the TWCOE biolubricant and other commercial lubricants with respect to time.

study [20]. Aravind et al. [18,48] reported that wear scar diameter for commercial lubricants is within the range of 0.51–0.87 mm.

Fig. 16 shows that the average wear scar diameter for the TWCOE biolubricant was 0.632 mm, which was slightly close to those of commercial mineral-based lubricants. The results suggest that the TWCOE biolubricant effectively forms a consistent lubricating film between the surfaces that come into contact, even when subjected to a high load of 40 kg. The TWCOE biolubricant demonstrated desirable anti-wear (WSD) and anti-friction properties due to the presence of fatty acid and ester components in the biolubricant. The ester group constitutes the polar component of lubricants derived from vegetable oil. Fatty acid chains consist of non-polar parts with different lengths, levels of unsaturation, and stereochemistry. In principle, the ester group strengthens the binding of the molecules, increasing the strength of the lubricating film, providing strong resistance to shear forces. In general, the wear scar diameter increases as the normal load increases. When the normal load increases, the two rolling surfaces move closer to each other due to the high surface pressure, thereby increasing the wear scar diameter [18]. The TWCOE biolubricant provided lubrication to the steel surface, leading to the formation of smoother and less pronounced scars compared with the LB15W40 lubricant, as shown in Fig. 17. Based on these results, the TWCOE biolubricant appears to protect surfaces better because it has ester functional groups that form a film that sticks to metal surfaces and keeps them from contacting each other. Nevertheless, the lubricating film has a limited lifespan. The presence of deep grooves and material transfer on the metal surface lubricated with LB15W40 lubricant clearly indicates a high level of abrasiveness, as shown in Fig. 17.

3.6.3. *Worn surface characteristics*

Fig. 18 shows the surface morphologies of the TWOCE biolubricant-lubricated steel balls, which were examined using scanning electron microscopy (SEM). This measurement complies with the ASTM D4172 standard, where the load, temperature, rotational speed, and duration of the four-ball wear test were 392 N, 75 °C, 1200 rpm, and 3600 s, respectively. Fig. 17 shows that the maximum wear scar diameter for the TWCOE biolubricant was 931 μm, whereas the average wear scar diameter was 897 μm. The wear scar areas on the stationary steel balls lubricated with the LB15W40 lubricant shown in Fig. 17 serve as an important reference for understanding the surface morphology of the steel balls immersed in this lubricant. The steel ball surfaces lubricated with LB15W40 lubricant showed negligible wear. The average wear scar area of 0.632 mm for the TWCOE biolubricant was lower than that obtained by Kamyab et al. [23], who produced TMP ester from canola oil using two-step transesterification, and the wear scar diameter was 0.8 ± 0.023 mm [23]. Fig. 18 shows the surfaces of the stationary steel balls lubricated with the TWCOE biolubricant. SEM images A, B, and C correspond to the first, second, and third stationary steel balls, respectively. The surface of the steel balls typically exhibited shallow scratches or abrasion, characterised by abrasion wear (A), as well as deeper adhesion wear and abrasion wear, alongside surface smoothing resulting from friction. Deeper abrasion wear was present on the surface of the third steel ball (C). Shear wear results from friction between the stationary and rotating steel balls, while adhesion wear arises when melted or softened material from the rotating steel ball adheres to the surface of the stationary steel ball. Melted material can develop due to friction generated at high rotational speeds between the surfaces of the stationary and rotating balls. High rotational friction increases the temperature of the biolubricant, leading to a decline in the efficacy of the ester group intended to protect the steel ball surface. This results in the formation of shallow scratches on the steel ball surface, as evidenced from the SEM images. Further studies can be conducted to enhance the performance of biolubricants, particularly through the incorporation of additives in order to improve their tribological characteristics [1,46]. Overall, the results indicate that the performance of the TWCOE biolubricant is comparable to those of commercial lubricants, suggesting its potential as an alternative lubricant additive to enhance the performance of lubricants sourced from renewable and environmentally sustainable materials.

Table 8
Tribological characteristics of the TWCOE biolubricant and other commercial lubricants.

