

High Oleic Pentaerythritol Tetraester Formation via Transesterification: Effect of Reaction Conditions

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Abstract: Pentaerythritol tetraoleate esters synthesized from high oleic palm oil methyl ester (POME) have potential as biolubricant base stock. In the present study, the chemical transesterification of POME and pentaerythritol (PE) using sodium methoxide as a catalyst was conducted under vacuum. The effect of operating variables such as reaction temperature, catalyst concentration, the molar ratio of POME to PE, vacuum pressure, and stirring rate on the yield of PE tetraoleate was examined. The ideal conditions for the reaction were at a temperature of 160 °C, 1.25% (w/w) catalyst concentration, the molar ratio of POME to PE at 4.5:1, vacuum pressure at 10 mbar, and stirring speed at 900 rpm. PE tetraoleate with a yield of 36% (w/w), was successfully synthesized under this condition within 2 h of reaction time.

Keywords: transesterification; pentaerythritol tetraester; optimization; biolubricant

■ INTRODUCTION

Pentaerythritol (PE) tetraester can be synthesized from various vegetable oils and fatty acid esters. The synthesis of polyol esters can be carried out via chemical synthesis or enzymatic synthesis. However, enzymatic synthesis is inappropriate for high temperature reaction. Besides, chemical synthesis is a more economical process as the catalyst cost, and catalyst consumption will be much lower, compared to enzymatic synthesis [1]. The chemical synthesis method can be conducted via transesterification and esterification methods. Most of vegetable oil-based lubricants are synthesized via transesterification because of its lower cost and higher conversion at milder operating conditions. High oleic vegetable oils are potential candidates for mineral oil replacement as a base oil for lubricants and synthetic ester due to its excellent oxidative stability. A higher oleic content with relatively low trans and saturated fatty acid contents requires less additional processing steps to improve its oxidative stability. Furthermore, vegetable

oil-based polyol ester lubricants have excellent thermal stability, high viscosity, and biodegradable [2-4].

Previous research by Aziz et al. [5] reported that the highest yield of PE tetraoleate ester obtained via transesterification of palm oil methyl ester (POME) with PE was 37.56%. The reaction was conducted under vacuum to remove the methanol byproduct; thus, minimize the reverse reaction and move the reaction forward. The study also reported the performance parameters for the transesterification to achieve high PE ester conversion. These parameters include reaction temperature, reaction time, catalyst concentration, and the molar ratio of POME to PE. The performance parameter has been optimized with the catalyst concentration, and the molar ratio of POME to PE was found to be the most significant parameter to achieve a high yield of PE tetraoleate ester. Nonetheless, the yield of tetraester is still too low, thus require further studies to deliberate further on how to increase the conversion to tetraester, and thus improve its yield.

Even though the effect of the mixing rate and vacuum pressure plays an important role in increasing the rate of reaction, both parameters have not been investigated. In this reaction, mixing is important to ensure PE is soluble and form a homogeneous mixture with POME. Mixing increases the reaction area between the reactants and not only occurs at the interface; hence, it increases the rate reaction to form a product with the presence of catalyst [6]. Furthermore, the effect of vacuum pressure in transesterification reaction is important for the removal of methanol and to promote the forward reaction [7]. Effective methanol removal may lead to the high formation of the desired yield, which is PE tetraester. Therefore, in this study, the effect of vacuum pressure and mixing rate on the transesterification process of POME and PE via transesterification in batch scale reactions were carried out.

The lubricating properties of the polyol ester depend on the structures of these esters. Thus, it is important to achieve high reaction conversion to obtain high tetraester using the feasible method. The method must be able to produce high conversion to tetraester, simple and economical. Aziz et al. [5] studied the transesterification reaction of PE with palm oil methyl ester (POME) in a batch reactor. The method used sodium methoxide as a catalyst is found to be more feasible, and the reaction time is shorter than the method using an acid catalyst. In this study, the interaction parameters for the transesterification of POME and PE to produce tetraester are elucidated. The effects of reaction parameters such as reaction temperature, catalyst concentration, the molar ratio of POME to PE, vacuum pressure and stirring rate to the formation of products, i.e., PE monooleate (monoester), PE dioleate (diester), PE trioleate (triester) and PE tetraoleate (tetraester) were observed.

■ EXPERIMENTAL SECTION

Materials

Palm oil methyl ester (POME) and pentaerythritol (PE) alcohol were obtained from Solution Engineering (M) Sdn Bhd and Fischer Scientific, respectively. The analytical grade sodium methoxide was used as a catalyst. Transesterification reaction of POME and PE was carried out in the batch reactor.

Reactor Setup

The reactor setup includes 500 mL of the flat bottom three-necked flask as a batch reactor, a reflux condenser, thermometer, a hot plate, and a magnetic stirrer bar. A reactor equipped with a thermometer, a sampling port, and a condenser was immersed in a silicon oil bath and connected to a vacuum pump. A hot plate stirrer was used to provide heat as well as to control the stirring speed of reaction mixture in the reactor. A magnetic bar was used to ensure uniform mixing of the reaction mixture. A thermometer was used to measure the temperature of the reaction, and the reflux condenser was used to condense and return the palm oil methyl ester to the reactor due to its low boiling point. A vacuum pump equipped with a pressure transmitter was connected to the reflux condense to allow for the reaction to take place under various vacuum conditions. An air relief valve was placed in between the reflux condenser and vacuum pump to adjust the vacuum level. The reactor was immersed in a silicon oil bath to ensure uniform temperature reaction throughout the reaction and prevent heat loss.

