



Synthesis and Characterization of Palm Kernel Oil Based Trimethylolpropane Ester

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(Received: 7 February 2013;

Accepted: 21 October 2013)

AJC-14268

Palm kernel oil based trimethylolpropane ester for biolubricant base stock was produced. Trimethylolpropane ester was synthesized *via* esterification of palm kernel free fatty acids (PKFFA) with trimethylolpropane. The mole ratio of PKFFA to trimethylolpropane was held constant at 4:1. The reaction was carried out for 5 h at 150 °C. 1 % (w/w) of sulphuric acid was added as catalyst. Analysis was performed by Fourier transform infrared spectroscopy, nuclear magnetic resonance and gas chromatography (GC-FID) using a high-temperature capillary column for characterization of trimethylolpropane ester. The trimethylolpropane ester was tested for the physical and chemical properties. The results showed that the trimethylolpropane ester was successfully synthesized with 68 % yield. The physical and chemical properties of trimethylolpropane ester showed high flash point (above 300 °C), pour point (3 °C), high viscosity index (157) with 219 of saponification value and 16 of iodine value.

Key Words: Biodegradable lubricant, Trimethylolpropane ester, Trimethylolpropane, Palm kernel, Fatty acid ester, Polyol ester.

INTRODUCTION

Palm kernel based trimethylolpropane (TMP) ester is one of potential base stock for biolubricant. It was also known as polyol ester. Esters derived from fatty acids and polyhydric alcohol such as neopentyl glycol (NPG), trimethylolpropane or pentaerythritol was known as polyol esters^{1,2}. Previous studies show that plant oil-based polyol esters have been produced from fatty acids and fatty acid methyl ester (FAME). Palm oil methyl ester (POME) and palm kernel oil methyl ester (PKOME) has been used as starting material for synthesis of trimethylolpropane ester. The result for trimethylolpropane esters from palm kernel oil methyl esters showed that trimethylolpropane ester derived contains 98 % w/w triesters with viscosity at 40 °C in the range of 39.7-49.7 cSt, pour point between -1 to 1 °C and high viscosity indices in the range of 167-187. The reactant molar ratio was maintained at 3.9:1, with 0.9 % w/w sodium methoxide as catalyst. The pressure of 20 mbar was applied with 130 °C in 1 h³.

In other development, ester was synthesized by transesterification of trimethylolpropane and rape seed oil methyl ester both by enzymatic and chemical means both in bench and pilot scales. *Candida rugosa* lipase was used as biocatalyst and an alkaline catalyst in chemical transesterification. In biocatalyst the maximum total conversion to trimethylolpropane esters of up to 98 % was obtained at 42 °C, 5.3 kPa and 15 %

added water. The maximum conversion of about 70 % to triester was obtained at the slightly higher temperature of 47 °C. In the chemical synthesis triester yields increased when the temperature was first held at 85 to 110 °C for 2.5 h and subsequently increased up to 120 °C for 8 h. The ester produced had good cold stability, friction and wear characteristics and resistance against oxidation at elevated temperatures⁴. Esters of neopentylpolyols were prepared by an esterification reaction between pentaerythritol and erucic acid in xylene, *p*-toluene sulphonic acid (*p*-TSA) was added and heated to 200 °C. Dean stark trap was used and nitrogen was applied throughout the experiment⁵. Polyol ester based on plant and animal fats was also prepared by using the Dean-Stark cap. The purpose of using Dean Stark cap is to carry out the azeotropic distillation of methanol-isooctane. The methanol formed by the reaction was continuously removed by increasing the temperature of the reaction mixture to their boiling point. The reaction was carried out for 20 h. The synthesis of final products were performed by alcoholysis of fatty acid methyl esters, obtained from natural fats studied, with the appropriate polyhydric alcohol using sodium methoxide as a catalyst. The results showed the neopentyl glycol and trimethylolpropane esters synthesized had viscosity at 40 °C in the range of 13.5-37.6 cSt, pour point at -10.5 and -17.5 °C compared with natural lard 33 °C and high viscosity indices, higher⁶ than 200.

