Synthesis of Biolubricant from Various Based Methyl Esters

Nurazreen Shazwin binti Kamarudin, Harumi Veny

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract—**Recently, the research on biolubricant production has been rising in order to fulfil biodegradable base stock. The purpose of this research was to emphasize on the production of eco-friendly biolubricant from various based methyl ester by using the process of two stages transesterification. Biolubricant from trimethylolpropane (TMP) triesters from methyl ester based of waste cooking oil (WCOME) and rubber seed oil (RSOME) were synthesized via transesterification reaction with TMP in the three-necked bottom flask. 2 % (w/w) of para-Toluenesulfonic acid (*p*-TSA) was added as catalyst in the reaction. In this study, the effect of time, temperature and molar ratio of FAME to TMP were observed on transterification reaction based on the percentage conversion of FAME as reactant to be converted into the final product, biolubricant. Analysis of resulting biolubricant was carried out by Gas Chromatograph-Mass Spectrophotometer (GC-MS) system to determine the composition of the synthesized biolubricant while the presence of ester functional group was displayed by performing Fourier Transform Infrared Spectroscopy (FTIR) analysis. The synthesized lubricant were characterized according to American Society for Testing and Materials (ASTM) standard method based on these properties: Cloud point (ASTM D97), Pour point (ASTM D97), Specific gravity (ASTM D941-55) and Viscosity (ASTM D445). Experimental results has reviewed that the optimum condition for the production of WCOME based biolubricant were found at the following conditions such as temperature 150°C, 4 h reaction time, 3:1 ratio of FAME to TMP and 2% (wt/wt) of *p*-TSA as catalyst. A comparative study for biolubricant between WCOME and RSOME based were also studied. In addition, these polyol based esters exhibit appropriate basic properties as a lubricant because both methyl ester based demonstrate comparable characteristic to the requirement of standard lubricant ISO VG46.**

Keywords*— *biolubricant, rubber seed oil methyl ester, transesterification, trimethylolpropane triester, waste cooking oil methyl ester

I. INTRODUCTION

High demand for various application of lubricant has giving a rise towards the increase of lubricant price and environmental issues due to their properties; non-biodegradable and toxic which can directly harm and polluted if discharge into the environment and exposed with land, water and air system [1]. Thus, the development of an environmental friendly based lubricant has become a greater interest to the researchers in utilizing the renewable resource. Vegetable oil based is preferred as the feedstock for production of biolubricant because of having criteria being a renewable resource, economical and non-toxic.

Vegetable oil can be classified into edible and non-edible oil. Edible oil is easily accessible since it is required for food source. However, non-edible oil have either little impact on global food cost or production because they can be grown on nutrient-deficient land and at the same time reducing the competition within the current agricultural resources [2]. Hence, it gives advantage for the biolubricant production from non-edible oil to be applied for research development. Thus, the focus in developing biolubricant can be considered based on those factors. The idea of biolubricant synthesis is not a new thing in oleochemical field since previous researchers has found that biolubricant gives similar lubricating properties as mineral based lubricant. There are few studies reported for biolubricant production from the application of vegetable oil based such as palm oil, Jatropha curcas oil, rubber seed oil, karanja oil, rapeseed oil, waste cooking oil and sesame oil [3]–[8]. In this study, feedstock for production of biolubricant is utilizing waste cooking oil (WCO) because its usage can reduce the waste deposition [9]. Another reason behind this is because WCO is much lower in price compared to unused vegetable oils [10]. In contrast, rubber seed oil (RSO) is another feedstock for synthesizing biolubricant. This is accounted for its characteristic containing glycoside which is toxic and not suitable to be used by human [2].

Recently, biolubricant derived from vegetable oil has been developed and shows great chances as a new generation of lubricant. However, the failure of performance due to the structure of vegetable oil has affect its lubrication properties such as oxidation stability, hydrolytic instability and low temperature properties [4]. Therefore, modification should be proposed in order to improve the oil performance. The most common method of study to synthesis biolubricant is from the transesterification process between FAME and polyhydric alcohol or polyol, which consist of more than one hydroxyl group. Commonly used polyol are neopentyl glycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PET). Further to this, TMP is chosen compared to other polyols because it has been widely used to produce environmental lubricant with having cheaper price and also low melting point [11].Synthesis of polyol based esters can be produced either from fatty acid or fatty acid methyl ester and were catalyzed by the presence of acid, base or enzyme. Since both feedstock used in this study contains high amount of free fatty acids (FFA), therefore, it is an advantage to catalyze the reaction by acid catalyst. Due to the fact that acid catalyst demonstrates no measurable susceptibility to FFA, this can be attained by methodologies based on acid-catalyzed reactions. Transesterification catalyzed by acids preferably by sulfonic, sulphuric acids, hydrochloric acids and phosphoric acids. A previous study by Kamalakar *et.al*, transesterification reaction of rubber seed oil has result in higher yield in the range of 91-96.5% yields [5]. Thus, this study follows to perform transesterification reaction catalysed by *p*-TSA.

