



# The Effects of Various Acid Catalyst on the Esterification of *Jatropha Curcas* Oil based Trimethylolpropane Ester as Biolubricant Base Stock

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**Abstract:** Biolubricant production of trimethylolpropane ester (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% wt/wt concentrated catalyst (based on weight of FA). Different catalyst was used in this reaction such as perchloric acid, sulfuric acid, *p*-toluenesulfonic acid, hydrochloric acid, and nitric acid. 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 (<sup>1</sup>H-NMR and <sup>13</sup>C-NMR) spectra. 70% of ET was successfully synthesized using perchloric acid in this research. The pour point of the product was observed as low as -23 °C, flash point is >300 °C and viscosity index is 150.

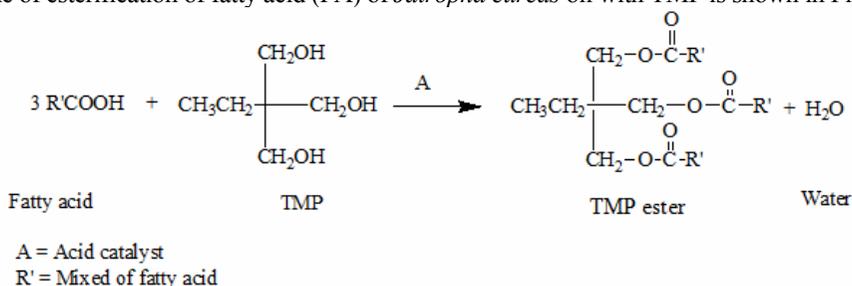
**Keywords:** *Jatropha curcas*, Biolubricant, *Jatropha* oil fatty acid, Esterification, Trimethylolpropane ester

## 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 environmental friendly. The searching for using alternative sources in the preparation of lubricants has begun to actively investigate. Biolubricant production using vegetable oil gives the various advantages that is the source of renewable, cheap, biodegraded and no adverse effects on nature<sup>1</sup>. The problems faced by vegetable oil are that it has low thermal and oxidative stability due to the existing double bond<sup>2</sup> and the presence of active sites in the  $\beta$  hydrogen of triacylglycerol 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 gives valuable products 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 content in crude oil are 42-44% oleic acid, linoleic acid 33-34% and 6-7% saturated fatty acids<sup>3</sup>. The observed major triacylglycerol (TAG) composition was PLL (20.40%) and OOL (17.98%)<sup>4</sup>. The oil was used as a diesel substitute during the World War II. JCO is available locally and it is non-edible vegetable oil due to its high toxicity. The utilisation of non-edible and renewable crops such as *Jatropha* in biofuels production is crucial to minimize the utilisation of edible food crops (corn, soya, *etc.*) as it is expected to create a short supply of food for human consumption. In addition, increasing environmental awareness and diminishing petroleum resources leads research on alternative non edible crops for biofuel production<sup>5</sup>.

However, due to the presence of hydrogen in the structure of glycerol- $\beta$  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 TMP ester. 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<sup>6</sup>. Chemical modification such as transesterification of vegetable oils with polyols has shown increased levels of oxidative stability of vegetable oil-based lubricants<sup>7</sup>. 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- $\beta$  in the structure of the ester oil is made with high thermal and oxidative stability<sup>8</sup>. The scheme of esterification of fatty acid (FA) of *Jatropha curcas* oil with TMP is shown in Figure 1.



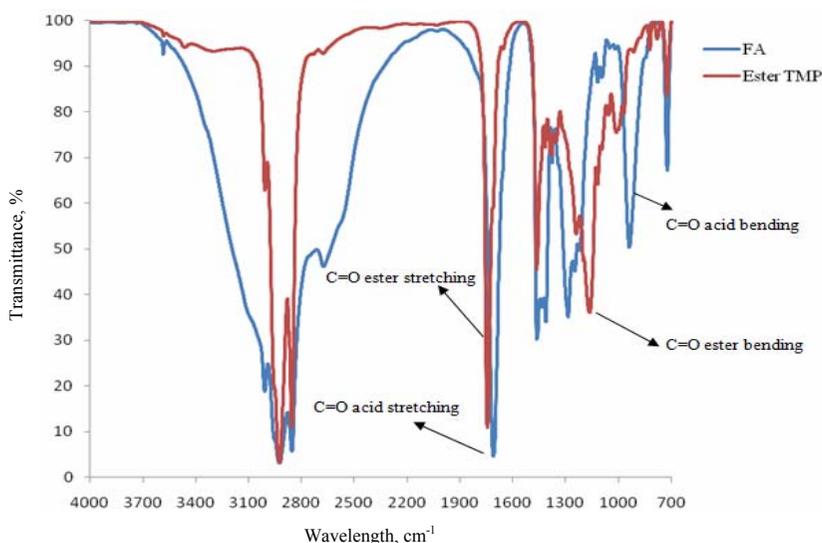
**Figure 1.** Esterification of fatty acid (FA) of *Jatropha curcas* oil with trimethylolpropane (TMP)

