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SYNTHESIS AND CHARACTERISATION OF BIOBASED GREASE DERIVED FROM CHEMICALLY MODIFIED WASTE COOKING OIL

Abstract: As the global population rises, the dependency on edible oils also rises. The used oil possesses environmental concerns due to improper waste oil disposal. This study emphasises the feasibility of repurposing waste cooking oil (WCO) for eco-friendly lubricating grease production, emphasising enhanced stability and performance through chemical modifications. Chemical modifications, primarily transesterification, enhance the oxidative stability and chemical properties of WCO. Gas chromatography and mass spectroscopy analyse the fatty acid profile, and the hot oil oxidation test (HOOT) assesses the oxidative characteristics of WCO. The formulated grease using WCO undergoes tribological testing and penetration value testing. Results indicate post-transesterification improvements in chemical and oxidative stability, with lowered acid and peroxide values. Modified waste cooking oil (MWCO) exhibits enhanced thermal stability with higher flash and fire points. Viscosity results suggest the potential of MWCO as a lubricant with superior oxidative stability. Tribological properties reveal an improved characteristic value for MWCO, establishing its potential as an eco-friendly grease. Cone penetration tests categorise the formulated grease as NLGI grade 2, indicating a softer consistency with potential advantages for specific applications. The findings offer insights into the sustainable development of the lubricant industry, presenting MWCO as a promising alternative to conventional lubricants.

Keywords: biogrease, lubricants, sustainability, transesterification, waste cooking oil

Introduction

The development of eco-friendly lubricants addresses the increasing demand for energy, driven by population growth. The use of lubricants plays a pivotal role in human civilisation, significantly influencing development and machining standards [1]. Alternatives to conventional lubricants such as vegetable oils exhibit remarkable qualities, boasting high flash points, excellent lubricity, a better viscosity index, and renewable attributes, with their most crucial quality being biodegradability [2]. Biomass, which includes organic materials derived from plants, agricultural residues, and other biological sources, has emerged as a versatile and renewable feedstock in this context [3, 4]. By using industrial and agricultural waste, its use in the manufacturing of biolubricants not only

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takes advantage of its availability but also supports sustainability and the circular economy [4, 5].

Despite these advantages, vegetable oils face challenges such as weak cold flow characteristics and limited oxidation stability, leading to polymerisation and deterioration [6]. To overcome these limitations inherent to vegetable oils, chemically modified versions are developed [7, 8]. This modification aims to remove or rectify deficiencies, enhancing the overall performance and application range of vegetable oil-derived lubricants.

The significance of developing these biolubricants mainly extends to developing nations where agriculture serves as the primary economic driver. Biolubricants, characterised by the biodegradability of vegetable oils, offer environmental benefits [9, 10]. The term "biolubricants" is assigned to lubricants that are both biodegradable and safe for both people and the environment, yet their application remains limited compared to mineral oil-based lubricants [11, 12].

Waste cooking oil (WCO), costing two to three times less than fresh vegetable oil, emerges as a potential substitute for vegetable oils in biolubricant manufacturing [13]. However, the management of used cooking oils and fats poses challenges due to disposal issues and the potential contamination of water and land resources. While some residual cooking oil finds a secondary use in soap production, a substantial portion is still released into the environment. The United States alone generates around 100 million gallons of used cooking oil daily, averaging 9 pounds per person [14].

WCO is currently under investigation as a potential source for biodiesel production [1, 14, 15]. Exploring the use of WCO in producing biolubricants holds promise for various applications, including engine lubricants, compressor oils, milling applications, biological applications, and machining. This approach presents a potential future solution to the waste management problem [16]. In the machinery sector, base oils and environmentally friendly lubricants are scrutinised for their economic and environmental significance. The chemical alteration of vegetable oils to create alternatives to petroleum-based products is a captivating area of study [17, 18]. Additionally, the production of biolubricants from used cooking oil and cyclic oxygenates is achievable through a four-step catalytic process [19]. The avenue of these research contributes to the ongoing exploration of sustainable alternatives in the lubricant industry.

Vegetable oils primarily consist of triglycerides, featuring ester connections and three long-chain fatty acids. The triglyceride structure comprises three hydroxyl groups esterified with fatty acid carboxyl groups, leveraging its high molecular weight to benefit from long and polar glycerides [20]. Vegetable oils encompass diglycerols, free fatty acids, sterols, and tocopherols along with triglycerides [21]. These components contribute to the creation of a tribofilm, adhering to surfaces and reducing the coefficient of friction (COF) and wear in the system [22].

Chemical modifications such as transesterification enhance the oxidative and thermal stability of bio-lubricant base-stocks by eliminating the β-hydrogen atom from the vegetable oil substrate [23]. Significantly, the transesterification process applied to jatropha oil using ethanol and sodium hydroxide in the presence of trimethylolpropane (TMP) has showcased enhanced lubrication properties [24]. Likewise, the transesterification of canola oil with diverse alcohol blends has elevated the oil’s characteristics in alignment with ASTM standards, with ethyl ester displaying the highest level of lubricity [25]. The non-edible oils are preferred to undergo chemical modifications due to the high

acid content which may eventually limit its potential use as a base stock if left untreated [26, 27].

