

# Production of Lauric Acid and Pentaerythritol Based Biolubricant

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## Abstract

Production of a biolubricant based on lauric acid and pentaerythritol (PE) was carried out. The esterification reaction at 180°C-200°C for 6-7 hours in the presence of sulphuric acid as catalyst. The end product (PE ester) was confirmed through the determination of Fourier Transformation Infrared spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR), GC-FID. The characterization of PE ester's of viscosity index, pour point, flash point and oxidative stability. The PE ester showed flash point at 250°C, pour point at 25°C, viscosity index 162 and the oxidative stability at 216°C respectively. The PE ester produced is plausible to be used as potential biolubricant.

**Keywords:** biolubricant; lauric acid; pentaerythritol; pentaerythritol ester

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## 1. INTRODUCTION

Lubricant generally is a material in liquid form that been put in between two moving surface to mitigate the friction between the two surface and also prevent damages of the surfaces. Today's lubricants are a mixture of mixture of base fluids (90%) which is normally from petroleum and a range of other materials added to improve performance[1]. Nowadays the increasing demands on lubricant and the decreasing in minerals oils from petroleum production act as a major force for change to the development of lubricant based from oils and fats of vegetable and animal origin depending on the amphiphilic nature of those molecules chosen. Another strong factor is the biodegradability problems of minerals oils which when the lubricant is spilled or has to be dispose.

This kind of lubricant are called as biolubricant. Biolubricant production using vegetable oil gives the various advantages that is the source of renewable, cheap, biodegradated and no adverse effects on nature [2]. The problems faced by vegetable oil are that it has low thermal and oxidative stability due to the existing double bond [3] and the presence of active sites in the  $\beta$  hydrogen of triasilglicerol 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 Lauric acid is used as the main source for the biolubricant production, meanwhile pentarytritol is used as the additive to improve the problems faced by lauric acid to make great biolubricant. Lauric acid is a medium-chain ( $C_{12}$ ) saturated fatty acid whit the linear packed structure. Lauric acid did not have any double bond chains which make it in saturated acids groups. The main source of lauric acid is from coconut and palm kernel oil. Generally Lauric acid is non toxic, act as anti microb agent and safe to handle and also cheap. It's solid in room temperature and gradually melting in boiling water.

Lauric acid structure is not branched and contains no double bonds which make it happen to have high oxidative stability but bad in cold condition as it tend to form macro-crystal which prevent the lubrication in low temperature. Lauric acid is very environmental friendly and have been used in various industry. To turn Lauric acid into biolubricant some modification to overcome the problems been carried out. Due to the presence of hydrogen in the structure of glycerol- $\beta$  of the Lauric acid which is causing the oil has low thermal and oxidative stability, Lauric acid will be reacted with polyol such as Pentaerytritol (PE) to produce PE ester. PE polyol is selected because of the branching structure which also do not have any  $\beta$  hydrogen 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 [4]. 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 [5]. 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 [6].

Previous study has been reported that so many production of biolubricant from polyol ester. Usually the polyol that been used to produce biolubricant in previous research is trimethylpropane (TMP) , neopentyl glycol (NPG) and pentaerytritol (PE). The previous study from esterification of fatty acid and PE showed that the product contains 4 types of ester which is monoester, diester, triester and tetraester. This give more benefits to ester PE compared to TMP ester [7].

## **2. MATERIALS & METHODS**

Lauric acid were obtained by purchased from Riedel-de Haën. Pentaerytritol was purchased from Merck, sulfuric acid was purchased from System, toluene was purchased from Merck, ethyl acetate, sodium bicarbonate and sodium chloride was obtained from System.

