



Research Article

Investigation on Synthesis of Trimethylolpropane (TMP) Ester from Non-edible Oil

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Abstract

Trimethylolpropane (TMP) ester is an eco-friendly lubricant that fully biodegradable and known as bio lubricant. In this study, TMP ester was produced from waste cooking oil and rubber seed oil through a two-step synthesis approach. The reaction is two stages transesterifications, in which the waste cooking oil and the rubber seed oil were first transesterified with methanol to produce methyl ester, followed by transesterification with TMP using para-Toluenesulfonic acid (*p*-TSA) as catalyst. Various effects of operating conditions were observed, such as reaction time, temperature and molar ratio of reactants. The TMP ester formation was determined based on the quantity of reactant conversion. The synthesized TMP ester was compared and characterized according to their properties. The results showed that the TMP ester from waste cooking oil (WCO) has shown better conversion compare to TMP ester from rubber seed oil (RSO), within a similar operating condition. The highest TMP ester conversion from WCO is 71%, at temperature of 150 °C with molar ratio of FAME to TMP of 3:1 and catalyst amount of 2% (wt/wt). In addition, these polyol based esters from WCO and RSO exhibit appropriate basic properties for viscosity when compare with requirement standard of lubricant ISO VG46. Copyright © 2020 BCREC Group. All rights reserved

Keywords: biodiesel; rubber seed oil; waste cooking oil; biolubricant; transesterification; trimethylolpropane triester

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1. Introduction

Various application of lubricant has been giving rise on its demand and increase its price. However, lubricant is non-biodegradable and toxic when directly discharged into the environ-

ment and exposed with land, water, and air system [1]. Thus, the development of an environmentally friendly-based lubricant has become a greater interest by utilizing renewable resources. Recently, biolubricant derived from vegetable oil has shown great chances as a new generation of lubricants. Vegetable oil-based is preferred as the feedstock for biolubricant because it can be renewable, economical and non-

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toxic. The structure of the triglycerides in vegetable oil gives many advantages, such as: low volatility due to high molecular weight of triacylglycerol molecule, good boundary lubrication characteristics due to polar ester group, also high solubilizing power and high viscosity index for polar contaminants and additive molecules [2]. Vegetable oil can be classified into edible and non-edible oil. Edible oil can be consumed and is easily accessible, since it is an abundant source. Non-edible oil, on the other hand, cannot be consumed and have either little impact on global food cost or production because it can be either a waste or from plant that can be grown on nutrient-deficient land. Hence, the use of non-edible oil as feedstock for biolubricant may reduce the competition within the current agricultural resources [3]. There are few studies reported for biolubricant production from vegetable oil based such as palm oil, *Jatropha curcas* oil, rubber seed oil, Karanja oil, rapeseed oil, waste cooking oil and sesame oil [4–9].

However, the structure of vegetable oil may also affect its lubrication properties, such as: oxidation stability, hydrolytic instability, and low-temperature properties [5]. Therefore, the modification should be proposed to improve oil performance. There are two available syntheses for biolubricant production from vegetable oil, and both consist of two series of reactions.

The first reaction is a series of transesterification, where the triglyceride is synthesized with methanol to produce FAME using chemical catalysts or biocatalyst. The second step is carried on by reacting to the intermediate FAME formed from the first transesterification with TMP to produce TMP triester, also called biolubricant [10]. The two-consecutive series of transesterification process are written below:



where TG is triglyceride, M is methanol, TMP is Trimethylolpropane, GLY is glycerol, respectively.

The second series of reactions are hydrolysis of triglyceride followed by esterification of fatty acid with TMP [11]. In hydrolysis, the reaction can speed up with catalysts, either chemical or biocatalyst, such as: alkali metal hydroxide (base catalyst), organic sulphonic acid (acid catalyst) and lipase [12,13]. Alkali catalyst gives higher reaction rate about 4000 times faster compare to acid catalyst at standard reaction temperature when using low quality feedstock

[12]. Immobilized enzyme from lipase is suitable biocatalyst for hydrolysis, as presence of water in reaction is sufficient for the lipase activity, Lipase is surface active enzyme that will bind with substrates at the oil-water interface thus oil and water can separate [13].

