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## Study on Effect of Hydroxyl Group on Lubrication Properties of Palm Based Trimethylolpropane Esters: Development of Synthesis Method

Anita Abu Bakar, Robiah Yunus, A. Luqman Chuah and A. Fakhru'l-Razi  
Department of Chemical and Environmental Engineering, University Putra Malaysia,  
43400, Serdang, Selangor, Malaysia

**Abstract:** Some concerns have been raised regarding the oxidative stability of vegetable oil-base fluids. Thus, wide ranges of palm-based trimethylolpropane esters, which contain different percentages of partial esters, were synthesized. The palm-based TMP were esterified from Palm Oil Methyl Esters (POME) with trimethylolpropane [2-ethyl-2-(hydroxymethyl)-1,3-propanediol;TMP] and sodium methoxide ( $\text{CH}_3\text{ONa}$ ) as catalyst. Quantification of methyl esters, mono, di- and tri-TMP esters were performed using a gas chromatography (GC), with a high temperature capillary column (SGE HT5), operated at a temperature gradient of  $6^\circ\text{C min}^{-1}$  starting from 80 to  $340^\circ\text{C}$ . The influence of operating variables (temperature, pressure, molar ratio of palm methyl esters to TMP and catalyst amount) on diesters formation was studied and analyzed. Palm oil TMP ester containing 10-30% partial esters (monoesters and diesters) was successfully synthesized.

**Key words:** Partial esters, transesterification, gas chromatography, methyl esters

### INTRODUCTION

Vegetable oil in its natural form has limited use as industrial fluids due to poor thermal and oxidative stability. It was reported (Schlosberg *et al.*, 2001; Hwang and Erhan, 2001) that the oxidative stability was low due to the glycerol moiety present in the oil. The secondary hydroxyl group in the glycerol is thermally unstable and easily loses the elements of water in the presence of acid. Further, it was also found an alternative triol that provides a stable structure in which there is no hydrogen  $\beta$ -to the OH groups such trimethylolpropane (TMP). The chemical synthesis of palm oil trimethylolpropane esters was conducted via transesterification of Palm Oil Methyl Esters (POME) with trimethylolpropane (TMP). The problem with the Pour Point (PP) associated with the level of saturation in palm oil was resolved, as the Pour Point (PP) was successfully lowered to  $-36^\circ\text{C}$ . However, the TMP ester that exhibits better lubricating characteristics has pour point of only  $-30^\circ\text{C}$ . This is because the reduction in pour point has negative effect on oxidative stability as well as the wear and friction. Yunus *et al.* (2003a) also found that the presence of hydroxyl group (partial ester) in the lubricant provides marginal resistance on the oxidative and thermal stability. It was reported that the partial polyol esters has more resistant to thermal and oxidative environment due to its longer decomposition time than full converted esters (Gryglewicz and Piechocki, 2003).

The objective of this study is to develop the synthesis method for palm based TMP polyol esters (TMPE) which exhibit high thermal and oxidative stability by varying the percentages of partial esters (diesters) in the reaction products.

### MATERIALS AND METHODS

**Materials:** The High Oleic Palm Oil Methyl Esters (HOPOME) used for the experiments were extracted from palm oil methyl esters which were obtained from Carotech Malaysia Sdn Bhd (Perak); Trimethylolpropane (TMP) was purchased from Merck-Schuchardt (Germany). The purified, dry sodium methoxide with an assay of 96% was provided by Sigma Aldrich Chemicals Co. and N,O-Bis (trimethylsilyl) trifluoroacetamide (BSTFA) was a product from Fluka Chemie AG (Switzerland).

