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DEVELOPMENT OF OPTIMUM SYNTHESIS METHOD FOR TRANSESTERIFICATION OF PALM OIL METHYL ESTERS AND TRIMETHYLOLPROPANE TO ENVIRONMENTALLY ACCEPTABLE PALM OIL-BASED LUBRICANT

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ABSTRACT

Chemical synthesis of palm oil trimethylolpropane esters was conducted via transesterification of palm oil methyl esters (POME) with trimethylolpropane (TMP). The palm oil TMP esters are potential biodegradable base stock for lubricant production. The influence of the main operating variables, namely, temperatures and pressures, molar ratio of palm methyl esters to TMP, and catalyst amount was studied and analysed. The effects of temperature (80°C to 140°C) and reduced pressure (0.1, 10, 50, 100 and 500 mbar) were investigated and found to have a significant impact on the reaction. On the contrary, the amount of catalyst (% w/w) and molar ratio of POME to TMP had little influence on the conversion but affected the overall yield of the reaction. The optimal reaction conditions are as follows: duration: 1 hr; temperature: 130 °C; pressure: 20 mbar; catalyst: sodium methoxide at 0.8% w/w; molar ratio of POME:TMP at 3.9:1. Palm oil TMP ester containing 98% w/w triesters was successfully synthesized in less than an hour.

Keywords: biodegradable lubricant, palm oil methyl esters, transesterification, trimethylolpropane esters.

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INTRODUCTION

The global drive towards the use of biodegradable products is increasing despite early commercial resistance due to their cost and performance consideration (Davidson and LaPierre, 1998). Biodegradable polyol esters derived from the transesterification of vegetable oils and branched neopolyols such as TMP and pentaerythritol (PT) have been developed for various biodegradable lubricant applications (Uosukainen *et al.*, 1998; Pavlovicova and Cvengros, 1999; Schlosberg *et al.*, 2001). The fluids have excellent thermal stability, better lubricity, low volatility, and resist hydrolysis better than other esters (Kohashi, 1990). However, these esters suffer the disadvantage of seal-swelling tendencies due to their high degree of polarity. Nonetheless, there are applications where ester-based fluids are inevitable to overcome the high or low temperature limitations of vegetable oil-based lubricants. For instance, long-chain polyol esters have been used successfully in the steel-rolling industry, hydraulic fluids and outdoor lubricants, particularly in forestry, waterways and construction (Remmelmann and Murrenhoff, 1998).

Burmah Castrol Ltd (GB) was reported to have invested substantially in a research project to develop palm-based lubricants for a two-stroke engine (Bahaman, 1993). The company patented the product in 1994 which uses palm olein as base fluid (European patent, 93307853.7). The invention provides a lubricating oil for a two-stroke lubricant which comprises 30%-99% w/w olein, 0%-30%

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w/w other base fluids, 0%-25% w/w diluents, 0%-30% w/w smoke suppressant and up to 18% w/w additives in order to improve its lubricating properties. In its original form, palm olein suffers various setbacks particularly its high pour point at 22°C and poor oxidative stability. Hence, new polyol esters from palm oil with improved pour point and oxidative stability will be synthesised in this work to provide high performance base fluids for biodegradable lubricants.

For the lubricants to be economically viable, both the lubricating characteristics and the method of synthesis are important. Earlier studies have reported slow reaction rates caused by sterically hindered components (Schlosberg *et al.*, 2001). Since the lubricating properties of the polyol esters depend primarily on the structures of these esters, it is important that a high conversion to triesters be achieved in all runs (Eychenne *et al.*, 1998). The synthesis of the polyol esters can be carried out either via chemical or enzymatic reactions (*Figure 1*). Typical catalysts include sodium methylate (Uosukainen *et al.*, 1998), sulphuric acid, *p*-toluene sulphonic acid (Eychenne *et al.*, 1998), tetraalkyl titanate, anhydrous sodium hydrogen sulphate, phosphorous oxides and stannous octanoate. Immobilized lipases from *Candida rugosa* (Linko *et al.*, 1995), *Mucor* or *Rhizomucor miehei* (Hallber *et al.*, 1999; Hayes and Kleiman, 1996) have also been employed in the synthesis of diol and polyol esters.