Viscosity, a critical property in lubrication, significantly influences the effectiveness of lubricants. The viscosity index (VI) was devised to illustrate the impact of temperature changes on oil viscosity, given the sensitivity of lubricating oil viscosity to operating temperature [2]. However, the triglyceride structure of natural vegetable oils imposes a limited viscosity range, due to which their application in various industries is constrained [16]. To address this constraint, vegetable oils undergo transesterification to yield fatty acid alkyl esters with varying chain lengths. Commonly, mineral acids and bases act as catalysts in this process. The resultant fatty acid alkyl esters serve various purposes, including applications as fuel, biodiesel, and lubricants, thereby broadening the versatility of vegetable oils [28]. In biodiesel manufacturing from Calophyllum inophyllum oil, a two-stage transesterification process is commonly employed [29]. A noteworthy advancement in potential biodegradable base stocks for lubricant development is the Trimethylolpropane fatty acid triester stands out due to its exceptional lubricity, biodegradability, favourable viscosity-temperature properties, and low volatility, making it a promising candidate in the field [30, 31].

In the realm of lubrication, grease plays an irreplaceable role due to its distinctive characteristics. Unlike liquid or solid lubricants, grease forms a three-dimensional network within its thickener, creating a colloidal dispersion [32]. This unique feature enables grease to be applied to hard-to-reach surfaces, adhering to contacting surfaces effectively. With its ability to provide semi-permanent lubrication, grease has become widely utilised, offering superior load-carrying capacity, reducing friction and wear, and preventing corrosion by sealing work surfaces. However, a significant drawback is that approximately 90 % of greases produced globally rely on petroleum-derived materials, which are neither biodegradable nor environmentally friendly. Only a mere 1 % of the total grease production is allocated to bio-grease [33]. Some publications have explored the use of jatropha and modified Karanja oil to create greases with enhanced tribological properties and favourable extreme pressure characteristics [28, 34].

From the available literature, it is observed that the studies regarding the production and characterisation of biobased greases are very limited. The concept of chemically altering WCO to create biolubricants is mentioned in some studies [2, 31]. This innovative approach aims to address both the disposal challenges associated with WCO and the need for environmentally friendly lubricants. Furthermore, biodegradable greases, derived from byproducts of the palm oil industry, have been discussed by researchers [35]. These greases, formulated with organic chemicals harmless to the environment, hold the promise of being both eco-friendly and biodegradable [36].

The present study focuses on the chemical modification of WCO to create bio-lubricants, considering the modified oil as a capable base oil for eco-friendly lubricants. The investigation encompasses the analysis of various properties of these biolubricants, including viscosity index, viscosity, pour point, cloud point, oxidative and tribological properties. Through this exploration, the aim is to contribute to the development of environmentally sustainable lubrication solutions to the world.

Materials and methods

Materials

The base oil used in the present study- waste cooking oil is procured from an oil disposal facility - Hasinar, Kochi, India. The waste cooking oil collected by Hasinar predominantly originates from palm oil, as it is widely used in the preparation of food by many restaurants and local hotels owing to its abundant availability. All additional chemicals required for the assessment of chemical properties and the implementation of transesterification processes were generously provided by Sigma-Aldrich.

Fatty acid profile

The fatty acid profile of base oil has been evaluated using gas chromatography-mass spectrometry (GC-MS) to analyse vegetable oils quantitatively. Natural variations in fatty acid compositions are observed based on the plant and species. The fatty acid content of WCO plays a crucial role in determining its tribological properties. Fatty acids with longer carbon chains contribute to reducing wear and friction at the boundary. Agilent System (USA) is the manufacturer of the GC-MS apparatus (GC Model 7890A and MS Model 5975C). With the triple-axis detector mass spectrometer, a dura bond (DB) diphenyl dimethyl polysiloxane column (30 m length, 0.25 mm diameter, and 0.25 m thickness) is employed as a coupling element. The temperature is initially increased to 40 °C and maintained for 5 minutes in an isothermal condition. The temperature is then raised to 280 °C at a steady rate of 5 °C/min, and after 10 minutes, an isothermal condition is applied. The injection port and detector are kept at temperatures of 230 °C and 250 °C, respectively. Helium is the chosen carrier gas, with a flow rate of 1 mL/min. When the oil undergoes the transformation into its corresponding methyl esters and is introduced into the apparatus, the esters vaporise, leading to the separation of various components. To identify the analysed compounds, the retention times of these compounds are matched with the retention times of standard compounds.

Chemical modification of WCO and preparation of biogrease

Transesterification is carried out using methanol in the presence of sulfuric acid and potassium hydroxide, serving as the acid and base, respectively [37]. Temperature plays a noteworthy role in the reaction due to the potential for a saponification reaction. To obtain a triester with excellent surface lubrication properties, TMP is used in the presence of sodium methoxide as a catalyst. Due to the increased concentration of the available free fatty acids, transesterification of WCO in a two-stage process is essential.