The palm kernel oil was not directly reacted with trimethylolpropane to produce ester because of the glycerol. Glycerol is a component of triglyceride molecule that is readily destructible at high temperatures. This advantageous property stems from the presence of hydrogen atoms in position β relative to the hydroxyl group in the glycerol molecule. The structure feature is conducive to the partial defragmentation of molecule and the formation of unsaturated compounds. The compounds formed undergo polymerization, increasing the liquid's viscosity and resulting in the formation of precipitate particles. Thus, direct application of natural triglycerides in lubrication technology was not applicable because of a low resistance to both oxidation and high temperature treatment. They are also easily undergoing hydrolysis⁷.

In order to overcome the situation, fatty acid esters that derived from combination of fatty acids and numerous alcohols were developed to produce esters with good physical properties and performance. Fatty acid esters have superior properties and performances relative to mineral oils. The excellent properties of fatty acid ester such as good lubricity, good thermal and oxidative stability, low volatility, high viscosity index, excellent low temperature fluidity made it suitable to be used as synthetic lubricant. Monoesters, diesters and polyol esters are three types of ester that being used as lubricant⁸.

In this experiment the free fatty acids of palm kernel was used to react with trimethylolpropane. Palm kernel is derived from the fruit kernel of the *Elaeis guineensis*. Palm kernel free fatty acids were first synthesized by hydrolysis of the palm kernel oil. The polyhydric alcohol selected was trimethylolpropane, as it is branched and has a relatively low melting point. The transesterification reaction involves cleavages of an ester group, RCOO-, from fatty acid by the -OH group of trimethylolpropane to produce the new palm kernel-based trimethylolpropane esters. Since there are three -OH groups in the trimethylolpropane, the process yields intermediate formation of monoesters, diesters and triesters. Water is the by product that is removed to ensure completion of reaction⁹. The lubricating properties of the trimethylolpropane esters. Based oil with high triesters content has superior temperature behaviour compared to the oil with more monoesters and diesters. The remaining hydroxyl groups present in these partial esters have caused the thermal stability of the oil to fall¹⁰.

EXPERIMENTAL

RBD palm kernel oil was obtained from Jomalina Sdn. Bhd. (Teluk Panglima Garang, Selangor, Malaysia). Trimethylolpropane was supplied by Fluka Chemie AG (Buchs, Switzerland), sulphuric acid, toluene, sodium chloride, anhydrous sodium sulphate, sodium bicarbonate, potassium hydroxide, hydrochloric acid, ethanol, methanol, ethyl acetate, *n*-hexane are from System, GC grade ethyl acetate, *N,O*-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) and GC standards for esters analysis was purchased from Sigma Aldrich (Steinheim, Germany).

Hydrolysis of palm kernel oil: Reaction was performed in 500 mL two-necked flask equipped with a thermometer and a reflux condenser. The reaction was immersed in water bath. The reactor was filled with 50 g palm kernel oil and 300 mL ethanolic KOH (1.5 N) solution. The mixture was swirled

and heated for 2 h at 60 °C. After the reaction stopped and cool the mixture was put into the separating funnel. Water (200 mL) and 100 mL (6 N) of hydrochloric acid were added. The fatty acid was extracted three times by adding 100 mL of *n*-hexane. The collected solvent was washed with 50 mL distillate water. Anhydrous sodium sulphate was put to remove trace of water that remains in the product. The fatty acids that obtained were tested to determine the composition by using GC-FID analysis, FTIR analysis, NMR analysis and others physical and chemical properties¹¹.