### **2.1 Esterification of Lauric Acid with Pentaerytritol**

In this study direct esterification of fatty acid with polyhydric alcohol or polyol was chosen because it will help to ease the determination of ester functional group which attached with the product from the esterification using FT-IR. The esterification reaction in this study was refer according to Gryglewicz *et al.* (2003)[8] and some modification has been made to fulfill the need of study which taking other important information from Yunus *et al.* (2003)[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 PE and toluene were placed in the flask under constant stirring provided by the magnetic stirrer. The weight of PE 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 180 °C, time of reaction was 6 hours molar ratio of LA:PE was 4.9:1, and 2 % w/w catalyst (based on weight of LA). Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) 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 70 °C.

### 2.3 Instrumentation

Samples were confirmed by FTIR (Figure 2),  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Figure 3 and Figure 4) and analysed at certain time intervals for fatty acid, monoesters (ME), di-esters (DE), tri-esters (TrE) and tetra-ester (TtE) 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  $\times$  0.25 mm, i.d. 0.10  $\mu\text{m}$  (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.

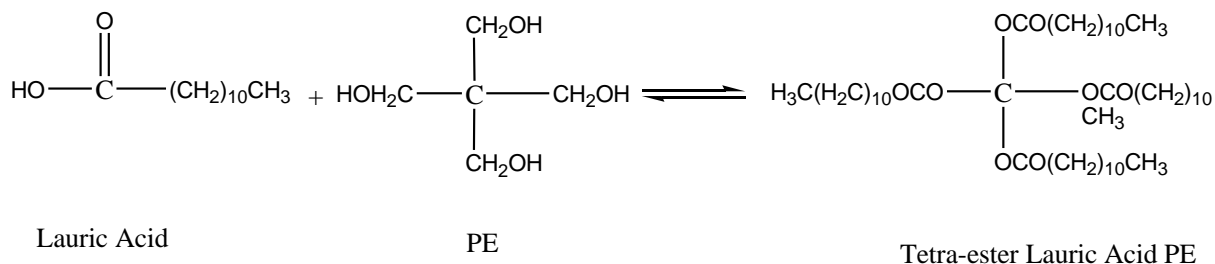
In this study also make the confirmation of physico-chemistry test which is using Thin Layer Chromatography (TLC) to compare with GC data obtained.

### 2.4 Lubrication Characteristics

The pour point, the flash point and the viscosity of the ester-PE were measured according to ASTM D 97-87, ASTM D 92-05a and ASTM D 445 (Brookfield RV-I. A spindle of S0<sub>3</sub> was used at 100 rpm at room temperature) [10]. The oxidative stability were measured using DSC.

