PREPARATION AND CHARACTERIZATION OF TRIMETHYLOLPROPANE ESTERS FROM PALM KERNEL OIL METHYL ESTERS

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ABSTRACT

Palm-based polyol esters are potential biodegradable base stocks for environmentally friendly lubricants. The synthesis of palm kernel oil trimethylolpropane (TMP) esters was performed by transesterification of palm kernel methyl esters with TMP using sodium methoxide as a catalyst. Approximately 98% w/w conversion to palm kernel TMP triesters was obtained. Temperature and vacuum pressure were found to be the key parameters because of their effects on the rate and reversibility of the reaction. A reduced pressure of at least 20 mbar was crucial for high product yield at which the optimal operating temperature was 130°C. The basic lubrication properties of the non-additived palm and palm kernel TMP esters were the following: viscosity at 40°C in the range of 39.7 to 49.7 cSt, pour point between -1°C to 1°C and high viscosity indices in the range of 167-187. Other chemical and lubrication properties compared well with the commercial vegetable oils-based TMP esters.

INTRODUCTION

Owing to growing concern on the environment, vegetable oils are finding their way into lubricants for industrial and transportation applications. They have the attractions of being natural, renewable, non-toxic, non-polluting and cheaper than synthetics. In general, synthetic lubricants cost four to eight times higher than the mineral oil-based lubricants (Bartz, 1993). Vegetable oil-based lubricants are 50% cheaper than synthetic oils but they are easily degradable and have poor lubricity. Nevertheless, they are plentiful in supply and can be used as biodegradable lubricant base stocks. Despite their enormous potential to be cost and performance competitive to mineral-based fluids, research and development in these biofluids are needed to overcome their inherent shortcomings such as oxidative and thermal stability (Johnson, 1999; Wu et al., 1998).

Chemical modifications namely epoxidation and transesterification of vegetable oils with polyols have been shown to improve the oxidative stability of vegetable oil-based lubricants (Gryglewicz et al., 2003; Wu et al., 1998; Uosukainen et al., 1998; Glancey et al., 1998; Adhvaryu and Erhan, 2002). Uosukainen et al. (1998) described the synthesis of biodegradable TMP esters from rapeseed oil methyl ester via both chemical and enzymatic methods. The catalyst employed was sodium methylate (0.5% w/w) and the reaction mixture was refluxed under a reduced pressure of 3.3 kPa. Approximately 99% total conversion was achieved at 110°C-120°C in 10 hr. Using 40% w/w *Candida rugosa* lipase, only 64% of the TMP was converted to triesters in 24 hr at 5.3kPa and 47°C. With immobilized *Rhizomucor miehei* (50% w/w), the highest conversion to the TMP triesters of about 90% was achieved in 66 hr.

In another development, esters of neopentylpolyols were prepared by an esterification reaction between pentaerythritol and erucic acid catalysed by 4-toluene sulphonic acid (*p*-TSA) in xylene (Eychenne et al., 1998). The reaction mixture was heated to 200°C under nitrogen. Since pentaerythritol becomes the backbone of the new

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esters, four types of esters were obtained: tetra, tri, di and monoesters. Animal fat was also used to synthesize polyol esters using calcium methoxide but the rate of reaction was slow with a yield of 85%-90% after 20 hr of reaction (Gryglewicz *et al.*, 2003). A two-stage low temperature crystallization process was used to improve the pour points.

It was demonstrated in an earlier paper (Yunus *et al.,* 2003a) that palm oil TMP esters containing 98% w/w triesters had been successfully synthesized in less than an hour which has never been achieved before. Earlier studies have reported slow reaction rates caused by sterically hindered components (Schlosberg *et al.*, 2001) resulting in long reaction times of between 10 to 20 hr (Uosukainen *et al.*, 1998; Gryglewicz *et al.*, 2003). The chemical transesterification of TMP with palm oil methyl esters was attainable under a reduced pressure of at least 20 mbar, T=120°C, 3.9:1 molar ratio employing sodium methoxide as catalyst. The optimum molar ratio was established at 3.9:1 and the catalyst required was less than 1.0% w/w, a quantity far less than the lipase required for enzymatic transesterification at 40%-50% w/w (Linko *et al.*, 1995; Uosukainen *et al.*, 1998).

