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Batch Production of Trimethylolpropane Ester from Palm Oil as Lubricant Base Stock

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Abstract: A batch process for the transesterification of Palm Oil Methyl Ester (POME) with trimethylolpropane (TMP) to TMP ester was investigated in a mini pilot reactor. The process was equipped with a high vacuum pump. The experimental studies explored effects of vacuum pressure, temperature, molar ratio, catalyst amount and agitator speed on the overall conversion. Five liters of TMP esters containing 83 to 87 w/w % triesters (TE) were successfully synthesized after 2 h of reaction time. Application of vacuum pump enhanced conversion of TE (w/w %) for the process. High catalyst amount resulted in higher conversion of TE (w/w %) but increased in solid content of the product. This has reduced the product yield due to inefficient separation by gravity settling.

Key words: Biolubricant, batch production, mini pilot reactor, palm oil TMP ester

INTRODUCTION

Recently, the interest in the biolubricants derived from renewable resources like vegetable oil is growing due to their biodegradability, low toxicity and environmentally benign nature (Dharma, 2002). The biodegradable lubricant could be derived from the transesterification of vegetable oil with polyol ester such as neopentyl glycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE). The TMP esters are widely used in synthetic lubricant formulations and are excellent base stocks for crank case lubricant, 2-cycle oils, high temperature greases, compressor oil, hydraulic fluid etc. (Helena *et al.*, 2001). These products are designed to offer high performance lubricant that exhibit excellent lubrication properties as well as non-toxic and biodegradable. However no specific information has been reported on the large scale production of TMP esters (Valérie *et al.*, 2001).

A growing number of companies are manufacturing and distributing agricultural-based lubricant, including Cognis Oleochemicals. BioLube is Cognis's full line of naturally derived based oil from TMP ester. This Biolubes provide an exceptionally high performance paired with the greatest possible environment compatibility. However, the non-toxic biodegradable fluids are designed for use in heavy machinery. Several processes for biolubricant production were developed by transesterification using alkaline catalyst which is capable to increase the production yields in short reaction time. Previous research on biolubricant (Robiah *et al.* 2003) showed

good potential for various applications such as hydraulic fluids, metalworking fluids and general lubricating oil. The technology was successfully demonstrated at lab-scale (500 mL reactor), by using Palm Oil Methyl Ester (POME) and trimethylolpropane (TMP) as a raw material and catalyzed by sodium methoxide (Robiah *et al.*, 2003).

However, due to its limited production capacity, the lubricant could not be tested for commercial application. Thus based on the previous study by Robiah *et al.* (2003), this study focused on batch production of large capacity of palm oil TMP ester and optimization of the operating conditions.

MATERIALS AND METHODS

Raw material palm: Oil methyl esters (POME) were obtained from Carotech (Malaysia) Sdn Bhd. Trimethylolpropane, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) was purchased from Fluka Chemie AG and alkaline catalyst, sodium methoxide was purchased from Sigma Aldrich Chemicals Co. Others chemical such as N, O-Bis (trimethylsilyl) trifluoroacetamide (BSTFA) and ethyl acetate were purchased from Fluka Chemie AG.

Transesterification reaction: Batch transesterification reactions were performed in 10 L high vacuum reactor. Initially Palm Oil Methyl Ester (POME) was dried overnight in an oven at 105°C in order to reduce the moisture content. Five liter Palm Oil Methyl Ester and

known amount of TMP were added into the reactor. The reactants were heated by 2 kW oil bath heater by circulating silicon oil through the vessel double jacketed wall. The anchor agitator was used to agitate the reactants. The speed was controlled by a frequency inverter. Vacuum model RV12 manufactured by Edward BOC was applied gradually after catalyst (sodium methoxide) was added in to the system. The thermostatic circulation bath was set at 20°C and used to circulate water to the reflux condenser. After the reaction was completed, the product was withdrawn from the vessel and placed in the container to settle for one day to allow for the separation of product and catalyst.

