ANALYSING THE LUBRICANT RHEOLOGY-PRESSURE RELATION FOR BIODIESEL DERIVED WASTE PALM COOKING OIL (WPCO)

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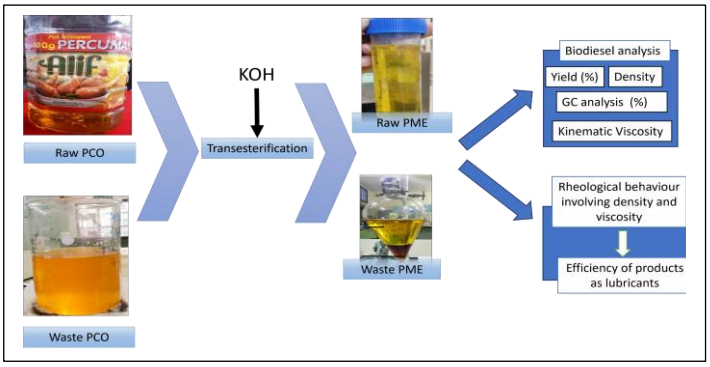
GRAPHICAL ABSTRACT



ABSTRACT

Given that its primary energy sources are reported to be dwindling daily, the pursuit for new alternatives to fossil fuel is essential. Biodiesel is perceived as a viable option for achieving sustainable and renewable energy in response to this challenge. The present study demonstrates the potential of Waste Palm Cooking Oil, Raw Palm Cooking Oil, Waste Palm Methyl Ester, and Raw Palm Methyl Ester as lubricants. This study's objective is to analyze the rheological behaviour of produce biodiesel lubricant from two distinct feedstocks, namely WPCO and Raw PCO at increasing temperature from 25°C to 100°C. Both WPCO and Raw PCO are subjected to a transesterification reaction, which is facilitated by potassium as a catalyst to remove the free fatty acid (FFA) present. This study discovered that the biodiesel production efficiency for waste palm methyl ester (WPME) was 82.5%, whereas the yield for raw palm methyl ester (RPME) was 96.4%. A qualitative analysis was carried out by Gas Chromatography Analysis to identify the presence of Fatty Acid Methyl Ester (FAME) in the biodiesel produced from Waste Palm cooking oil (WPCO) and Raw Palm Cooking Oil (RPCO). The physicochemical properties of all four varieties of oils were evaluate. WPCO, WPME, Raw PCO, and Raw PME had densities of 895 kg/m^3, 865 kg/m^3, 898 kg/m^3, and 867 kg/m^3 at 40 °C, respectively. The density that was acquired was subsequently employed to calculate the kinematic viscosity of the lubricants. At a temperature of 40 °C, a comparison was made between the kinematic viscosity of the lubricants and the standard kinematic viscosity of motor oil as specified by the SAE. The evaluation of WPCO, WPME, Raw PCO, and Raw PME in comparison to SAE motor oils standard reveals that none of the aforementioned oil types exhibit the necessary properties to function as a pourable engine lubricant.

KEYWORDS
Waste Cooking Oil, Lubricants, Rheology

INTRODUCTION

Since the industrial revolution of the 18th century, the world's energy consumption has increased by approximately 5% per year [1]. The global increase in the consumption of fossil fuels has given a negative drawback to the environment. Thus, many nations are shifting towards renewable energy sources such as biodiesel [2]. The United States, for instance, generated biodiesel from soybeans, whereas Europe utilised rapeseed oil and sunflower oil. Asia, Malaysia, Indonesia, and the Philippines produce biodiesel from palm oil and coconut oil, respectively, while Bangladesh has identified rubber seed oil as a potential feedstock in biodiesel production [3].

However, the high dependence on virgin oils such as palm oil causes some controversial issues, including lubricant vs. food competition in palm oil usage, which increases commodity prices. Considering this issue, cheaper feedstocks such as waste cooking palm oil are preferable to reduce its production cost by up to 70 to 90%[4].