Procedure

Synthesis of PE esters via transesterification

The reaction conditions were varied based on parameters to be studied, i.e., reaction temperature, catalyst concentration, vacuum pressures, the ratio of POME to PE, and stirring rate. By adapting the optimum reaction conditions obtained by Aziz et al. [5], the effects of reaction parameters on the formation of PE tetraester were examined. The reaction was conducted at temperature of 140 to 170 °C, molar ratio of POME to PE of 4.00:1 to 5.00:1, catalyst concentration of 0.5% (w/w) to 1.5% (w/w) and vacuum pressure ranged from 5 mbar to 50 mbar were employed while stirring rate fixed at 600 rpm and 1.2% catalyst w/w at 600 rpm. For the effect of stirring rate, the experiments were conducted at 300, 600, and 900 rpm, while the other parameters were kept constant at a temperature of 160 °C, the molar ratio of reactant 4.50:1, catalyst concentration 1.25% (w/w) and vacuum pressure of 10 mbar. Product samples were collected at certain time intervals to monitor the ester content. All PE disappeared in 1 h of reaction. However,

the synthesis was prolonged for up to 2 h to ensure complete conversion of PE.

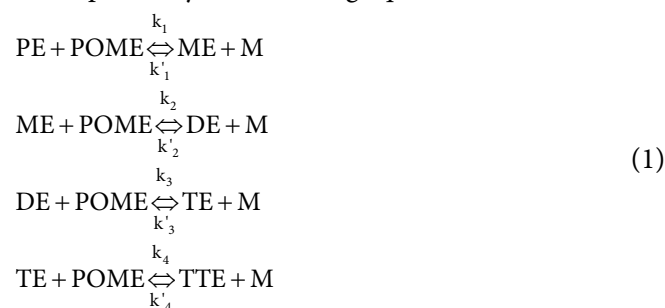
Analysis of the sample

The sampling procedure must be carried out within the possible shortest time to minimize the changes in the reaction system. The product sample was taken from the flask reactor and kept in the vial. The reaction sample was immediately diluted with ethyl acetate and BSTFA and swirled to prevent sample degradation and reverse reactions. The composition of product samples was analyzed using GC analysis method developed by Yunus et al. [8]. DB-HT5 capillary column with $15\text{ m} \times 0.32\text{ mm} \times 0.1\text{ }\mu\text{m}$ i.d., was used to perform the separation in the gas chromatography system. The reaction sample was diluted with 1 mL ethyl acetate and then swirled. Afterward, 0.5 mL of BSTFA was added into the mixture and swirled again. Before being injected into the GC, the prepared samples were heated for 10 min at $50\text{ }^\circ\text{C}$. The oven temperature was set at $80\text{ }^\circ\text{C}$ initially and held for 3 min. Then, it was ramped to $380\text{ }^\circ\text{C}$ at $6\text{ }^\circ\text{C}/\text{min}$ and held for another 6 min. The temperature of the detector and injector was set at 360 and $300\text{ }^\circ\text{C}$, respectively. The carrier gas used was hydrogen with a flow rate of $26.7\text{ mL}/\text{min}$, and the split ratio was done at 1:1.

RESULTS AND DISCUSSION

Transesterification Mechanism of PE Esters

The mechanism of the reaction is proposed to occur via four stepwise series reactions with the formation of intermediates. The reaction began with the formation of intermediate PE monoester, followed by PE diester, then the formation of PE triester, and finally, the product PE tetraester. Fig. 1 shows the overall step of transesterification of pentaerythritol esters. The formation of PE triester and PE tetraester increased significantly in the first 30 min of reaction. The steps can be simplified by the following equations.



The overall reaction is:

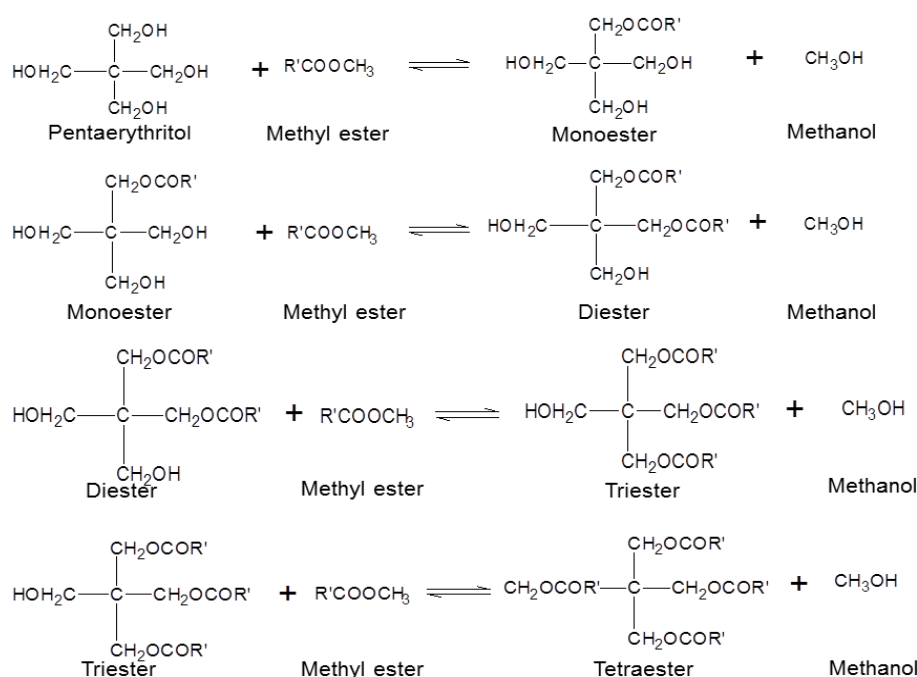


Fig 1. The overall transesterification of palm oil methyl ester with pentaerythritol where R' is C₁₇H₃₃