Commonly used polyol reactant in both reactions is neopentyl glycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PET). Most of the synthetic esters biolubricant are manufactured based on branched polyols, especially neo-pentyl glycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE) [14]. These type of bio-lubricant have been accepted broadly as the bio-lubricant with better performance, by replacing glycerol with polyols [15]. Nevertheless, among the three polyols, TMP is considered more environmentally friendly, as it has relatively low melting point and moderate price [15]. In this study, TMP ester was synthesized through two series of transesterification from waste cooking oil (WCO) and rubber seed oil (RSO). The waste cooking oil was selected, because it has low in price when compared to RBD vegetable oils and its usage can reduce the waste deposition [10,16]. Rubber seed oil (RSO) is also non-edible oil that is considered as waste which contain of glycoside and not suitable for humans [3]. Furthermore, TMP is chosen compared to other polyols, because it has been widely used to produce environmental lubricants, cheaper in price, and has low melting points [17]. Synthesis of polyol based esters can be produced either from fatty acid or fatty acid methyl ester, using catalysts from acid, base or enzyme. Both feedstocks used in this study contains a high amount of free fatty acids (FFA), thus an acid catalyst is more suitable for the reaction. Because acid catalysts, such as: sulfonic, sulphuric acids, hydrochloric acids and phosphoric acids, demonstrates no measurable susceptibility to FFA. A previous study by Kamalakar *et al.* reported transesterification reaction of rubber seed oil using an acid catalyst, such as toluene-4-sulfonic acid, has obtained high yield in the range of 91-96.5% [6]. Thus, this study follows to perform transesterification reaction catalyzed by *p*-TSA.

In this research, TMP ester was produced from two different based feedstocks of methyl ester which were synthetically derived from Waste cooking oil (WCOME) and Rubber seed Oil (RSOME). These Methyl esters (FAME) undergone transesterification reaction with TMP to produce TMP ester or biolubricant. Various operating conditions to produce high conver-

sion of TMP esters were observed, such as temperatures, reactant molar ratios and reaction time. The biolubricant produced from both feedstocks are compared. The properties of biolubricant are then compared with standard lubricant ISO VG46. The result from this study is expected to be an alternative for producing more environmentally and sustainable lubricant.

2. Materials and Methods

2.1 Materials

Waste cooking oil methyl ester and rubber seed oil methyl ester were previously obtained from transesterification with methanol. 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) ($\geq 99\%$) and Toluene-4-sulfonic acid monohydrate (*p*-TSA) (99%) were obtained from Merck, Malaysia. Other solvents, such as: hexane (analytical grade) was used directly without purification.

2.2 Synthesis of Biolubricant

Figure 1 displays the experimental setup for the biolubricant production via transesterification reaction. The reaction occurs in the three-necked round bottom flask, attached with the

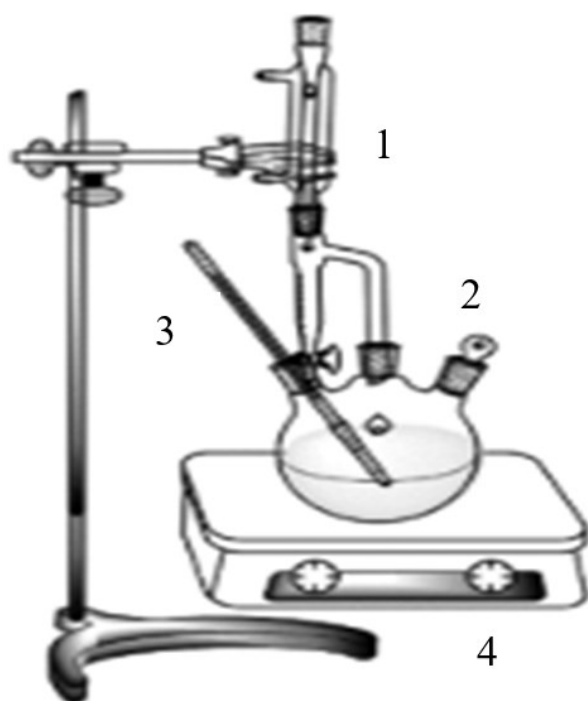


Figure 1. Experimental setup for TMP ester through double transesterification reaction [17]; (1) Condenser, (2) Three Neck Flask, (3) Thermometer, (4) Stirring Hotplate

reflux condenser, a thermometer, and a sampling port. The transesterification reaction between the reactant of FAME and TMP was carried out by initially heated the TMP at 60 °C with continuous stirring. This temperature was maintained for about 15 minutes to remove moisture. The FAME was then poured at a known amount of molar ratio. The reaction was then proceeded according to the set temperature. After the desired temperature has been reached, *p*-TSA as a catalyst was added into the reaction. The sampling was the taken for every one hour and then it was purified by centrifugation. The formation of TMP ester or biolubricant is defined as conversion of biolubricant based on reduction of reactants (FAME), as shown below:

$$\text{Conversion (\%)} = \frac{\text{Initial Fatty acid or FAME} - \text{Final Fatty acid or FAME}}{\text{Initial Fatty acid or FAME}} \times 100\% \quad (3)$$