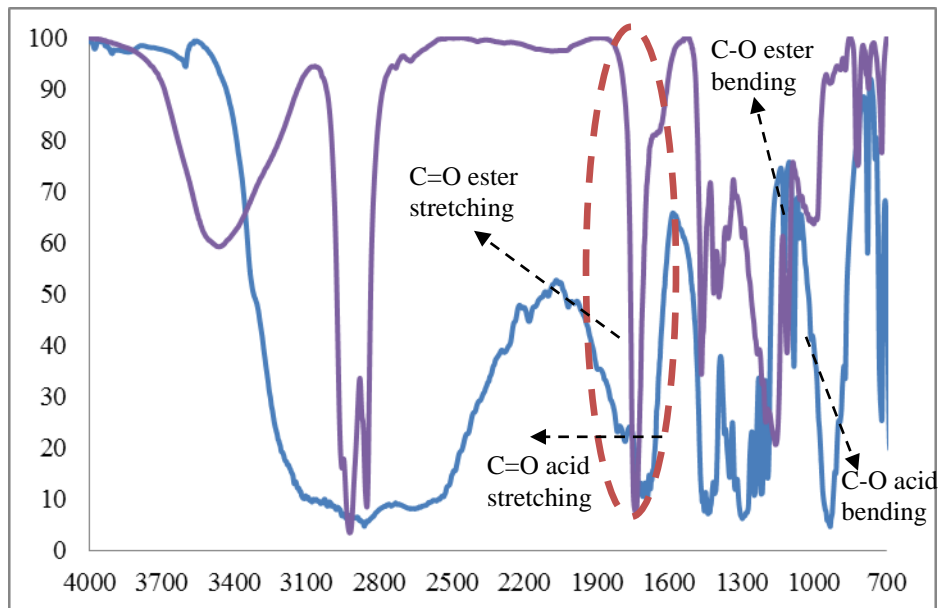
## 3. RESULTS & DISCUSSION

Fatty acid reacted with PE using sulfuric acid as catalyst producing PE ester and water as byproduct by using Den-Stark apparatus under nitrogen gas atmosphere. More than 55% of product yields was successfully synthesized in this research. The presence of ester group of PE ester is determined by the infrared spectrum (FTIR) as illustrated in Figure 1. The comparison between the FTIR spectrums of lauric acid and PE with the spectrum of PE ester after esterification is shown in Figure 2.



**Figure 1:** Esterification of Lauric Acid with PE

Based on the comparison of the FTIR spectrum of Lauric acid with PE, the wavelength of the presence of alcohol (-OH) ( $3300\text{-}3100\text{cm}^{-1}$ ) showed different bend shape from PE ester. This indicates that the -OH bond from PE is reacted with Lauric acid. From the spectrum also it also showed obvious shift in the wavelength of C=O stretch at the value of  $1692\text{ cm}^{-1}$  which shift the value of wavelength into  $1738\text{ cm}^{-1}$  after the esterification process done between lauric acid with PE. The existence of  $1738\text{ cm}^{-1}$  stretch wavelength proved the formation of ester as the according to Pavia et al. 2009 the formation of ester group wavelength is at  $1735\text{ cm}^{-1}\text{-}1740\text{ cm}^{-1}$ . In addition the value of  $1709\text{ cm}^{-1}$  is carboxylic acid functional groups and after the process of esterification, ester formation produced at the wavelength  $1738\text{ cm}^{-1}$ .



**Figure 2:** IR comparison spectrum of Lauric Acid and Ester PE

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 [11]. The resulting spectrum of  $^1\text{H}$  NMR analysis that provides some important guidance in determining the structure for the PE ester have been produced (Figure 3).

The results of the analysis found that the existence of signals of methylene protons bound to  $-\text{O}$  of the carboxylic acid ester group,  $-\text{OOR}$  that is the major ester of PE in the study. Signals at 4.0-4.6 ppm are for the methylene protons at the (methylene) carbon are formed in PE ester. Based on information from the software Chemdraw and the reference in Pavia et al. 2009 [11], the value is respectively 4.00 ppm. Thus, the existence of the signal is then established that the ester product is PE ester. Besides, proton signals at 2.038 ppm is appeared which is refer to the proton of  $-\text{OH}$  proton that the values are also present in the analysis Chemdraw and the reference in Pavia et al. 2009 [12]. While the signal proton at 7.269 is a signal from the chloroform,  $\text{CDCl}_3$  solvent that been used as solvent in sample dilution before NMR analysis was carried out. According to Lathi & Mattiasson (2007)[13] the existance of glycerol backbones can be detect at signal range at 4.0-4.44 ppm.