Fig. 2 shows the distribution curve of PE ester formation after 2 h of reaction at 160 °C and 10 mbar. From the analysis, it is evident that more PE triester and tetraester was formed compared to monoester and diester during the first few minutes of reaction. It indicates that the rate reaction of monoester from pentaerythritol was very fast. Once the monoester formed, it reacts with POME immediately to form diester. The result also indicates that the composition of monoester was maintained below 0.5% throughout the reaction. Lower composition of diester was observed during the first few minutes of reaction, probably due to the competitive reaction to produce triester from diester. After 45 min of reaction, the composition of diester was between 6.0% and 7.0%. Even though almost all monoester was subsequently converted to diester, not all diester was converted to triester, as indicated in the composition of PE ester after 2 h of reaction. Triester compositions were found between 24.0% to 28.0% whereas the composition of tetraester was between 26% to 35% after 45 min of reaction. The lower composition of PE tetraester at the end of the reaction might be due to the lower rate of reaction of triester to form tetraester because of greater steric hindrance of tetraester compared to the triester. In between 60 min to 105 min reaction, the composition of tetraester formed was lower than the triester. This might occur due to the accumulation of methanol in a reaction mixture that drives the PE tetraester reversed back to the triester. The slowest formation of tetraester from the triester also indicates that this step is rate-determining step with forwarding rate reaction constant, k_4 .

Effect of Reaction Time

In this study, the interaction parameters for the transesterification of POME and PE to produce tetraester are elucidated. The effects of reaction parameters such as reaction temperature, catalyst concentration, the molar ratio of POME to PE, vacuum pressure and stirring rate to the formation of products, i.e., PE monooleate (monoester), PE dioleate (diester), PE trioleate (triester) and PE tetraoleate (tetraester) were observed. A preliminary study has been conducted to obtain optimum reaction time, and it indicated that the highest conversion

was achieved after 2 h of reaction. Fig. 3 shows the comparison of product formation at 1 h reaction and 2 h reaction. Pentaerythritol alcohol reactant still exists in the product mixture after a 1 h reaction. However, when the reaction extends up to 2 h, pentaerythritol alcohol completely disappeared and formed PE esters that are PE monoester, PE diester, PE triester, and PE tetraester, and the composition was presented in Table 1. Further increment of reaction time decreased the formation of PE tetraester decreased due to some reverse reactions.

Effect of Reaction Temperature

The reaction temperature was varied from 140, 150, 160 °C, and 170 °C to study the dependency of transesterification reaction on temperature. The other parameters were fixed at constant values; reactants molar ratio of 4.25:1, 1.2% w/w sodium methoxide catalyst,

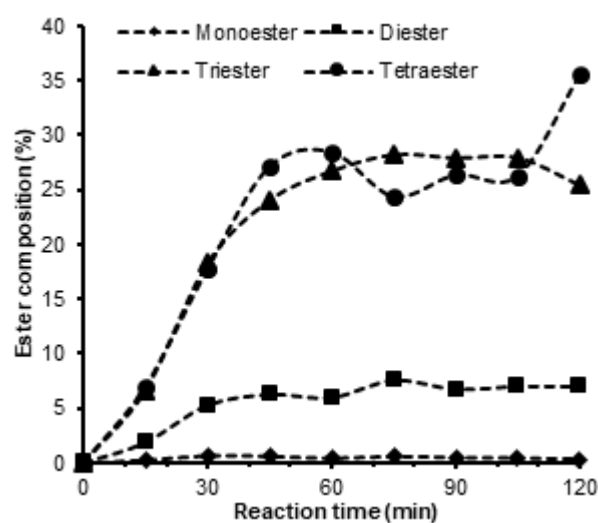


Fig 2. Composition change of PE ester products versus reaction time at 160 °C. (POME:PE, 4.5:1; 10 mbar; 1.25% w/w sodium methoxide; 900 rpm)

Table 1. Composition of PE oleate esters at optimum conditions

Products	Composition (% w/w)
Pentaerythritol monooleate (PE monoester)	0.4%
Pentaerythritol dioleate (PE diester)	6.7%
Pentaerythritol trioleate (PE triester)	25.5%
Pentaerythritol tetraoleate (PE tetraester)	36.0%
Remaining POME	31.4%