2.3 Analysis of FAME

The composition of FAME was determined using a GC-MS. GC-MS is the technique of analysis which developed to separate the sample according to the molecular mass and resulting from the data composition [18]. In this study, the composition of fatty acid present in the product from transesterification of FAME and TMP were analyzed with GC-MS. The GC-MS used in this analysis is the combination of Varian 450-Gas Chromatograph with Varian 240-Mass Spectrometer Ion Trap. The column used was DB wax with 30 m long, with 0.25 mm i.d. and 0.25 μm film thickness. The helium used as carrier gas at the head pressure of 0.55 atm and a split injection system at ratio 50:1. The inlet temperature was 250 °C and the detector temperature was 280 °C. The prepared sample for 1 mL each was injected into the GC system. Confirmation of ester functional group in the synthesized biolubricant was also then identified FTIR.

2.4 Analysis of Biolubricant Properties

Basic properties of biolubricant were characterized based on the American Society for testing and material (ASTM) methods. The properties being investigated were cloud point, pour point, specific gravity and viscosity. These properties were carried out to observe the potential of lubricant characteristics.

2.4.1 Cloud point (ASTM D97)

Cloud point can be defined as the minimum temperature where the sample becomes clouded when wax crystals are started to form. Cloud point was analyzed by using Cloud and Pour Point Apparatus. An amount of biolubricant sample was poured into a graduated jar until the level was marked with a line. The jar was closed tightly with a cork and was placed in the cooling bath. The sample was chilled until it is noted to become clouded at the bottom of the jar. The temperature at this point happen was recorded. The measurements were taken with every decrement of 2 °C.

2.4.2 Pour point (ASTM D97)

Pour point is used to determine the flow properties of the fluid. A similar procedure to measure the cloud point was taken, however further chilling was continued until the biolubricant sample ceases to flow. The observation of sample flow was made by tilting the jar horizontally for 5 seconds and the temperature at which the sample shows no longer movement was recorded.

2.4.3 Specific gravity (ASTM D941-55)

Specific gravity is the ratio of the density of the used lubricating oil to the density of the equal volume of water. This was measured by using a hydrometer. The property was observed, and the value was recorded.

2.4.4 Viscosity (ASTM D445)

Viscosity was analyzed by using an Automated Micro Viscometer (AMVn). The capillary block of the clean viscometer was filled with the biolubricant sample while immersed in a

thermostat. The temperature was set at 40 °C and the result was tabulated.

3. Results and Discussion

The synthesise of biolubricant from WCOME and R SOME were studied over the effects of reaction time, temperature and molar ratio of FAME to TMP. Throughout this study, the biolubricant was analyzed based on the conversion of reactant (FAME) into the product. The conversion of FAME to biolubricant was verified with GC-MS and FTIR. The synthesized product was characterized using ASTM standard by comparing with the standard lubricant.

3.1 Preliminary Study on Reaction Time for Transesterification of WCOME based Biolubricant

Determination of optimum reaction time for biolubricant production was obtained by carried out a preliminary study of transesterification between WCOME and TMP. The transesterification reaction conditions were as follows: temperature 140 °C, 3:1 ratio of WCOME to TMP with 2 wt% of *p*-TSA as the catalyst. The molar ratio used in the reversible reaction is theoretically created from the general transesterification reaction of FAME and TMP as written in equation 2. The stoichiometric ratio for the forward reaction requires 3 moles of FAME and 1 mole of TMP. Figure 2 shows the effect of FAME conversion versus reaction time in the transesterification reaction. The major constituent of FAME which is hexadecenoic acid methyl ester was investigated based on the sample taken at every one (1) hour interval. The reaction time was varied from 0 to 5 hours.

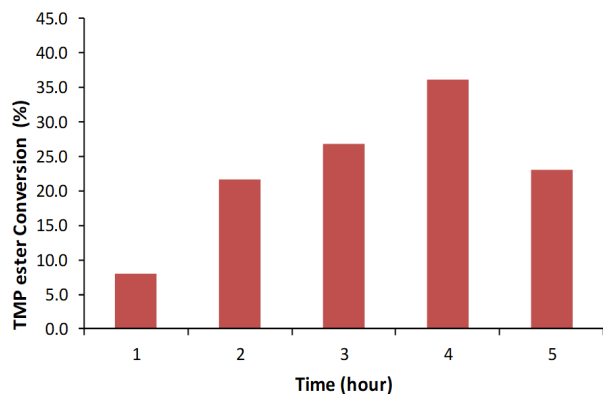


Figure 2. Effect of reaction time based on conversion of biolubricant in transesterification of WCOME using *p*-TSA as catalyst.