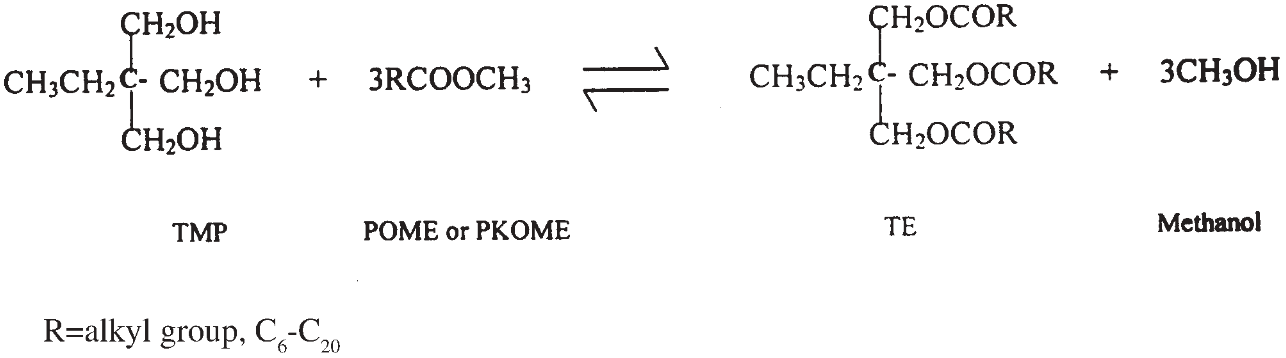

Figure 1.

To develop an optimum synthesis method, the effects of various operating conditions on the chemical transesterification of POME and TMP must be studied. These include the effects of temperatures, vacuum pressures, substrate ratio and catalyst. Chemical synthesis as opposed to enzymatic synthesis was used since the reaction temperature has to be maintained above the melting point of TMP, which is too high for enzymes. The objective of this work was to develop an optimum process for the synthesis of palm oil lubricant via chemical transesterification of POME and TMP.

MATERIALS AND METHODS

Materials

POME were obtained from Carotech (Malaysia) Sdn. Bhd. The fatty acid compositions of these samples were determined according to the standard methods for oil and fats analysis (PORIM, 1995) and shown in *Table 1*. TMP was purchased from Merck-Schuchardt (Germany), sodium methoxide and reference standards were purchased from Sigma Aldrich Chemicals Co.

Synthesis of Palm Oil Trimethylolpropane (TMP) Esters

The reactions were performed in a 500-ml three-neck flask equipped with a thermometer, a sampling port and a reflux condenser. The condenser was connected to a vacuum line equipped with a relief valve, accumulator and a vacuum trap. The reactor was immersed in a temperature-controlled oil bath. The reactor was filled with 200 g of POME and a known amount of TMP and was under constant stirring provided by the magnetic stirrer. The weight of TMP was determined based on the required molar ratio and the calculated mean molecular weight of the POME. The mixture was then heated to the reaction temperature after which the catalyst was added. The vacuum was gradually applied to the system until it reached the desired pressure and maintained at the same pressure until the reaction was completed (Malaysian patent application pending: PI20030943). Samples were analysed at certain time intervals for POME, monoester (ME), diesters (DE), triesters (TE) and TMP compositions (weight %) by gas chromatography as described earlier (Yunus *et al.*, 2002a).

The effects of temperature and pressure were examined at a molar ratio of POME to TMP of 3.9:1 and 0.9% catalyst (w/w). Experiments were conducted at temperatures between 80°C-140°C at 0.2, 10 and 20 mbar vacuum using POME. To

TABLE 1. AVERAGE FATTY ACID COMPOSITIONS OF PALM OIL-BASED METHYL ESTERS (POME)

Fatty acid	POME (%)
10:0	-
12:0	0.9
14:0	1.5
16:0	41.5
16:1	0.3
17:0	0.1
18:0	2.7
18:1	40.6
18:2	11.9
18:3	0.3
Others	0.2

examine the effects of vacuum on the reaction, vacuum pressures ranging from 0.1 to 500 mbar were employed at 130°C throughout the experiments.

The experiments on the effects of reactants molar ratio and catalyst were conducted at 130°C and 10 mbar. The range of molar ratio selected was from 3.1:1 to 3.9:1 using 0.9% catalyst (w/w). For the catalyst, it was reported that the optimum weight percentage lay between 0.1% to 2.0% (Uosukainen *et al.*, 1998). However, in this study, the catalyst quantity was varied within the range of 0.1% to 1.2% using the reactants with a molar ratio of 3.9:1.