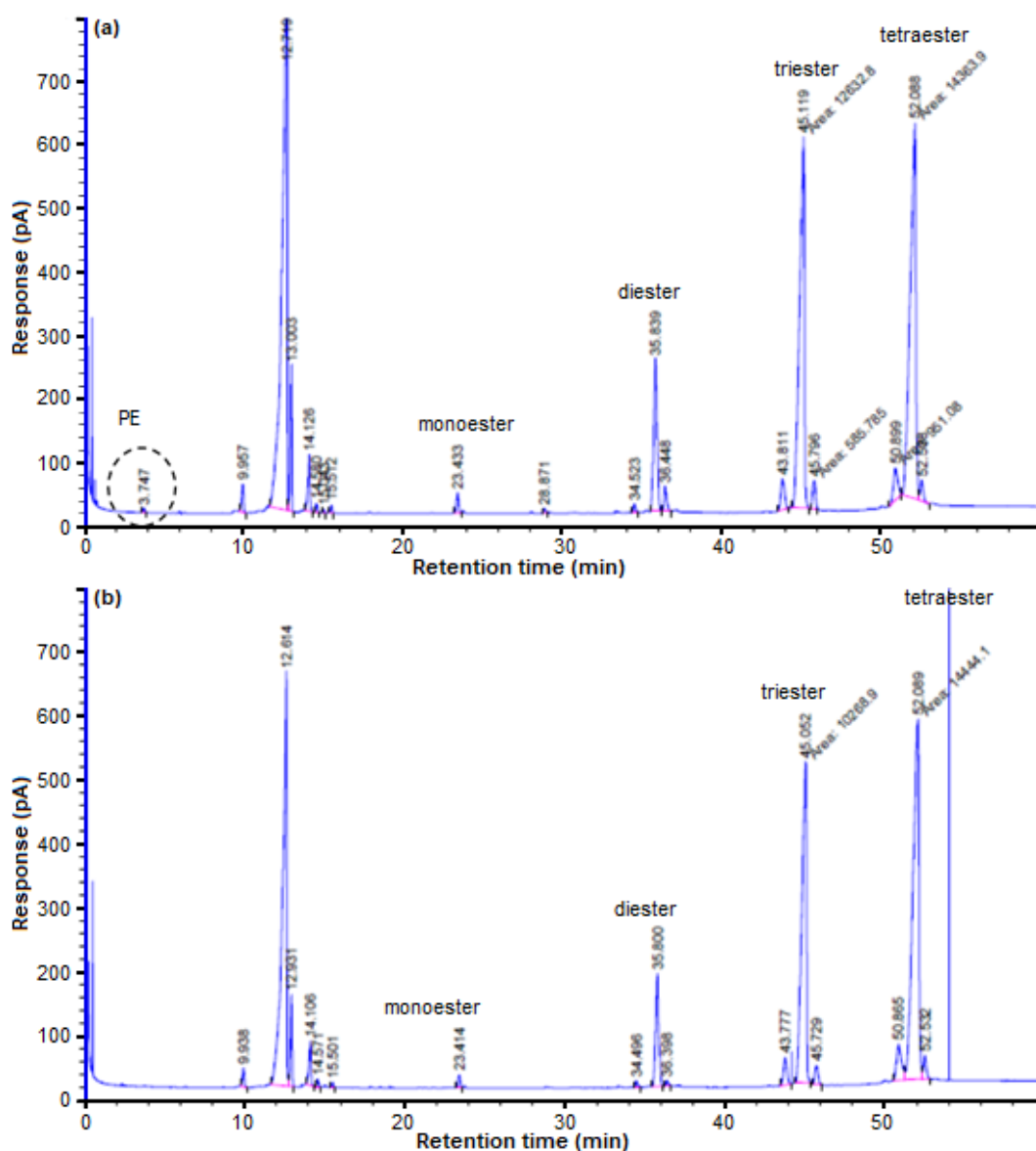


Fig 3. Gas chromatography of PE esters formation at (a) 1 h reaction and (b) 2 h reaction

10 mbar vacuum pressure, and 600 rpm stirring rate. The samples were collected after 1, 2, and 3 h, and then analyzed using the GC to determine the composition of the product. However, it was observed that the reversible reaction occurred after 3 h reaction and most of the PE tetraester reversed back to form triester. Thus, all reactions were stopped after 2 h. Moreover, the synthesis of PE tetraester was performed below 180 °C to avoid sublimation of pentaerythritol. Due to this consideration, the reaction temperature was set in between 140 to 170 °C.

The effect of reaction temperature on the formation of PE esters at 1 h reaction is shown in Fig. 4, and the

formation of PE esters at 2 h reaction is shown in Fig. 5. The yield of PE tetraester at 1 h reaction were 13.4, 24.0, 28.5 and 20.9% at 140, 150, 160 and 170 °C respectively. Fig. 4 shows that the effect of temperature is more obvious after 2 h of reaction. At the same temperature, the composition of PE esters rose to 17.36, 29.43, 36.73, and 20.71%, respectively. The improvement in reaction conversion from 1 to 2 h shows a similar trend with responding to the increase in temperature. The results indicated that the yield of tetraester increased with temperature and the maximum yield was obtained at 160 °C. However, the yield of tetraester was slightly

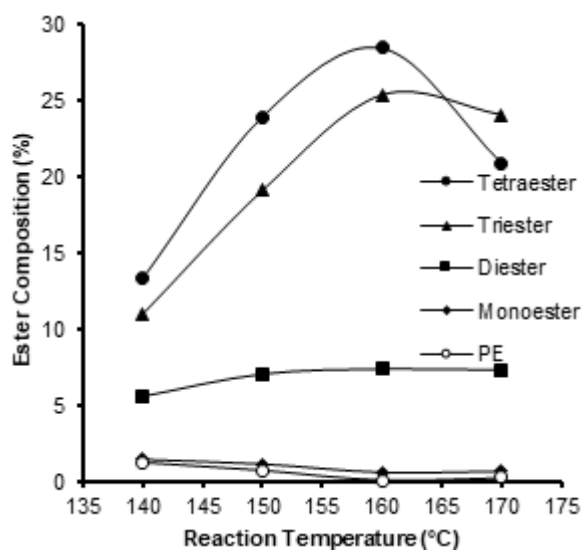


Fig 4. Effect of temperature on PE ester yield at 1 h reaction (POME: PE, 4.5:1; 10 mbar; 1.25%w/w sodium methoxide, 600 rpm)

dropped when the temperature was further increased to 170 °C. This may occur due to a higher rate of the backward reaction that reverses the tetraester back to the triester. These findings concur with similar transesterification reaction of TMP triester reported by Yunus et al. [7] and Koh et al. [9]. At higher temperatures, the rate of reverse reaction of TMP triester to diester was represented by kinetic reaction rate constants, $k_{3,r}$ was significantly larger than $k_{2,r}$ [10].