Synthesis of trimethylolpropane ester from palm kernel fatty acids: The reaction was performed in a 500 mL three-necked flask equipped with a thermometer, magnetic stirring and a reflux condenser of Dean Stark apparatus. The flask mouth was fitted with a Dean Stark cap in order to carry out the azeotropic distillation of water-toluene. The reactor was filled with 20 g of palm kernel free fatty acid, a known amount trimethylolpropane (TMP) and 80 mL of toluene. The known amount trimethylolpropane added in the reactor was depended on the reactants mole ratio 4:1 of FFA: trimethylolpropane. The reaction mixture was stir and heat up to 150 °C which was above the boiling point of reaction mixture. Sulphuric acid was added into the reaction as catalyst with amount of 1 % (w/w). The esterification was carried out for 5 h. The water which is the by product that formed by the reaction was continuously removed.

Removal of catalyst and unreacted free fatty acids: When the reaction was completed, the synthesized ester was separated from the catalyst and remaining unreacted free fatty acids by adding the saturated sodium chloride solution and saturated sodium bicarbonate solution. Fatty acid was removed from the ester by washing it with methanol for several times. The sample was then extracted with ethyl acetate and washed with water. The esters obtained were tested for Fourier transforms infrared (FTIR), gas chromatography (GC-FID), nuclear magnetic resonance (NMR) and other physical and chemical properties test¹¹.

Derivatization of sample for GC analysis: About 0.03 ± 0.005 g of sample was weighed exactly into a 2 mL vial and diluted with 1 mL ethyl acetate. The sample was swirled for a few minutes to dissolve the mixture. 0.5 mL of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) was then added to the mixture and swirled. The vial was then transferred to water bath held at 40 °C for 10 min. The sample was left to cool to room temperature then injected on the GC-FID¹⁰. Derivative samples will be stored in the freezer to help extend their lifespan.

Gas chromatography: The separation on the GC system was performed using the capillary column DB-5ht. 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 temperature were at 300 and 400 °C, respectively. Hydrogen was used as the carrier gas at flow rate. 1 μ L of sample was injected into the GC system.

RESULTS AND DISCUSSION

FTIR analysis of FFA, trimethylolpropane and trimethylolpropane ester: Fig. 1 shows comparison of the infrared spectra of the palm kernel fatty acid, trimethylolpropane

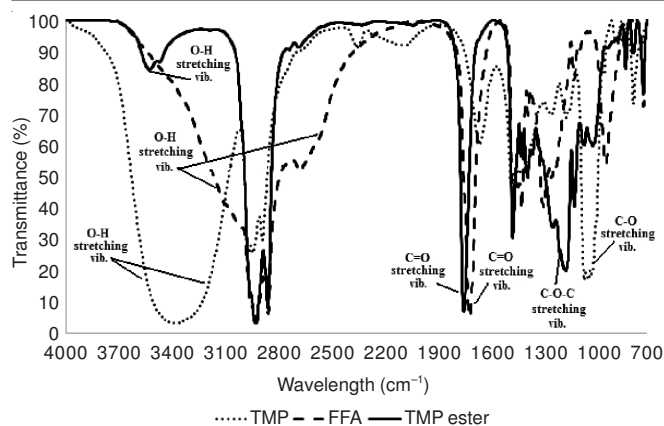


Fig. 1. Infrared spectra of trimethylolpropane, FFA and trimethylolpropane ester

and trimethylolpropane ester. The structure of trimethylolpropane ester produced from esterification of palm kernel fatty acids with trimethylolpropane was confirmed from the infrared spectra by the disappearance peak of the C=O stretching vibration for fatty acid at 1710 cm^{-1} and appearance of the C=O stretching vibration for ester peak at 1743 cm^{-1} . In the comparison, the presence of broad band at $3300\text{--}2500\text{ cm}^{-1}$ can be seen in free fatty acid infrared spectra due to the O-H stretching vibration in carboxylic acid and the presence of broad band at 3391 cm^{-1} for trimethylolpropane. In the trimethylolpropane ester infrared spectra, both intensity of broad band for fatty acid and trimethylolpropane become weak and the shift in O-H stretching band can be seen at 3526 cm^{-1} . This indicated the evidence of trimethylolpropane ester was produced with some partial ester of monoester and diester. Another evidence of trimethylolpropane ester produced was the reducing intensity of primary alcohol of trimethylolpropane peak at $1090\text{--}1000\text{ cm}^{-1}$ and appearance of C-O-C stretching vibration peak of trimethylolpropane ester at $1160\text{--}1050\text{ cm}^{-1}$.