Initially, 64 mL of methanol and 2 mL of sulfuric acid are added to a 200 g WCO sample. The mixture is then continuously stirred in a water bath at 75 °C. The mixture is transferred into a separate funnel and left undisturbed after 2 hours. The unreacted sulfuric acid layer that develops on top of the separating funnel is removed after six hours. A mixture consisting of 2 g of KOH and 55 mL of methanol is then added to the residual oil. Once more, the mixture is continuously mixed in a 65 °C water bath. The mixture is then poured into a separate funnel and left undisturbed for 1 hour. The glycerol that builds up at the bottom of the separating funnel is removed after six hours, and the mixture is then rinsed with hot deionised water. Deionised water is held at a temperature of roughly 70 °C. The surplus water in the oil is then removed after heating the mixture with an electrical

heater and vacuum pump. Trimethylolpropane is then added in a 1 : 4 ratio to the modified oil to modify the two-stage transesterified oil. As a catalyst, 1 % sodium methoxide is added. After two hours of continuous stirring at a temperature of 80 °C, the mixture is filtered to achieve the finished product. Figure 1 shows the WCO after transesterification. Figures 2 and 3 demonstrate the chemical processes of transesterification.

The grease preparation procedure involves combining base oil and lithium hydroxide soap in a grease kettle, with proportions of 90 % - 96 % and 3 % - 5.5 % by weight respectively. The mixture is then heated to a temperature ranging from 130 °C to 240 °C and stirred for a duration of 4 h - 9 h. In this study, 2.5 g of lithium hydroxide is dissolved in 100 mL of WCO, along with 12.5 mL of water. Simultaneously, 16.95 g of stearic acid is heated above 69 °C, its melting point. The lithium hydroxide solution is slowly added to the stearic acid with continuous stirring. The mixture is stirred until it transforms into soap, and the temperature is monitored, reaching approximately 220 °C. The mentioned procedure ensures the proper preparation of the bio-grease. The prepared biogrease is shown in Figure 4.

Fig 1. WCO after chemical modification

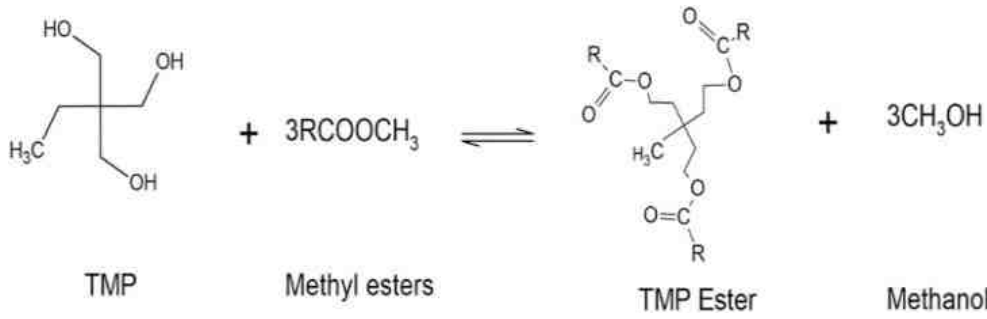

Fig. 2. Formation of methyl esters (Transesterification - first stage) [18]

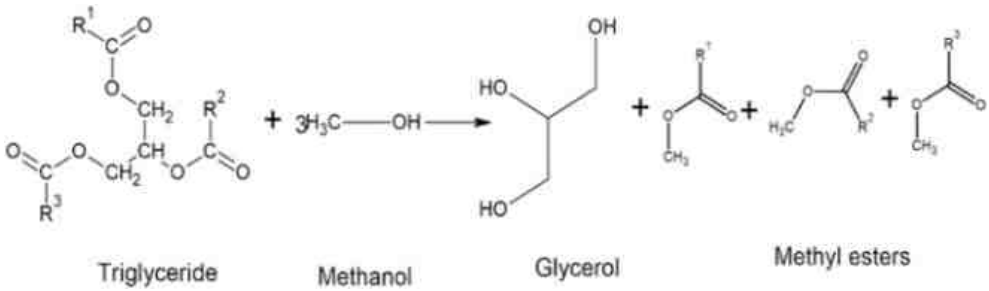

Fig. 3. Formation of TMP esters (Transesterification - second stage) [18]

Fig. 4. Bio-grease from MWCO

Evaluation of physicochemical properties

The physical characteristics of the oils, such as colour and density, were observed. To gauge the density, a specific gravity container was used. Using the titration method in accordance with IS: 548 (Part 1) - 1964, the chemical characteristics of all the samples, such as the acid value, peroxide value, and iodine value, have been assessed. The WCO's acid and peroxide values provide an indirect indicator of the potential for oxidation in the oil [38], while the amount of unsaturation in the oil is determined by the iodine value. For estimating the degree of unsaturation and to determine the amount of primary oxidation we are doing acid, peroxide and iodine tests including para-anasidine for conformation for peroxides as per IS: 548 (Part 1) - 1964 and ISO 6885. The acid value gauges the free fatty acid content in the oil, determined by the base needed for neutralisation. Peroxide value measures peroxide content, primarily hydroperoxides, indicating potential oxidation and rancidity. Critical sites like β-carbon and unsaturated bonds in the oil are prone to oxidation, indirectly measured by both acid and peroxide values. The iodine value expresses unsaturation, highlighting the susceptibility of unsaturated fatty acids to oxidation and oil rancidity.