At higher temperatures, the rate of reaction increases; thus, it increases the yield of PE tetraester. However, the reactant POME can also evaporate at high temperatures, resulting in the occurrence of reverse reaction which reduces the yield of PE tetraester. Hence, it is very important to use cold water in the condenser to condense the evaporating POME and return to the reaction flask. Furthermore, the sublimation of pentarerythritol may also occur. If the reaction temperature is too high, both POME evaporation and pentarerythritol sublimation could take place, resulting in the low yield of PE ester. Therefore, the optimum reaction temperature is proposed at 160 °C which produced the highest yield of tetraester.

Effect of Catalyst Concentration

The use of enzymes as a catalyst for this transesterification reaction is not suitable because of the

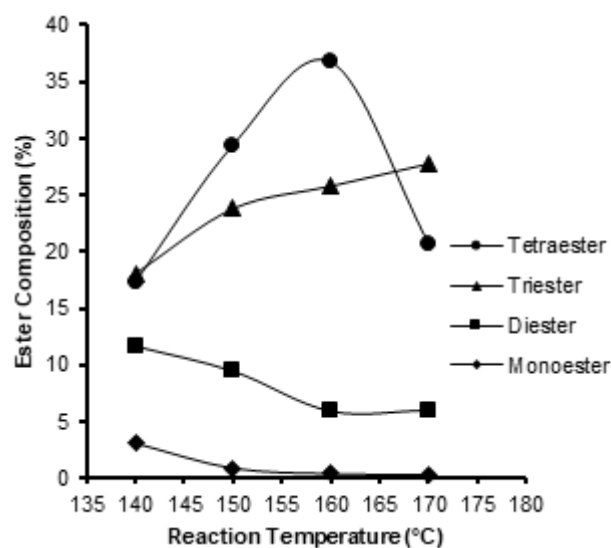


Fig 5. Effect of temperature on PE ester yield at 2 h reaction (POME: PE, 4.5:1; 10 mbar; 1.25%w/w sodium methoxide, 600 rpm)

higher melting point of pentaerythritol, which is at 260 °C. Furthermore, some of the acid catalysts are toxic, and the reaction is longer to obtain high yield. A homogeneous acid catalyst such as sulfuric acid or hydrochloric acid is corrosive, and the main problem is that this hazardous strong acid generates much wastewater during product purification. Furthermore, the reaction with the acid catalyst requires a long reaction time for completion [11].

On the contrary, most of the alkaline catalyst is non-toxic, and the reaction is much faster. Thus, sodium methoxide was used as a catalyst for the transesterification reaction of PE and POME to form PE tetraester. However, sodium methoxide catalyst is easily oxidized in the air; hence, the reaction should be maintained under anhydrous condition [5].

The effect of catalyst concentration on the transesterification reaction was evaluated in the range of 0.5% to 1.5% (w/w), while the other parameters such as temperature, reactants molar ratio, vacuum pressure, and stirring rate were kept constant at 160 °C, 4.25:1, 10 mbar and 600 rpm, respectively. The reaction was carried out for 2 h. Fig. 6 shows the effect of catalyst concentration of the PE ester formed in which the catalyst concentration was varied at 0.5, 0.75, 1.00, 1.25, and 1.5%, respectively. The catalyst concentration has a positive effect on the PE tetraester composition. At the

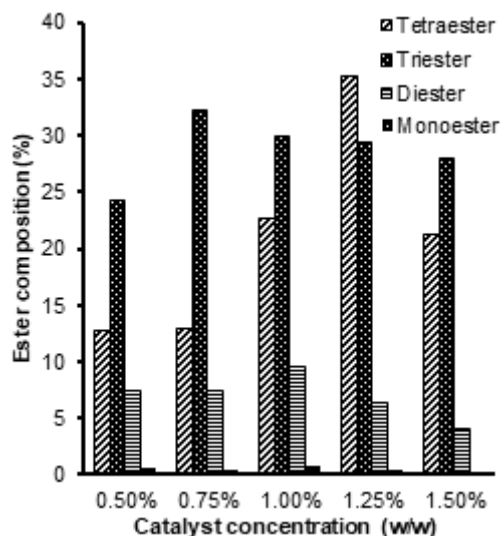


Fig 6. Effect of catalyst concentration on PE ester yield at 2 h reaction (POME: PE, 4.5:1; 10 mbar; 160 °C; 600 rpm)

lowest catalyst concentration, 0.5% w/w, the percentage of tetraester was low at 12.8%. There is no significant effect of catalyst concentration increment from 0.5% to 0.75% w/w on the tetraester composition, which remained at 12.8%. However, when the catalyst was at 1.0% w/w, the composition of tetraester increases to 22.7%. The results are comparable with a transesterification of PE tetraester by Aziz et al. [5], where increasing the catalyst concentration from 0.75% to 1.0% w/w significantly increased the composition of PE tetraester. A similar finding was observed when sodium methoxide used as a catalyst in transesterification of TMP triester, where the highest triester composition was obtained at a catalyst concentration of 1.0% w/w. There is no significant effect on the TMP triester yield increment when the sodium methoxide catalyst used at a concentration between 0.5% w/w to 0.7% w/w [12]. In a transesterification of biodiesel from karanja oil using sodium methoxide, a similar result was observed where the highest composition of karanja oil methyl ester was obtained at a catalyst concentration of 1.0% w/w [13].