Description	TWCOE	LB15W40	HB0W30	ATF9
Experimental conditions	Load: 40 kg, rotation 1200 rpm, temperature: 75 °C, duration: 3600 s.			
Average coefficient of friction	0.045	0.062	0.088	0.089
Average wear scar diameter (mm)	0.632	0.501	0.212	0.169
Average wear scar diameter obtained from microscopic images (μm)	906	853	553	464

4. Conclusions

In this study, the process variables of TWCOE biolubricant synthesis was optimised by RSM, and the physicochemical properties and tribological characteristics of the TWCOE biolubricant were assessed and compared with those of commercial lubricants. The following conclusions were drawn based on the key findings of this study:

- The TWCOE biolubricant, synthesised via a two-step transesterification process, attained a predicted maximum yield of 97.06 % under optimal conditions: (1) reaction time: 180 min, (2) TMP-to-WCOME ratio: 25 % (w/w), and (3) sodium methoxide catalyst concentration: 1 % (w/w). The TWCOE biolubricant yield obtained from experiments was 96.12 %, which showed very good agreement with the predicted TWCOE biolubricant yield, with an R^2 value of 98.88 %.
- The physicochemical properties of the TWCOE biolubricant were evaluated. The kinematic viscosities of the TWCOE biolubricant at 40 and 100 °C were 41.55 and 6.93 mm^2/s, respectively. The viscosity index was 125.30, the flash point was 222.2 °C, and the acid value was 0.4 mg KOH/g. The physicochemical properties of the TWCOE biolubricant closely aligned with those of ISO VG 46 lubricant standard, showing its potential as a lubricant additive for gear shaping, tool lubrication, and industrial metalworking applications, as well as a hydraulic fluid.
- The TWCOE biolubricant demonstrated effective boundary lubrication properties, exhibiting lubrication performance comparable to commercial lubricants, with a coefficient of friction of 0.045 and an

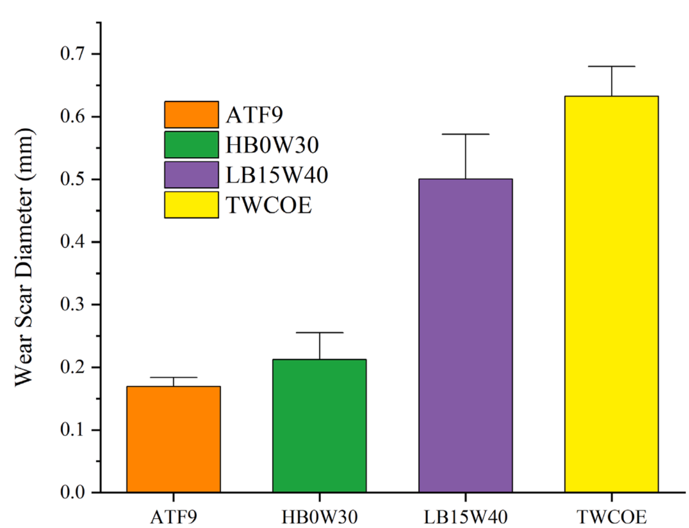

Fig. 16. Average wear scar diameters for the TWCOE biolubricant and other commercial lubricants.