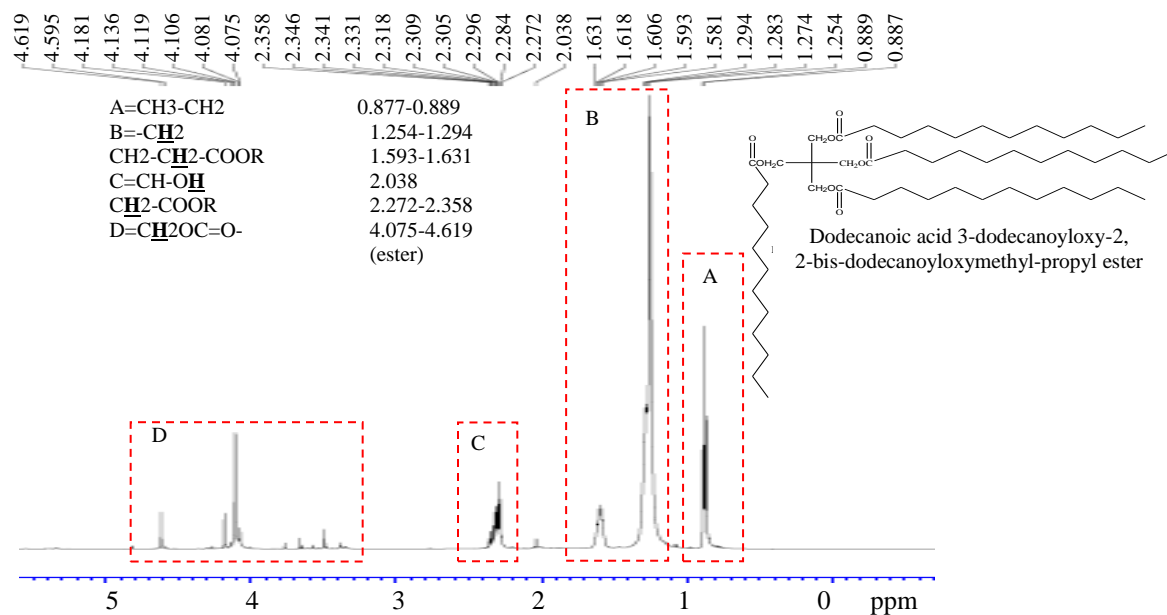
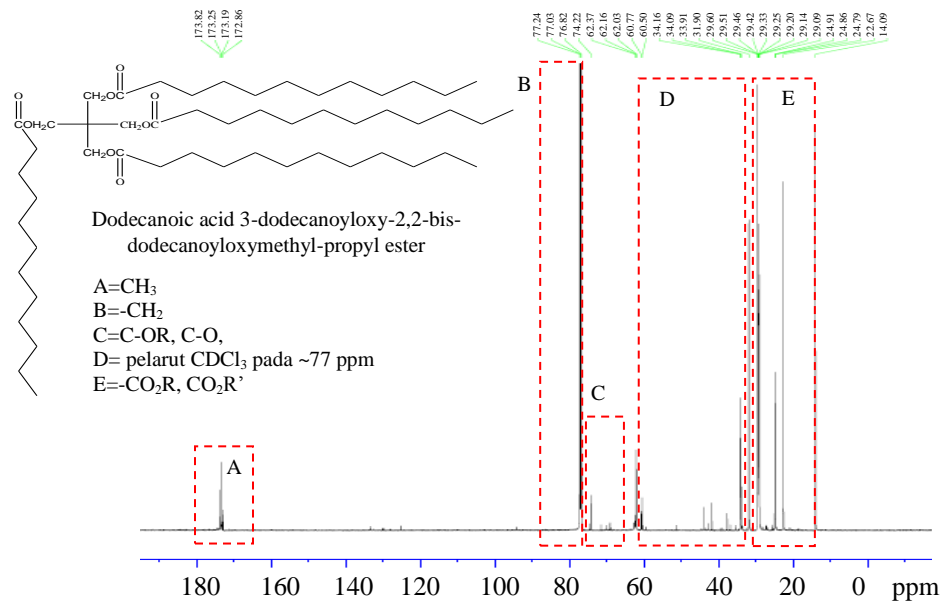