In this study, the highest PE tetraester composition, which is 35.2%, was obtained with 1.25% w/w of catalyst. It shows that increasing catalyst concentration will accelerate the reaction and formed more PE esters. On the increasing of catalyst to 1.5% w/w, the composition of tetraester drastically reduced to 21.3%. The amount of

monoester and diester at all catalyst concentration were below 0.5 and 10.0%, respectively. Whereas, the total composition of triester was in the range of 25.0% to 32.0% at all concentrations.

This finding is similar to the PE ester transesterification reaction by Aziz et al. [5] but the highest tetraester composition was obtained in 1 h. However, the reaction was conducted for 2 h in this study to ensure pentaerythritol completely reacted to form PE tetraester. This is because a small amount of pentaerythritol still left in the reaction mixture when the reaction was conducted in 1 h, and only a small amount of PE tetraester was formed. It might be due to a very slow reaction during the first minute due to the mixing and dispersion of reactants and catalysts. Furthermore, the temperature of the reaction mixture slightly reduced about 10 °C to 15 °C as soon as the sodium methoxide catalyst was added. This is because transesterification is an endothermic reaction that adsorbed energy from the surrounding, consequently reduce the temperature of the reaction mixture. Based on the observation, the reaction required 10 min to 15 min to increase to the desired reaction temperature. Therefore, the rate formation was slow at 1 h of reaction, and a lower amount of PE tetraester produced.

The increment of catalyst concentration from 1.25% to 1.5% w/w decreased the amount of PE ester formed. The presence of a large amount of alkaline catalyst in the reaction could lead to the formation of fatty acid soap. The hydrolysis of methyl ester will produce fatty acid and lead to fatty acid soap formation in the presence of metal catalyst [5,14]. Therefore, the formation of PE ester will be affected. The yields of PE ester component were reduced at the highest catalyst concentration 1.5% w/w, as shown in Fig. 6. A similar result was noticed when sodium methoxide was used for transesterification of high oleic TMP triester [12] and transesterification of biodiesel from karanja oil [13], where a higher amount of catalyst reduced the yield of TMP triester and karanja oil methyl ester, respectively. When homogeneous sodium methoxide was employed for transesterification of POME to TMP triester, a low catalyst concentration of 1.0% w/w catalyst was required

to achieve 92.6% TMP triester composition [12]. However, a high catalyst concentration of 1.25% w/w catalyst was required to obtain a high yield of PE tetraester. Therefore, it can be observed as an optimum catalyst concentration for the examined conditions.

Effect of Molar Ratio of POME to PE

The molar ratio of reactants is one of the important parameters that affect the rate of reaction in the transesterification process [1,15-16]. The molar ratio of POME to PE from the stoichiometric is 4 to 1. However, the amount of POME used was in excess to enhance the forward reaction and hinder the backward reaction [16]. The molar ratio of POME to PE was varied at 4:1, 4.25:1, 4.5:1, 4.75:1, and 5:1 to study the effect of the molar ratio of reactants on the PE tetraester formation. The other reaction parameters were kept constant at reaction temperature 160 °C, vacuum pressure at 10 mbar, and 1.25% w/w sodium methoxide. The reaction was carried out up to 2 h at 600 rpm.

The effect of the molar ratio of POME to PE on the formation of PE ester is shown in Fig. 7. The composition of PE tetraester was very low at the stoichiometric ratio of 4:1, which is around 5.0%. The composition of tetraester increased to 19.1 and 35.2% when the ratio of reactants was increased to 4.25:1 and 4.5:1, respectively. However,

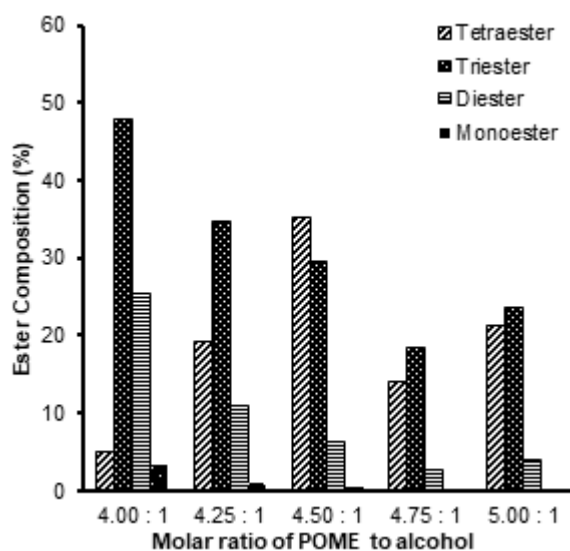


Fig 7. Effect of the molar ratio of POME to PE on PE ester yield at 2 h reaction (10 mbar; 160 °C; 1.25% w/w sodium methoxide, 600 rpm)

the composition of tetraester decreased drastically to 13.9% when the ratio of the reactants was further increased to 4.75:1. At a molar ratio of 5.00:1, the composition of tetraester was slightly increased to 21.2%. At a very high ratio of POME to PE, i.e., at 10:1 and 12:1, the composition of tetraester was markedly decreased to 12.0% and 6.7%, respectively.

There is no significant effect of using the high molar ratio of reactants since the reaction was based on the stoichiometric molar ratio. The highest composition of tetraester was obtained at the molar ratio of 4.5:1. At a molar ratio of 4.00:1 and 4.25:1, the reaction was assumed incomplete since a large proportion of ME and DE still exist. The excess of POME was used to ensure the reaction is complete. When the large excess of POME was used in the reaction, the interaction between the catalyst and the reactants was reduced due to the dilution effect. Thus, the best molar ratio of POME to PE is 4.5:1.