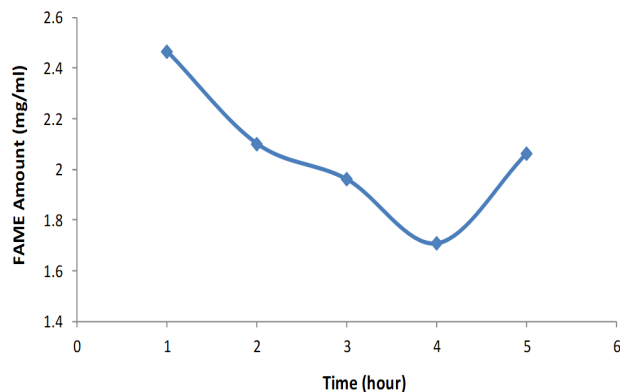


Figure 3. Time profile in transesterification of WCOME based on FAME amount using *p*-TSA as catalyst.

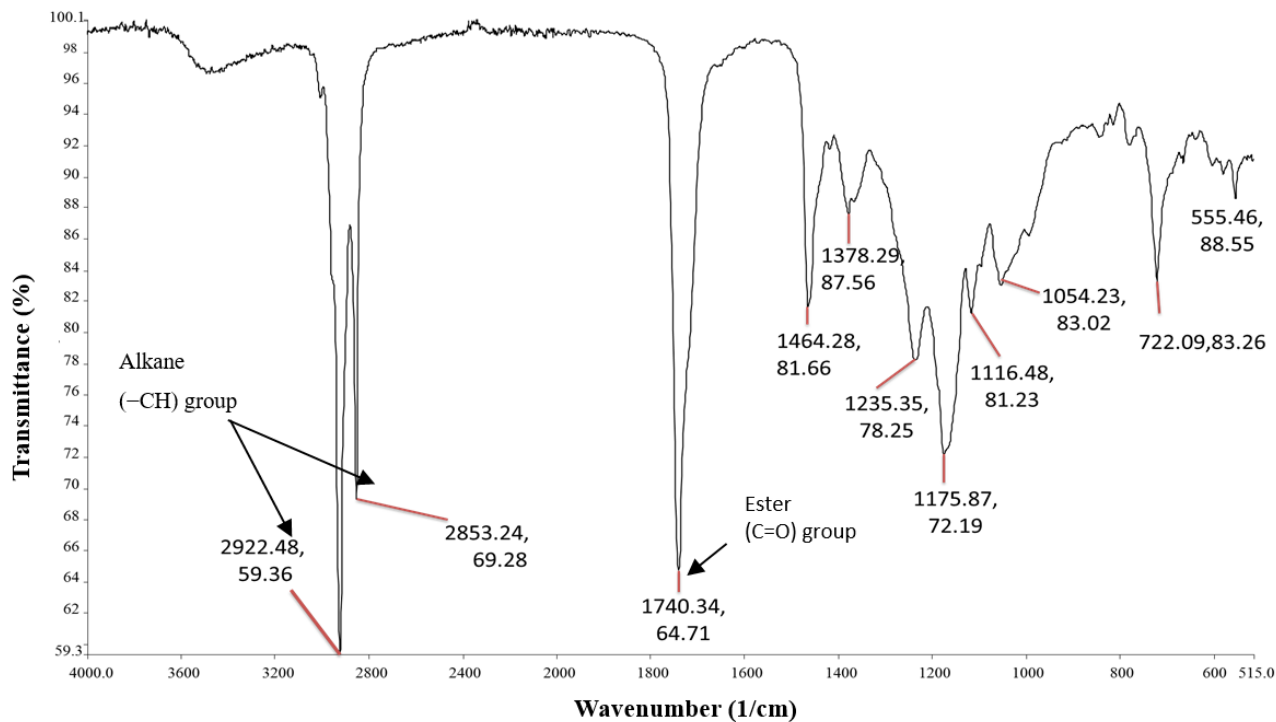


Figure 4. FTIR spectrum of WCOME based biolubricant (TMP ester).