RESULTS AND DISCUSSIONS

Effect of Temperature

The reactions were carried out at 80°C, 90°C, 100°C, 110°C, 120°C, 130°C and 140°C with the aim of observing the effect of temperature on TMP ester conversions. Experiments were conducted at a 3.9:1 molar ratio of POME to TMP, 0.9% w/w catalyst, and 0.2 mbar. The GC chromatogram of the palm oil TMP esters is shown in *Figure 2*.

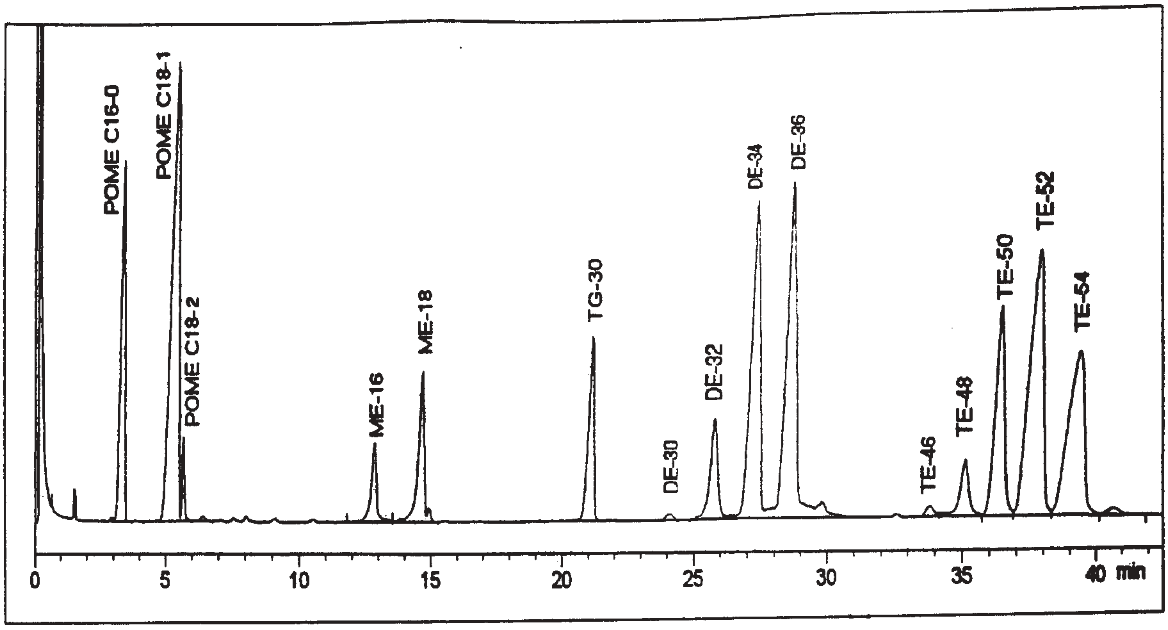

Figure 2. GC chromatogram of palm oil trimethylolpropane esters. POME-palm oil methyl ester, ME-monoester, DE-diesters, TE-triesters. TG 30 (trilaurin) is the internal standard.