**Transesterification:** The reaction was performed according to the procedures described in the previous papers (Yunus *et al.*, 2003a, b; Glyglewicz and Piechocki, 2003). The apparatus used were a 250 mL reactor equipped with a magnetic stirrer, thermometer, sampling port and capped with a reflux condenser. The condenser was connected to a vacuum line equipped with a relief valve, accumulator and vacuum trap. The reactor was immersed in a silicon oil bath. A known amount of TMP was first dissolved in 100 g of POME in the reactor under slight heating and stirring. The catalyst was then added to the

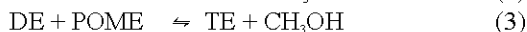
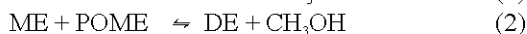
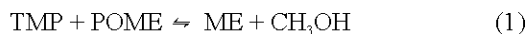
mixture under constant stirring. The vacuum was applied gradually after adding the catalyst in order to avoid spill over of the reaction material. The timing was started immediately after the vacuum was switched on. Samples were analyzed at certain time intervals for POME, monoesters (ME), di-esters (DE), tri-esters (TE), fatty acids (FA) and TMP by gas chromatography. The yield of each product was determined from the GC chromatogram calibrated against the known samples according to the procedure described (Yunus *et al.*, 2002). The additional experiments were conducted to study the effects of temperature, vacuum pressure, reactant molar ratio and amount of catalyst on trimethylolpropane esters formation.

**Product purification:** When the reaction was completed, the catalyst was separated from the product mixture using vacuum filtration. The un-reacted methyl ester was removed from the filtered product by high vacuum distillation.

**Analytical procedure:** The separation on the GC system was performed according to the procedure described by Yunus *et al.* (2002), using capillary column SGE HT5, 12×0.53 mm, i.d., 0.15 μm (SGE, Melbourne, Australia). The oven temperature was set initially at 80°C, held for three minutes, then increased at the rate 6°C min<sup>-1</sup> to 340°C and held for another 6 min. The injector and detector temperature were at 300 and 360°C, respectively. Hydrogen was used as the carrier gas at flow rate of 26.7 mL min<sup>-1</sup>. The split ratio was set at 1:1 and 1.0 μL of sample was injected into GC system. This procedure provides a complete separation of reaction product, TMP, methyl esters, monoesters (ME), di-esters (DE) and tri-esters (TE).

## RESULTS AND DISCUSSION

**Transesterification reaction:** The transesterification reaction consists of three consecutive and equilibrated reactions involving intermediate formation of mono- and diesters. The stoichiometry requires one mol of TMP and three mol of POME, however, in this study, excess amount of POME were used in order to avoid the backward reaction. An overall reaction follows as:



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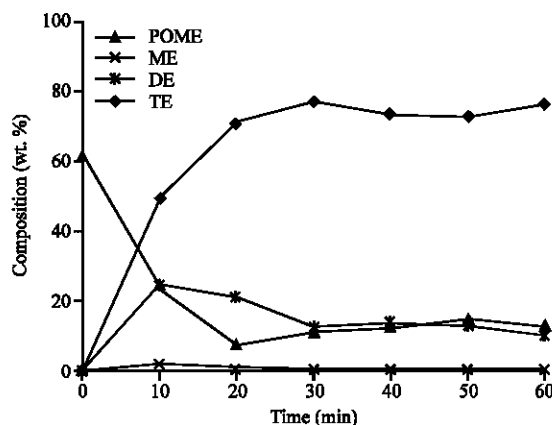
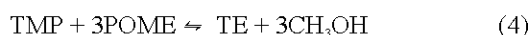


Fig. 1: Effect of time on transesterification reaction at 130°C vacuum pressure 50 mbar, catalyst amount 0.7% (wt/wt), POME: TMP; 3.9:1 and reaction time 60 min

**Effect of time on product distribution:** It appears from Fig. 1 that the reaction is very rapid; the TMPE conversion is nearly 70% after 20 min and stabilized at around 80% after 40 min. The conversions of intermediate esters (mono and diesters) are very fast. Monoesters were completely converted to diesters after 10 min while the concentration of the diesters stabilizes around 10%. After removal of unreacted POME, the final product contains around 90% of TE.

**Effect of temperature on DE formation:** The rate of trimethylolpropane esters conversion was studied at different temperatures, 110, 120, 130 and 140°C. A POME-to-TMP molar ratio of 3.9:1 and 0.9% of NaOCH<sub>3</sub> by total weight of HOPOME and TMP were used. The effect of temperature on the transesterification of HOPOME with TMP at 50 mbar is shown in Fig. 2. It was noticed that temperature is a sensitive parameter for the reaction. The maximum effects were observed at 10 and 20 min, respectively. Afterwards only marginal effect of temperature on conversion is detected.