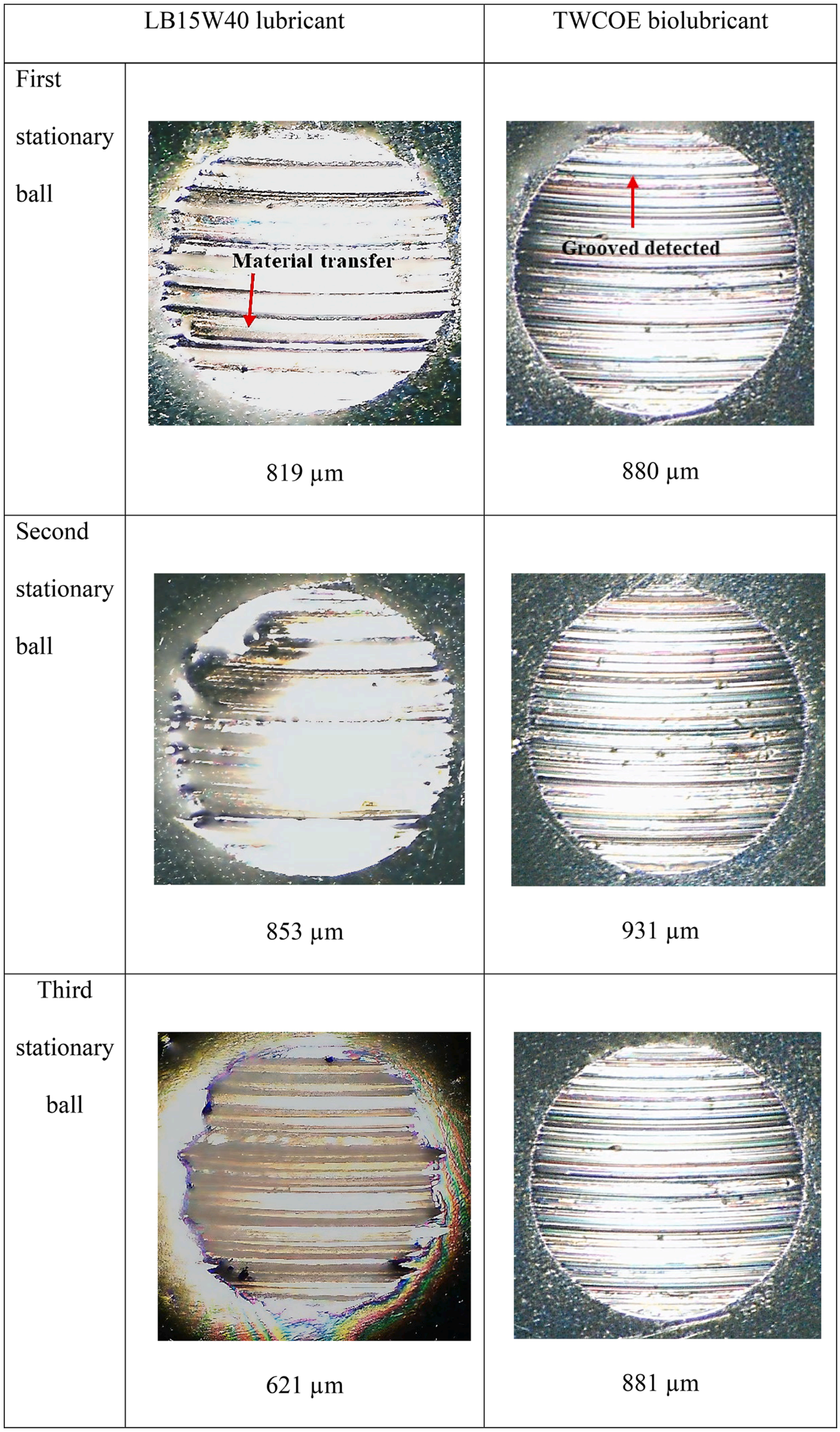

Fig. 17. Microscopic images of the wear scar areas of the stationary steel balls lubricated with TWCOE biolubricant and LB15W40 lubricant. The wear scar diameters are presented below the microscopic images.

average wear scar diameter of 0.632 mm. The results showed that the TWCOE biolubricant had a lower coefficient of friction and a wear scar diameter comparable to those of SAE15W40, SAE0W30, and ATF9 commercial lubricants, demonstrating its potential as an effective lubricant for industrial equipment and as an additive to enhance existing commercial lubricants.

CRediT authorship contribution statement

Teuku Meurah Indra Riayatsyah: Writing – original draft, Resources, Methodology, Investigation, Data curation, Conceptualization. **Arridina Susan Silitonga:** Writing – review & editing, Supervision, Funding acquisition, Data curation, Conceptualization. **Md Abul Kalam:** Writing – review & editing, Supervision, Resources,