To assess the potential of palm kernel oil-based TMP esters as base stock for biodegradable lubricants, a similar study was carried out on the transesterification of palm kernel methyl esters with TMP using sodium methoxide as a catalyst. The vacuum pressure and temperature were identified as the key parameters because of their effects on the rate and reversibility of the reaction. The effects of palm methyl esters to TMP ratio and the amount of catalyst were found to be marginal (Yunus *et al.,* 2003a) thus, it is not reported here. In this study, the influence of only the main operating variables, namely, temperature and vacuum on transesterification of palm kernel oil methyl esters with TMP, was studied. The lubrication characteristics of palm and palm kernel oil TMP esters were analysed according to the standard methods for materials testing (ASTM, 1995) and AOCS methods (AOCS, 1998).

EXPERIMENTAL PROCEDURES

Palm kernel oil methyl esters (PKOME) were obtained from Cognis (M) Sdn Bhd (Selangor, Malaysia). The fatty acids compositions of the esters were determined according to the standard methods for oil and fats analysis (PORIM, 1995) as follows; (FA wt%); C10:0, 0.1; C12:0, 48.9; C14:0, 18.8; C16:0, 10.2; C18:0, 2.7; C18:1, 17.0; C18:2, 2.2. TMP was supplied by Merck-Schuchardt (Hohenbrunn, Germany), sodium methoxide and other chemicals were purchased from Sigma Aldrich Chemicals Co. N,O-Bis (trimethylsilyl) trifluoroacetamide (BSTFA) was purchased from Fluka Chemie AG (Buchs, Switzerland).

Transesterification of Palm Oil-Based Trimethylolpropane (TMP) Esters

The reactions were performed according to the procedures described in the earlier paper (Yunus *et al.,* 2003a). A 500-ml three-neck flask equipped with a thermometer, a sampling port and a reflux condenser was filled with 200 g of PKOME and heated to the desired temperature. The vacuum was maintained constant throughout the process by using the vacuum controller. A known amount of TMP was then added and the mixture was heated to the operating temperature before the catalyst was added. The vacuum was applied gradually after adding the catalyst to avoid spill over of the reaction materials. The reactions were carried out at temperatures between 80°C to 140°C and the effect of temperature on the ester conversion was observed. The reactant molar ratio was maintained at 3.9:1, with 0.9% w/w catalyst added. The effect of vacuum was examined at 0.2, 10 and 20 mbar while the temperature was maintained at 130°C throughout these experiments. Samples were analysed at certain time intervals for PKOME, monoester (ME), diesters (DE), triesters (TE), fatty acids (FA) and TMP by gas chromatography as shown in *Figure 1*. The yield of each product was determined from the GC chromatogram calibrated against the known samples according to the procedure described elsewhere (Yunus *et al.*, 2002).
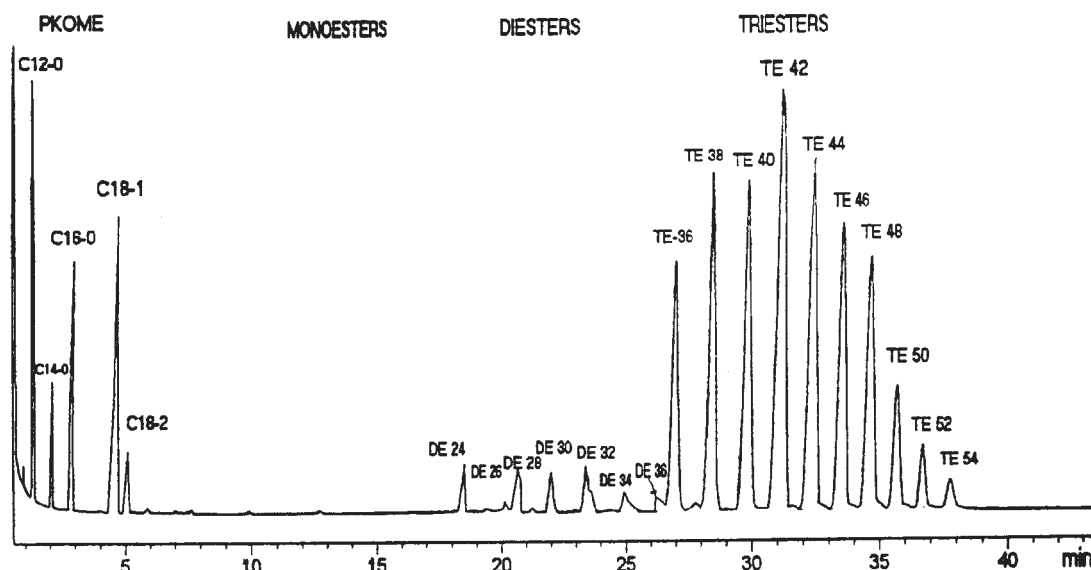
Figure 1. GC Chromatogram of palm kernel oil trimethylolpropane esters.