The synthesis of biolubricant was proposed through two stages of transesterification reaction. The first stage of the reaction occurs between triglyceride and methanol to prepare FAME, also known as biodiesel. The second step is carry on by reacting the intermediate FAME formed from the first stage with TMP to produce TMP triester, also called biolubricant with the presence of catalyst. The general equation of 1 and 2 takes place for two stages transesterification process as written below:

Stage one:

$$1\ \text{TG} + 3\ \text{M} \leftrightarrow 1\ \text{GLY} + 3\ \text{FAME} \qquad (1)$$

where TG is triglyceride, M is methanol and GLY is glycerol, respectively.

Stage two:

$$1\ \text{TMP} + 3\ \text{FAME} \leftrightarrow \underset{\text{(Biolubricant)}}{1\ \text{TMP Triester}} + 3\ \text{M} \qquad (2)$$

In this research, based stocks of FAME are synthetically derived from WCOME and RSOME will undergo transesterification reaction with TMP to produce biolubricant. Therefore, the potential of reactant conversion, which is FAME based, producing high quality and yield of biolubricant is studied.

II. METHODOLOGY

A. Materials

The feedstocks utilized in this experiment were waste cooking oil methyl ester and rubber seed oil methyl ester. Both feedstocks were obtained from the previous undergraduate research. 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) and Toluene-4-sulfonic acid monohydrate for analysis (*p*-TSA) was obtained from Merck, Shah Alam, Malaysia. Other solvent such as hexane was analytical grade and were used directly without purification.

B. Methods

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 reflux condenser, a thermometer and a sampling port.

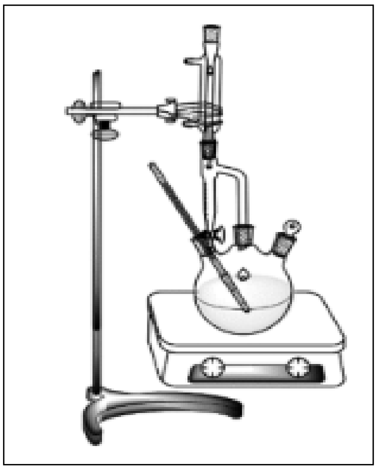

Figure 1. Experimental setup for transesterification reaction [11]

The process started by the transesterification reaction between the reactant of FAME or biodiesel and TMP. The FAME was first centrifuge around 6000 rpm for about 15 to 30 minutes. TMP was then added into the flask and melted by heating at 60ºC with continuous stirring. The temperature was maintained at 60ºC for about 15 minutes in order to remove moisture. Next, FAME was poured at known amount of molar ratio. FAME and TMP react in the flask was then heated to the desired reaction temperature. After the desired temperature has been reached, *p*-TSA was added into the reaction as catalyst. The reaction time for sampling start and the first sample is taken out of the flask through sampling port after every 1 h. The samples collected were repeated until it reached the reaction time. The sample product was purified by centrifuge to remove any solid particle left in the sample.

Sample Preparation for GC-MS Analysis

The sample preparation for GC-MS analysis was completed by taking 100 µl of product dissolved in 3900 µl hexane as solvent. The prepared sample was homogenized by taking to vortex mixer. There were two vials at every 1 h time interval of samples collected, each containing 1 mL of the prepared sample to be sent for analysis. To study the conversion of reactant into product, the analysis of FAME conversion by GC-MS was determined by equation 3:

$$\text{Conversion (\%)} = \left(\frac{\text{Initial amount of ME} - \text{Final amount of ME}}{\text{Initial amount of ME}}\right) \times 100 \qquad (3)$$

Analysis of Product

The composition of FAME in the final methyl ester (ME) product was determined using a GC-MS system. GC-MS is the technique of analysis which developed to separate the sample according to the molecular mass and resulting of the data composition [12]. In this study, the composition of fatty acid presence in the finishing product of transesterification between FAME and TMP was being analyzed. The system of GC-MS consist of the combination between Varian 450-Gas Chromatograph with Varian 240-Mass Spectrometer Ion Trap. The column spec is 30 m long, with 0.25 mm i.d. and 0.25 µm film thickness. The column use helium as carrier gas at the head pressure of 0.55 atm and a split injection system at ratio 50:1. The column temperature was held at 50ºC throughout the entire 6 min run. Temperature initiated at 50ºC at the rate of 25ºC min^{-1} to reach a temperature of 200ºC. The inlet temperature was 250ºC and the detector temperature was 280ºC. The prepared sample for 1 mL each was injected into the GC system. Confirmation of ester functional group in the synthesized biolubricant was then identified by analysis using FTIR.