NMR analysis of trimethylolpropane ester: Palm kernel based trimethylolpropane ester was confirmed by ^{13}C nuclear magnetic resonance (NMR) from Fig. 2 and Table-1 and ^1H NMR from Fig. 3 and Table-2.

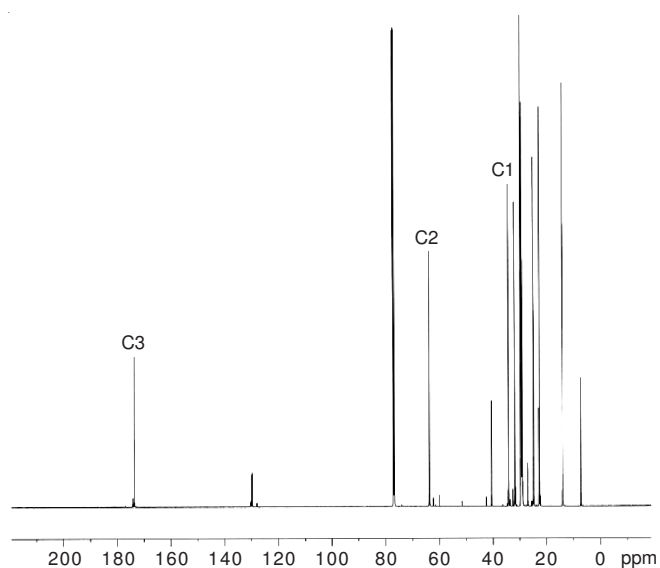


Fig. 2. ^{13}C NMR spectra of palm kernel based trimethylolpropane ester

TABLE-1
NUCLEAR MAGNETIC RESONANCE (NMR) ^{13}C ,
CHEMICAL SHIFT (ppm) OF PALM KERNEL
BASED TRIMETHYLOLPROPANE

Compound	Chemical shift (ppm)	Theoretical chemical shift (ppm) ¹²
C1 R-CH ₂ -COOR	34.2	15-55
C2 R-COO-CH ₂ -	63.7	40-80
C3 -C=O	173.5	158-185

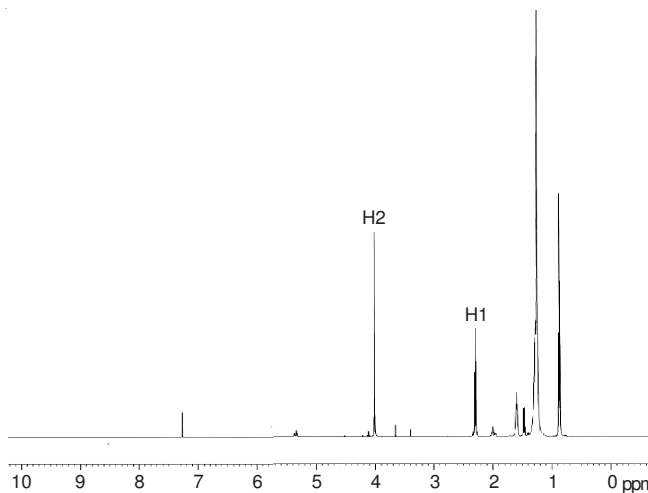


Fig. 3. ^1H NMR spectra of palm kernel based trimethylolpropane ester

TABLE-2
NUCLEAR MAGNETIC RESONANCE (NMR) ^1H ,
CHEMICAL SHIFT (ppm) OF PALM KERNEL
BASED TRIMETHYLOLPROPANE

Compound	Chemical shift (ppm)	Theoretical chemical shift (ppm) ¹²
H1 R-CH ₂ -COOR	2.3	2.1-2.5
H2 R-COO-CH ₂ -	4.0	3.5-4.8