Esterification reactions are normally catalysed by acidic or basic based catalysts. The most common acid catalysts are *p*-toluenesulphonic acid, phosphoric acid, sulphuric acid, sodium hydroxide, sodium ethoxide and sodium methoxide<sup>9</sup>. Using basic homogenous catalyst would result in high amounts of soap formation in the reaction. This is due to this feedstock has a high amount of free fatty acid (FFA) which is much higher than the maximum amount suitable to be used with basic homogeneous catalysts. Therefore, alternative ways should be employed, to avoid this reaction, for example with a homogeneous acid catalyst, solid resins, or enzymes<sup>10</sup>. For enzyme catalyst's, the features of the substrates selected influence the properties of the ester manufactured.

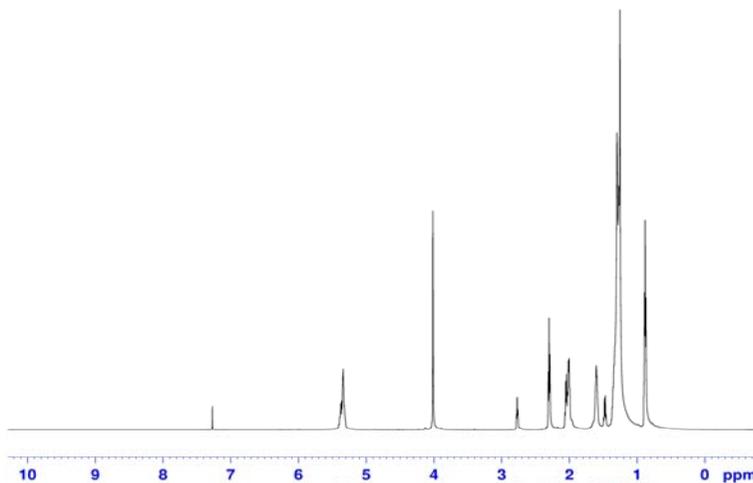
Previous study has been reported that ester production was carried out by esterification reaction of TMP with isovaleric acid and *n*-valerik. 85% of the esters produced by using 7% sodium bisulphate catalyst at a temperature of 110-120 °C for 2 hours. The use of 1% sulfuric acid catalyst in the same reaction resulted in 78% ester at a temperature of 110-120 °C for 60 hours<sup>11</sup>. 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)<sup>12</sup>. 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<sup>13</sup>. 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<sup>14</sup>. In this paper, we report the effects of various acid catalyst on the esterification of *Jatropha curcas* oil based trimethylolpropane ester as biolubricant base stock.

## Experimental

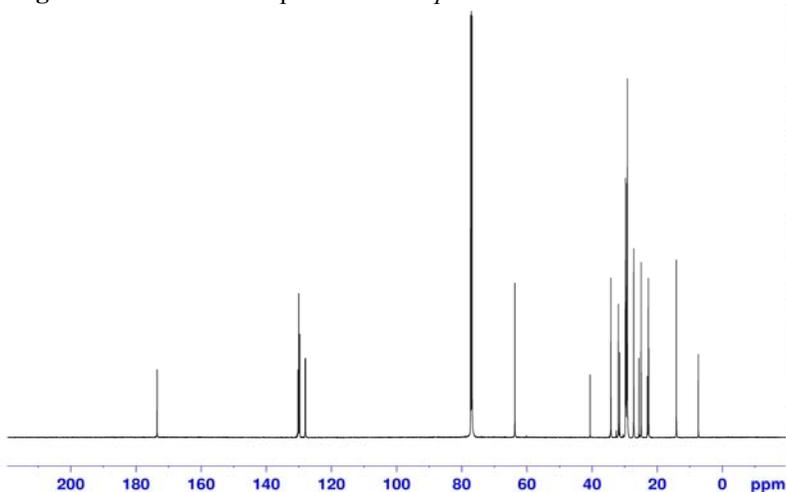
*Jatropha curcas* were obtained from House Plant in National University of Malaysia. Fatty acid was prepared according to modified PORIM Test Method<sup>15</sup>. TMP was purchased from Fluka, perchloric acid, sulfuric acid, *p*-toluenesulfonic acid, hydrochloric acid nitric acid, ethyl acetate, sodium bicarbonate and sodium chloride was purchased from System, and toluene was purchased from Merck. Samples were confirmed by FTIR (Figure 2), <sup>1</sup>H and <sup>13</sup>C NMR spectra (Figure 3 and Figure 4) and analysed at certain time intervals for fatty acid (FA), monoesters (ME), diesters (DE) and triesters (TE) 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.