Analysis of Biolubricant Properties

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

Cloud point (ASTM D97)

Cloud point can be defined as the minimal 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 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. Temperature at this point happen was recorded. The measurements were taken with every decrement of 2ºC.

Pour point (ASTM D97)

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

Specific gravity (ASTM D941-55)

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

Viscosity (ASTM D445)

Viscosity was analysed 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 40ºC and the result was tabulated.

III. RESULTS AND DISCUSSION

The experimental results for the biolubricant production were presented and studied in detail. The experimental condition for synthesizing biolubricant from WCOME and RSOME based were studied over the effects of reaction time, temperature and molar ratio of FAME to TMP towards transesterification reaction. Throughout this study, the production of biolubricant was analyzed based on the conversion of reactant, FAME into product. The resulting FAME conversion to product was verified by analyzing using GC-MS and FTIR. The synthesized product was characterized using ASTM standard by comparing with the standard lubricant.

A. Preliminary Study on Reaction Time for Transesterification of WCOME based Biolubricant

Determination of optimum reaction time for biolubricant production was obtained by carried out preliminary study of transesterification between WCOME and TMP. The transesterification reaction was conducted under the following conditions as follows: temperature 140ºC, 3:1 ratio of WCOME to TMP with 2 wt% of *p*-TSA as catalyst. The molar ratio used in the reversible reaction is theoretically created from 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 against reaction time on transesterification reaction. The major constituent of FAME which is hexadecanoic acid methyl ester was investigated based on the sample taken at every time interval of 1 h. The reaction time was varied from 0 to 5 h.

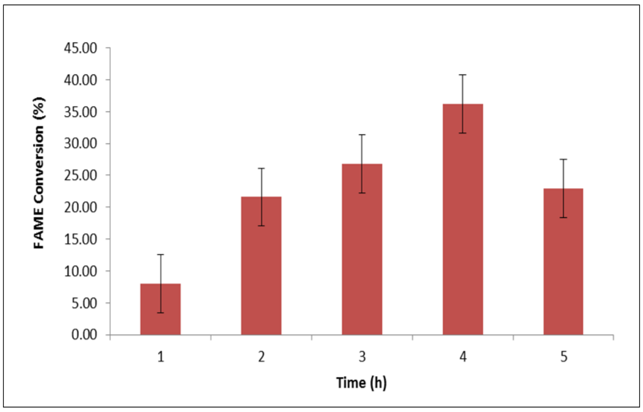

Figure 2. Effect of reaction time against FAME conversion at the following condition: temperature of 140ºC, molar ratio of 3 FAME: 1 TMP and 2% (wt/wt) of *p*-TSA as catalyst.

As can be seen from figure 2, the conversion of FAME increased obviously as the reaction time increased from 0 to 4 h. The conversion of FAME at 4 h reaction time is the highest which is up to 36%. Further increase of reaction time to 5 h led to adverse impact on FAME conversion where the conversion decreased to 23%. The decrement at longer reaction time probably influence by the achievement of reaction completion and the backward reaction in transesterification process. Besides, increase in higher reaction time will led to higher usage in terms of energy and time as stated by Wang *et al.* [1]. However, higher yield can be gained from acid-catalyzed transesterification by conducting the reaction at high temperature above 100ºC as it prolonged reaction time more than 3 h [13].

It can be seen that as the reaction goes over time, the reaction utilize FAME from the feedstock of WCOME based for the product formation. This parameter was evaluated in order to observe the time profile of FAME amount during the experiment was held. The result of FAME amount against time is expressed in figure 3.

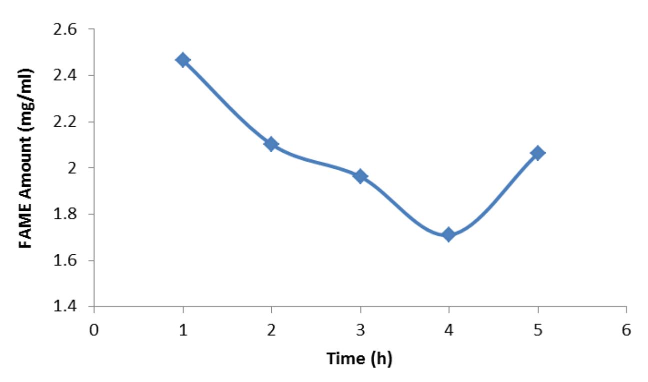

Figure 3. Time profile of FAME amount at the following condition: temperature of 140ºC, molar ratio of 3 FAME: 1 TMP and 2% (wt/wt) of *p*-TSA as catalyst.

Through the experiment based on figure 3, FAME amount is higher at the beginning of the experiment. The obtained amount is 2.47 mg/ml for 1 h sample collected. The outcome shows FAME amount to be lowered and decreased as implements longer reaction time of the experiment. FAME has been used up and reacted with TMP until its amount reached 1.71 mg/ml at 4 h. However, an amount of 2.06 mg/ml was gained at 5 h where this time had reversed back the reaction. In reversible reactions, as the reactants react with other reactants to form products, the products are reacting with other products to form reactants. Thus, it can be concluded that 4 h was an optimum reaction time used as a reference time for transesterification reaction on parameter studies of temperature and molar ratio. The resulting condition also was applied for the production of biolubricant from RSOME based.