Removal of Catalyst and Unreacted Methyl Esters

When the reaction was completed, the catalyst was separated from the product mixture (180 g) before the properties of the sample were analysed. This was carried out using either one of these methods, namely, vacuum filtration or washing with acidic water (10% w/w orthophosphoric acid) followed with warm water. The trace water was removed from the sample by using rotavap or drying in a desiccator overnight. The unreacted methyl ester was removed from the filtered product by high vacuum distillation. The sample (160 g) was filled into the flask and distilled in the constant-temperature oil bath at 180°C-200°C under reduced pressure (0.2 mbar). Approximately 135 g of final product was produced from each experiment.

Lubrication Characteristics

The pour points (PP) were measured according to the ASTM method D97 [14]. The sample was first heated to 45°C in a water bath maintained at 48°C and then cooled down to 27°C in another water bath at 24°C (Petrotest Instruments, Germany). PP is defined as the temperature at which there is no movement of the oil when the test jar is held in a horizontal position for 5 s. The kinematic viscosities at 40°C and 100°C were measured based on the method described in ASTM D445 [14]. The experiments were carried out in the constant temperature bath of Tamson Zoetermeer, Holland, model TV4000 using Ubbelohde capillary tube viscometers. The viscosity index was calculated according to ASTM D2270 based on the kinematic viscosities at 40°C and 100°C. The chemical properties such as acid number or value, base number or hydroxyl value, saponification value, iodine value, density and flash point were determined based on the methods described by AOCS (AOCS, 1998).

RESULTS AND DISCUSSIONS

Effect of Temperature

The effect of temperature on the transesterification of PKOME with TMP is shown in *Figure 2*. As expected, the yield of TE increased with temperature until it reached the optimum value at 130°C. Above this temperature, the yield of TE markedly dropped which may have been due to a lower rate of conversion of DE to TE and/or persistent occurrence of the reverse reaction, *i.e.* breakdown of TE to DE. In addition, high temperature may cause excessive evaporation of PKOME from the reactor, thus suppressing the forward reaction to form TE from DE. A similar response was also observed at 20 mbar and 130°C (*Figure 3*) but the TE yield was very much lower at 80.4% w/w as compared to 88.6% w/w at 0.2 mbar.