Suzihaque et al. reported an estimated 540 000 tonnes of WCO derived from vegetable and animal fats are discarded annually without being treated as waste in Malaysia [5]. Untreated waste cooking oil (WCO) solidifies and accumulates within the sewerage system, leading to a 70% blockage rate in Malaysia and threatening water quality, soil contamination, and aquatic biodiversity [6]. Therefore, a potential approach for addressing these issues is the utilisation of WCO as raw materials for biodiesel, which is more cost-effective and environmentally beneficial.

Biodiesel is a liquid fuel that is biodegradable, renewable, clean, and environmentally friendly. It is a lipid-derived fuel produced through transesterification in the presence of an appropriate catalyst. Compared with conventional diesel, one of the most notable qualities of biodiesel is its high level of lubricity, reducing friction and corrosion on sliding engine components and prolonging engine life [7], [8].

Due to its high lubricating power, higher viscosity, and reduced attrition on engine parts, outperforms commercial lubricants when used as a lubricant. Canola lubricating oil is utilised in chain bar lubricants, penetrating oils, food-grade lubricants, tractor transmission fluids, hydraulic oils and metalworking fluids. While gear lubricants and greases are manufactured with castor oil, rolling lubricants and greases are made with palm lubricating oil. Safflower, sunflower, and jojoba oils were employed as hydraulic oil in addition to soybean lubricating oil [9, 10].

To develop a lubricant, it is necessary to obtain specific physicochemical properties, including its density and kinematic viscosity. Hence, the transesterification process is crucial to convert vegetable oils to biodiesel. In the presence of a catalyst, a natural oil triglyceride composed of animal lipids or vegetable oils reacts with a short-chain alcohol, methanol, or ethanol, to produce fatty acid alkyl esters [11]. Figure 1 illustrates the conversion procedure for vegetable oil. Standard of Automotive Engineers (SAE) lubricating oil must satisfy all lubrication requirements in the various tribological pairs present in the engine.

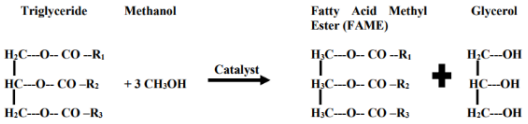


Figure 1: Equation of Transesterification Process [12].

This study used waste cooking palm oil and raw cooking palm oil to synthesise waste cooking palm methyl ester and raw cooking methyl ester by transesterification with potassium catalyzed to remove free fatty acid (FFA). The produce bio-lubricants are characterized by chromatography (GC) analysis. The density and kinematic viscosity are then evaluated to acknowledge its rheological behaviour at increased temperature from 25 to 100 °C.

METHODOLOGY

The samples of raw palm oil (RPO) and waste palm cooking oil (WPCO) utilized in this study were obtained from the Alif brand. The WPCO had been previously used three consecutive times for frying chicken. All chemicals utilised in the study were of analytical grade and procured from Sigma-Aldrich.

Transesterification Reaction of WPCO and PCO.

Both feedstocks were filtered and pre-treated by heating them at 65 °C for 30 minutes to remove all insoluble impurities.

Biodiesel samples were produced through transesterification using a 6:1 methanol to oil ratio with the aid of Potassium catalysed (KOH) at 55°C for 30 minutes. The product was then decanted to settle in the separating funnel for 24 hours. The bottom layer of glycerine, methanol, and KOH was

removed, while the clear upper layer was collected as methyl ester (ME).

The produce methyl ester from both feedstocks was further purified thrice with distilled water. It was then heated at 48°C for 30 minutes to remove excess distilled water. As the process of evaporation takes place in the methyl ester, the apparent clarity of the solution is enhanced. The process was then repeated for the production of RPME. The biodiesel yield (%) of WPME and RPME was calculated by using equation (1) [13] :

$$\text{Volume Yield (\%)} = \frac{Amount\ of\ biodiesel\ produced}{Amount\ of\ oil} \times 100 \quad (1)$$

Analysis of Methyl ester produced.