Effect of Vacuum Pressure

The vacuum was used in the reaction to remove the methanol from the process and promote the forward reaction. In order to study the effect of vacuum pressure on the transesterification reaction, the experiments were conducted at 5 mbar, 10 mbar, 20 mbar, and 50 mbar. The other parameters were fixed at a reaction temperature of 160 °C, POME to PE 4.5:1, and at 1.25% w/w sodium methoxide. The reaction was run for 2 h.

The effect of vacuum pressure on the yield of PE esters is shown in Fig. 8. The highest composition of PE tetraester was obtained at 10 mbar, which was at 36.7%. When the vacuum level increased to 20 mbar and 50 mbar, the composition of tetraester drastically decreased to 16.7 and 19.3%, respectively. At low vacuum (high pressure), not all POME was converted to PE esters. For example, 45% of PE esters at 20 mbar and 50 mbar were still in intermediates forms of esters (monoester, diester, and triester). This may occur due to an inadequate vacuum that unable to prevent the backward reaction and reverse the PE esters back to POME. The removal of methanol was slow at a low vacuum; the reaction between methanol with PE esters may have occurred and resulted in the reverse reaction to form POME. It can be seen from the

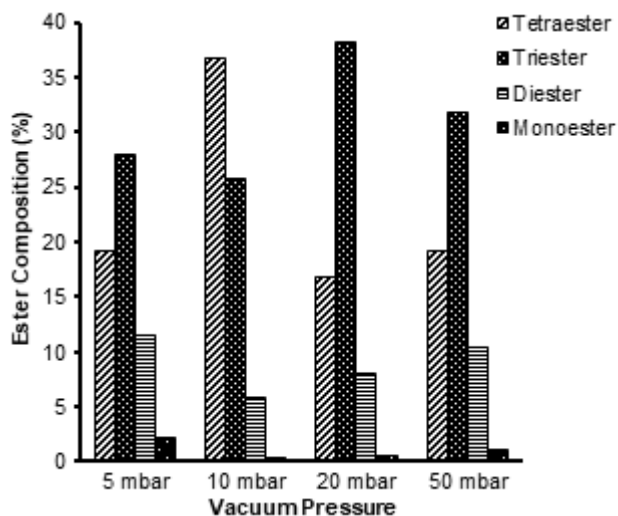


Fig 8. Effect of vacuum pressure on PE ester yield at 2 h reaction (POME: PE, 4.5:1; 160 °C; 1.25% w/w sodium methoxide, 600 rpm)

composition of POME at 20 mbar and 50 mbar, which is higher compared to the composition of POME at 5 mbar and 10 mbar. This observation is similar to previous research on the transesterification reaction of TMP esters conducted by Yunus et al. [7] and Kamil et al. [17].

However, at 5 mbar, the composition of tetraester obtained was reduced to 19.1%. This is because if the vacuum is too high (low pressure), POME will be sucked away together with methanol from the system, resulting in the lower formation of PE esters. POME may evaporate from the reaction system because of lower boiling point properties. Hence, it will change the stoichiometric ratio of reactants in the reaction. The backward reaction may have occurred to reverse the tetraester back to partial esters due to the insufficient quantity of POME. In economic consideration, high vacuum requires high energy and increase the cost of equipment and process.

Therefore, for the transesterification of POME with PE, the optimum vacuum pressure was found to be at 10 mbar for the synthesis temperature between 140 °C to 170 °C. The high yield of PE tetraester was formed under this condition. In contrast with the synthesis of TMP triester using sodium methoxide catalyst, the optimum vacuum pressure was obtained at 20 mbar at a synthesis temperature between 100 °C to 130 °C.

Effect of Stirring Rate

Mixing is very important in transesterification reactions involving POME and PE. PE is solid, and the POME is liquid. In order to make sure PE is soluble and form a homogenous mixture with POME in the presence of a catalyst, good mixing is crucial. This will provide a good mass and heat transfer and maintain uniform conditions in the reaction system. Furthermore, mixing will enhance the mixing of particles or molecules of reactants, thus reduced reaction time [9]. These conditions can be achieved by conducting the reaction in the turbulent flow which can be promoted with the addition of baffles. In a batch system, the reaction can be conducted by providing external mixing using rotary agitation [18]. In a small-scale batch reaction, a stirred batch reactor will be used to conduct the reaction.

In this study, the mixing process in a batch reactor was achieved by providing the stirring of the mixture using magnetic stirrer. The stirring speed played an important role in speeding up the reaction rate. The stirring speed was varied at 300, 600, and 900 rpm, and the other parameters were kept constant at 160 °C, 10 mbar, 1.25% sodium methoxide, and POME to PE at 4.5:1. The sample was taken at 15 min interval, and the reaction was conducted for 2 h. The effect of stirring speed on the composition of PE esters is shown in Fig. 9.

A good mixing between the reactants, i.e., POME, PE, and sodium methoxide catalyst, resulted in effective collisions between the reactants molecules and catalysts. Therefore, enough energy is gained to overcome the potential energy barrier for the reactions to occur and obtain the desired product [9]. Fig. 9 shows that, as the stirring rate increases, the yield of PE tetraester increases. At the lower stirring speed of 300 rpm, the rate formation of PE esters was slow. It can be seen in Fig. 9(a) that the rate of tetraester formation from triester was slow at the beginning, and slightly increased up to 90 min of reaction. At 90 min to 105 min, the rate suddenly increased and thus increased the composition of PE esters. However, the composition of the triester is higher than the tetraester, along with the reaction. It may be