Interestingly when the vacuum was reduced to 10 mbar, the effect of temperature was minimal. Under moderate vacuum, increasing the temperature did not play a significant effect on the product yield because the molecules were already at the optimum energy state for collision. The yield of esters reached the maximum at 100°C and increasing the temperature did not affect the yield but the rate of reaction as shown in *Figure 4*. Since the effect on the rate is marginal, it is concluded that the optimum temperature for PKOME at 10 mbar is between 110°C-130°C.
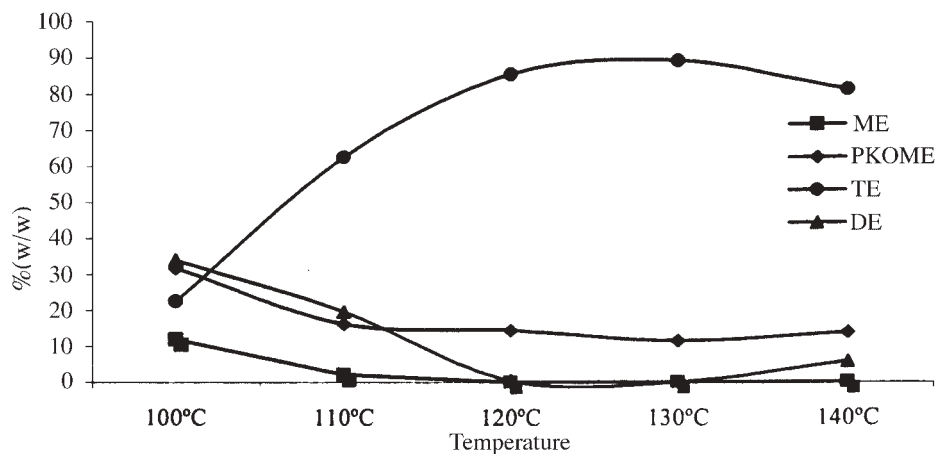
Figure 2. Effect of temperature on transesterification of palm kernel oil methyl esters with trimethylolpropane at 0.2 mbar.
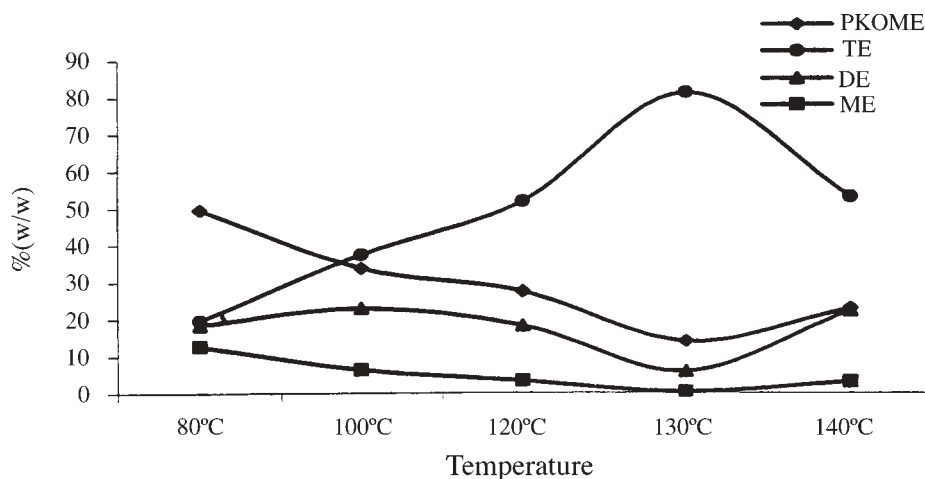

Figure 3. Effect of temperature on transesterification of palm kernel oil methyl esters with trimethylolpropane at 20 mbar.
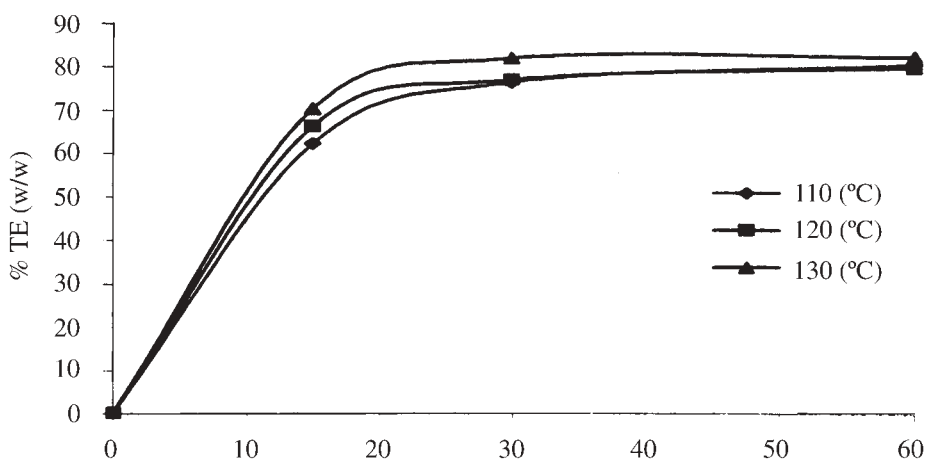