Figure 3:  $^1\text{H}$  NMR Ester PE Spectrum

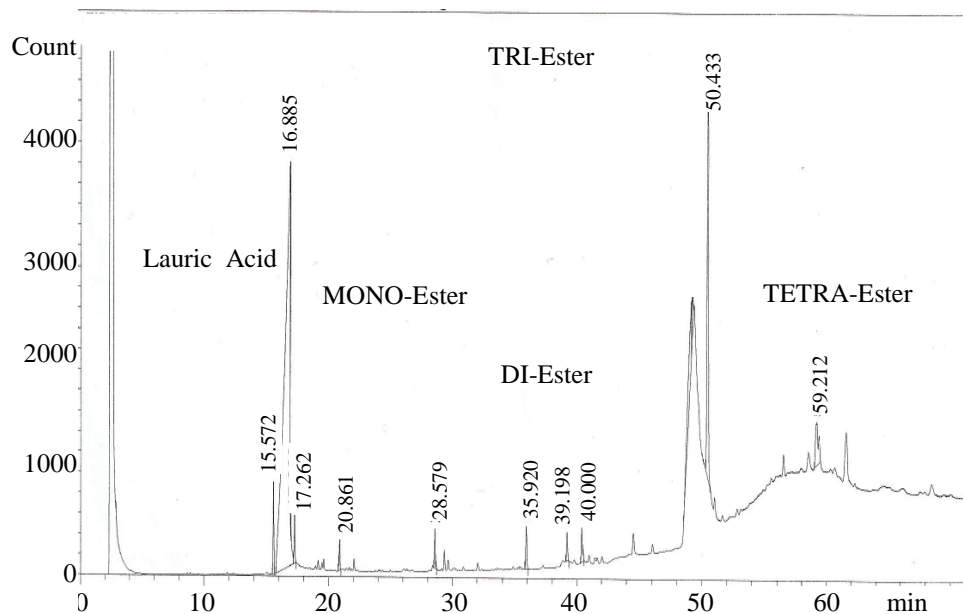
The  $^{13}\text{C}$  NMR spectrum also plays an important role in displaying the important features of PE ester produced (Figure 4). Ester carbonyl signals in the range of 173-174 ppm are very important in this study. The signal at the range is representing the functional group ester carbonyl at the end of the esterification of PE. In this study of polyol ester, ester carbonyl signals appear in the range of 172.86-173.82 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 76.02-77.24 ppm, which refers to the chloroform signal,  $\text{CDCl}_3$ . After successfully interpreting NMR data, the result of the expected PE ester obtained are shown in Figure 3 and Figure 4.



**Figure 4:**  $^{13}\text{C}$  NMR Spectra of Ester PE obtained

To confirm accurately the existence the composition of PE ester obtained from this study, GC-FID was carried out. Generally information from GC's data obtained which generate different peaks height and length to give the clarification of the composition of all components that occupy in the sample and also the total of composition obtained from sample. This data from GC is important is this study to prove the pureness of the ester PE. GC chromatogram of PE esters is shown in Figure 5. The peaks appeared was identified and labeled based on the number of alkyl carbon groups that attached to PE backbone.

The esters formed are identified by making comparisons by standard or by using the standard of fatty acids [14] and by comparing with other data from published journal. The composition of products 53% FA, 1.7% monoester, 3.3% di-ester, 1.7% and 37.6% of tri-ester and tetra ester PE 4.4 % (Table 1). The percentages of Lauric acid is higher than any other component is because the esterification is a reversible reaction which in this study lauric acid is a saturated and linear chain fatty acid was reacted with polyol PE ester which easily to form into crystal structure although PE is branched polyol but the structure is symmetric and is granular solid.



**Figure 5:** GC-FID based on the number of alkyl carbon groups that attached to PE backbone.

**Table 1:** Composition of product of esterification of ester PE

Composition	Percentages (%)
Lauric Acid	53.0
Mono Ester	1.7
Di Ester	3.3
Tri Ester	37.6
Tetra Ester	4.4

As the result data from the GC spectra not showing the tetra-ester PE peak, the TLC was carried out to determine through physico-chemistry analysis. The TLC analysis of ester PE was carried out according to Linko et al. (1995)[15] with some



modification to fix with the product condition. Through TLC result obtained by measured the retention time of every spot that appeared on TLC plate after colored and dried from Kalium Manganate (VII). Every pattern of spot from starting spot to final spot and the retention time was measured. From the TLC plate there were 5 different spots appeared with different distance spot from starting point which is fatty acid, monoester, di-ester, tri-ester and tetra-ester PE. Table 2 showed the retention time and distance of every spot detected from the best product of PE ester. The solvent for this TLC is diethyl-ether: n-hexane ; 5:5. The first of spot appeared on the plate is considered most polar compound, while the last spot appeared which take more retention time is more non polar compound.