B. FTIR Analysis of Biolubricant

The functional group found in the WCOME based biolubricant has been diagnosed by infrared spectrum as presented in figure 4. The conversion of FAME to TMP based ester obtained from transesterification between TMP and WCOME can be confirmed through the peak appearance of ester functional group at 1740.34 cm^{-1}. A similar trend was obtained from the TMP ester of Jatropha oil based [14]. This shows the characteristic of the absorption band of an ester where the transesterification between FAME and TMP has well reacted with each other. A distinct peak also can be observed from the spectrum at wavenumber between 2800 to 3000 cm^{-1} resulting from $-CH_3$ stretching vibration and 1464 cm^{-1} indicates –CH bending, the existence of alkane group [15].

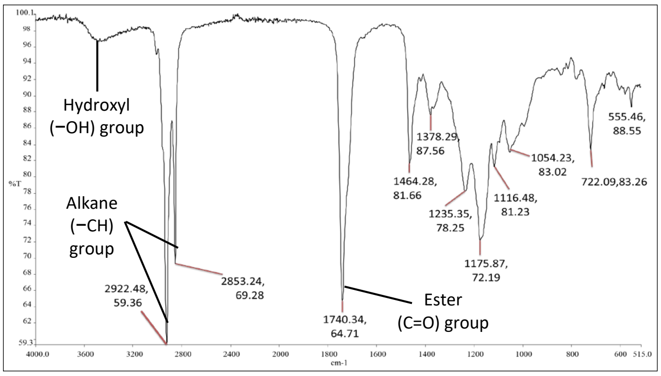

Figure 4. FTIR spectrum of WCOME based biolubricant at the following condition: time at 4 h, temperature of 140ºC, molar ratio of 3 FAME:1 TMP and 2% (wt/wt) of *p*-TSA as catalyst.

The formation of TMP triester is from the intemediates of monoester and diester. If hydroxyl groups were partially esterified, monoester and diester will be formed and triester if its hydroxyl groups were fully esterified [3]. The spectrum represents absence or unsignificant peak of hydroxyl group at a range of 3200-3600 cm^{-1}. According to Sanni *et al.* (2017), no specific bond in the molecule may exist at the area without peaks since it represents no photons are being absorbed at that frequency. No appearance of O-H bond shows that TMP has successfully reacted with FAME to produce TMP triester, which similar result has been reported in the previous research [17]. This is another prove that indicates the formation of TMP triester from the transesterification reaction.

C. *The Effect of Temperature on the Transesterification Reaction of WCOME based Biolubricant*

Reaction temperature gives significant effect in most of the chemical reactions including transesterification. This research has studied the effect of reaction temperature on the synthesis of WCOME based biolubricant by performing the experiment at 130ºC, 140ºC, 150ºC and 160ºC for 4 h. The other reaction conditions were fixed in this series of experiment at 3:1 ratio of FAME to TMP and 2 wt% *p*-TSA as catalyst. Figure 5 illustrates the influence of reaction temperature towards the conversion of FAME. About 71% conversion was observed, indicated that FAME has been converted into product, occurred at the reaction temperature of 150ºC.

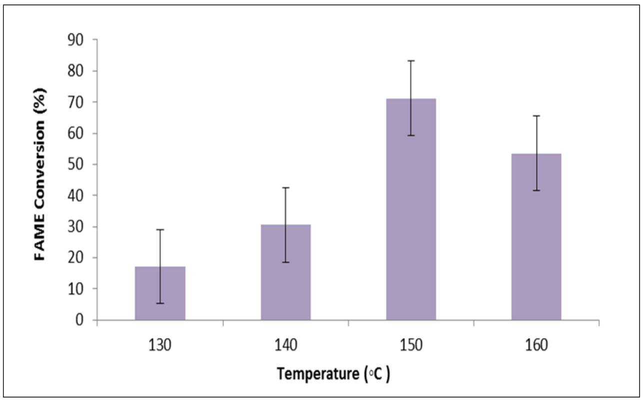

Figure 5. Effects of reaction temperature on FAME conversion at various temperature with following condition: time at 4 h, molar ratio of 3 FAME:1 TMP and 2% (wt/wt) of *p*-TSA as catalyst.