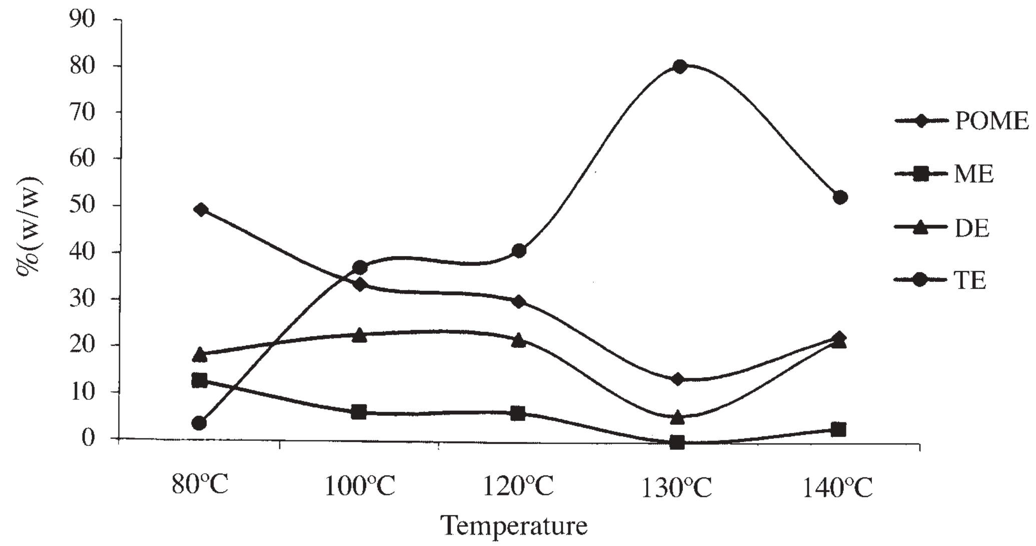

Figure 3. Effect of temperature on transesterification of palm oil methyl esters with trimethylolpropane (POME:TMP, 3.9:1; catalyst 0.9% w/w; 10 mbar, 4 hr). POME-palm oil methyl ester, ME-monoester, DE-diesters, TE-triesters.

The effect of temperature on the transesterification of POME with TMP at 10 mbar is shown in *Figure 3*. The samples were analysed for TE, DE, ME and POME content by gas chromatography (Yunus *et al.*, 2002a). Initially, the yield of TE (wt %) increased with temperature but dropped slightly at 120°C. Although, the yield at 130°C was lower than at 120°C, the amount of diesters at 120°C was notably higher. At high temperature, the amount of POME in the reactor was low due to vaporization, thus occurrence of the reverse reaction (*Figure 4)* could not be suppressed. Consequently, there was a high concentration of diesters in the product composition.

$$\mathrm{TMP} + \mathrm{POME} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \mathrm{ME} + \mathrm{CH_3OH} \tag{1}$$

$$\mathrm{ME} + \mathrm{POME} \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} \mathrm{DE} + \mathrm{CH_3OH} \tag{2}$$

$$\mathrm{DE} + \mathrm{POME} \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} \mathrm{TE} + \mathrm{CH_3OH} \tag{3}$$

The overall reaction is:

$$\mathrm{TMP} + 3\mathrm{POME} \underset{k_0'}{\overset{k_0}{\rightleftharpoons}} \mathrm{TE} + 3\,\mathrm{CH_3OH} \tag{4}$$

Figure 4.

However, if the vaporized POME were recondensed back into the reactor, the reverse reaction would be contained and the esterification of DE to TE would prevail. This is evident from the product composition at 130°C. Hence, it is very important that water used in the condenser is cold enough to condense all the vaporized POME back to the reactor. Otherwise, the POME would escape with methanol and result in lower conversion of the TE as shown at 120°C. At higher temperatures, most of the POME escaped with the vacuum and resulted in backward reaction of TE to form DE. Similar results were discovered in the transesterification of PKOME with TMP. Hence, high temperatures are not recommended for these reactions.

Effect of Pressure

The effect of pressure on the rate of transesterification between POME and TMP at 130°C is shown in *Figure 5*. Although the highest yield of POME TE was obtained at 0.1 mbar, considerable energy would be needed to achieve this high vacuum condition. The composition of TE at 0.1 and 10 mbar were 82.6% and 79.9% w/w, respectively.

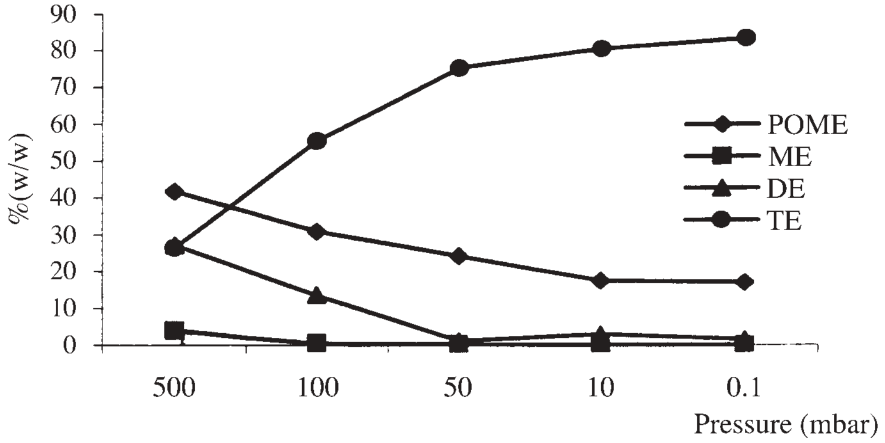

Figure 5. Effect of reduced pressure on product composition in transesterification of palm oil methyl esters with trimethylolpropane (POME: TMP was 3.9:1, catalyst 0.9 % wt., 130°C). POME-palm oil methyl ester, ME-monoester, DE-diesters, TE-triesters.