Determination of fatty acid and trimethylolpropane ester composition: The fatty acids composition that produced from hydrolysis of palm kernel oil as shown in Table-3, were determined using GC-FID. The result showed that palm kernel oil consist of eight types of fatty acids which are 2 % of caprylic acid, 3.1 % of capric acid, 51 % of lauric acid, 16.4 % of myristic acid, 7.9 % of palmitic acid, 2 % of stearic acid, 15.3 % of oleic acid and 2.2 % of linoleic acid.

TABLE-3
AVERAGE FATTY ACID COMPOSITIONS
OF PALM KERNEL OIL

Free fatty acids	Composition (%)	Free fatty acids	Composition (%)
C 8:0	2.0	C 16:0	7.9
C 10:0	3.1	C 18:0	2.0
C 12:0	51.0	C 18:1	15.3
C 14:0	16.4	C 18:2	2.2

Trimethylolpropane ester composition that produced *via* esterification of palm kernel fatty acids with trimethylolpropane was also determined by using high temperature column GC-FID. Fig. 4 shows gas chromatogram for palm kernel oil based trimethylolpropane ester. GC method was preferred than HPLC because it gives better separation. Separation of TAG molecules in GC is according to the number of carbon atoms where each peak is referred according to its carbon number in the

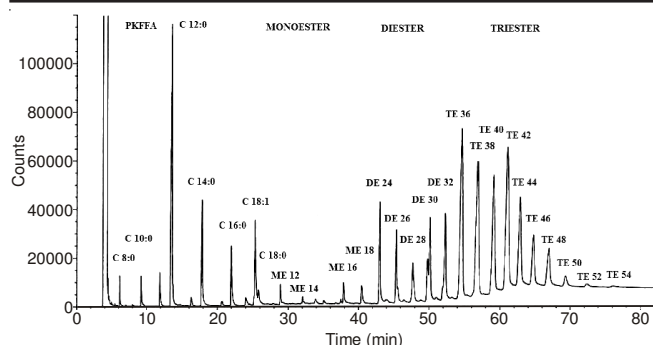


Fig. 4. Gas chromatogram of palm kernel based trimethylolpropane ester

acyl chain of the TAG molecules. The same carbon number of TAG will elute together as one peak. Thus, the same terminology was used to identify the trimethylolpropane ester. For example, trilaurin with three lauric acid (C12) chains is referred to TAG 36 and oleolaurin with two lauric acid chains and one oleic acid chain is TAG 42 while in trimethylolpropane ester, trilaurate with three lauric acid chains is referred to triesters 36 and oleolaurate with two lauric acid chains and one oleic acid chain is triesters 42¹⁰.

Trimethylolpropane ester will produce three types of polyol esters which are monoester (ME) and diester (DE) if its -OH groups were partially esterified and triester (TE) if its -OH groups were fully esterified. All components in trimethylolpropane ester such as fatty acids, monoester, diester and triester were well separated by GC because the sample was derivatized. All of the OH groups in polar compounds such as monoesters and diesters are replaced with the methylsily (-SiMe₃) in silylation which is improves the separation. Hence, all peaks were grouping according to their groups and carbon numbers as shown in Fig. 2. In order to identify and label each peak, standards for trimethylolpropane ester was prepared by reaction of pure fatty acid such as lauric acid, palmitic acid and stearic acid with trimethylolpropane. The retention times of each of these standards were compared with GC peaks of trimethylolpropane ester⁹. Table-4 showed the composition of palm kernel based trimethylolpropane ester from GC-FID analysis. The yield of trimethylolpropane ester obtained was 68 %.