By analysing its physicochemical properties, the biodiesel qualities were determined. The Free Fatty Acid (FFA) conversion and Acid Value of WCPME and RCPME were selected via an American Society for Testing and Materials (ASTM) standardized test procedure.

1 mL of the internal standard of methyl heptadecanoate was prepared by dissolving it in hexane. The samples were prepared by dissolving 50 mg of crude biodiesel in 1 mL internal standard. 0.1µL methyl ester was injected into the GC column. The programmed temperature was set to 190 °C for 5 minutes, then elevated by 5 °C/min to 230 °C for 5 minutes.

Viscosity and Rheological Properties of WPCO, WPME, Raw PCO and Raw PME.

Rheological properties, namely density and kinematic viscosity for the lubricant's properties, were measured at temperatures 25 °C, 40 °C, 60 °C, 80 °C and 100 °C before and after tribology testing. In the current study, the dynamic viscosity of a sample was determined using a Brookfield Dial Reading Viscometer with a large cylindrical spindle number 1. A heating plate was used to heat the sample to the desired temperature. To determine the kinematic viscosity, the density of the samples was measured at the corresponding temperature using a density metre [14]. The kinematic viscosity was then calculated by using Equation 2:

$$Kinematic\ viscosity\ (v) = \frac{\eta}{\rho} \quad (2)$$

Where η is dynamic viscosity, while ρ is density.

Results and Discussion

Biodiesel yield.

Alif Waste Palm Cooking Oil (WPCO) and Alif Raw Palm Cooking Oil (Raw PCO) were utilised in this study. Prior research on Waste cooking Oil (WCO) did not classify the oil's manufacturer or the number of times it had been used for frying or cooking. However, the cooking oils used in this project were monitored. Table 1 demonstrates the biodiesel yield percentage of WPME and RPCME

Table 1: Biodiesel Yield

Type of Biodiesel	Percentage Yield, %
WPME	82.5
Raw PME	96.4
Waste Cooking Methyl Ester [15]	90

By using the similar methanol to oil parameter in biodiesel synthesis of RPCO and WPCO, from the result, WPCO has a lower yield of WPCME of 82.5% compared to Raw PME, which shows a higher yield at 96.4%. This is because the source of WPME biodiesel was WPCO, which contains higher FFA content than Raw PCO from the frying activities. This can lead to saponification and separation difficulties, resulting in a low FAME yield.

Determination of FAME in WPME and PME by Chromatography

The FAME properties of WPME and raw PME were evaluated by GC-FID analysis. Table 2 tabulated the dominance of linoleic acid methyl acid ester in WPME and raw PME at 14.04% and 11.90%, respectively. Also detected in the studied samples were Stearic Acid Methyl Ester and Palmitic Acid Methyl Ester.

Table 2: Fatty acid methyl ester by GC-FID analysis.

Component	Structure	Area, %
Waste Palm Methyl Ester (WPME)		
Palmitic Acid Methyl Ester	C16:0	0.03
Stearic Acid Methyl Ester	C18:0	9.92
Linoleic Acid Methyl Ester	C18:2	14.04
Total Area % = 23.99		
Raw Palm Methyl Ester (Raw PME)		
Palmitic Acid Methyl Ester	C16:0	0.10
Stearic Acid Methyl Ester	C18:0	9.36
Linoleic Acid Methyl Ester	C18:2	11.90
Total Area % = 21.36		

The area percentage of WPME Palmitic Acid Methyl Ester is 0.03%, while that of Raw PME is 0.10%. In contrast, the percentage area of Stearic Acid Methyl Ester for WPME and Raw PME is 9.92% and 9.36%, respectively. Regarding Linoleic Acid Methyl Ester, WPME has a percentage area of 14.04 percent, while Raw PME has a percentage area of 11.90 percent. Orsavova et al. [16] summarized in their study the GC-FID analysis of methyl ester composed of 1.6% to 79.0% linoleic acid (C18:2), while palmitic acid (C16:0) has a percentage area between 4.6% and 20.0%. Singh et al. [17] reported biodiesel from palm and waste cooking oil composed of 9-12% and 55.2% linoleic acid. In contrast, the composition of its palmitic acid was 39 to 48% for palm oil biodiesel and 8.5% for waste cooking biodiesel.