The reaction was slowest at temperature 130ºC with the lowest conversion. This can be due to the low reactant mobility which ends up in a low reaction rate [18]. Reactions at low temperature cause in a slower rate because the reacting particles have less kinetic energy for the product formation [19]. Owing to the fact that the synthesis of TMP triester is an endothermic reaction , it is a plus point to conduct the reaction at high temperature, however, the temperature must not be too high [1]. The result obtained in this study proved that reaction at even higher temperature was found to be unnecessary as a result may contributed by vaporization of reactant volatile substance, enhancing the occurrence of a reverse reaction. The aim of this study is to concentrate on the higher FAME conversion to product at certain range of temperature. Therefore, it is sufficient to operate the reaction at 150ºC as the optimum temperature for the transesterification of WCOME with TMP.

D. *Composition of WCOME based Biolubricant*

The chromatogram plot of FAME present in the resulting WCOME based biolubricant was determined by using GC-MS as demonstrates in figure 6. 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 with the standard from previous study [20]. The peaks in the gas chromatogram were examined by introducing compounds from the reaction between FAME with TMP.

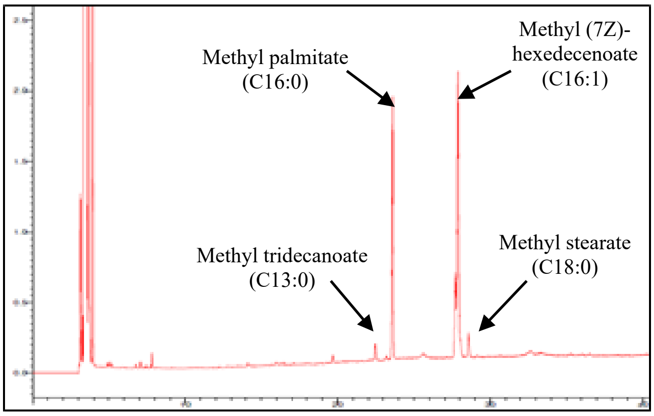

Figure 6. GC-MS chromatogram of WCOME based biolubricant synthesis at temperature 150ºC for 4 h

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)-hexedecenoate (42.06%), methyl stearate (4.58%), and methyl tridecanoate (0.83%). Overall, biolubricant synthesized from WCOME based produced a mass fraction of 57.93% for saturated FAME and a mass fraction of 42.06% for unsaturated FAME. From the analysis, it can be concluded that higher saturation content in the biolubricant product will lead to higher resistance towards oxidative-thermal treatment [14]. On top of that, high degree of saturated FAME also could develop a lubricant with high biodegradability and good low temperature performance [21].

Table 1
The percentage composition of FAME in WCOME based biolubricant

FAME name and formula	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 (7Z)-	42.06

methyl ester (C16:1)	hexadecenoate

E. The Effect of Molar Ratio on the Transesterification Reaction of WCOME based Biolubricant

Based on the general transesterification reaction, 3 mole of FAME is required with 1 mole of TMP to initiate a forward reaction. Investigations on the effect of molar ratio of FAME to TMP for the synthesis of WCOME based biolubricant were varied at three different ratio which are 3:1, 4:1 and 5:1 while all other conditions were kept constant throughout the experiment such as follows: temperature 150 ºC, 4 h reaction time and 2% (wt/wt) of *p*-TSA as catalyst. Figure 7 describes the result achieved in terms of percent conversion of FAME against molar ratio of FAME to TMP. From the resulting data, it could be observed that 3:1 ratio possess the highest conversion of 71%, 4:1 ratio at 46% conversion followed by 5% conversion occurred for 5:1 ratio.

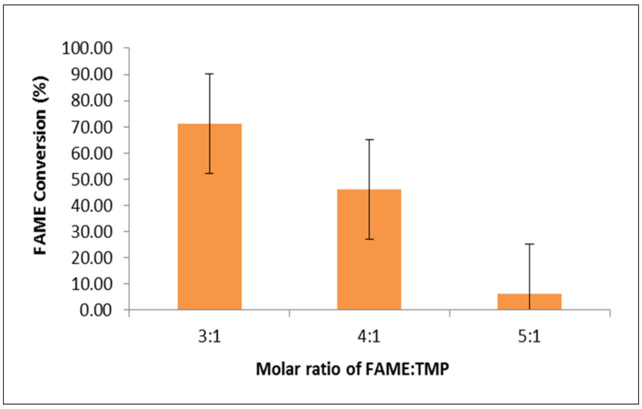

Figure 7. Effects of molar ratio of FAME:TMP on FAME conversion (WCO) at the following condition: time at 4 h, temperature of 150°C, molar ratio of 3 FAME:1 TMP and 2% (wt/wt) of *p*-TSA as catalyst.