Evaluation of thermal properties

Thermal stability emerges as a pivotal factor playing a crucial role in both safety considerations and operational effectiveness. This study employs key parameters such as flash point, fire point, pour point, and thermal degradation to analyse the thermal properties of both WCO and MWCO. The flash point and fire point of WCO are significant indicators for assessing the safety of the lubricant in practical use. Defined by ASTM D92, the flash point represents the minimum temperature at which the lubricant emits sufficient vapour to ignite in the presence of a testing source. On the other hand, at the fire point, the lubricant sustains combustion for at least 5 seconds after ignition. Higher values for flash and fire points, indicative of ASTM D92 standard tests, suggest a lower risk of the lubricant catching fire in the event of leakage or spillage. The elevated flash and fire points also imply greater safety in high-temperature applications, requiring hotter conditions for ignition and combustion. The low-temperature behaviour of the lubricant is elucidated through two vital parameters: pour point and cloud point. The pour point signifies the lowest temperature at which the lubricant flows under gravity, while the cloud point marks the temperature at which the lubricant begins to exhibit a cloudy appearance due to the precipitation of waxes or other solid components. Evaluated by ASTM D97 and ASTM D2500, respectively, a lower pour point and cloud point denote superior low-temperature characteristics, making the lubricant suitable for application in cold weather conditions [37].

The DSC experiments utilised the TA Instruments DSC-Q20 model (UK) with a computer-based controller [39]. Approximately 10 mg of oil was sealed in an aluminium hermetic pan and analysed alongside an empty reference pan. The sample was rapidly heated to 110 °C to dissolve waxy materials and remove moisture, then gradually cooled to –50 °C at 10 °C/min. Heat flow versus temperature plots were generated and compared with pour points determined via ASTM D97 for similar oils. The TGA analysis employed the TA Instruments Q50 model (UK), with a heating rate of 10 °C/min from 30 °C to 600 °C in an oxygen atmosphere at 100 mL/min. Platinum pans contained 5 mg - 10 mg of analyte. The onset degradation temperature was determined from the TGA curve at 98 % mass [40]. Data from three measurements were averaged to produce TGA curves to evaluate the onset degradation temperature.

Evaluation of oxidative stability

The susceptibility of vegetable oils to oxidation is attributed to the presence of polyunsaturated acids in oils. To evaluate the oxidative stability of the oil samples in this study, the HOOT was conducted following the American Oil Chemists Society (AOCS Cd-12-57) standard. The testing was expedited in a hot air oven at 100 °C for 120 h to accelerate oxidation processes. Monitoring changes in kinematic viscosity served as a key parameter in assessing oxidative stability. The viscosity of all oil samples was measured every 24 h at 40 °C, as the occurrence of oxidative by-products tends to increase viscosity. A Cannon-fenske opaque viscometer was employed to evaluate the kinematic viscosity of the samples. The sample displaying the lowest percentage increase in viscosity after 120 h signifies higher oxidative stability, providing valuable insights into the comparative performance of the oil samples in resisting oxidation.

Evaluation of rheological properties

The rheological characteristics of the oils were assessed through the examination of dynamic viscosity and viscosity index [41]. Dynamic viscosity variations in the temperature range of 20 °C - 120 °C were determined for both WCO and MWCO utilising Anton Paar MCR 102 rheometers in rotation mode with parallel plate geometry. The viscosity index of the oil samples was calculated in accordance with ASTM D2270. This analysis provides how the dynamic viscosity of the oils changes over a temperature range and offers a standardised measure of their viscosity characteristics.

Evaluation of tribological properties

The tribological characteristics of all samples, including wear scar diameter (WSD) and coefficient of friction (COF), were evaluated using a standard four-ball tester following ASTM D 4172 guidelines. The test employed chrome alloy steel balls. Initially, acetone was used for cleaning both the balls and the ball pot. Following this, the oil sample has been placed into the ball pot alongside three test balls. A mandrel, connected to the motor spindle, held the fourth ball securely fastened to the collet. The experimental conditions encompassed a temperature of 75 °C, spindle speed set at 1200 rpm, and the application of a 392 N load, all maintained for a period of 1 hour [42].

Grease worker roll stability test

Grease worker stability was used to gauge the bio-grease's consistency after it was developed [43]. In this study, the unworked penetration value for the formulated greases was assessed using a standard cone penetrometer in accordance with ASTM D 217. This method measures the depth of penetration of a standard cone into an undisturbed grease sample over a 5-second duration. The reported results in this study represent the average of three repeated tests conducted with a fresh grease sample.

Results and discussion

Various standard experiments have been conducted to assess the properties of different oils, with the results averaged. The investigational findings are presented in graphs and tables. The characteristic fatty acid profile of the oil has been determined using gas chromatography-mass spectrometry (GC-MS) and compared with the palm oil fatty acid profile. The GC-MS method revealed the fatty acid profile of WCO oil, with the outcomes detailed in Table 1. The area beneath the peak in the chromatogram directly corresponds to the percentage quantity of the component. As per Table 1, the primary substances in WCO are oleic acid (35.9 %) and palmitic acid (44.3 %). The total saturated and unsaturated acids constitute 49.4 % and 45 %, respectively.