At 50 mbar, the product contained 75% TE, 1 % DE and 24% excess POME, while at 10 mbar, the product consisted of 79.9% TE, 2.8% DE and 17.3% excess POME. Since the difference was marginal, it is anticipated that a vacuum between 10-20 mbar, is appropriate for the palm oil-based TMP ester synthesis. Although the amount of unreacted POME would be slightly high, it would eventually be removed by distillation. Under a moderate vacuum of 50 mbar, the backward reaction to regenerate POME was not suppressed, hence resulting in high percentages of unreacted POME. However, the higher content of DE at high vacuum (low pressure) condition indicates that there might have been occurrence of a backward reaction to convert the TE to DE due to depletion of the methyl esters. In the absence of sufficient quantity of methyl esters, the backward reactions could no longer be suppressed. This is shown in the results obtained at higher pressures, 100 and 500 mbar. There were high percentages of unconverted partial esters (mono and diesters) in the reaction products due to the backward reactions which could be detrimental to the wear behaviour of the palm oil-based TMP esters (Yunus *et al.*, 2002b).

Effect of Reactants Molar Ratio

One of the methods to promote forward reaction is by using the excess amount of one of the reactants. Since POME are relatively cheaper compared to polyol, *i.e.* TMP, the reaction was subjected to excess methyl esters. The stoichiometric molar ratio between the POME and TMP is 3:1. In the analysis of the effects of temperature and vacuum on the extent of reaction, a molar ratio of at least 3.8:1 was used throughout the experiments. This was to ensure that the reaction was not constrained by the effect of excess reactant. The investigation on the effects of POME: TMP and POME: TMP molar ratio on the conversion to TMP esters was carried out at 130°C and 10 mbar in 4 hr. The amount of catalyst was maintained at 0.9% w/w in all experiments.

The effect of molar ratio of POME:TMP on product composition is shown in *Figure 6*. The yield of TE somewhat fluctuated at higher ratios, decreased at 3.5:1 and 3.7:1 and then increased at 3.9:1. Increasing the ratio to 3.9:1 from 3.3:1 provided marginal improvement to TE conversion. When the amount of POME was included in the weight percentage calculation, the mass of the residual POME appeared to override the effect on the conversion. Hence, there was no clear benefit of increasing the molar ratio of reactants since the ratio increased proportionately with the weight of the POME. However, the effect of molar ratio was more evidenced when the weight of POME was excluded in the weight percentage calculations *(Figure 6b)*. The TE yield increased proportionately with the molar ratio, thus no substantial conclusion could be made from the study.

In the chemical and enzymatic transesterifications of rapeseed methyl ester with TMP, maximum conversion was obtained at 3.3:1 and 3.5:1, respectively (Uosukainen *et al.*, 1998). For palm oil TMP ester synthesis, the results showed a proportional increase between the TE conversion and molar ratio excluding POME. In a similar esterification study, two- to three-fold excess of acids