**Figure 2.** The comparison between the IR spectra of *Jatropha curcas* oil fatty acid and *Jatropha curcas* oil based TMP ester



**Figure 3.** The  $^1\text{H}$  NMR spectra of *Jatropha curcas* oil based TMP ester



**Figure 4.** The  $^{13}\text{C}$  NMR spectra of *Jatropha curcas* oil based TMP ester

A two stage process was used in the preparation of 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.

The esterification reaction in this study was refer according to Itsikson *et al.* 1967<sup>11</sup>. 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 azeotropic 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% wt/wt catalyst (based on weight of FA). Different catalyst was used in this reaction such as perchloric acid, sulfuric acid, *p*-toluenesulfonic acid, hydrochloric acid and nitric acid. When the reaction was complete, the solution washed and neutralized using water and alkaline solution to remove catalyst. The solvent removed using a rotary evaporator under reduced pressure at 80 °C.

For the lubrication characteristics, the pour point, flash point, viscosity index, viscosity at 40 °C and 100 °C of the TMP ester were measured according to ASTM D 97, ASTM D 92 ASTM D 2270 and ASTM D 445 (Rheometer Model Anton Paar. A spindle of CP25-2 used at 40 °C and 100 °C at room temperature)<sup>16</sup>.

## Results and Discussion

The presence of ester group of TMP ester is determined by the infrared spectrum (FTIR). The comparison between the FTIR spectrums of fatty acid after hydrolysis with the spectrum of TMP ester after esterification is shown in Figure 2. Based on the comparison of the spectrum of FA with ET, the wavelength of the presence of alcohol, -OH (3300-3100  $\text{cm}^{-1}$ ) does not look directly at the spectrum of TMP ester. This indicates that the OH bond in TMP react fully with the fatty acids to form TMP ester.

In addition, there is a shift in the wavelength of 1711  $\text{cm}^{-1}$  for the spectrum of fatty acids to the wavelength of 1743  $\text{cm}^{-1}$  for the spectrum of TMP ester. The value of 1711  $\text{cm}^{-1}$  is carboxylic acid functional groups and after the process of esterification, ester formation produced at the wavelength 1743  $\text{cm}^{-1}$ . There is also a wavelength that appears after the esterification is at 1056  $\text{cm}^{-1}$  which shows the functional group of the CO bond as the result of the formation of TMP ester<sup>17</sup>.

The use of NMR methods is very important for determining the molecular structure of a chemical. 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<sup>18</sup>.

The resulting spectrum of <sup>1</sup>H NMR analysis that provides some important guidance in determining the structure for the TMP ester has been produced (Table 1). The results of the analysis found that the existence of signals of methylene protons bound to -O of the ester group, -OOR that is the major methyl ester of TMP in the study. Signals at 4.004 ppm are for the methylene protons at the (methylene) carbon are formed in TMP ester. Based on information from the software Chemdraw and the reference<sup>17</sup>, the value is respectively 4.00 ppm. Thus, the existence of the signal is then established that the ester product is TMP ester. 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<sup>17</sup>.

**Table 1.** <sup>1</sup>H-NMR data for *Jatropha curcas* oil based TMP ester.

Compound	Chemicals shifts, ppm	Chemical shift, ppm (Theoretical, Pavia <i>et al.</i> 2009)	Conclusion
ET	4.004	4.0	RCO-O-C-H (Ester)
	5.301, 5.356, 5.374	5.3-5.4	C=C-H

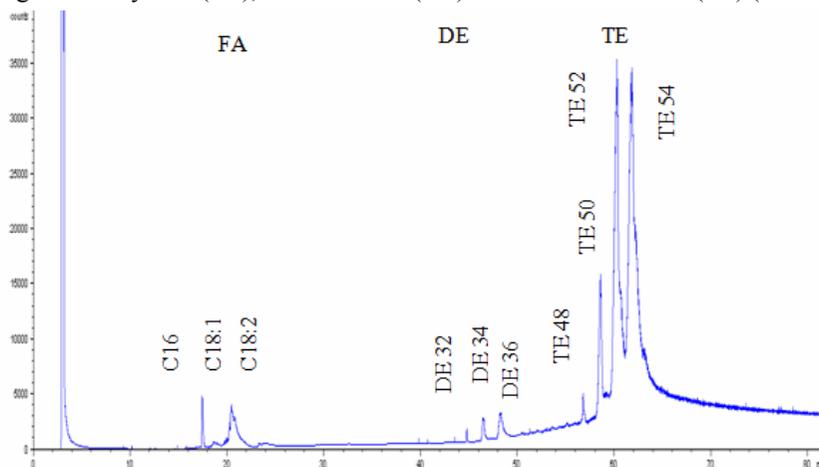
<sup>13</sup>C NMR spectrum also plays an important role in displaying the important features of TMP ester produced (Table 2). Ester carbonyl signals in the range of 173-174 ppm are very important in this study. The signal at the range is representing the functional group ester carbonyl at the end of 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  $^{13}\text{C}$  NMR spectrum, there is also a clear signal at 77.25 ppm, which refers to the chloroform signal,  $\text{CDCl}_3$ . After successfully interpreting NMR data, the result of the expected TMP ester obtained are shown in Table 1 and Table 2.

