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Synthesis And Characterization Of Ester Trimethylolpropane Based *Jatropha Curcas* Oil As Biolubricant Base Stocks

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Abstract

Biolubricant production of ester trimethylolpropane (ET) was conducted via esterification of fatty acid (FA) of *Jatropha curcas* oil with trimethylolpropane (TMP). The condition for this reaction was as follows: temperature was 150°C, time of reaction was 3 hours, molar ratio of FA: TMP was 4:1, and 2 % w/w catalyst (based on weight of FA). Sulfuric acid was used as the catalyst in this reaction. The composition of ET was determined by gas chromatography (GC-FID). The ester group was confirmed by fourier transform infrared spectroscopy (FTIR) and the structure was confirmed by proton and carbon Nuclear Magnetic Resonance (^{1}H-NMR and ^{13}C-NMR) spectra. 55% of product was successfully synthesized in this research. The pour point of the product was observed as low as –30°C, flash point was >300 °C and viscosity was 79 cP.

Keywords: *Jatropha curcas*; biolubricant; *Jatropha* oil fatty acid; ester trimethylolpropane.

1 INTRODUCTION

Increase awareness among the community of environmental pollution by petroleum-based oils for use as industrial lubricants cause the switch to vegetable oil which is more environmentally friendly. The searching for using alternative sources in the preparation of lubricants has begun to actively investigate. Bioubricant production using vegetable oil gives the various advantages that is the source of renewable, cheap, biodegradated and no adverse effects on nature [1]. The problems faced by vegetable oil are that it has low thermal and oxidative stability due to the existing double bond [2] and the presence of active sites in the β hydrogen of triasilgliserol ester. To overcome this problem, modifications to the study carried out on crude oil to produce better quality of biolubricant which has better oxidative stability and pour point.

In this study, *Jatropha curcas* oil (JCO) is used as the source for the biolubricant production. *Jatropha curcas* is a species of the family *Euphorbiaceae* which is widely grown in South America, South-West Asia, India and Africa. This species has a high resistance to hot and dry climate. It can grow in many places, even in arid or sandy soil. Oil from *Jatropha* seeds is a valuable product with features that have low acidity, high oxidative stability compared to soybean oil, low viscosity compared with castor oil, and better cooling characteristics of palm oil. Fatty acids contained in crude oil are 42-44% oleic acid, linoleic acid 33-34% and 6-7% saturated fatty acids [3]. The observed major triacylglycerol (TAG) composition was PLL (20.40%) and OOL (17.98%) [4]. The oil was used as a diesel substitute during the World War II. JCO is locally available and non-edible of vegetable oil. The utilisation of non-edible and renewable crops such as *Jatropha* is expected to minimize the problem which is the utilisation of edible food crops (corn, soya, etc.) for the production of biofuels are expected to create a short supply of food for human consumption. In addition, increased environmental awareness and diminishing petroleum resources that leads to increased research on alternative non edible crops for biofuel production [5].

However, due to the presence of hydrogen in the structure of glycerol-β of the oil which is causing the oil has low thermal and oxidative stability, fatty acid of *Jatropha curcas* oil will be reacted with a polyol such as trimethylolpropane (TMP) to produce ester TMP. TMP polyol is selected because of the branching structure and has a low melting point. Polyol esters are excellent substitutes for mineral oils because of their low volatility, high flash point, good thermal stability, low toxicity, and excellent biodegradability [6]. Previous study have been reported that chemical modification such as transesterification of vegetable oils with polyols has shown increased

levels of oxidative stability of vegetable oil-based lubricants [7]. Among the methods that can be used to improve the properties of vegetable oil as biolubricant is to change the structure of the oil to polyol ester of the branched polyol. The absence of a hydrogen atom at carbon-β in the structure of the ester oil is made with high thermal and oxidative stability [8].