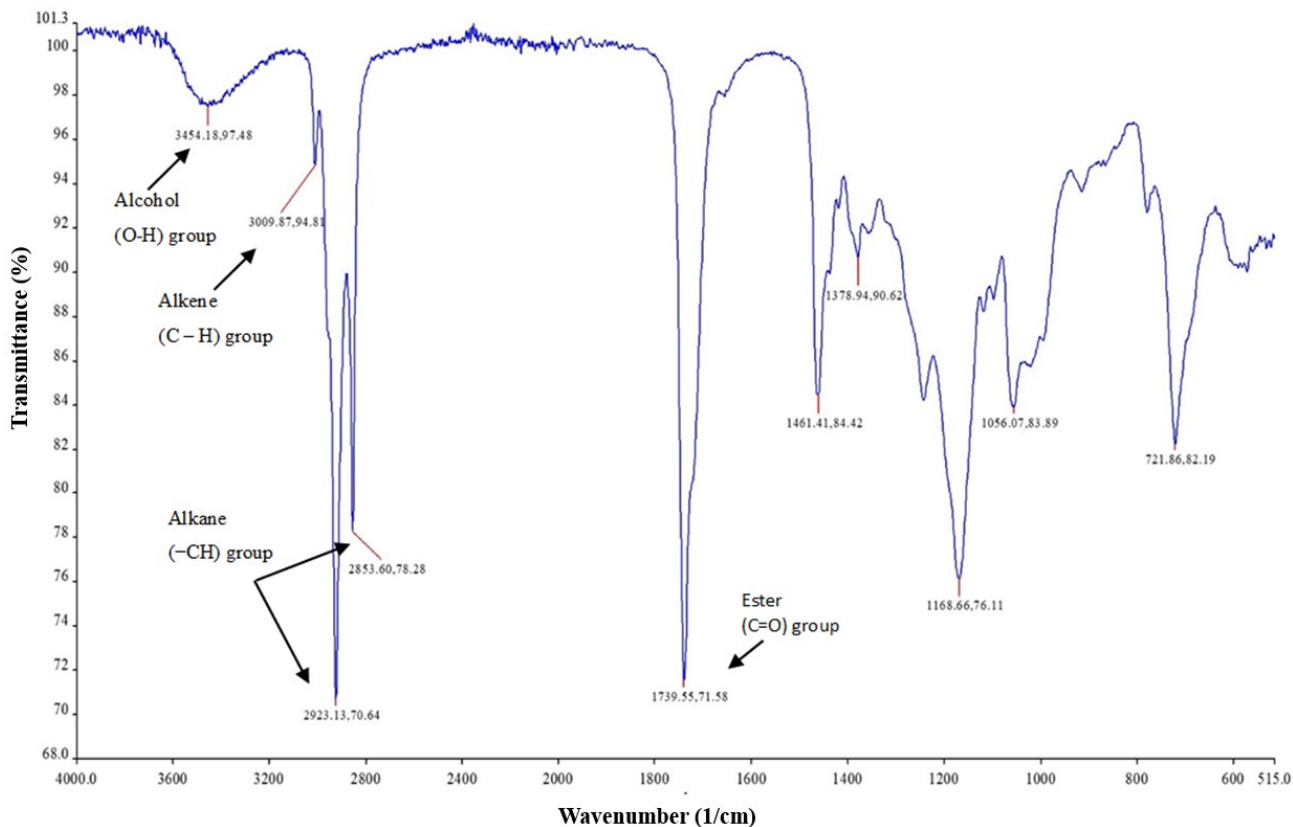


Figure 5. FTIR spectrum of RSOME based biolubricant (TMP ester).

As can be seen from Figure 2, the conversion of FAME increased obviously as the reaction time increased from 0 to 4 hours. The conversion of FAME at 4 hours reaction time is the highest which is up to 36%. Further increase of reaction time to 5 hours led to an adverse impact on FAME conversion, where the conversion decreased to 23%. This is most probably because the reaction has completed at 4 hours and further reaction time may lead to reverse of the product into reactant. Additionally, according to Wang *et al.* result, the increasing reaction time will lead to higher usage in terms of energy and time [1]. The result from this study is used to describe reaction profile based on reduction of FAME amount as seen in Figure 3.

Figure 3 shows that FAME amount is still high at the beginning of the experiment, which is 2.47 mg/mL after 1 hour of reaction. Afterward, FAME amount starts to decrease until 4 hours of reaction. The amount of FAME was decreasing until only 1.71 mg/mL was left. However, extending reaction time after 4 hours made the FAME amount started to increase to 2.06 mg/mL at 5 hours. This is most probably because of reversible reaction as explained earlier in Figure 2. Thus, it can be concluded that 4 hours was an optimum reaction time for further study in transesterification of WCOME and RSOME with TMP.