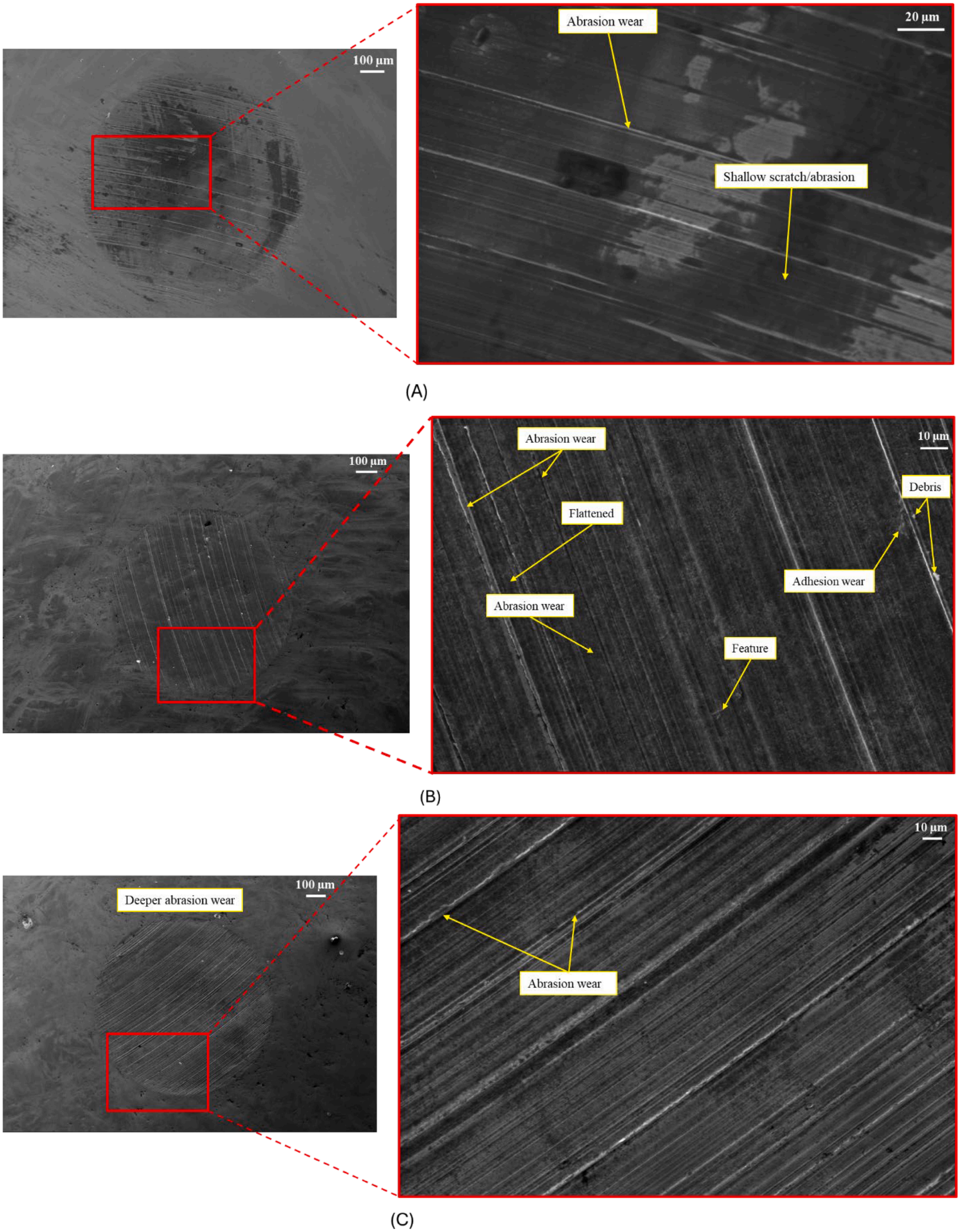

Fig. 18. Surface morphologies of worn surfaces lubricated with TWCOE biolubricant after wear tests at a load, temperature, rotational speed, and duration of 392 N, 75 °C, 1200 rpm, and 3600 s, respectively: (A) first stationary steel ball, (B) second stationary steel ball, and (C) third stationary steel ball.

Methodology, Conceptualization. **Islam Md Rizwanul Fattah:** Writing – review & editing, Validation, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.rineng.2025.104055.

Data availability

The data used in this study will be made available by the authors upon reasonable request.

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