Previous study has been reported that ester production was carried out by esterification reaction of TMP with isovaleric acid and n-valerik. 85% of the esters produced by using 7% sodium bisulphate catalyst at a temperature of 110-120 °C for 2 hours. The use of 1% sulfuric acid catalyst in the same reaction resulted in 78% ester at a temperature of 110-120 °C for 60 hours [9]. There are also the studies of TMP ester production carried out by transesterification reaction of palm oil methyl ester (POME) with trimetilolpropana (TMP) or palm kernel oil methyl esters (PKOME) with the yield of 98% triester (TE) [10]. Transesterification reaction is carried out at a temperature of 130 °C under a pressure of 20 mbar for 1 hour with the addition of 0.8% sodium methoxide catalyst [11]. Another study showed a 99% triester resulting from esterification reaction of rapeseed oil methyl ester with TMP. The reaction was carried out at temperature 110-120 °C for 10 hours under the pressure of 3.3 kPa with the addition of 0.5% catalyst sodium methylate [12]. The objective of this work was to study the esterification of fatty acid of *Jatropha curcas* oil (JCO) as starting material with trimethylolpropane by sulfuric acid as the catalyst for the production of biolubricant base stocks.

2 MATERIALS & METHODS

Jatropha curcas were obtained from House Plant at National University of Malaysia. Fatty acid was prepared according to PORIM Test Method [13]. Trimethylolpropane was purchased from Fluka, sulfuric acid was purchased from Systerm, toluene was purchased from Merck, ethyl acetate, sodium bicarbonate and sodium chloride was obtained from Systerm.

2.1 Fatty acid of Jatropha curcas

A two stage process was used in the preparation of fatty acid of *Jatropha curcas* oil. The first step was saponification with alkaline-ethanol solution that were refluxed for two hours. Then, the next step was hydrolysis. The hidrolysis reaction involves the uses of water and acidic solution to neutralized the alkaline solution. The solvent was then removed using rotary evaporator under reduced pressure at temperature of 70 °C. The sample was determined from the FTIR spectroscopy.

2.2 Esterification of fatty acid of Jatropha curcas oil with Trimethylolpropane (TMP)

The esterification reaction in this study was refer according to Itsikson et al. 1967 [9]. The reaction was performed in a three necked round bottom flask equipped with a Dean and Stark water separator. Twenty gram of fatty acid, known amount of TMP and toluene were placed in the flask under constant stirring provided by the magnetic stirrer. The weight of TMP was determined based on the required molar ratio of the fatty acid. The toluene used as azeotroping agent in this reaction. The temperature was raised to the boiling point of the reaction mixture after which the catalyst was added. The condition for this reaction was as follows: temperature was 150 °C, time of reaction was 3 hours molar ratio of FA:TMP was 4:1, and 2 % w/w catalyst (based on weight of FA). Sulfuric acid (H_2SO_4) was used as the catalyst in this reaction. When the reaction was completed, samples of reaction mixture were taken out and thoroughly washed with water and alkaline solution to remove catalyst. The solvent was removed using a rotary evaporator under reduced pressure at 80 °C.

2.3 Instrumentation

Samples were confirmed by FTIR (Figure 2), ^{1}H and ^{13}C NMR spectra (Figure 3 and Figure 4) and analysed at certain time intervals for fatty acid, monoesters (ME), diesters (DE), and triesters (TE) compositions (% peak area) by gas chromatography (Figure 5). The GC equipped with Flame Ionization Detector (FID) system was performed using the capillary column DB-5HT, 30 m × 0.25 mm, i.d. 0.10 µm (DB, United States). The oven temperature was set initially at 100 °C, held for 1 min, then increased at 5 °C/ min to 380 °C and held for another 25 min. The injector and detector temperatures were at 380 °C.

2.4 Lubrication Characteristics

The pour point, the flash point and the viscosity of the ester-TMP were measured according to ASTM D 97-87, ASTM D 92-05a and ASTM D 445 (Brookfield RV-I. A spindle of S03 was used at 100 rpm at room temperature) [14].

3 RESULTS & DISCUSSION

The presence of ester group of ester TMP is determined by the infrared spectrum (FTIR) as illustrated in Figure 1. Fatty acid reacted with

TMP using sulfuric acid as catalyst producing ester TMP and water as byproduct. 55% of product was successfully synthesized in this research. The comparison between the FTIR spectrums of fatty acid after hydrolysis with the spectrum of ester TMP after esterification is shown in Figure 2.