Figure 4. Effects of temperature and time on triesters composition in synthesis of palm kernel trimethylolpropane esters at 10 mbar.
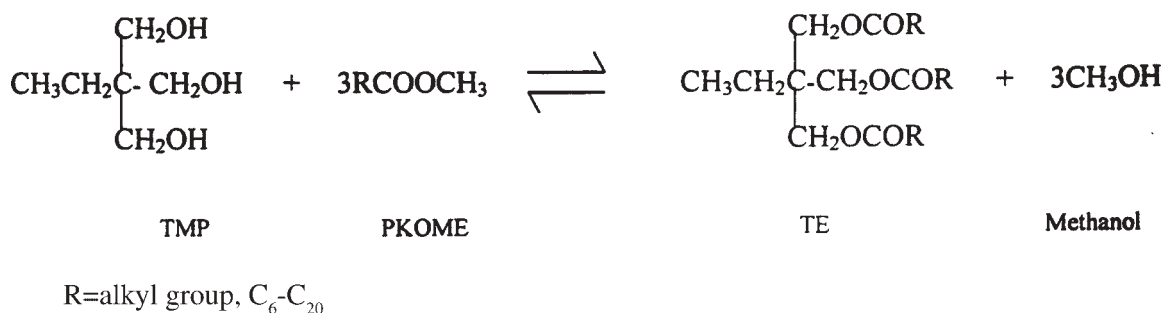
$$\underset{TMP}{CH_3CH_2C-CH_2OH} + \underset{PKOME}{3RCOOCH_3} \rightleftharpoons \underset{TE}{CH_3CH_2C-CH_2OCOR} + \underset{Methanol}{3CH_3OH}$$

R=alkyl group, C_6-C_{20}

Figure 5.

Effect of Pressure

Application of vacuum is vital in the transesterification of palm oil-based methyl esters with TMP (Yunus *et al.*, 2003b). The forward reaction shown in *Figure 5* is favoured by either continuous removal of methanol or the use of excess PKOME. Removal of methanol can be achieved by the application of a vacuum (Uosukainen *et al.*, 1998), high temperature system under nitrogen (Eychenne *et al.*, 1998) and the use of an azeotropic agent such as isooctane (Gryglewicz *et al.*, 2003). Under atmospheric pressure, an operating temperature of at least 200°C is required to produce a reasonable conversion to polyol esters (Eychenne *et al.*, 1998).

Since the optimum pressure found in the previous study on POME (Yunus *et al.*, 2003a) was between 20 to 0.1 mbar, the experiments on PKOME were conducted at 20, 10 and 0.2 mbar. The effect of vacuum on PKOME transesterification is shown in *Figure 6*. The TE compositions at these reduced pressures and 130°C were 80.4%, 83.2% and 88.6%, respectively, obtained in 45 min of reaction. These notably higher compositions were due to the lower percentage of methyl esters in the final products.

According to the overall material balance, approximately 21% of excess PKOME should be present in the product. However, at high vacuum, most of the PKOME with comparatively lower boiling point than POME will be carried away in the vacuum line. Thus, it has resulted in higher TE composition (% w/w) in the final product of palm kernel TMP ester synthesis. Under high vacuum, the rate increases due to the rapid removal of methanol, hence, promoting the forward reaction.

However, for commercial application, 20 mbar would be the most economical vacuum pressure, which can be readily achieved using a moderate vacuum pump. At this condition, not only the yield of PKOME is reasonably high but also the rate of reaction (*Figure 7*). The reaction rate was very fast in the beginning and slowed down as it approached the plateau. Although the DE content at 20 mbar was high (lower TE %), a moderate concentration of partial esters, *i.e.* DE in palm-based TMP esters, improve its lubricating characteristics particularly its wear and friction behaviour.