Transesterification is a reversible reaction and is accomplished by mixing the reactants of FAME and TMP. Since the structural TMP consist of three hydroxyl groups, the reaction mechanism of transesterification reaction should follow three consecutive steps so that those hydroxyl groups can be substituted with ester group, cleaved from the structure of WCOME to produce the final product, TMP triester. The step mechanisms of reaction were as follows in equation 4, 5 and 6 [22]. TMP monoester (TMPME) is first produced and reacted in the second reaction, hence, TMP diester (TMPDE) is formed as the intermediate products. This intermediate product is next used to complete the reaction in producing TMP triester (TMPTE).

$$\text{WCOME} + \text{TMP} \leftrightarrow \text{ME} + \text{M} \quad (4)$$
$$\text{WCOME} + \text{TMPME} \leftrightarrow \text{TMPDE} + \text{M} \quad (5)$$
$$\text{WCOME} + \text{TMPDE} \leftrightarrow \text{TMPTE} + \text{M} \quad (6)$$

Based on the three steps of reaction, the overall reaction is:

$$3\ \text{WCOME} + 1\ \text{TMP} \leftrightarrow 1\ \text{TMPTE} + 3\ \text{M} \quad (7)$$

On account of the stoichiometric reaction, the production of biolubricant can be much better accomplished by conducting the experiment at higher molar ratio of reactants to enhance the reaction completion [4]. It is preferable to excess the amount of reactant as the reaction is reversible to cover any vaporize or loss subtance in reactant. However, the performance of this parameter shows that increasing molar ratio of FAME to TMP favours decreased in FAME conversion to product formation. This occurrence may be considered from the higher content of FAME in the reaction, promoting the dilution of TMP concentration in the system and decreasing in the collision probability of the nucleophilic particle [11]. Moreover, 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 increase in molar ratio of FAME:TMP had a negative impact for synthezing biolubricant based on the FAME conversion to the final product.

F. Comparative Study on Various Based Methyl Esters for Biolubricant Synthesis

The comparison of biolubricant from WCOME based and RSOME based were studied based on the same operating condition carried out at temperature 140ºC, 3:1 molar ratio of FAME:TMP, 4 h reaction time and 2% (wt/wt) of *p*-TSA as catalyst. Figure 8 conveys the comparative study of FAME conversion on both feedstocks, which are biolubricant derived from based of WCOME and RSOME.

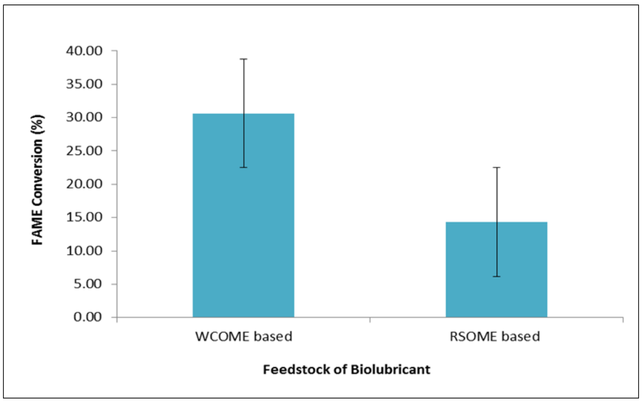

Figure 8. Comparative study of biolubricant feedstock on FAME conversion at the following condition: time at 4 h, temperature of 140ºC, molar ratio of 3 FAME:1 TMP and 2% (wt/wt) of *p*-TSA as catalyst.

The outcome of the experiment revealed that the production of biolubricant from WCOME based shows higher conversion at 31% than RSOME based at 14% on the same operating condition. The possible explanation is because the sample collected at the same temperature has turn out to be sludgy and viscous in terms of its oil structure. Likewise, higher reaction temperature could damage the appearance of the biolubricant and preventing a better yield of biolubricant [23]. Another reason that may contribute to lower conversion in RSOME based biolubricant is because the volatile component in the product has been vaporized as the experiment was handled at exact ratio instead of consuming the reactant in excess to generate a complete reaction into product. An early conclusion can be made is that RSOME based biolubricant might run the experiment lower than the stated temperature. On the other hand, chemical transesterification reaction usually requires a minor excess of reactant as under these conditions, the molar ratio of FAME probably higher than 3 mole and lower than 4 mole as beyond this, it could lower down the FAME conversion towards product synthesis.

G. Properties of Biolubricant

The properties of synthesized biolubricant were evaluated based on ASTM methods. The comparison of WCOME and RSOME based biolubricant were compared to an industrial lubricant ISO VG46. ISO VG46 is a grade lubricant which normally utilize for light gear applications, crankcase and as hydraulic fluid [12]. The overall result was tabulated in table 2.

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 ºC (cSt)	62.56	40.2	>41.4
Cloud Point (ºC)	14	2	N/A
Pour Point (ºC)	8	-4	-6

Viscosity is one of the important criteria to look for in selecting a lubricant. In this study, kinematic viscosity at 40ºC was measured by applying ASTM D445 method [24]. Viscosity of WCOME based biolubricant was found at 62.56 cSt where it is comparable to the specification of industrial oil ISO VG46. Viscosity of RSOME based biolubricant was determined at 40.2 cSt. Likewise, the study of biolubricant from rubber seed was reported by [5]. This shows a good comparison for RSO based biolubricant produced with other rubber seed oil based biolubricant.