Analysis: The samples were analyzed for TMP, ME, DE, TE and methyl ester by gas chromatography using capillary column SGE 12 m × 0.53 mm IDHT5 0.15 μm (SGE, Australia Pty. Ltd.) with hydrogen at 26.7 mL min⁻¹ as a carrier gas and split ratio of 1.1. The oven temperature was set at initial temperature 80°C, hold for 3 min, increased at 6°C min⁻¹ to 340°C and hold for another 6 min. The injector and detector temperature were set at 300 and 360°C, respectively (Robiah *et al.*, 2002).

RESULTS AND DISCUSSION

Effect of temperature: To determine the effect of temperature on ester formation for the transesterification reaction of POME with TMP at a molar ratio of 3.8:1 (POME/TMP) catalyzed by 0.9 w/w % sodium methoxide, four temperatures ranging from 110 to 140°C were examined as shown in Fig. 1. The results show that temperature has negligible effect on the reaction. However, the conversion of TE increased slightly from 110 to 120°C and dropped at temperature 130 and 140°C. This is because, at high temperature, POME tends to vaporize and easier to be pulled away via vacuum pressure (Robiah *et al.*, 2003). Higher conversion of TE (66.0 w/w %) was achieved at 120°C compared to 130°C, even though the amount of monoesters (ME) is relatively high (1.0 w/w %) at 120°C. However, the ME was separated together with the unreacted methyl ester during the final purification step. The yield of TE increased up to 86 w/w % after the final purification step.

Effect of pressure: One of the most important methods to depress the backward reaction in order to improve the yield is by applying vacuum pressure. In this reaction, the vacuum pressure was varied by changing the formation of triesters (TE) w/w %. A total of four vacuum conditions at 500, 100, 50 and 20 mbar were applied in this reaction. The speed of agitator, temperature, molar ratio and

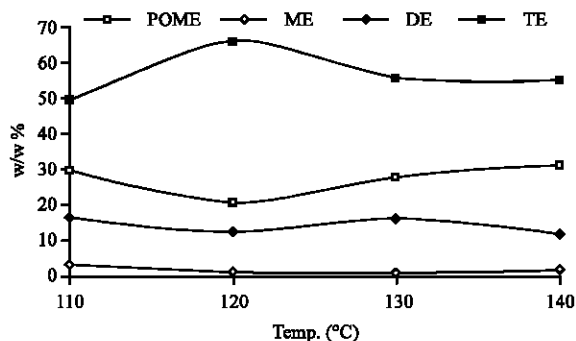


Fig. 1: Effect of temperature on transesterification of palm oil methyl esters with TMP molar ratio of POME:TMP was 3.8:1, catalyst 0.9% w, 20 mbar

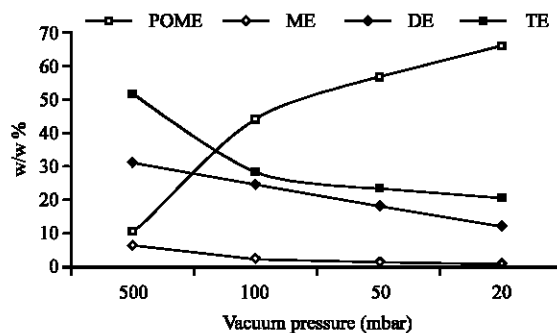


Fig. 2: Effect of vacuum on transesterification of palm oil methyl esters with TMP molar ratio of POME:TMP was 3.8:1, catalyst 0.9 w/w %, 120°C

catalyst amount were held constant at 180 rpm, 120°C, 3.8:1 and 0.9 w/w %, respectively. The results are shown in Fig. 2.

There is a proportional relationship between vacuum pressure and the formation of TE in w/w % (Fig. 2). An increase in vacuum pressure increases the conversion of TE. Figure 2 shows clearly that, the highest vacuum (20 mbar) resulted in the best product consists of 66 w/w % TE, 12.2 w/w % DE, 1.2 w/w % ME and 20.9 w/w % POME.