There is no report on the effect of vacuum on transesterification using chemical catalysts. However, Uosukainen *et al.* (1998) carried out similar
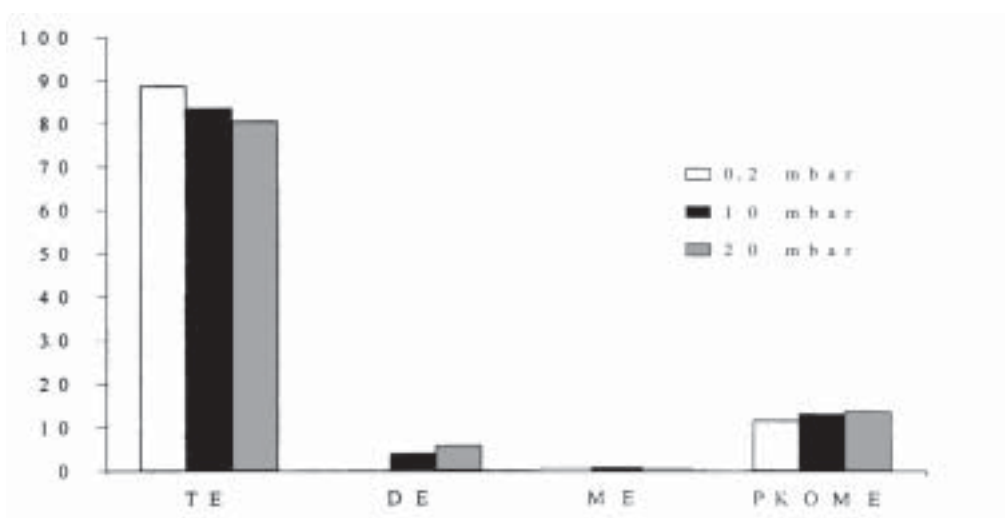

Figure 6. Effect of pressure on the relative product composition (% w/w) in transesterification of palm kernel oil methyl esters with trimethylolpropane at 130°C.
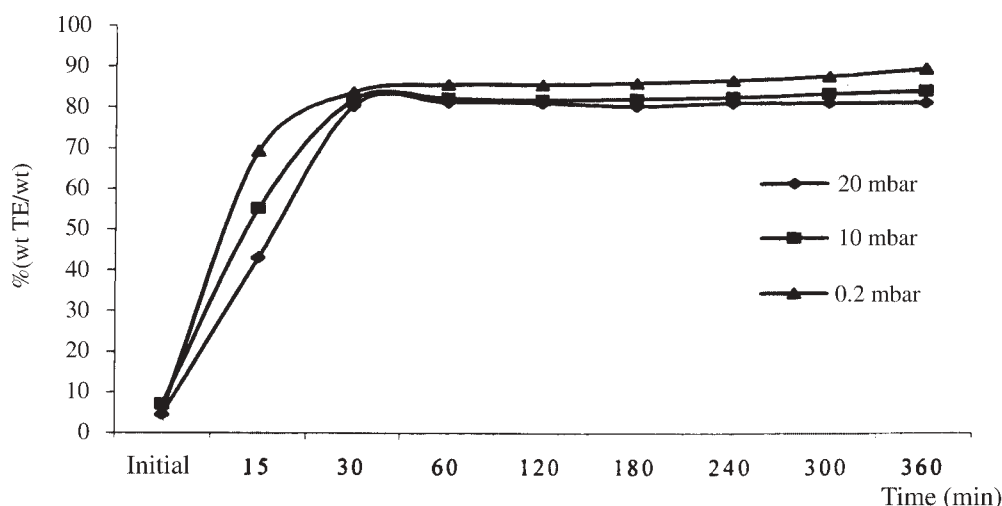
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Figure 7. Time courses of palm kernel trimethylolpropane ester synthesis at various vacuum pressures.

studies on enzymatic synthesis of rapeseed oil TMP ester. The TE conversion increased with vacuum: 8% at ambient, 18% at 120 mbar and 44% at 53 mbar. The maximum conversion to TE at 66% was obtained at 20 mbar. The synthesis was carried out at 37°C using 40% w/w *Candida rugosa* lipase. In similar studies, Linko *et al.* (1995) reported a 75% conversion to rapeseed TMP TE obtained at 53 mbar, 58°C using 20% (w/w) of immobilized enzyme, IM 20 in 24 hr. In chemical transesterification, they reported a conversion of 99.0% to total esters, which included all the partial esters. This was achieved at 33 mbar (3.3 kPa) and 120°C using a molar ratio of 1:3.2 in about 10 hr with no residual rapeseed oil.