**Table 2 :** R<sub>f</sub> value of production of ester PE

	Ester PE 1	Ester PE 2	Ester PE 3	Ester PE 4
Distance of middle spot from starting point (cm)	Spot 4: 8.0	Spot 4: 7.9	Spot 4: 7.9	Spot 4: 8.1
	Spot 3: 5.8	Spot 3: 5.6	Spot 3: 5.4	Spot 3: 5.7
	Spot 2: 1.7	Spot 2: 1.7	Spot 2: 1.7	Spot 2: 1.8
	Spot 1: 1.3	Spot 1: 1.3	Spot 1: 1.3	Spot 1: 1.3
Distance of solvent from starting point (cm)	8.5	8.5	8.5	8.5
R <sub>f</sub> value	Spot 4: 0.94	Spot 4: 0.93	Spot 4: 0.93	Spot 4:0.95
	Spot 3: 0.68	Spot 3: 0.65	Spot 3:0.64	Spot 3:0.67
	Spot 2: 0.20	Spot 2: 0.20	Spot 2: 0.20	Spot 2:0.21
	Spot 1: 0.15	Spot 1: 0.15	Spot 1: 0.15	Spot 1:0.15

### 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 [16]. Based on Table3, the resulting viscosity of the PE ester is 162.75. 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 lauric acid. This resulted in viscosity values were also higher than the oil.

**Table 3:** Characterization of Lauric Acid, PE, and Ester PE as biolubricant based stocks.

Characterization	Lauric acid	PE	Ester PE
Pour point °C	27°C	-	25°C
Flash point °C	110 °C	240 °C	250°C
Viscosity index Oxidative	-	-	162.75
Stability	183 °C	-	216.15 °C

The pour point of PE ester obtained in this study is 25°C. At low temperature, oil composition capable of forming macro-crystal 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. But the result show the pour point is high, this is cause by the behavior and structure of lauric acid and polyol PE itself. Lauric Acis and PE is both in granular form or in solid form therefore as the esterification is a reversible reaction the behaviour both of the component influence the pour point of PE ester. The results of the analysis found that the flash point of PE ester produced was >250°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 PE ester has a high potential for the production of lubricants.

The viscosity index for PE ester is quite high which is 162, the calculation was carried out according to ASTM D 2270 [17] Oxidative stability for the PE ester in this study is 216.15 °C which is more higher than oxidative stability from lauric acid which only 183 °C according to Litwinienko et al. (1999)[18]. Oxidative stability is one of most important properties to improve the performance level of lubricants. The more higher temperature of oxidative stability will give more benefits to the lubricants performance as it also give longevity performance because it prevent the corrosive on the metal surface.

#### **4. CONCLUSIONS**

In this study, 55% of product was successfully synthesized in this research using lauric acid with pentaerythritol (PE) in the presence of sulfuric acid as catalyst. The results obtain suggest that the following reaction time: 6 hours, temperature: 180-200 °C, molar ratio of LA: PE is 4.9:1 and catalyst concentration: ±1 % w/w (based on weight of FA) are sufficient for the esterification of PE ester as biolubricant base stocks. In addition, the pour point of the product was observed is 25°C, flash point is >250°C, oxidative stability 216 °C and viscosity is 162 that resulting PE ester has a potential for the production of lubricants with suitable requirement with the properties of PE ester obtained.