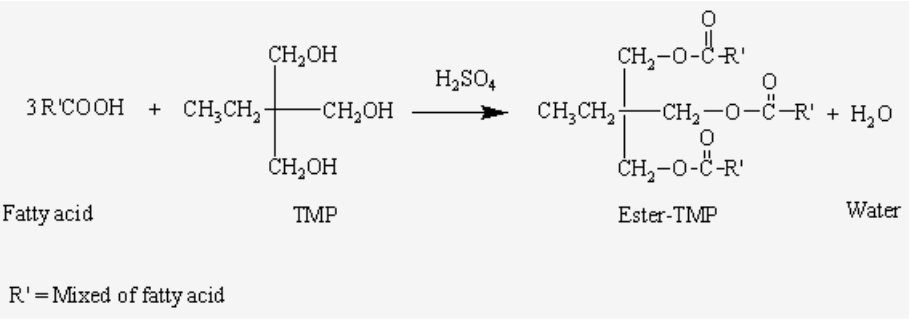

Figure 1 : Esterification of fatty acid (FA) of *Jatropha curcas* oil with trimethylolpropane (TMP).

Based on the comparison of the spectrum of FA with ET, the wavelength of the presence of alcohol, -OH (3300-3100 cm^{-1}) does not look directly at the spectrum of ester TMP. This indicates that the OH bond in TMP react fully with the fatty acids to form TMP triester. In addition, there is a shift in the wavelength of 1709 cm^{-1} for the spectrum of fatty acids to the wavelength of 1743 cm^{-1} for the spectrum of ester TMP. The value of 1709 cm^{-1} is carboxylic acid functional groups and after the process of esterification, ester formation produced at the wavelength 1743 cm^{-1}. There is also a wavelength that appears after the esterification is at 1056 cm^{-1} which is shows the functional group of the CO bond as the result of the formation of ester TMP [15].

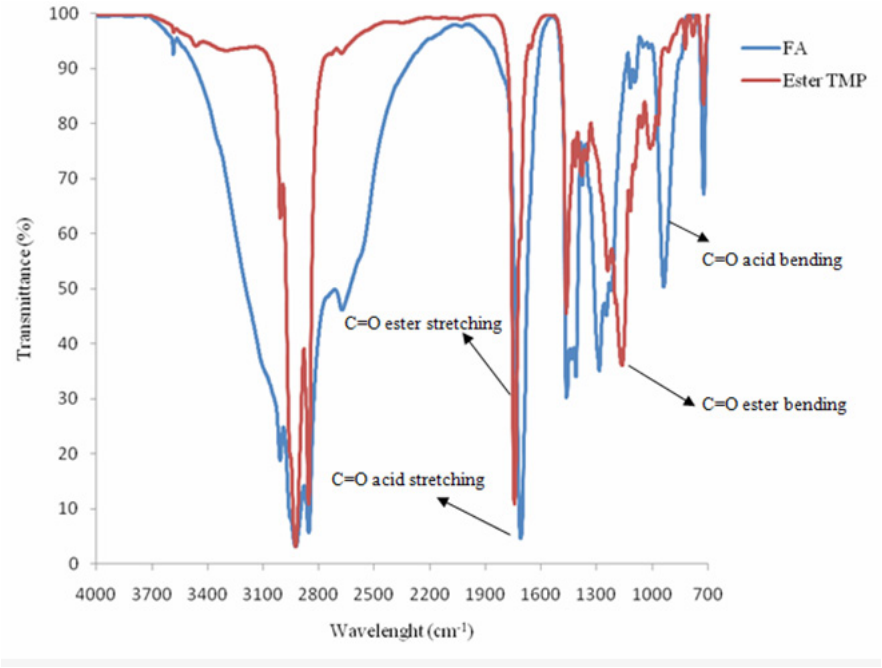

Figure 2 : Comparison between the IR spectra of fatty acid and ester TMP.

The use of NMR methods is very important for determining the molecular structure of a chemical as a whole. The result of merging data from infrared spectroscopy (to determine the function of a compound) and NMR (provides information on the number of each type of hydrogen) is sufficient to determine more about an unknown structure [16].

The resulting spectrum of ^{1}H NMR analysis that provides some important guidance in determining the structure for the ester TMP have been produced (Figure 3). The results of the analysis found that the existence of signals of methylene protons bound to –O of the carboxylic acid ester group,-OOR that is the major methyl ester of TMP in the study. Signals at 4.016 ppm are for the methylene protons at the (methylene) carbon are formed in ester TMP. Based on information from the software Chemdraw and the reference in Pavia et al. 2009, the value is respectively 4.00 ppm. Thus, the existence of the signal is then established that the ester product is ester TMP. Besides, proton signals at 5.3-5.4 ppm is appeared which is refer to the proton of C=C-H proton of olefin that the values are also present in the analysis Chemdraw and the reference in Pavia et al. 2009 [15].