At low temperature, the diesters concentration are lower than at high temperature, may be due to the amount of POME in the reactor. At high temperature, the amount of POME was low due to vaporization, thus occurrence of the reverse reaction could not be suppressed. Consequently, there was a high concentration of diesters (Yunus *et al.*, 2003a, b). By increasing temperature to 130 and 140°C; there are a progressive coloration of the reaction medium from yellowish to dark orange was noted. This may be caused by oxidation of the oil.

**Effect of vacuum pressure on DE formation:** At high vacuum (5 mbar) the reaction rate are very fast for the first

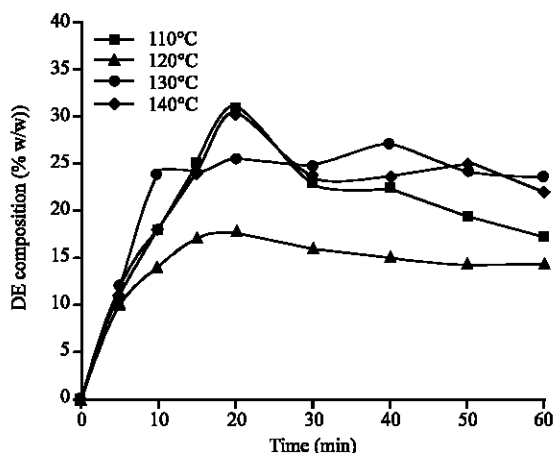


Fig. 2: Effect of temperature on DE formation at vacuum pressure 50 mbar, catalyst amount 0.7% (wt/wt), POME: TMP; 3.9:1

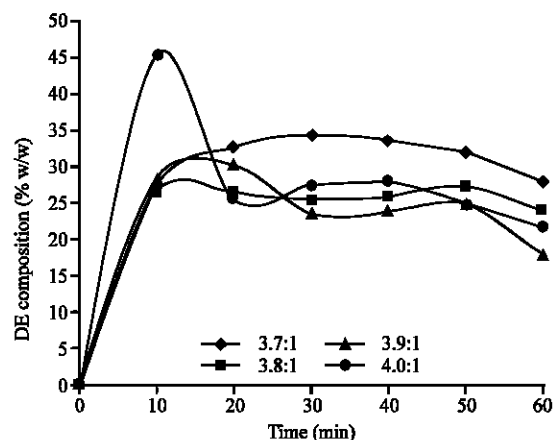


Fig. 4: Effect of reactant molar ratio on DE formation at 130°C; 0.7% (wt/wt) catalyst, vacuum pressure 50 mbar

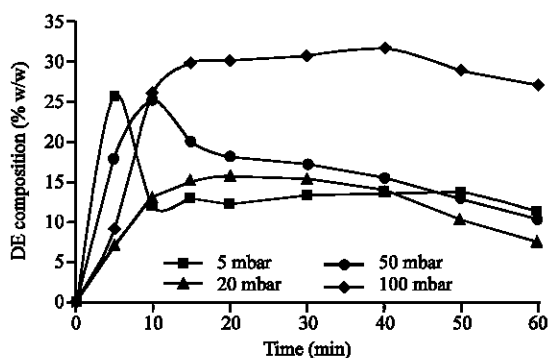


Fig. 3: Effect of pressure on DE formation at 130°C, catalyst amount 0.7% (wt/wt), POME: TMP; 3.9:1

10 min due to rapid removal of methanol, but after that the concentration (Fig. 3). The effect of vacuum pressure on the rate of transesterification between POME and TMP at 130°C is shown in Fig. 3. At high vacuum (5 mbar) the reaction rate are very fast for the first 10 min due to rapid removal of methanol, but after that the concentration of De was increased slowly, high content of DE at high vacuum indicate that might be occurrence of backward reaction where the TE decomposed to DE due to depletion of POME (Yunus *et al.*, 2003a, b).