3.2 FTIR Analysis of Biolubricant

The functional group found in the WCOME based biolubricant was diagnosed by the infrared spectrum (FTIR). The conversion of FAME to TMP based ester obtained from transesterification between TMP and WCOME can be confirmed through the peak appearance of ester

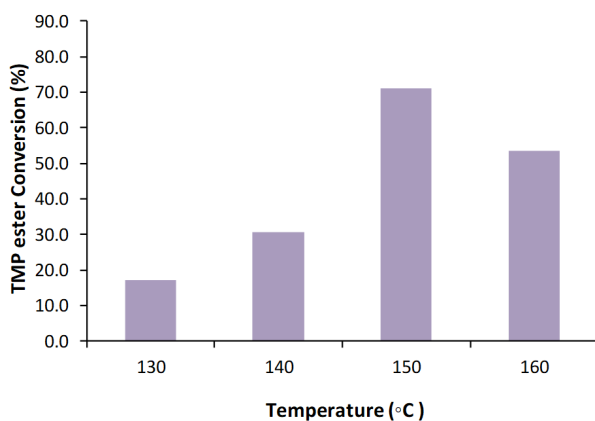


Figure 6. Effects of temperature on conversion in transesterification of WCOME using *p*-TSA as a catalyst.

functional group at 1740.34 cm^{-1} . A similar trend was obtained from the TMP ester of Jatropha oil-based [19]. A distinct peak also can be observed from the spectrum at wave-number between 2800 to 3000 cm^{-1} resulting from $-\text{CH}_3$ stretching vibration and 1464 cm^{-1} indicates $-\text{CH}$ bending, the existence of alkane group [20].

The formation of TMP triester is from the intermediate of monoester and diester. If hydroxyl groups were partially esterified, monoester and diester will be formed. Triester, on the other hand, will be formed, when its hydroxyl groups were fully esterified [4]. The FTIR spectra for WCMOE based biolubricant shows in Figure 4. The hydroxyl (O-H) functional group is insignificant in WCOME spectra, as it is exhibited weaker IR absorbances compared to other groups. It shows that TMP has successfully reacted with FAME to produce TMP triester. Similar result has been reported by Musa *et al.* where the spectrum represents insignificant peak of hydroxyl group at a range of 3200-3600 cm^{-1} [21]. According to Sanni *et al.* result, no specific bond in the molecule may exist in the area without peaks, because it represents no photons are being absorbed in that frequency [22]. Different IR spectra for Hydroxyl functional group was obtained with RSOME based TMP ester as shown in Figure 5. The O-H functional group is quite clear at wavelength 3454 cm^{-1} for RSOME based TMP ester.

3.3 The Effect of Temperature on the Transesterification Reaction of WCOME

Reaction temperature gives a significant effect on most of the chemical reactions including transesterification. This research observed the effect of reaction temperature on the synthesis of WCOME based biolubricant by experimenting 130, 140, 150 and 160 $^{\circ}\text{C}$ for 4 hours. The other reaction conditions were fixed in this series of experiments at 3:1 ratio of FAME to TMP and 2 wt% *p*-TSA as a catalyst. Figure 6 illustrates the influence of reaction temperature towards the conversion of FAME. The highest amount of FAME converted into TMPE ester is about 71% at the temperature of 150 $^{\circ}\text{C}$. Comparable study from Panchal *et al.* also showed that conducting the reaction at high temperature above 100 $^{\circ}\text{C}$ may obtained higher yield, as it prolonged reaction time more than 3 hours [23].

In Figure 6, the lowest conversion is achieved at temperature 130 $^{\circ}\text{C}$. This can be due to the low reactant mobility in which ends

up in a low reaction rate [24]. Reactions at low temperatures cause a slower rate because the reacting particles have less kinetic energy for product formation [25]. Since the synthesis of TMP triester is an endothermic reaction, it is a plus point to conduct the reaction at high temperature, but the temperature must not be too high [1]. The result obtained in this study proved that reaction at higher temperatures than the optimum, would give low conversion. This may also be contributed from vaporization of reactant volatile substance as well as enhancing the occurrence of a reverse reaction. Therefore, it is sufficient to operate the reaction at 150 °C for the optimum temperature of the transesterification of WCOME with TMP.

3.4 Composition of WCOME based Biolubricant

The chromatogram of FAME from WCOME based biolubricant was determined by using GC-MS. The GC-MS chromatogram peaks refer to the number of carbon contained in the sample product. The peak component in the chromatogram was identified by comparing it with the standard from the previous study [26].