^{13}C NMR spectrum also plays an important role in displaying the important features of ester TMP produced (Figure 4). Ester carbonyl signals in the range of 173-174 ppm are very important in this study. The signal at the range is representing the functional group ester carbonyl at the end of the esterification of TMP. In this study of polyol ester, ester carbonyl signals appear in the range of 173.5 ppm. According to the software Chemdraw, ester carbon signal is present at about 172 ppm. Based on the ^{13}C NMR spectrum, there is also a clear signal at 77.25 ppm, which refers to the chloroform signal, CDCl3. After successfully interpreting NMR data, the result of the expected ester TMP obtained are shown in Figure 3 and Figure 4.

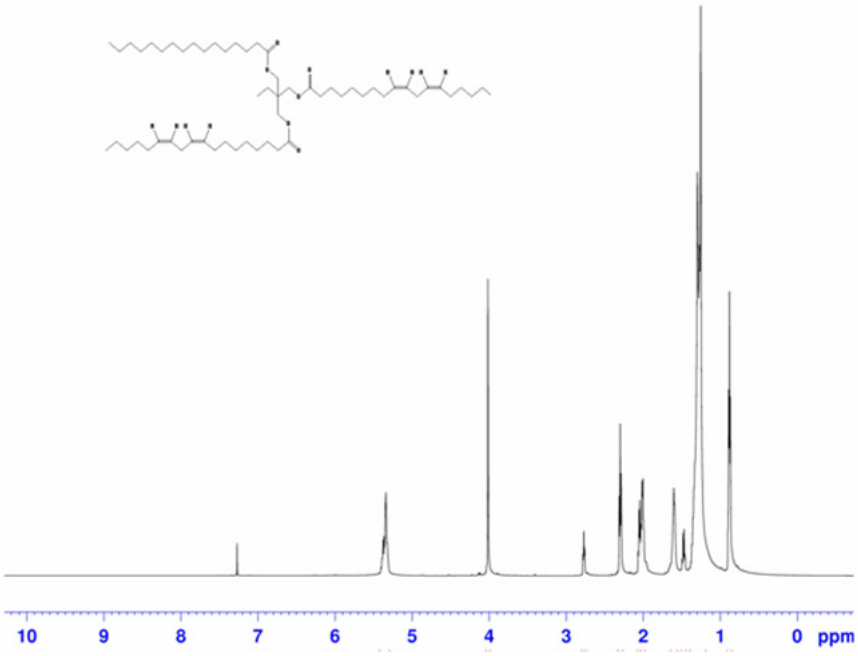

Figure 3 : The ^{1}H NMR spectra of ester TMP.

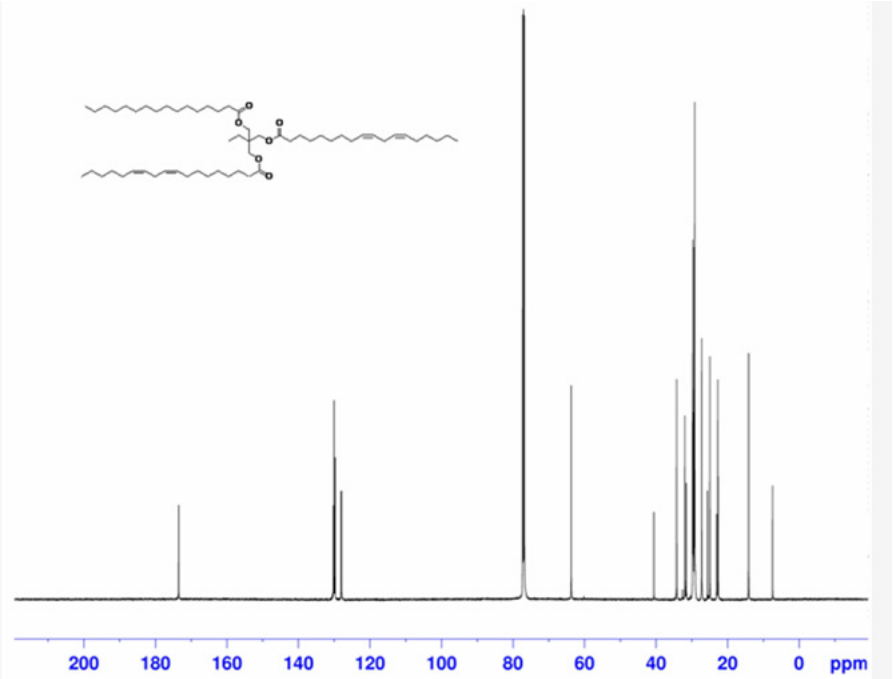

Figure 4 : The ^{13}C NMR spectra of ester TMP.