Saturated fatty acids exhibit exceptional oxidation steadiness owing to the absence of double bonds, but their solid state at room temperature results in negligible low-temperature performance. Monounsaturated fatty acids offer an optimal steadiness of thermal and oxidative stability, along with notable tribological and low-temperature properties. Given its higher concentration of monounsaturated fatty acids, WCO oil is deemed suitable as a base stock for the potential development of lubricants.

The physicochemical properties, including density, acid, peroxide, P-Anisidine, and iodine values, were assessed and are presented in Table 2.

Table 1

Fatty acid profile

Constituents	Nature	Waste cooking oil [%]	Palm oil [%]
Myristic acid	Saturated	1.0	1.0
Palmitic acid	Saturated	44.3	43.5
Stearic acid	Saturated	4.1	4.3
Oleic acid	Mono-unsaturated	35.9	36.6
Linoleic acid	Poly unsaturated	9.1	9.1

Table 2

Physiochemical evaluation results

Oil/Test	Acid [mg KOH/g]	Peroxide [Meq/kg]	Iodine [g I_2/100 g]	P-Anisidine [Meq/kg]	Density [g/cm^3]
WCO	2.16 ±0.21	4.72 ±0.47	75.86 ±1.01	4.41 ±0.87	0.916 ±0.008
MWCO	1.65 ±0.18	0.32 ±0.11	70.13 ±1.22	0.69 ±0.15	0.904 ±0.005

Results indicate that the chemical modifications have positively impacted the chemical properties of the oil. The acid value, indicative of free fatty acids, measured 2.16 ± 0.75 mg KOH/g for pure WCO i.e., the acid values of MWCO exhibited a reduction of 23.71 % in comparison to WCO. The reduction in acid value is attributable to the transesterification process, which converts Free fatty acids (FFAs) into more stable esters by removing glycerol molecules. These molecules are susceptible to primary and secondary oxidation, and hence their removal effectively lowers the concentration of the reactive sites. A lower acid value implies the enhancement of the oil's oxidative stability, thus prolonging its shelf life [44]. The peroxide values of MWCO samples were also significantly decreased by 93.22 % compared to WCO, indicating improved oxidative stability. The substantial decrease suggests that the transesterification process effectively eliminated oxidation-prone sites by removing unstable hydroperoxides. This is particularly advantageous for lubricant applications where oxidative stability is critical to performance, as it suppresses the initiation of oxidative degradation [37]. The reduced p-Anisidine value further highlights the more effective reduction of the lower secondary oxidation products in MWCO, which reflects minimal degradation and oxidative exposure [41]. This indicates that the chemical modification significantly improved the oil's resistance to oxidative stress, making it more suitable for high-performance applications. The reduction in chemical properties after modification indicates that transesterification has significantly enhanced the stability of the oil. In addition to this, the transesterification process removes components with higher densities than FAMEs, thus resulting in a reduction in overall density of MWCO when compared to WCO [18].

The thermal stability results are tabulated in Table 3.

Table 3

Thermal properties of oil samples

Sample	Flash point [°C]	Fire point [°C]
WCO	163 ±2	171 ±1
MWCO	180 ±2	188 ±2

Analysing the provided data, it is evident that MWCO demonstrates higher thermal stability compared to WCO. This conclusion is drawn from the flash and fire point data

presented in Table 3. A higher flash point signifies greater thermal stability, indicating that the oil requires a higher temperature to release flammable vapours. The fact that MWCO has a higher flash point suggests superior thermal stability compared to WCO. Similarly, a higher fire point is indicative of increased thermal stability, and the higher fire point exhibited by MWCO further supports its superior thermal stability compared to WCO. The pour point and cloud point also show a considerable increment. Higher flash and fire points make a lubricant safer against fire threats. In this context, the flash and fire points of MWCO surpass those of WCO, ensuring the secure utilisation of MWCO in elevated temperature conditions. Enhancing the pour point of MWCO remains a crucial aspect for it to effectively compete with mineral oil in lubricant applications.

The enhanced thermal stability of MWCO can be attributed to the presence of TMP, known for its strong chemical bonds. TMP contributes to improving the stability and thermal resistance of the oil, leading to higher flash and fire points. The robust bonds in TMP play a critical part in enhancing the overall stability and resistance of MWCO to thermal degradation. In summary, the data in Table 3 indicates that the transesterification process and the addition of TMP have significantly improved the thermal properties and stability of waste cooking oil, making MWCO more suitable for applications where thermal stability is a critical factor.