Even though the amount of unreacted POME is slightly high, but it can be removed by distillation. At vacuum 50 and 100 mbar, the conversion of TE slightly decrease (from 66 to 56.8 w/w % and 44.1 w/w %) while the partial ester increase twice (DE: from 12.2 to 18.1 w/w % and 24.8 w/w % and for ME: from 1.2 to 1.5 w/w % and 2.4 w/w %). Thus, it indicates that there is a methanol (in small amount) in the system and causes the backward reaction to decompose triesters to diesters and diesters to monoesters. Hence it reduces the conversion of TE and increase the formation of partial ester (such as mono and diesters) (Robiah *et al.*, 2003).

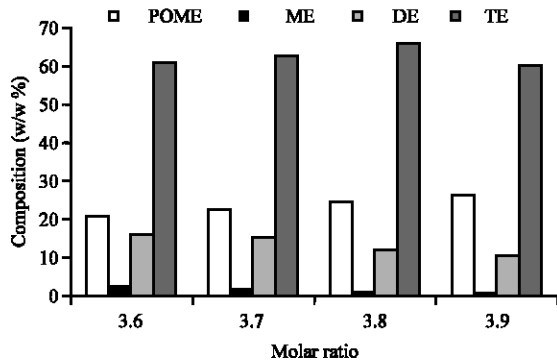


Fig. 3: Effect of molar ratio on transesterification of palm oil methyl esters with TMP at Temperature 120°C, catalyst 0.9 w/w %, 20 mbar and 180 rpm

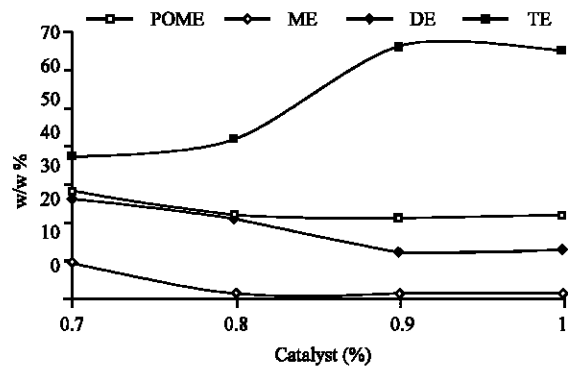


Fig. 4: Effect of catalyst on transesterification of palm oil methyl esters with TMP at Temperature 120°C, molar ratio 3.8:1, 20 mbar and 180 rpm

While at low vacuum pressure (500 mbar) the product consists of 10.7 w/w % TE, 31.2 w/w % DE, 6.7 w/w % ME and 51.4 w/w % of excess POME. It reveals that the reaction is inefficient at low vacuum pressure due to low percentage of TE in the product. Under low vacuum (higher pressure) there is not enough energy to pull the methanol away from the system. Therefore, it would not prevent the backward reaction. As a result, the TMP esters decomposed into methyl ester and resulted in higher percentage of unconverted methyl ester and partial esters in the final product.

Effect of molar ratio: Figure 3 reveals that there is negligible effect of molar ratio of POME to TMP on reaction conversion. When the ratio was varied between 1:3.6 and 1:3.9, the amount of TE formed from each varied between 60.1 and 65.6 (w/w %) only. It also indicates that, 3.8 is the optimum molar ratio since the amount of TE decrease when molar ratio increased to 3.9.

When molar ratio was high (1:3.9) the amount of partial ester in the product, especially monoesters was reduced which is important in the lubrication behavior (Robiah *et al.*, 2003; Zhang *et al.*, 2003; Schuchardt *et al.*, 1998).

Effect of catalyst amount: To determine the effect of catalyst amount, experiments were carried out with 0.7, 0.8, 0.9 and 1% catalyst based on total weight of POME and TMP. The other reaction conditions were as follows, duration 2 h, temperature: 120°C, molar ratio: 3.8:1 (POME/TMP) and agitator speed: 180 rpm. The complete results are shown in Fig. 4.