Consequently, the FAME yield of Palmitic Acid Methyl Ester is lower than expected, whereas the FAME yield of Linoleic Acid Methyl Ester falls within the desired range. In conclusion, the total percentage area of FAMEs determined was small compared to FAMEs examined in the literature. This could be due to the heating oil's elevated WPCO and Raw PCO acid values.

Physicochemical characteristics of Biodiesel.

The analysis of prepared methyl ester by both RPCO and WPCO, including density, kinematic viscosity, and Acid value, was tabulated in Table 3.

Table 3: Comparison of physicochemical characteristics of biodiesel from WPCO and Raw PME with standard.

Properties	Standard Biodiesel (ASTM D6751)	Raw Palm Methyl Ester (RPME)	Waste Palm Methyl Ester (WPME)
Density @ 40°C (kg/m^3)	860-900	867	865
Kinematic Viscosity @ 40°C (mm^2/s)	1.96 – 6.0	5.80	3.4789
Acid Value (mg KOH/g max.)	<0.5	0.517	0.947

The standard Biodiesel (ASTM D6751 and EN 14214) stipulates that the range of biodiesel density at 40 °C should be between 860 and 900 kg/m^3. Both varieties of biodiesels produced were within the Standard Biodiesel Density range, with WPME having a density of 865 kg/m^3 and raw PME having a density of 867 kg/m^3. It is crucial to measure the density of biodiesel because it has a substantial impact on engine performance [18], [19]. Singh et al. [17] stated the fuel injection pump can dispense varying quantities of fuel, as the fuel delivered by fuel injection pumps is measured by volume. Fuel with high density has a greater mass than fuel with low density. The density of fuel has an impact on the energy quantity and air-fuel ratio within the combustion chamber. The density of biodiesel fuel is subject to various factors, such as the profile of methyl ester, the type of feedstock, and the biodiesel production process.

The present study measured the kinematic viscosity of all four types of oils. WPCO and Raw PCO had kinematic viscosities of 33.89 and 40.09mm^2/s, respectively, more significant than Standard Biodiesel. In contrast, WPME and Raw PME have kinematic viscosities of 3.4789 and 5.8004 mm^2/s, respectively. Using ASTM D675 as a reference, the kinematic viscosity of both WPME and Raw PME falls within the Standard range (1.96 – 6.0 mm^2/s), whereas EN 14214 revealed that neither oil fell within the Standard range. Chemical modifications by transesterification reaction can reduce the viscosity and alter the physicochemical characteristics of the feedstock [20]. Therefore, methyl ester obtained from WCOME and RCPME had shown lower viscosity values than raw oil due to the reduction of higher molecular weight of the esters of glycerol present in oil samples into straight chain methyl ester by transesterification process.

Rheological Properties of WPCO, Raw PCO, WPME and Raw PME.

This section measured the rheological behaviour of the four types of lubricants before and after the tribology test.

Density and kinematic viscosity of WPCO, Raw PCO, WPME and Raw PME before Tribology Test.

Figure 2 illustrates the density for WPCO, WPME, Raw PCO and Raw PME against temperature before and after the tribology test. At lower temperatures (40 °C), Raw PCO and WPCO have the highest density of 0.898 g/cm^3 and 0.895 g/cm^3 respectively. WPME and Raw PME have the lowest density of 0.862 g/cm^3. Density plays a vital role in viscosities as it inherently affects the lubricant's flow properties[21]. The high density of lubricants shows heavier (high mass per volume) lubricants and will demonstrate a low tendency to flow compared to low-density lubricants. The inadequate distribution of lubricant throughout the engine's moving components can pose a challenge, potentially resulting in escalated levels

of mechanical abrasion.