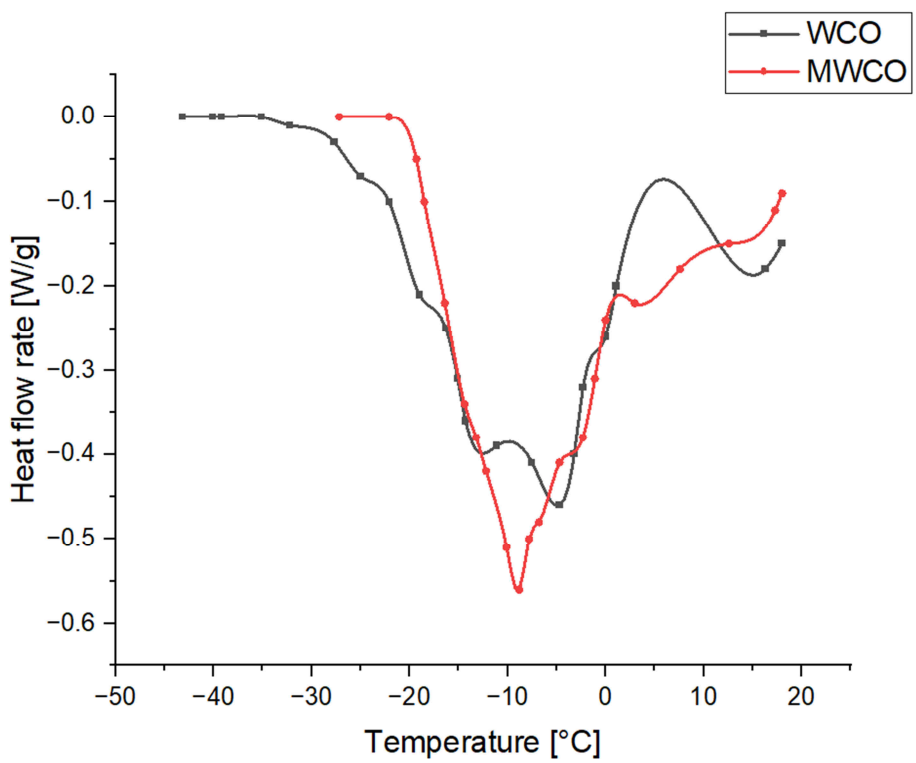

Fig. 5. DSC graph

Upon heating the oil samples from 110 °C to - 46° C, a notable endothermic peak appears in the DSC heating curve signifying a phase transition as depicted in Figure 5. Table 4 outlines the peak endothermic values for different samples by defining the pour points marked by the solidification of oil. The results highlight that the pour point of WCO is significantly lower than that of MWCO, suggesting the need for improvement in MWCO's pour point to compete with mineral oil.

Table 4

Pour point of oils

Sample	Pour point [°C]
WCO	–4.72 ±0.47
MWCO	–8.34 ±0.54

The chemical modification results in changes to the molecular structure, including increased unsaturation or branching of carbon chains. This in turn alters the intermolecular forces, thereby enhancing the flow properties at low temperatures. The introduction of branched methyl esters after the addition of TMP to modified WCO extends the chain length [45-47]. Thus, the elongation prevents dense packing of molecules during cooling, leading to the observed improvement in the pour point of WCO.

The mass loss curve displays two distinct regions for both WCO and MWCO. In the initial stage, decomposition begins around 150 °C for WCO, followed by the second stage or complete devolatilisation region. At around 400 °C, the MWCO marks the point of maximum mass loss. At about 170 °C, an early mass loss of about 10 wt.% is observed for WCO, while MWCO exhibits a similar early mass loss, approximately 10 wt.%, but at a higher temperature of 225 °C. A minor peak or dip around 170 °C corresponds to the evaporation, or loss of moisture, present in the sample as an impurity, constituting approximately 2 %. The mass loss curve highlights the impact of heating rate on reaction temperature. Notably, the heating rate exhibits minimal influence on mass loss in all cases, as the bio-lubricants display consistent degradation patterns throughout the entire temperature range. This thermal behaviour suggests that the synthesised biolubricant may be more susceptible to thermal degradation specifically at higher temperatures.

Figure 6 illustrates the TGA results of the oil samples, where onset temperatures for thermal degradation are determined at 98 % weight to accommodate the elimination of volatile compounds and moisture present in the oils [40]. The onset temperatures are presented in Table 5.

The results indicate that MWCO exhibits superior thermal stability, with an onset temperature of 109.4 °C, compared to WCO, which has an onset temperature of 186.1°C. During chemical modification, the addition of TMP to the transesterified WCO leads to the formation of TMP esters. These esters possess a more branched and complex structure compared to the simpler triglycerides in unmodified WCO. The branching introduced by TMP contributes to a higher molecular weight and increased thermal stability, making the modified oil more resistant to thermal breakdown [48, 49]. Moreover, the chemical modification often involves a reduction in the level of unsaturated fatty acids. Unsaturated bonds are more prone to oxidation and thermal degradation, leading to lower thermal stability in unmodified oils like WCO. By decreasing the number of double bonds, the thermal stability of MWCO is significantly enhanced, as the oil becomes less susceptible to oxidative breakdown at elevated temperatures [50]. This suggests that MWCO is

well-suited for application over a wide range of temperatures. The TGA results consistently demonstrate the enhanced thermal stability of MWCO in comparison to WCO, reinforcing its suitability for diverse temperature conditions.