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## REFERENCES

- [1] Frank D. Gunstone. 2004. The Chemistry of oils and fats , sources , composition, properties and uses. Blackwell Publishing. pgs 53, 270-271.
- [2] Asadauskas, S. & Erhan, S.Z. 1999. Depression of Pour o f Vegetable Oils by Blending with Diluents Used for Biodegradable Lubricants. *Journal of the American Oil Chemist's Society* 76(3): 313-316.
- [3] Lathi, S.P. & Mattiason, B. 2006. Green Approach for the Preparaof Biodegradable Lubricant Base Stock from Epoxidized Vegetable Oil. *Journal of Applied Catalysis B: Environmental* 69: 207-212.
- [4] Hwang, H.S., Adhvaryu, Atanu & Erhan, S.Z. 2003. Preparation and Properties of Lubricant Basestocks from Epoxidized Soybean Oil and 2-Ethylhexanol. *Journal of American Oil Chemistry Society* 80: 811-815.
- [5] Wu, X., Zhang, X.S., Yang, H.C. & Wang, D. 1998. The study of epoxidized rapeseed oil used as a potential biodegradable lubricant. *J. Amer. Oil Chem. Soc.* 75: 1557-1563.
- [6] Wilson, B. 1998. Lubricants and Functional Fluids from Renewable Sources. *Ind. Lubr. Tribol.* 50: 6-15.
- [7] Jumat Salimon, Nadia Salih, Emad Yousif . 2010 .Biolubricants :Raw material. Chemical modification and eviromental benefits. *European Journal of Lipid Scientific Technology.* 2010, 112,519-530
- [8] Gryglewicz, S., Piechocki, W. & Gryglewicz, G. 2003. Preparation of Polyester based on vegetable and animals fats. *Bioresource Technology* 87 (1): 35-39

- [9] Robiah, Y., Fakhru'l-Razi, A., Ooi, T.L., Iyuke, S.E dan Idris, A. 2003a. Development of Optimum Synthesis Method for Transesterification of Palm Oil Methyl Esters and Trimethylolpropane to Environmentally Acceptable Palm Oil-Based Lubricant. *Journal of Oil Palm Research* 15 (2): 35-41.
- [10] ASTM. 1995. Annual Book of ASTM Standards, Petroleum Products, Lubricants and Fossil Fuels. 5th ed. American Society for Testing and Materials, Philadelphia.
- [11] Pavia, D.L., Lampman, G.M. & Kriz, G.S. 2001. Introduction to Spectroscopy. 3rd ed. United States: Thomson Learning, Inc.
- [12] Pavia, D.L., Lampman, G.M. & Kriz, G.S. 2009. Introduction to Spectroscopy. 4<sup>th</sup> ed., United States: Thomson Learning, Inc.
- [13] Lathi, P.S. & Mattiason, B. 2007. Green approach for the preparation of biodegradable lubricants base stock from epoxidized vegetable oils. *Applied Catalyst B: Environment* 69: 207-212
- [14] Robiah, Y., Ooi, T.L., Fakhru'l-Razi, A. & Shahnor, B. 2002. A Simple Capillary Column GC Method for Analysis. *Journal of the American Oil Chemist's Society* 79: 1075-1080.
- [15] Linko, Y.Y., Lämsä, M., Huhtala, A. & Rantanen, O. 1995. Lipase Biocatalysis in the Production of Esters, *Ibid.* 172: 1293-1299
- [16] Sharma, B.K., Doll, K.M. & Erhan, S.Z. 2008. Ester hydroxy derivatives of methyl oleate: Tribological, oxidation and low temperature properties. *Bioresources Technology* 99: 7333-7340.
- [17] ASTM D2270 1998. Standard Practice for Calculating Viscosity Index From Kinematic Viscosity at 40 and 100°C *An American National Standard British Standard* 4459
- [18] G. Litwinienko, A. Daniluk, & T. Kasprzycka-Guttman 1999. A differential scanning calorimetry study on the Oxidation of C<sub>12</sub>-C<sub>18</sub> Saturated Fatty acids and their Esters. *Journal of the American Oil Chemists' Society* 76(6) : 655-657