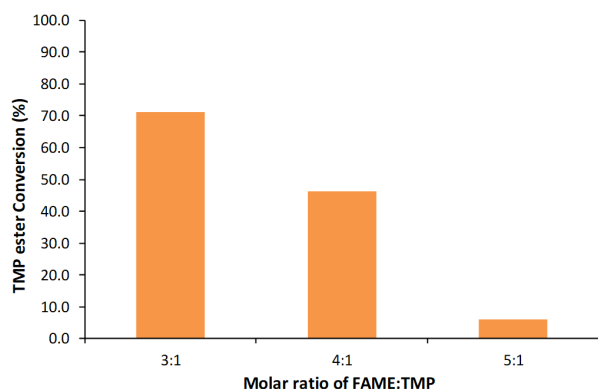
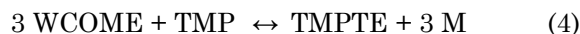


Figure 7. Effects of molar ratio of FAME:TMP on conversion in transesterification of WCOME using *p*-TSA as catalyst.

The percentage composition of ME in the production of biolubricant from WCOME based is tabulated in Table 1. The finding shows that saturated methyl esters were the major component in the synthesized biolubricant. Highest composition of methyl ester consists of methyl palmitate (52.52%) followed by methyl (7Z)-hexadecenoate (42.06%), methyl stearate (4.58%), and methyl tridecanoate (0.83%). Overall, biolubricant synthesized from WCOME produced high saturated FAME at a mass fraction of 57.93% compare to unsaturated FAME with mass fraction of 42.06%. This is promising, because high saturation content in the biolubricant product will lead to higher resistance towards oxidative-thermal treatment [19]. On top of that, a high degree of saturated FAME also could develop a lubricant with high biodegradability and good low-temperature performance [27].

3.5 The Effect of Molar Ratio on the Transesterification Reaction of WCOME

Based on the general transesterification reaction, 3 moles of FAME are required to initiate a forward reaction with 1 mole of TMP, as shown below:



Transesterification is a reversible reaction and is accomplished by mixing the reactants of FAME and TMP. The synthesis of biolubricant from transesterification with presence of catalyst involves three phases of reactions. Initially, TMP monoesters (TMPME) is produced and it will be converted to form intermediates of TMP diesters (TMPDE) and finally become the final product, TMP triester (TMPTE).

Investigations on the effect of molar ratio of FAME to TMP for the synthesis of WCOME based biolubricant were varied at three different ratios which are 3:1, 4:1 and 5:1. Other op-

Table 1. The percentage composition of FAME in WCO based biolubricant.

FAME name	Common name	Percentage of total mass (%)
Saturated FAME		
Tridecanoic acid methyl ester (C13:0)	Methyl tridecanoate	0.83
Hexadecanoic acid methyl ester (C16:0)	Methyl palmitate	52.52
Octadecanoic acid methyl ester (C18:0)	Methyl stearate	4.58
Unsaturated FAME		
7Z-Hexadecenoic acid methyl ester (C16:1)	Methyl (7Z)-hexadecenoate	42.06

erating conditions were kept constant throughout the experiment, such as: temperature 150 °C, 4 h reaction time and 2% (wt/wt) of *p*-TSA as catalyst. Figure 7 describes the result achieved in percent conversion of FAME versus molar ratio of FAME to TMP. From Figure 7, it could be observed that 3:1 molar ratio possesses the highest conversion of 71%, 4:1 ratio at 46% conversion followed by 5% conversion occurred for 5:1 ratio. Thus, the optimum molar ratio for this study was at stoichiometric molar ratio of 3:1.

On account of the stoichiometric reaction, the production of biolubricant can be much better accomplished by experimenting with a higher molar ratio of reactants to enhance reaction completion [5]. However, in our study, increasing molar ratio of FAME to TMP above its stoichiometric molar ratio, decreased the conversion of reactant to biolubricant. This occurrence may be because higher content of FAME in the reaction, promoting the dilution of TMP concentration in the system and decreasing the collision probability of the nucleophilic particle [17]. Moreover, the previous study by Wang *et al.* stated that more energy will be needed to be recovered for excess amount of unreacted FAME [1]. As the consequences, that is why the increase in molar ratio of FAME:TMP had a negative impact on synthesizing biolubricant