Cloud point is analyzed by ASTM D97 method [25]. Cloud point obtained is higher compared to the previous study in synthesizing WCOME biolubricant [26]. It tells that triglyceride of WCOME is susceptible to form macro crystalline structures at low temperature that will limit the flow of the fluid cause by the loss of kinetic energy of individual molecules.

Another property to be observed is pour point. This property is a concern to measure the flow properties of a fluid at low temperature which has been conducted similar to cloud point. As shown in the table, the pour point of WCOME and RSOME based biolubricant is 8ºC and -4ºC, respectively. The previous study that derived biolubricant from WCOME shows a lower pour point at -3ºC [27]. Lower pour point was also obtained for RSOME based biolubricant which is -6ºC [5]. This shows that higher pour point is achieved in this study probably contributed from the higher level of saturation since the biolubricant consist of high palmitic content (52.52%) as it removes the effect of Cis-unsaturation in biolubricant [14]. A good lubricant should possess a low pour point so that any solid form is not allowed in pipeline transportation during cold weather. This condition is attainable by the usage of shorter chain length with a greater branching degree of carboxylic acid [28]. A similar finding was also found where higher pour point increase its thermal stability and can endure mechanical stress better than petroleum lubricants [29]

CONCLUSION

Expansion in using two-steps transesterification process provides a cost saving method for synthesis of biolubricant since non-edible vegetable oil based can be used as the feedstock without having substantial impact towards environment issue. In transesterification reaction, temperature and molar ratio are the variables that display significant impact towards the product completion. The properties of synthesized biolubricant are much better to meet the requirement of the standard lubricant as it is safer to be used for industrial lubricant. Biolubricant establishment from feedstock based of WCOME and RSOME by acid-catalyzed transesterification in the current study shows a promising alternative to replace the market lubricant as well as fulfill the current demand and improving the oil performance. Additionally, the characteristic of the lubricant properties were comparable and did not shows significant difference in the biolubricant performance. In fact, this is one of the examples of support in the production of biolubricant along with the encouragement for further research on using renewable natural sources. For further research on biolubricant, it is highly recommended to utilize the non-edible based since the competition is much less within other agricultural resources as well as intensely study on variety ways and condition to produce a great biolubricant for future industry.

REFERENCES

[1] E. Wang *et al.*, “Synthesis and oxidative stability of trimethylolpropane fatty acid triester as a biolubricant base oil from waste cooking oil,” *Biomass and Bioenergy*, vol. 66, pp. 371–378, 2014.

[2] J. McNutt and Q. S. He, “Development of biolubricants from vegetable oils via chemical modification,” *J. Ind. Eng. Chem.*, vol. 36, pp. 1–12, 2016.

[3] N. Salih, J. Salimon, and F. N. Jantan, “Synthesis and characterization of palm kernel oil based trimethylolpropane ester,” *Asian J. Chem.*, vol. 25, no. 17, pp. 9751–9754, 2013.

[4] M. C. Menkiti, O. Ocheje, and C. M. Agu, “Production of environmentally adapted lubricant basestock from jatropha curcas specie seed oil,” *Int. J. Ind. Chem.*, vol. 8, no. 2, pp. 133–144, 2017.

[5] K. Kamalakar, A. K. Rajak, R. B. N. Prasad, and M. S. L. Karuna, “Rubber seed oil-based biolubricant base stocks: A potential source for hydraulic oils,” *Ind. Crops Prod.*, vol. 51, pp. 249–257, 2013.

[6] U. C. Sharma, S. Sachan, and R. K. Trivedi, “Viscous flow behaviour of karanja oil based biolubricant base oil,” *J. Oleo Sci.*, vol. 67, no. 1, pp. 105–111, 2018.

[7] Y. Wang, C. Zhou, G. Zheng, and Y. Sun, “Synthesis and Optimization of Trimethylolpropane Rapeseed Oil Ester,” *Adv. Mater. Res.*, vol. 1015, pp. 610–614, 2014.

[8] G. S. Dodos, F. Zannikos, and E. Lois, “Utilization of Sesame Oil for the Production of Bio-based Fuels and Lubricants,” *3rd Int. CEMEPE SECOTOX Conf.*, vol. 1, no. 1, pp. 623–628, 2011.

[9] D. Karonis and D. Chilari, “A Comparison Between Of Sodium Methoxide And Sodium Hydroxide Catalysts For Ethyl Esters Production,” no. September, pp. 5–7, 2013.

[10] V. B. V. Ivana B. Bankovi´c-Ili ´c, Olivera S. Stamenkovi´c, “Biodiesel production from non-edible plant oils,” *Renew. Sustain. Energy Rev.*, pp. 3621– 3647, 2012.

