Activity of Calcium Methoxide Catalyst for Synthesis of High Oleic Palm Oil Based Trimethylolpropane Triesters as Lubricant Base Stock

6 AUTHORS, INCLUDING:

Hassan Masood
University of New South Wales
8 PUBLICATIONS   66 CITATIONS

SEE PROFILE

Robiah Yunus
Putra University, Malaysia
165 PUBLICATIONS   1,638 CITATIONS

SEE PROFILE

Umer Rashid
Putra University, Malaysia
157 PUBLICATIONS   1,751 CITATIONS

SEE PROFILE

Dayang Radiah
Putra University, Malaysia
56 PUBLICATIONS   809 CITATIONS

SEE PROFILE

Activity of Calcium Methoxide Catalyst for Synthesis of High Oleic Palm Oil Based Trimethylolpropane Triesters as Lubricant Base Stock

Teck-Sin Chang,[†,‡] Hassan Masood,[†] Robiah Yunus,*[,†,§] Umer Rashid,[§] Thomas S. Y. Choong,[†] and Dayang Radiah Awang Biak[†]

[†]Department of Chemical and Environmental Engineering, Faculty of Engineering, and [§]Institute of Advanced Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
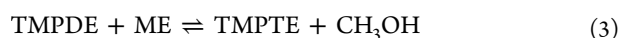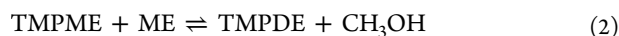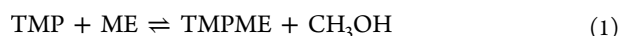
[‡]Solution Engineering Sdn. Bhd., No. 3, Jalan TPK 2/4, Taman Perindustrian Kinrara, 47100 Puchong, Selangor, Malaysia

ABSTRACT: High oleic palm oil based trimethylolpropane triesters (TMPTE) are potential biodegradable base stocks for lubricant production. Calcium methoxide was used as a catalyst for the synthesis of TMPTE through chemical transesterification of high oleic palm oil methyl esters (POME) with trimethylolpropane (TMP). The effects of the main operating variables, i.e., temperature, pressure, molar ratio of TMP to POME, and the catalyst amount, on the yield of TMPTE were appraised. The amount of soap produced under these conditions was examined. The optimum conditions for the reaction were the reaction temperature set at 170 °C, molar ratio of TMP:POME set at 1:6, pressure of the system maintained at 50 mbar, and mass ratio of calcium methoxide set at 0.3% per weight of reaction mixture. Trimethylolpropane esters containing 98% w/w triesters were successfully synthesized under these conditions within 8 h reaction time. Saponification occurred under these conditions; however, the soap formation was less than that produced when homogeneous catalyst was used.
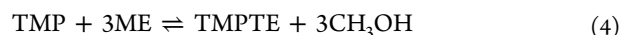
1. INTRODUCTION

Vegetable oils are becoming an integral part of lubricant products due to their environmentally friendly nature. Lubricants based on vegetable oils are rapidly and completely biodegradable, and they have low ecotoxicity compared to mineral oil based lubricants.[1] However, there are some performance limitations associated with them, e.g., thermal, oxidative, and hydrolytic stability, and inadequate low temperature fluidity due to high pour points.[2] These limitations can be minimized by means of chemical modification through transesterification of vegetable oils with polyhydric alcohols or polyols.[3] This process causes the elimination of a hydrogen atom from the β-carbon of the vegetable oil structure and provides esters with a high degree of oxidative and thermal stability which is seldom found in vegetable oils.[4] Several studies have evidenced the improvement in performance of vegetable oils through their structural modification.[5−9] In a similar manner, trimethylolpropane triesters (TMPTE) had been synthesized as base oils for various types of lubricating oils by using trimethylolpropane (TMP) and vegetable oil methyl esters as starting materials.[10−13]

The transesterification reaction involves three consecutive mechanisms with the presence of catalyst. Trimethylolpropane monoesters (TMPME) and trimethylolpropane diesters (TMPDE) are formed as the intermediate products toward the completion of the reaction producing TMPTE. The overall reaction stoichiometry requires 1 mol of trimethylolpropane (TMP) and 3 mol of methyl esters (ME). The reaction scheme is shown below:

$$\text{TMP} + \text{ME} \rightleftharpoons \text{TMPME} + \text{CH}_3\text{OH} \qquad (1)$$

$$\text{TMPME} + \text{ME} \rightleftharpoons \text{TMPDE} + \text{CH}_3\text{OH} \qquad (2)$$

$$\text{TMPDE} + \text{ME} \rightleftharpoons \text{TMPTE} + \text{CH}_3\text{OH} \qquad (3)$$

The overall reaction is as follows:

$$\text{TMP} + 3\text{ME} \rightleftharpoons \text{TMPTE} + 3\text{CH}_3\text{OH} \qquad (4)$$

Catalyst generally plays a crucial role in the production of TMPTE for obtaining better yield in less time. Uosukainen et al.[14] achieved 99% conversion to triesters in 10 h while using homogeneous sodium methoxide, 64% in 24 h with *Candida rugosa* lipase and 90% in 66 h by employing immobilized *Rhizomucor miehei*, for production of TMPTE from rapeseed oil methyl esters. Moreover, Gryglewicz et al.[15] obtained a yield of 85−90% after a reaction time of 20 h for the transesterification of TMP with methyl esters of animal fat in the presence of calcium methoxide as heterogeneous catalyst. It is probable that the steric hindrance of components is responsible for the slow reaction rate in these studies.