Reactions under low vacuum produced high percentage of unconverted DE as a result of the backward reaction. However, there is no significant effect on DE concentration at moderate vacuum, accept for the first 10 min. At early stage of reaction, the reaction rate of 20 mbar is faster than 50 mbar due to rapid removal of methanol. Subsequently, the DE concentration stabilized at constant value for both situations.

**Effect of reactant molar ratio on DE formation:** The effect of molar ratio of alcohol to vegetable oil has been stated by many investigators and considered to be the most important variables affecting the transesterification reaction (Yunus *et al.*, 2003b; Uosukainen *et al.*, 1998). According to Le Chatelier's principle, an excess of alcohol increase the ester conversion by shifting the equilibrium to the right. Since POME are relative cheaper compared to TMP, so, in this study, the reaction was subjected to excess POME. Four different molar ratios of POME to TMP were studied, 3.7:1; 3.8:1; 3.9:1 and 4.0:1. The molar ratio 3.9:1 gave the best results in terms of TE formation as shown in Fig. 4.

Yunus *et al.* (2003a), has developed the transesterification process with optimum conditions; ratio POME to TMP 3.8:1; 120°C; 0.9% catalyst and 20 mbar. According to this author, the conversion to TE increased from 83 to 86% as the ratio was increased from 3.5:1 to 3.7:1 but with more POME residue and also a slight of DE. Figure 4 also shows that higher amount of POME to TMP ratio had little effect on DE formation in the product. At 4.0:1, the formation of DE is higher compared to at 3.8:1 and 3.9:1. This can be reduce by improved the mixing process (stirrer) in order to encourage a better contact between the solid catalyst and substrates (Wu *et al.*, 1998).

**Effect of catalyst amount on DE formation:** It is important to study the effect of catalyst on the transesterification process of POME with TMP and NaOCH<sub>3</sub> as catalyst. The catalyst is very expensive compared to POME and TMP. Beside that it also provides an additional cost during the

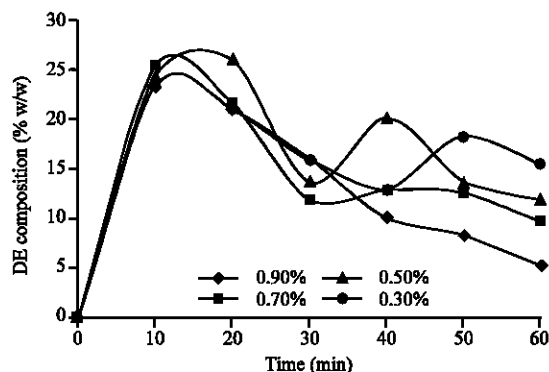


Fig. 5: Effect of catalyst amount on DE formation at 130°C; POME:TMP 3.9:1; vacuum pressure 50 mbar

production process because it is necessary to remove it from the end product. Four catalyst concentrations; 0.3% (wt/wt), 0.5% (wt/wt), 0.7% (wt/wt) and 0.9% (wt/wt) were studied. Previous study (Yunus *et al.*, 2002) found that, the conversion of TE was always greater than 70% if using catalyst percent ranging from 0.7 to 1.2%. Figure 5 shows the effect of catalyst on DE formation at 130°C, POME to TMP ratio, 3.9:1, vacuum pressure 50 mbar and reaction time 60 min. From the Fig. 5, it can be seen that increasing of the catalyst amount does not show impact on the DE concentration for the first 30 min. However DE concentration decreases slightly with catalyst amount after 30 min reaction.

### CONCLUSIONS

The operating variables for transesterification of POME with TMP and sodium methoxide as catalyst were found to be marked effects on the concentration of the intermediate products (mono- and diesters). It is very hard to evaluate the duration of when monoester converted to diesters due fast reactions. However, the optimum operating parameters to synthesize the product with partial esters content ranging from 10 to 30% are: Reaction time; 30-60 min, 130°C; pressure 50 mbar; catalyst at 0.7% w/w and molar ratio of POME to TMP at 3.9:1.

### ACKNOWLEDGMENTS

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