Table 5

Onset temperature of degradation in oil samples

Oil sample	Onset temperature of degradation [°C]
WCO	109.4 ±1.6
MWCO	186.1 ±2.7

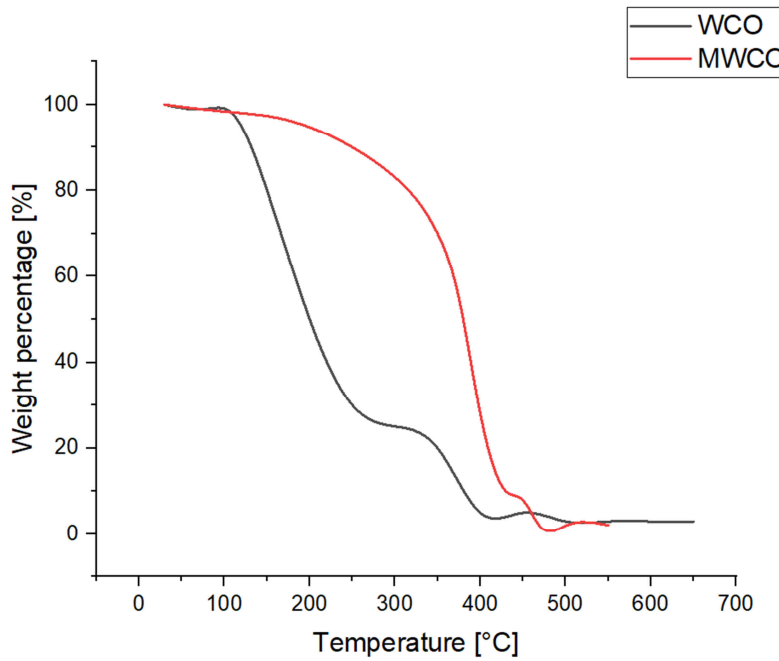

Fig. 6. TGA graph

The viscosity and Viscosity Index (VI) of oils are examined and presented in Figure 7 and Table 6, respectively. All vegetable oils exhibit a high VI, indicating minimal changes in viscosities with temperature, a valuable property in lubrication.

Among the oils, MWCO stands out with the highest viscosity index. The viscosity of MWCO is greater than that of WCO at the selected operating temperatures. This suggests that MWCO has the potential to serve as a commercial lubricant, provided the viscosity is further improved. Additionally, the viscosity range of MWCO could be enhanced through the incorporation of suitable viscosity improvers, making it even more suitable for various applications [51, 52].

Viscosity measurements obtained before and after the High Oxidation and Oxidative Stability Test (HOOT) are evaluated to assess the oxidative characteristics of the oil. The variation in viscosity is computed and presented in Table 7. The significant percentage increase in viscosity noted in WCO can be ascribed to its elevated free fatty acid content

and reactive oxidative sites. These sites enhance oxidation, resulting in the generation of larger molecular compounds such as aldehydes, hydroperoxides, peroxides, and ketones. This process ultimately contributes to the formation of agglomerates, silt, and sludge [53, 54].

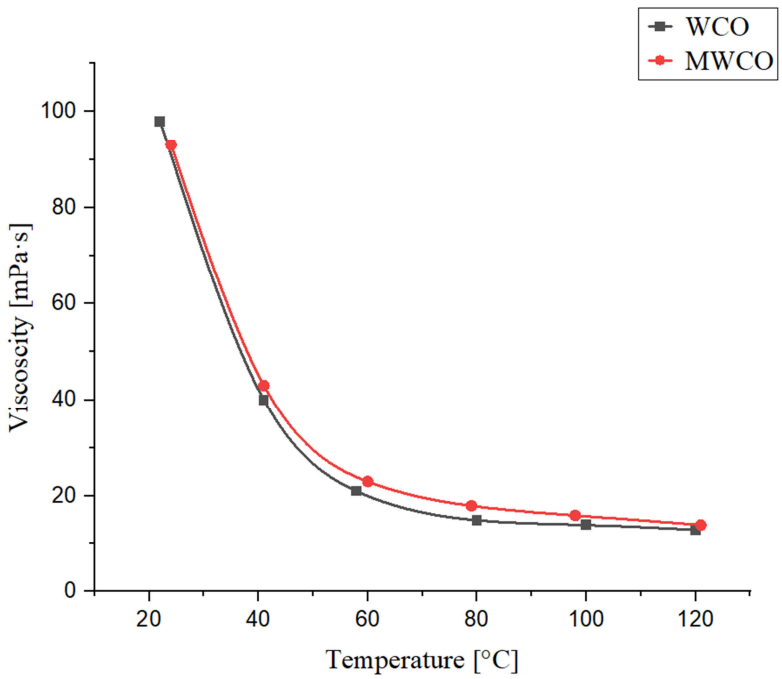

Fig. 7. Viscosity variation from 20 °C to 120 °C

Table 6

Viscosity index of samples

Sample	Temperature [°C]	Kinematic viscosity [mm²/s]	Viscosity index
WCO	40	46.05 ±0.32	170.7 ±3.8
	100	8.77 ±0.09	
MWCO	40	49.77 ±0.33	251.8 ±3.7
	100	12.21 ±0.11	

Table 7

Oxidative characteristics of samples

Oil sample	Viscosity at 40 °C before HOOT [mPa·s]	Viscosity at 40 °C after HOOT [mPa·s]	Increment in viscosity due to oxidation
WCO	41.23 ±0.22	54.61 ±0.41	13.38 ±0.19
MWCO	43.72 ±0.19	46.22 ±0.29	2.52 ±0.11

The oxidative stability of WCO is notably enhanced after the transesterification reaction. The increase in viscosity is attributed to the oxidation of oil and the growth of polymeric compounds during HOOT [55]. This result is promising for high-temperature

applications involving prolonged heat cycles, indicating improved oxidative properties of the oil after the chemical modification process.