Compound	Composition (%)	Compound	Composition (%)
FFA	5.8	Diester	18.2
Monoester	1.5	Triester	74.5

Chemical and physical properties: Chemical and physical properties of palm kernel based trimethylolpropane ester have been determined and are shown in Table-5. Each method was based on the methods described by¹³ and methods from ASTM 1995¹¹ with some modification.

The result showed, palm kernel based trimethylolpropane had saponification value of 219 and iodine value of 16. The pour point of trimethylolpropane ester obtained was good at 3 °C. The previous study showed that trimethylolpropane ester

TABLE-5
CHEMICAL AND PHYSICAL PROPERTIES OF
PALM KERNEL BASED TRIMETHYLOLPROPANE

Property	Method	PKO (raw material)	TMP ester (product)
Pour point (°C)	ASTM D-97	29	3
Flash point	ASTM D-92	240	> 300
Viscosity at 100 °C (cSt)	ASTM D-445	Pending	6.4
Viscosity at 40 °C (cSt)	ASTM D-445	Pending	28.9
Viscosity index	ASTM -2270	Pending	157
Saponification value	Ref. 13	207	219
Iodine value	Ref. 13	17	16

derived from palm kernel oil methyl ester had pour point of 2 °C¹⁰. Pour point was determined to indicate the temperature at which the lubricant started to loss its fluidity¹⁴. The flash point of trimethylolpropane ester was high (above 300 °C) and high viscosity index of 157. Lubricant with higher viscosity index (VI) showed that the viscosity of the lubricant is less affected by temperature change. Excellent lubricant has the same viscosity at all temperatures and pressures. Thus, the lubricant is applicable to be used over a wider range of temperatures¹⁴.

Conclusion

The trimethylolpropane ester was successfully synthesized from palm kernel fatty acid with 68 % yield. trimethylolpropane ester obtained also shows good physical and chemical properties of lubricant and plausible to be use for environmental friendly biolubricant application.

ACKNOWLEDGEMENTS

The authors thank to Universiti Kebangsaan Malaysia for funding (Code UKM-AP-2011-17, DPP-2013-054 and UKM-MI-OUP-2011).

REFERENCES

- J. Salimon, N. Salih and E.Yousif, *Arabian J. Chem.*, **5**, 135 (2012).
- S. Gryglewicz, W. Piechocki and G. Gryglewicz, *Bioresour. Technol.*, **87**, 35 (2003).
- J. Salimon, N. Salih and E. Yousif, *Arabian J. Chem.*, **5**, 193 (2012).
- N. Salih, J. Salimon and E. Yousif, *J. King Saud Univ.-Sci.*, **24**, 221 (2012).
- V. Eychenne, Z. Mouloungui and A. Gaset, *J. Am. Oil Chem. Soc.*, **75**, 293 (1998).
- J. Salimon, N. Salih, E. Yousif, *J. Saudi Chem. Soc.*, **15**, 195 (2011).
- N. Salih, J. Salimon and E. Yousif, *Turk. J. Eng. En. Sci.*, **35**, 115 (2011).
- J. Salimon, N. Salih and E. Yousif, *Sains Malaysiana*, **41**, 1239 (2012).
- Y. Robiah, A.F. Razi, T.L. Ooi, D.R. Biak and S.E. Iyukie, *J. Am. Oil Chem. Soc.*, **81**, 497 (2004).
- Y. Robiah, A.F. Razi, T.L. Ooi, S.E. Iyukie and A. Idris, *J. Oil Palm Res.*, **15**, 42 (2003).
- American Society for Testing Materials (ASTM), Annual Book of ASTM Standards, Petroleum Products, Lubricants and Fossil Fuels, American Society for Testing and Materials, Vol. 5 (1995).
- J. Salimon, N. Salih and E. Yousif, *J. Oleo Sci.*, **60**, 613 (2011).
- N. Salih, J. Salimon and E. Yousif, Improved the Properties of Biolubricant Basestock, Lambert Academic Publishing, Germany (2011).
- J. Salimon, N. Salih and E. Yousif, *Ind. Crops Prod.*, **38**, 107 (2012).