Figure 4 shows that at 0.7 w/w % the amount of catalyst was not sufficient to initiate the reaction of POME with TMP, thus very low TE content has been detected. It indicates that only 37.2 w/w % TE was converted while the conversion to partial ester such as

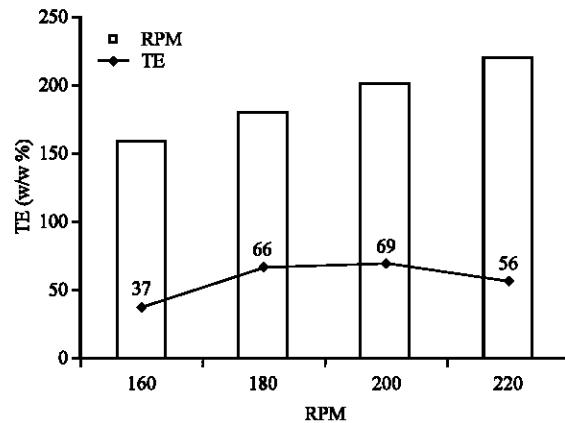


Fig. 5: Effect of agitator speed on transesterification of palm oil methyl esters with TMP at Temperature 120°C, molar ratio 3.8:1, vacuum pressure 20 mbar and catalyst 0.9 w/w %

mono ester and diesters are high at 9 and 26 w/w %, respectively. The result also indicates the optimum point due to proportional increase between the TE conversion and catalyst amount. Higher catalyst amount increase the solid content in the product. This may reduced the yield of final product (Zhang *et al.*, 2003; Schuchardt *et al.*, 1998). Therefore, 0.9 w/w % of catalyst was selected as an optimum condition rather than 1 w/w %, even though it shows the highest percentage of TE.

Effect of agitator speed: Figure 5 shows that the highest formation of TE (69 w/w %) was obtained at 200 rpm, which also gave the lowest value of unreacted POME (12 w/w %). The product also contains high amount of partial ester, especially diesters (18 w/w %) which can effect the lubrication behavior. While at agitator speed 180 rpm, the product consists of 66 w/w % TE, 12 w/w %

DE, 1 w/w % ME and another 21 w/w % POME. Since the difference is marginal, hence it is anticipated that the agitator speed between 180 to 200 rpm would be appropriate for palm oil TMP ester synthesis. At lower temperature (initial stage) TMP is in solid form while POME is liquid. However, as soon as the temperature approaches 60°C, TMP melts and homogenous solution is formed.

In order to ensure the homogenous condition, an adequate agitation is required to create circulatory flow to dissolve the particle (TMP) by POME. If the particle (TMP) could not be dissolved completely, it may reduce the production yield after catalyst was added. Since this is an unbaffled reactor, the circulatory flow was induced by agitator (Piero and Ernesto, 1998; McCabe *et al.*, 1993).

When the agitator speed was increased, the vortex may occur deeply until it reached the agitator. Therefore POME was drawn down into the charge and dissolved the TMP which was settled down at the bottom layer. This is clearly evident from the slope of the curves in Fig. 5 which indicates that the formation of TE has increased proportionally by agitator speed (especially from 160 to 200 rpm).

However, a drastic reduction in formation of TE was observed at agitator speed 220 rpm. The decrease in formation of TE (49 w/w %) may be influenced by other factor. Since vacuum pressure is crucial in this reaction, the reduction of TE may be due to non-optimal vacuum conditions. Under low vacuum, the methanol could have been present in the system. As a result, the occurrence of reverse reaction could not be suppressed. Consequently it may cause breakdown of triesters back to diesters and resulted low amount of TE in the product.

CONCLUSIONS

Five liter palm oil TMP ester containing 86% w/w triesters was successfully synthesized after 2 h operation. The optimum conditions were established at temperature: 120°C, vacuum pressure: 20 mbar, molar ratio: 3.8:1, catalyst amount: 0.9 w/w % and agitator speed: 180 rpm. The presence of a small amount of diesters (DE) and Palm Oil Methyl Ester (POME) in the product may act as an additive and improved the anti-wear characteristic. This study has shown that the scale up production is successful and could be used to scale up the process to a full scale biolubricant production.

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