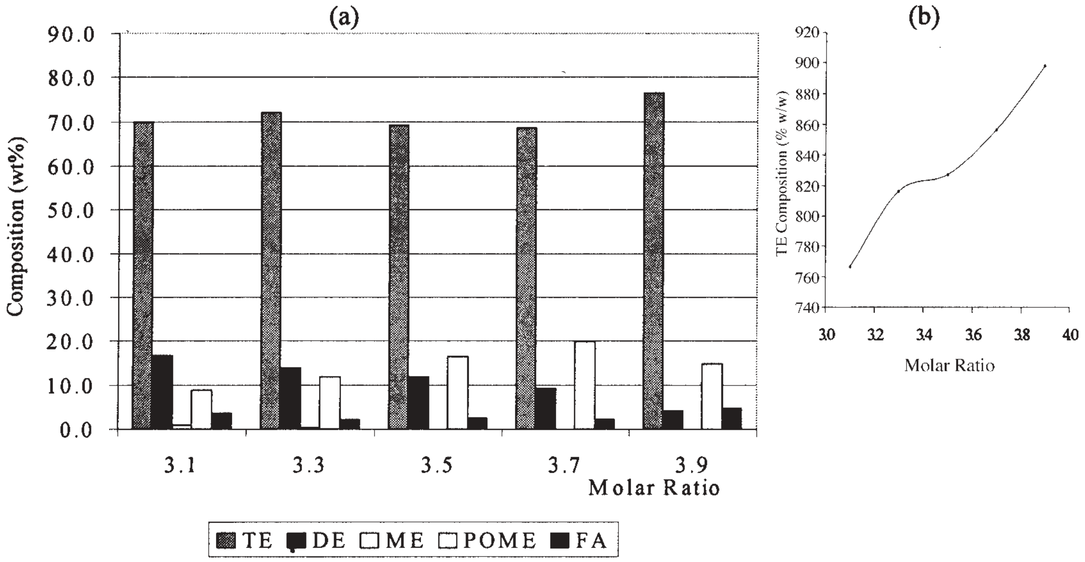

Figure 6. Effects of molar ratio on transesterification of POME with TMP (a) composition (% w/w) based on total weight including POME (b) % w/w without POME. POME-palm oil methyl ester, ME-monoester, DE-diesters, TE-triesters.

or esters was normally used to drive the reaction to completion. Freedman *et al.* (1998) employed a 10-fold excess of oil to eliminate the reverse reaction, which would have complicated their kinetics study. In this study, 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 residues. However, a small amount of DE is an added value to the properties of the lubricant and a large excess of unconsumed POME would require additional energy to remove them.

Effect of Catalyst

Previous works on transesterification of fats and oils had clearly suggested that the conversion of transesterification of POME to the desired TMP esters might be affected by the amount of catalyst. In this study, we employed an alkaline catalyst, namely, sodium methoxide. The advantages of using this type of catalyst to the acid catalyst were discussed by Liu (1994). The chemical synthesis was chosen over the enzymatic since the reaction temperature has to be maintained above the melting point of TMP (60°C), which is considered high for most enzymes. The amount of lipase required also was very high, 40% to 50% w/w (Linko *et al.*, 1995), compared to less than 1% for sodium methoxide.

In this study, the amount of catalyst (% w/w) had little influence on the transesterification of POME with TMP within the range covered in the experiment, 0.7% to 1.2% w/w. The conversion to TE was always greater than 70%. About 10% of the products were DE and the balance were excess methyl esters. Once the methyl esters were separated by vacuum distillation, the final product contained at least 90% TE and 10% DE. For palm kernel oil methyl ester transesterification, the highest conversion to TE was achieved at 0.7% catalyst while for POME transesterification, it was at 0.8% (w/w). These findings compare well with the results from rapeseed TMP esters synthesis (Uosukainen *et al.*, 1998). The highest conversion was obtained with 0.7% alkaline catalyst. With an acid catalyst and enzymes, a higher quantity of catalyst is usually required (Eychenne *et al.*, 1998; Linko *et al.*, 1995).

However, if a higher percentage of catalyst was used in the reaction, more fatty acids (FA) would be formed, which could lead to saponification of FA to fatty soaps in the presence of metal catalyst. Fatty soaps are solids materials that must be separated from the final product usually by vacuum filtration. In addition, if anhydrous condition could not be maintained in the system, the presence of alkaline catalyst could also lead to an irreversible hydrolysis of methyl esters to FA (Liu, 1994). However, in cases where the anhydrous condition is maintained in both the starting materials POME and TMP, and a moderate amount of catalysts is used in the reaction, the FA content is usually below 1% w/w.

CONCLUSION

It was demonstrated that chemical transesterification of TMP with POME to yield palm oil TMP TE was attainable under a reduced pressure of at least 20 mbar, T=120°C, 3.9:1 molar ratio employing sodium methoxide as catalyst. Palm oil TMP esters containing 98% w/w TE were successfully synthesized in less than an hour. The optimum molar ratio was established at 3.9:1 for palm oil TMP ester synthesis to get both the maximum yields of TE and reasonable methyl esters residues. The amount of catalyst required for the transesterification of POME and TMP was less than 1.0% w/w, a quantity far less than what is required in biocatalysis using lipase, 40%-50% w/w. In conclusion, the optimal reaction conditions are as follows: duration: 1 hr; temperature: 130 °C; pressure: 20 mbar; catalyst: sodium methoxide at 0.8% w/w; molar ratio of POME:TMP at 3.9:1.

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