[11] S. Qiao, Y. Shi, X. Wang, Z. Lin, and Y. Jiang, “Synthesis of Biolubricant Trimethylolpropane Trioleate and Its Lubricant Base Oil Properties,” *Energy & Fuels*, vol. 31, no. 7, pp. 7185–7190, 2017.

[12] M. F. M. Gunam Resul, T. I. Mohd. Ghazi, and A. Idris, “Kinetic study of jatropha biolubricant from transesterification of jatropha curcas oil with trimethylolpropane: Effects of temperature,” *Ind. Crops Prod.*, vol. 38, pp. 87–92, 2012.

[13] T. Panchal, D. Chauhan, M. Thomas, and J. Patel, “Bio based grease A value added product from renewable resources,” *Ind. Crop. Prod.*, 2014.

[14] E. K. Heikal, M. S. Elmelawy, S. A. Khalil, and N. M. Elbasuny, “Manufacturing of environment friendly biolubricants from vegetable oils,” *Egypt. J. Pet.*, vol. 26, no. 1, pp. 53–59, 2017.

[15] H. Masood, R. Yunus, T. S. Y. Choong, U. Rashid, and Y. H. Taufiq, “Synthesis and characterization of calcium methoxide as heterogeneous catalyst for trimethylolpropane esters conversion reaction,” *Appl. Catal. A Gen.*, vol. 425–426, pp. 184–190, 2012.

[16] S. E. Sanni, E. Emetere, V. E. Efeovbokhan, and J. D. Udonne, “Process Optimization of the Transesterification Processes of Palm Kernel and Soybean Oils for Lube Oil Synthesis,” *Int. J. Appl. Eng. Res.*, vol. 12, no. 14, pp. 4113–4129, 2017.

[17] U. Musa, I. A. Mohammed, M. M. Sadiq, F. Aberuagba, A. O. Olurinde, and R. Obamina, “Synthesis and Characterization of Trimethylolpropane-Based Biolubricants from Castor Oil,” *Proc. 45th Annu. Conf. NSChE*, pp. 248–253, 2015.

[18] K. L. Theam, A. Islam, Y. M. Choo, and Y. H. Taufiq-Yap, “Biodiesel from low cost palm stearin using metal doped methoxide solid catalyst,” *Ind. Crops Prod.*, vol. 76, pp. 281–289, 2015.

[19] R. Yunus and A. Idris, “Preparation and Characterization of Trimethylolpropane Esters From Palm Kernel Oil Methyl Esters,” *J. Palm Oil Res.*, vol. 15, no. December, pp. 42–49, 2003.

[20] R. Yunus, O. T. Lye, A. Fakhru’l-Razi, and S. Basri, “A simple capillary column GC method for analysis of palm oil-based polyol esters,” *J. Am. Oil Chem. Soc.*, vol. 79, no. 11, pp. 1075–1080, 2002.

[21] P. Nagendramma and S. Kaul, “Development of ecofriendly/biodegradable lubricants: An overview,” *Renew. Sustain. Energy Rev.*, vol. 16, no. 1, pp. 764–774, 2012.

[22] M. F. M. G. Resul, T. I. M. Ghazi, and A. Idris, “Temperature

dependence on the synthesis of jatropha biolubricant," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 17, no. 1, 2011.

[23] T.-S. Chang, H. Masood, R. Yunus, U. Rashid, T. S. Y. Choong, and D. R. A. Biak, "Activity of Calcium Methoxide Catalyst for Synthesis of High Oleic Palm Oil Based Trimethylolpropane Triesters as Lubricant Base Stock," *Ind. Eng. Chem. Res.*, vol. 51, no. 15, pp. 5438–5442, 2012.

[24] ASTM International, "Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)," 2011.

[25] ASTM International, "Standard Test Method for Pour Point of Petroleum Products," 2013.

[26] W. Li and X. Wang, "Bio-lubricants Derived from Waste Cooking Oil with Improved Oxidation Stability and Low-temperature Properties," *J. Oleo Sci. J. Oleo Sci*, vol. 64, no. 4, pp. 367–374, 2015.

[27] V. B. Borugadda and V. V. Goud, "Improved thermo-oxidative stability of structurally modified waste cooking oil methyl esters for bio-lubricant application," *J. Clean. Prod.*, vol. 112, pp. 4515–4524, 2016.

[28] D. Kania, R. Yunus, R. Omar, S. Abdul, and B. Mohamad, "A review of biolubricants in drilling fluids : Recent research , performance , and applications," *J. Pet. Sci. Eng.*, vol. 135, pp. 177–184, 2015.

[29] M. B. Alang, M. K. Ndikontar, Y. M. Sani, and P. T. Ndifon, "Synthesis and Characterisation of a Biolubricant from Cameroon Palm Kernel Seed Oil Using a Locally Produced Base Catalyst from Plantain Peelings," *Green Sustain. Chem.*, vol. 8, pp. 275–287, 2018.