**Table 2.**  $^{13}\text{C}$ -NMR data for *Jatropha curcas* oil based TMP ester

Compound	Chemicals shifts, ppm	Chemical shift, ppm (Theoretical, Pavia <i>et al.</i> 2009)	Conclusion
ET	173.5	155-185	C=O ester

GC chromatogram of TMP ester 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 monoglyceride (MG)<sup>19</sup>. The composition of products containing 0.8% fatty acid (FA), 1.13% diester (DE) and 98.1% of triester (TE) (Table 3).



**Figure 5.** GC chromatogram of *Jatropha curcas* oil based TMP ester.

**Table 3.** Composition of products of esterification of TMP ester

Products	Percentage, %
Fatty acid	0.8
Monoester	-
Diester	1.13
Triester	98.1

The catalyst is an important factor in esterification of TMP ester. Perchloric acid, sulfuric acid, *p*-toluenesulfonic acid, hydrochloric acid and nitric acid were used in this study because they are strong acids. These catalyst is neutralized at the end of the reaction to separate the product. From Table 4, it was found that perchloric acid gives higher % yield of TMP ester compared to sulfuric acid, *p*-toluenesulfonic acid, hydrochloric acid and nitric acid. It gives 70% of ET, while sulfuric acid gives 46% yield of ET, *p*-toluenesulfonic acid gives 42% yield of ET, hydrochloric acid gives 41% yield of ET and nitric acid gives 37% yield of ET. Perchloric acid is the inorganic compound with the formula  $\text{HClO}_4$  is a strong acid in strength comparable to sulfuric and nitric acids which is one of the strongest Brønsted-Lowry

acids. It's pKa is  $-10^{20}$ . It provides strong acidity without interference from potential nucleophiles such as sulfate or chloride that complicate the use of sulfuric and hydrochloric acids. This acid are not susceptible to hydrolysis, whereas it's favor the forward reaction of the esterification, thus increasing the yield of ET in this study. Therefore, perchloric acid are suitable reagent for esterification of TMP ester to increase biolubricant production of the reaction.

**Table 4.** % yield of TMP ester based on catalyst used

Catalyst	Amount of catalyst, %wt/wt	*Yield, %
Perchloric acid	2	70
Sulfuric acid	2	46
<i>p</i> -toluenesulfonic acid	2	42
Hydrochloric acid	2	41
Nitric acid	2	37

*Reaction conditions- temperature: 150 °C, time: 3 hours, molar ratio of FA: TMP: 4:1 and 2% wt/wt catalyst (based on weight of FA). \*The % yield is based on the weight of the product (% wt/wt)*

For the 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<sup>21</sup>. Based on Table 5, the resulting viscosity of TMP ester at 40 °C and 100 °C are 63.1 cSt and 12.1 cSt respectively. 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 5.** Characterization of JCO, FA and TMP ester as biolubricant base stock

Characterization	JCO	TMP Ester
Pour point, °C	10	-23
Flash point, °C	200	>300
Viscosity at 40 °C (cSt)	36.4	63.1
Viscosity at 100 °C (cSt)	8.7	12.1
Viscosity Index	164	150

Pour point of TMP ester obtained in this study is -23 °C. Formation of a complex chain and branched oils will have a lower pour point<sup>22</sup>. 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. This is because the presence of branches was able to create barriers around the congestion of each molecule and prevent crystallization. Therefore, it will lower the pour point<sup>21</sup>.

The results of the analysis found that the flash point of TMP ester 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 TMP ester has a high potential for the production of lubricants.

## Conclusion

In this study, TMP ester was successfully synthesized in this research using fatty acid of *Jatropha curcas* oil with trimethylolpropane in the presence of perchloric acid as catalyst with 70% yields of product. The results obtain suggested that the following reaction time: 3

hours, temperature: 150 °C, molar ratio of FA: TMP is 4:1 and amount of catalyst: 2% wt/wt (based on weight of FA) using perchloric acid are sufficient for the esterification of TMP ester as biolubricant base stock. In addition, the pour point of the product was observed as low as – 23 °C, flash point is >300 °C and viscosity at 40 °C and 100 °C are 63.1 cSt and 12.1 cSt respectively that resulting TMP ester has a high potential for the production of lubricants.

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