Yunus et al. did the transesterification of TMP with palm oil methyl esters (POME) in a batch reactor utilizing sodium methoxide as homogeneous catalyst and managed to obtain trimethylolpropane esters containing 98% w/w triesters in less than 1 h.[16] However, the presence of alkali metal catalyst contributed to saponification due to the formation of free fatty acids along the reaction. The fatty soaps formed were in colloidal form partially soluble in the reaction products, and hence were required to be separated from the final product through several complicated filtration and separation processes. Furthermore, it was essential to maintain the anhydrous conditions in the system as the presence of alkaline catalyst can lead to irreversible hydrolysis of methyl esters to fatty acids. This has restricted the use of a higher percentage of catalyst. In

addition, there was no possibility of separating the catalyst from the reaction mixture at the end of the reaction in order to use it for multiple cycles.

Previous studies reveal the inadequate performance of enzymatic catalysts for polyol ester production. Homogeneous catalysts showed good reaction activity by reducing the mass transfer resistance, but they suffered serious drawbacks in terms of saponification and troubling product purification. Heterogeneous calcium methoxide has offered a slow reaction rate under the process developed by Gryglewicz et al.,[15] but it provided excellent results in some of the transesterification research works.[17−19] This catalyst seemed to hold the potential to achieve better TMPTE conversion by optimizing the other influencing factors for transesterification reaction, such as temperature, molar ratio of TMP with POME, vacuum pressure, and catalyst loading. In addition to that, calcium methoxide has to show less contribution to saponification in order to gain environmental feasibility and economic reliability. The purpose of current study is to address all these aspects. Section 3.1 compares the catalytic activities of calcium methoxide and sodium methoxide in the transesterification of TMP with high oleic POME under fixed conditions. High oleic TMPTE yields and saponification are examined. Section 3.2 considers the optimization of various parameters influencing the transesterification of TMP with high oleic POME while using solid base calcium methoxide as catalyst.

2. MATERIALS AND METHODS

2.1. Chemicals. High oleic POME having 95% C18 were obtained from Carotino Sdn. Bhd (Malaysia). The methyl ester composition of POME is shown in Table 1. Trimethylolpro-

Table 1. Methyl Ester Composition of High Oleic POME

methyl ester	composition (wt %)
methyl myristate (C14:0)	0.4
methyl palmitate (C16:0)	3.7
methyl stearate (C18:0)	3.6
methyl oleate (C18:1)	74.9
methyl linoleate (C18:2)	17.4

pane, 2-ethyl-2-hydroxymethyl-1,3-propanediol (TMP) (assay >98%) purum grade, sodium methoxide solution (30% in methanol) technical grade, and calcium methoxide powder (97%) were purchased from Sigma Aldrich Sdn. Bhd. (Malaysia). For gas chromatography, ethyl acetate (GC grade) and n-hexane (HPLC grade) were acquired from Fisher Scientific Sdn. Bhd. (Malaysia), while N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) (98%) was purchase from Acros Organic, Belgium.

2.2. Synthesis of TMPTE. *2.2.1. Experiment Using Batch Reactor.* The batch reactor setup included a hot plate stirrer, a 500 mL flat bottom three-necked flask made of borosilicate glass (as the reactor), a PTFE coated magnetic stirrer bar, a reflux condenser, a mercury thermometer, and a sampling port. The hot plate stirrer provided heating as well as stirring to the reaction mixture in the glass reactor, the mercury thermometer indicated the reaction temperature, and the reflux condenser prevented the low boiling point fraction of high oleic POME from escaping the reactor. Samples were collected through the sampling port after predetermined intervals for product composition analysis. A rotary vane vacuum pump was coupled with the reflux condenser to conduct the reaction

under various vacuum conditions, and the vacuum level was controlled by an air leakage valve located between the reflux condenser and the vacuum pump.

Prior to the reaction, high oleic POME were dried in the rotary evaporator at 80 °C and 15 mbar vacuum for 1 h to eliminate the trapped moisture. After the reactor was set up as above, a predetermined amount of TMP was added to the reactor and was melted by heating at 80 °C with continuous stirring at 1000 rpm under 15 mbar vacuum. The temperature was maintained at 80 °C for about 15 min to remove moisture from the hygroscopic TMP. A calculated amount of POME according to the respective molar ratio of TMP:POME was then introduced into the reactor and the reaction mixture was heated to the desired temperature. The required amount of catalyst was charged in once the reaction temperature was reached. The reaction was then carried out under the required amount of vacuum until the desired span of time.

2.2.2. Separation of Catalyst. Once the reaction was completed, the solid products consisting of leftover catalyst and traces of soap were isolated from the liquid portion of product through vacuum filtration. Filter papers of 3 μm pore size were used for this purpose. After vacuum filtration, the liquid product was cooled to room temperature.