Application of vacuum removes methanol away from the system, hence, creating an environment which favours the forward reaction. However, if the vacuum is too high, it tends to entrain the methyl esters away with methanol and results in a lower product yield. However, the TE composition at high vacuum is higher as it is based on the weight percentage. The amount of palm-based methyl esters decreases as the weight percentage of TE increases. This was especially true when PKOME was used; since it is more volatile than POME, it could be gradually swept away with the methanol by the vacuum.

On the other hand, if the vacuum was too low, *i.e.* at 100 mbar, not all the methyl esters were converted to TMP esters. Furthermore, 20% of the TMP esters were still in partial ester forms, *i.e.* mono and diesters. Insufficient vacuum could have also promoted the reverse reaction to decompose the TMP esters back into the methyl esters. For the transesterification of PKOME with TMP, it is proposed that at least 20 mbar pressure be used in a synthesis temperature between 100°C-130°C.

Lubrication Characteristics

The lubrication characteristics, which have been determined for palm-based TMP lubricants based on the methods described by ASTM (ASTM, 1995) and AOCS (AOCS, 1998) are shown in *Table 1*. The low temperature properties of the TMP esters are inferior compared to other vegetable oil-based lubricants due to a higher level of saturation. The basic lubrication properties of the non-additive palm and palm kernel TMP esters were the following: viscosity at 40°C in the range of 39.7 to 54.1 cSt, pour point between -5°C to 4°C and high viscosity indices in the range of 177-198 (Yunus, 2003). The values of pour points of other vegetable-based TMP esters could be as low as -15°C reported for rapeseed-based polyol esters (Usoukainen *et al.*, 1999). Many previous authors published papers describing the poor low temperature properties of vegetable oils (Asadauskus *et al.*, 1997; Asadauskus and Erhan, 1999; Hwang and Erhan, 2001).

TABLE 1. CHEMICAL AND LUBRICATION PROPERTIES OF PALM-BASED LUBRICANTS

	Method	PPOTE	PKOTE	AG 310
Total acid number	ASTMD-664	0.3	0.16	0.05
Total base number	ASTM D-2896	0.37	0.1	0.15
Density @ 15°C	ASTM D-4052	0.9167	0.9206	0.9204
Hydroxyl value	ASTM D-664	10.0	9.0	3.7
Iodine value	AOCS Cd 1c-85	61.3	18.2	89.6
Saponification value	AOCS Cd 3a-94	202.2	223.1	199.9
Colour	ASTM D-1500	1.0	1.0	1.0
Noack volatility (%)	ASTM D-5800	1.8	1.6	0.4
Flash point	ASTM D-92	304	310	322
Copper corrosion	ASTM D-130	1b	1a	1b
Viscosity@100°C (cSt)	ASTM D-445	9.8	7.7	7.8
Viscosity@ 40°C (cSt)	ASTM D-445	49.7	39.7	34.9
Viscosity index	ASTM D-2270	187	167	210
Pour point (^{o}C)	ASTM D-97	-1	2	-15
Origin		POME	PKOME	Vegetable-based TMP esters

CONCLUSION

Almost complete conversion of TMP to palm kernel-based TMP esters was obtained in the transesterification of PKOME with TMP using sodium methoxide as catalyst. Under optimum reaction conditions, the overall reaction reached completion in an hour, a period far less than that reported earlier in the synthesis of rapeseed oil TMP ester of 10 hr (Uosukainen *et al.,* 1998) and lard TMP esters of 20 hr (Gryglewicz *et al.,* 2003). While lower reaction temperature and duration of completion was reported at a much higher ratio, economically it will not be viable for industrial application.   The lubrication characteristics of palm kernel TMP esters are comparable to palm oil TMP esters but the latter exhibits a better viscosity index and lower pour point.

ACKNOWLEDGEMENTS

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