Table 8

Tribological properties

Sample	WSD [µm]	COF
WCO	659 ±8	0.052 ±0.018
MWCO	601 ±6	0.048 ±0.016
Bio grease	582 ±6	0.041 ±0.014
Commercial grease	580 ±6	0.079 ± 0.043

Tribological properties, including WSD and COF assessed using the four-ball tester, are tabulated in Table 8. The formulated biogrease is also compared with commercial grease - Mobil XHP 222, of NLG grade 2.

The results indicate that the COF of MWCO is significantly lower than that of WCO, whereas the Biogrease outperforms commercial grease in COF and showcases a comparable WSD. The superior tribological properties of chemically modified oils, such as MWCO, are closely linked to the stable lubricant films formed by TMP esters. These films play a crucial role in reducing direct surface-to-surface asperity interactions, minimising both friction and wear [49, 56]. The stability of TMP esters is particularly advantageous at higher temperatures, where other oils may degrade [48, 49]. This thermal stability is due to the fatty acid composition of TMP esters, specifically the balance between saturation and monounsaturation levels, which significantly influences their tribological performance [50].

In terms of wear, the analysis of WSD revealed that MWCO demonstrated the lowest WSD, indicating superior wear protection compared to WCO. This reduction in wear is associated with the effective coating properties of TMP esters, which provide a protective layer on metal surfaces [18]. WCO showed higher WSD values, likely due to the elevated presence of pure short-chain fatty acids, unsaturation, and a high saponification value - factors that contribute to greater wear. Specifically, the significant presence of linoleic acid, a short-chain fatty acid, in WCO influences its WSD [57, 58]. The unsaturation levels in fatty acids can undergo reduction after chemical modification processes such as transesterification and the addition of TMP. This decrease in unsaturation, along with the increase in chain length, contributes to improved tribological properties by enhancing film stability and reducing wear [59, 60]. The introduction of branched methyl esters after the addition of TMP to modified WCO is the reason for extended chain length [45-47].

Chemical wear induced by oxidation is the primary wear that happens when using vegetable based-oils, where natural antioxidants like tocopherol and sterols play a role [61, 62]. The lower WSD of MWCO suggests its potential as an eco-friendly base stock for lubricant development. Further reduction in MWCO wear can be achieved by incorporating appropriate anti-wear additives into the lubricant formulation.

The cone penetration test results are tabulated in Table 9.

Table 9

Cone Penetration test results

Samples	Unworked penetration [mm/10 s]	Worked penetration [mm/10 s]
Commercial grease	215 ±3	184 ±3
Bio grease	292 ±2	226 ±3

The unworked penetration for commercial grease and Bio grease are 215 mm/10 s and 292 mm/10 s respectively. For NLGI grade 2 Worked Penetration Range: 220 to 250 mm/10 s. For NLGI grade 3 Worked Penetration Range: 185 to 215 mm/10 s. The difference in NLGI grades carries implications for the performance and suitability of the greases in various applications. Typically, greases with higher NLGI grades are preferred for applications where a higher degree of mechanical stability and resistance to leakage or displacement is required. Conversely, greases with lower NLGI grades are often more suitable for applications where ease of pumpability and flowability are important. Considering that our bio grease has a lower NLGI grade 2 compared to the NLGI grade 3 grease, it suggests that our grease possesses a softer consistency and is potentially more pumpable and flowable. This characteristic can be advantageous for applications that require easy dispensing or smooth flow of the grease. The cone penetration test values, our grease can be classified under NLGI grade 2, which is soft grease.

Conclusion

The investigations into the thermal, tribological, oxidative, rheological, and physicochemical properties of WCO yield several notable conclusions. Noteworthy thermal characteristics of MWCO include a high flash point (180 °C), high fire point (188 °C), and low pour point (–8.34 °C). These attributes ensure the suitability of WCO for lubricant use across a broad temperature range, establishing MWCO-based grease as suitable for diverse temperature conditions. MWCO demonstrates superior anti-wear characteristics, evidenced by the least WSD. Rheological studies indicate a higher viscosity index for MWCO. Despite a significant degree of unsaturation, MWCO exhibits improved oxidative stability attributed to the presence of natural antioxidants, although further development and enhancement are required. MWCO showcases excellent thermal and tribological properties, and also the MWCO-based grease has shown better tribological characteristics. This positions MWCO grease as a potential substitute for commercial grease based on the investigated properties. However, ongoing efforts for refinement and development are essential to fully harness its potential as a sustainable and effective lubricant.

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