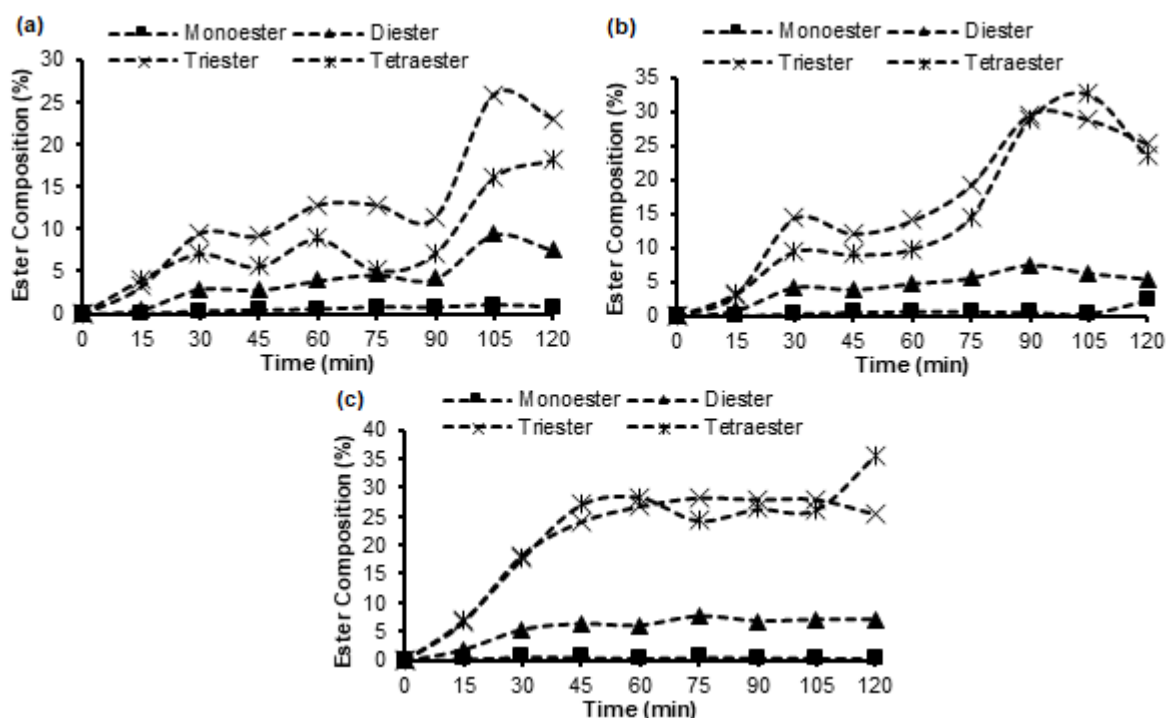


Fig 9. Effect of stirring speed on PE ester yield at 2 h reaction at (a) 300 rpm (b) 600 rpm and (c) 900 rpm (POME: PE, 4.5:1; 160 °C; 10 mbar; 1.25% w/w sodium methoxide)

due to insufficient energy to break the potential energy of triester to convert to tetraester at lower stirring speed. Furthermore, slow mixing may require a longer time to achieve a high composition of desired tetraester [13].

As the stirring speed was increased to 600 rpm, the rate reaction also increased. In the beginning, the composition of the triester is higher than tetraester until 90 min of reaction. The highest tetraester was found after 105 min reaction with tetraester composition at 32.6%. However, the composition of tetraester decreased to 23.5% when the reaction was prolonged to 120 min, as shown in Fig. 9(b). This may occur due to the occurrence of the reverse reaction. Once the reaction achieves its optimum yield, continued stirring will promote the reverse reaction which is competing with the optimality of system kinetics [19].

The highest tetraester composition was obtained when the reaction was conducted at 900 rpm, with a yield of 35.5% after 120 min of reaction. The rate formation of tetraester and triester gradually increased at the early 45 min of reaction. In between 45 min to 105 min, the reaction system produced more tetraester and triester as

shown in Fig. 9(c). Therefore, the stirring rate between 600 rpm to 900 rpm can be regarded as the best mixing speed for the reaction. Under these conditions, a reasonably high yield of PE tetraester can be obtained. Controlling the mixing speed is necessary for the optimum condition of PE esters formation. However, if the stirring speed is too high, it increases the rate of reverse reaction thus reduces the yield of tetraester.

■ CONCLUSION

Based on the results from the optimization study presented, the optimum parameters for the transesterification reaction of POME with PE were found. The temperature of reaction at 160 °C, molar ratio reactants, i.e., POME to PE at 4.5:1, sodium methoxide catalyst concentration at 1.25%, vacuum pressure at 10 mbar and stirring speed at 900 rpm were established as optimum conditions. All reactions were carried out for 2 h in a stirred batch reactor.

The transesterification reaction of POME and PE involved four steps of consecutive reactions to form PE monoester, PE diester, PE triester, and PE tetraester.

Pentaerythritol was not detected in the reaction product and has been fully converted into PE esters. The composition of monoester was below 0.5% at all reaction conditions. The highest composition of PE tetraester was achieved at 36%. The composition of PE tetraester obtained similarly with the previous study by Aziz et al. [5]. It might occur due to the slower rate formation to produce PE tetraester that has a bulky molecule structure. These steric effects would decrease the rate formation of PE tetraester because it has greater steric hindrance with four ester groups as compared to PE triester that consists of three ester groups. The substitution of large methyl oleate group into pentaerythritol by removal of -OH would make the molecule sterically crowded. When more -OH was replaced with methyl ester group, the steric effect would increase, and bulky ester molecule formed [20].

In this study, an efficient chemical synthesis to produce PE esters from palm oil is established. The transesterification reaction system using an alkaline catalyst and equipped with a vacuum system allows for faster reactions and suppress reverse reactions.

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