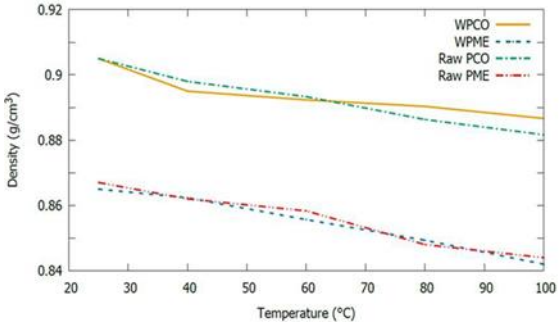


Figure 2: Density Temperature curve before the Tribology Test

As per Equation 2, the kinematic viscosity of a fluid is determined by dividing its dynamic viscosity with its density. Hence, alterations in density would have a significant impact on the kinematic viscosity of lubricants. Figure 3 depicts the kinematic viscosity of lubricants; it indicates a decrease in the kinematic viscosity as temperature increases due to the reduction in density.

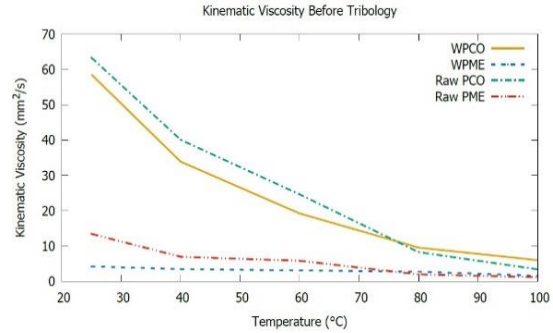


Figure 3 Kinematic Viscosity Temperature curve before Tribology Test

This observation demonstrated that temperature variations have a substantial impact on viscosity. According to Tutunea [22], a low temperature causes molecules to slide over one another very slowly. In contrast, increased temperature causes them to pass one another very quickly, making a liquid less viscous. According to Figure 3, Raw PCO and WPCO have the highest kinematic viscosities at 40 °C (40.089 and 33.892 mm^2/s, respectively), whereas Raw PME and WPME have the lowest viscosities at 5.8004 and 3.479 mm^2/s, respectively.

On the other hand, the trend of all lubricants shows a decrease in kinematic viscosity as temperature increases from 40°C to 100 °C. WPCO recorded the highest kinematic viscosity at 6.015 mm^2/s followed by Raw PCO with a kinematic viscosity of 3.403 mm^2/s whereas Raw PME and WPME have low kinematic viscosity of 1.185 mm^2/s and 1.583 mm^2/s respectively. Raw PCO and WPCO have greater kinematic viscosity at both temperatures than Raw PME and WPME because Raw PCO and WPCO contain more FFA and have a higher acid value than Raw PME and WPME.

According to Nadia Saleh et al. [23], the viscosity and density of triglyceride-containing vegetable oils are increased due to bigger molecular size. In addition, the high FFA content of biodiesel reduces its thermal and oxidative stability [24, 25]. According to Woma et al. [24], forming polar oxy compounds upon oxidative degradation of multiple double bonds limits their technical application. This resulted in insoluble deposits, increased oil acidity and viscosity, and increased corrosion attacks on lubricated parts [24].

Density and Kinematic viscosity of WPCO, Raw PCO, WPME and Raw PME before and after the Tribology Test.

After the tribology test, Raw PME and WPME show an increase in density at 40° C from 0.862 g/cm^3 to 0.871 and 0.887 g/cm^3, respectively. The increase in density after the tribological analysis of the lubricants might be due to degradation occurring through oxidation, particle, and water contamination[26]. Figure 4 depicts the effect of temperature on the density of WPCO, Raw PCO, WPME and Raw PME. While Figure 5 demonstrates the effect of temperature on WPCO, Raw PCO, WPME and Raw PME kinematic viscosity.