GC chromatogram of esters TMP is shown in Figure 5. The peaks appeared was identified and labeled based on the number of alkyl carbon groups that attached to TMP backbone. The esters formed are identified by making comparisons by standard or by using the standard of triglyceride (TG), diglycerides (DG) and monogliceride (MG) [17]. The composition of products containing 0.5% FA, 0.9% diester and 98.6% of triester (Table 1).

Table 1 : Composition of products of esterification of ester TMP.

Products	Percentage (%)
Fatty acid	0.5
Monoester	-
Diester	0.9
Triester	98.6

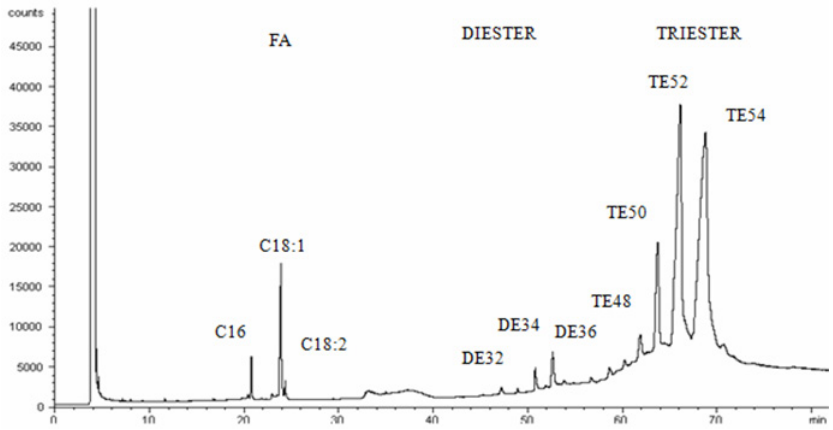

Figure 5 : GC chromatogram of ester TMP

3.1 Characterization of Biolubricant Base Stocks

The uses of branched chain are improving low temperature properties and hydrolytic stability. The higher degree of branching chain gives good low-temperature properties, high hydrolytic stability, and high viscosity index. In addition, the polar properties of a molecule capable of affecting the viscosity of polar molecule which is the higher viscosity [18]. Based on Table 2, the resulting viscosity of the ester TMP is 79 cP. Biolubricant produced from this study have a larger molecular chain and branched. Therefore, it has a higher molecular mass compared to the original structure of JCO. This resulted in viscosity values were also higher than the oil.

Table 2 : Characterization of JCO, FA and ester TMP as biolubricant base stocks.

Characterization	JCO	FA	ESTER TMP
Pour point (°C)	10	25	-30
Flash point (°C)	270	200	>300
Viscosity (cp)	77	55	79

The pour point of ester TMP obtained in this study is -30°C. Formation of a complex chain and branched oils will have a lower pour point [19]. At low temperature, oil composition capable of forming macrocistal for a uniform chain. The existence of branches in the fatty acid chains is able to retard the process of composition and temperature affect the extent of repairs to the cast. This is because the presence of branches was able to create barriers

around the congestion of each molecule and prevent crystallization. Therefore, the temperature will lower the pour point [18].

The results of the analysis found that the flash point of ester TMP produced was >300°C which is greater than origin oil. Flash point is influenced by the number of carbon contained in the structure. The more the number of carbon, the higher the flash point. The high values of flash point indicate that the resulting ester TMP has a high potential for the production of lubricants.

4 CONCLUSIONS

In this study, 55% of product was successfully synthesized in this research using fatty acid of *Jatropha curcas* oil with trimethylolpropane in the presence of sulfuric acid as catalyst. The results obtain suggest that the following reaction time: 3 hours, temperature: 150 °C, molar ratio of FA: TMP is 4:1 and catalyst concentration: 2 % w/w (based on weight of FA) are sufficient for the esterification of ester TMP as biolubricant base stocks. In addition, the pour point of the product was observed as low as –30°C, flash point is >300°C and viscosity is 79 cP that resulting ester TMP has a high potential for the production of lubricants.

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