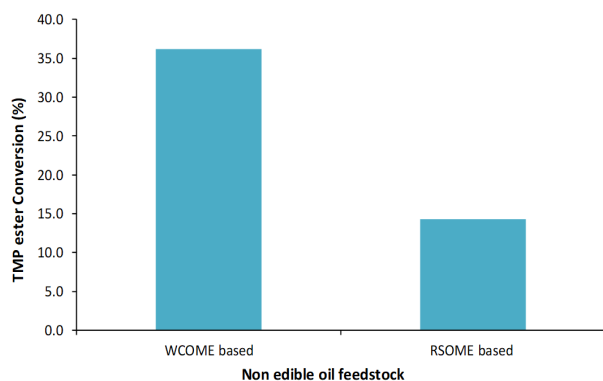


Figure 8. Comparison of conversion for biolubricant from Waste cooking oil (WCOME) and Rubber seed oil (RSOME) based in transesterification using *p*-TSA as a catalyst.

based on the FAME conversion to the final product.

3.6 Comparative Study on Various Based Methyl Esters for Biolubricant Synthesis

The comparison of biolubricant from WCOME and RSOME based were studied at stoichiometric molar ratio of FAME to TMP 3:1, 4 hours reaction time and 2% (wt/wt) of *p*-TSA as catalyst. Figure 8 conveys the comparative study of FAME conversion on both feedstock. It is found that the conversion of RSOME based is much lower than WCOME, although reaction was not carried out at optimum temperature. During the experiment with RSOME, it was seen that the sample tends to be sludgy and viscous. The biolubricant from WCOME has conversion of 36%, whereas conversion of RSOME based is 14%. Thus increasing temperature for comparison purposes is not effective and efficient, because a higher reaction temperature could damage the appearance of the biolubricant and preventing a better yield of biolubricant [28].

3.7 Properties of Biolubricant

The properties of synthesized biolubricant were evaluated based on ASTM methods. The WCOME and RSOME based biolubricant was compared to an industrial lubricant ISO VG46. The ISO VG46 is a grade lubricant which normally use for light gear applications, crankcase and hydraulic fluid [18]. The overall result was tabulated in Table 2.

Viscosity is one of the important criteria to look for when selecting a lubricant. In this study, kinematic viscosity at 40 °C was measured by ASTM D445 method [29]. Viscosity of WCOME based biolubricant was found at 62.56 cSt and Viscosity of RSOME based biolubricant was at 40.2 cSt. Only biolubricant's viscosity from WCOME is within the requirement of ISO VG46 lubricant which is above 41.2. Similar result was reported by Kamalakar *et al.* [6].

Cloud point and Pour point were analyzed by ASTM D97 method and compared with the standard lubricant [30]. Cloud point from both

Table 2. Properties of Biolubricant.

Specification	WCOME Biolubricant	RSOME Biolubricant	ISO VG46 [1]
Specific gravity (g/mL)	0.88	0.90	N/A
Viscosity at 40 °C (cSt)	62.56	40.2	>41.4
Cloud Point (°C)	14	2	N/A
Pour Point (°C)	8	-4	-6

WCOME and RSOME obtained higher values compared to study in from Li and Wang [31]. However, the values are not applicable for ISO VG46 lubricant standard. The pour point of WCOME and RSOME based biolubricant were not in the range of lubricant standard, which are 8 °C and -4 °C, respectively. Unlike current study, other reported study that derived biolubricant from WCOME shows a lower pour point at -3 °C [32]. Lower pour point was also obtained for RSOME based biolubricant which is -6 °C [6]. This probably due to high level of saturation from palmitic content (52.52%) that may remove the effect of cis-unsaturation in biolubricant [19]. According to Alang *et al.* result, a higher pour point increases thermal stability and can endure mechanical stress better than petroleum lubricants [33].

4. Conclusions

Trimethylolpropane (TMP) ester (biolubricant) has been successfully produced as alternatives lubricant from two different non-edible oil based, which are Waste cooking oil (WCO) and Rubber Seed Oil (RSO). The two-steps transesterification reaction was selected for the process, where WCO and RSO were first transesterified with methanol to form WCO methyl ester (WCOME) and RSO methyl ester (RSOME), followed by transesterification with Trimethylolpropane(TMP). The use of non-edible vegetable oil-based as the feedstock in this study can avoid impact on environment and food security's issues. Observation with various operating conditions have shown that TMP ester was best produced from Waste cooking oil. The biolubricant from WCOME was confirmed with Infra-Red spectra where strong formation of ester and alkene were detected without significant hydroxyl functional group. Comparison of biolubricant properties with lubricant standard of ISO VGA 46 depicts that only viscosities for both WCOME and RSOME based are meet the requirement. Thus, further study to improve the quality of biolubricant from Waste cooking oil and Rubber seed oil is recommended.

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