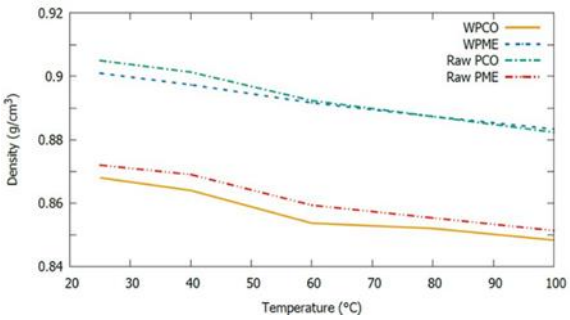


Figure 4: Density Temperature curve after the Tribology Test

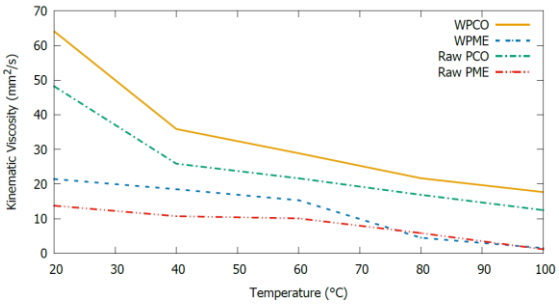


Figure 5: Kinematic viscosity Temperature curve after Tribology Test

The increase in density causes an increase in the kinematic viscosity of all lubricants. The comparison of the lubricant's rheology behaviour was essential for elucidating the lubricant's changes, which may be caused by aging and high-temperature pressure. Although density and viscosity play a crucial role in evaluating biodiesel lubrication, there is very little published information on the rheological study of biodiesel as an engine oil lubricant.

Comparison of WPME and RPME with specific standard performance of motor oils.

By referring to Table 3, the produced WPME and Raw PME fulfilled the kinematic viscosity from Standard Biodiesel ASTM D6751. However, the methyl ester produced from both feedstocks does not fulfill biodiesel lubricant characteristics, as the Society of Automotive Engineers (SAE) stated. Hence, the application of WPME and RPME was unsuitable for utilization as a lubricant due to very low viscosity compared with the specification fixed by SAE. Khuong et al. [27] stated viscosity should be high enough to resist the internal flow and low sufficient to prevent substantial energy loss. In an engine's lubrication system, a change in engine oil viscosity due to fuel dilution is undesirable because it affects lubricating efficacy and oil film thickness. Insufficient oil viscosity impacts lubricating film and load-bearing capacity, resulting in excessive attrition of bearings, journals, and other moving components, low oil pressure, and poor oil economy.

Table 4: Standard for Performance of Motor Oils by Society of Automotive Engineers (SAE)

Type	Kinematic Viscosity @ 40 °C (mm^2/s)
SAE15W40	105.10
SAE10W40	93.274
SAE5W40	90.903

Conclusion

The primary aim of this investigation is to generate a biodiesel lubricant utilising two distinct feedstocks, namely Waste Palm Cooking Oil (WPCO) and Raw Palm Cooking Oil (Raw PCO). As mentioned above, the goal is attained through the generation of Waste Palm Methyl Ester (WPME) and Raw Palm Methyl Ester (Raw PME). The comparison between Raw PME and WPME reveals that the former exhibits a higher biodiesel yield percentage at 96.4% and 82.5%, respectively. The rheological behaviour of WPCO, WPME, Raw PCO, and Raw PME shows the increase in temperature reduces the density and kinematic viscosity of the lubricants. Utilising WPME and RPME as lubricants is unsuitable as it has a lower viscosity than standard specifications from SAE. Viscosity was one of the essential factors to consider in applying waste cooking oil as a source in bio-lubricant manufacturing.

The challenge of using vegetable oil as a lubricant could be surmounted by modifying its properties, including additives, chemical modification, and thermal modification [28].

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