2.3. Analysis of Product. The samples were analyzed to determine the yield of TMPTE by gas chromatography (GC) through a method described in an earlier paper.[20] Approximately 0.03 ± 0.005 mL of sample was taken in a 2 mL autosampler vial and diluted with 1 mL of ethyl acetate and 0.5 mL of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA). The vial was then heated in a water bath for 10 min at 40 °C. The sample was allowed to cool at room temperature, and it was then injected into the GC system. The capillary column (SGE HT5) was used in the GC system with hydrogen as carrier gas at a flow rate of 26.7 mL min^{-1} and a split ratio of 1:1. The oven temperature was set initially at 80 °C and was maintained for 3 min, and then was increased at 6 °C min^{-1} up to 340 °C and was maintained for another 6 min. The injector and detector temperatures were set at 300 and 360 °C, respectively.

3. RESULTS AND DISCUSSION

3.1. Comparison of Calcium and Sodium Methoxides as Transesterification Catalysts. Performances of both heterogeneous calcium methoxide and homogeneous sodium methoxide in the synthesis of high oleic TMPTE were studied. The TMPTE yields and saponification after different time intervals were determined and compared. Experiments were conducted at 140 °C, TMP:POME = 1:3.9; 0.1 mbar, and 0.9% w/w catalyst. The results summarized in Table 2 show 91.75% of Na$^+$ was converted into soap at the end of reaction, while

Table 2. Contribution of Catalysts toward Saponification

calcium methoxide			sodium methoxide		
time (h)	total soap (g)	catal conv to soap (%)	time (h)	total soap (g)	catal conv to soap (%)
1	0.54	10.56	0.08	1.89	38.91
2	0.86	17.01	0.16	2.92	60.13
3	1.11	21.77	0.5	3.78	77.72
4	1.15	22.69	1	4.33	89.04
6	1.39	27.25	2	4.46	91.75
8	1.64	32.18			
10	1.73	34.03			

only 34.03% of Ca^{2+} got transformed into soap. This might be due to the homogeneous form of sodium methoxide with respect to reaction products, but calcium methoxide remained solid throughout the reaction. For sodium methoxide, saponification reaction occurred spontaneously with esters and free fatty acids as a competing reaction to the transesterification.[21] However, transesterification and saponification occurred on the surface of calcium methoxide, resulting in rather less conversion into soap.

The amount of soap produced per gram of the reaction mixture after 10 h by calcium methoxide was 18 mg/g, which is much less than the amount of soap produced while employing sodium methoxide after 2 h under the same reaction conditions, i.e., 46 mg/g (Figure 1). Meanwhile, the yield of
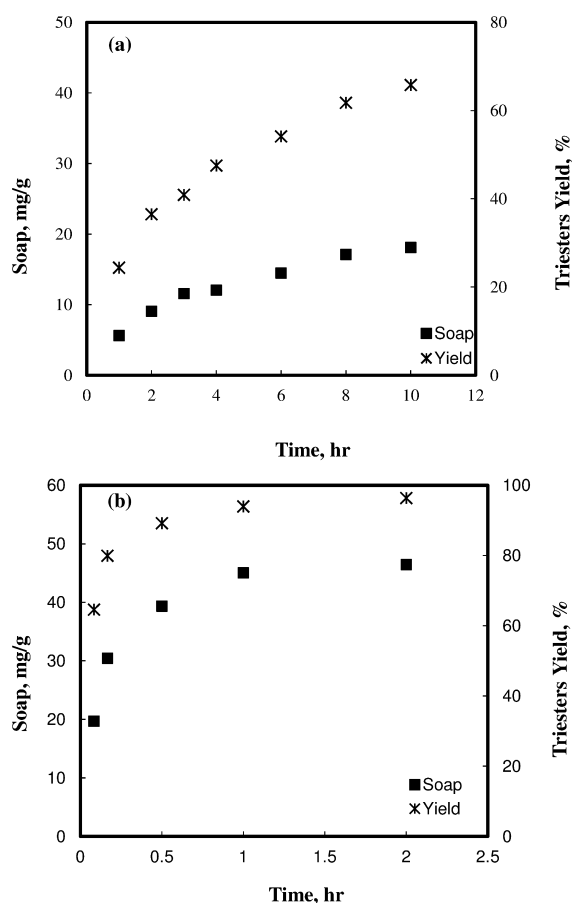

Figure 1. Amount of soap and yield of triesters generated by (a) calcium methoxide and (b) sodium methoxide.

triesters in the case of calcium methoxide was 65.78%, which is considerably less than the 96.38% generated by sodium methoxide. Sodium methoxide reduced the mass transfer residence due to its homogeneous nature, which led to good reaction efficiency but at the same time created more soap compared to its heterogeneous counterpart. From these results, calcium methoxide has demonstrated an encouraging potential as the transesterification catalyst in the production of high oleic TMPTE; however, optimization is required to obtain reasonable reaction conditions. Section 3.2 reports the optimization of reaction conditions using calcium methoxide as the transesterification catalyst.

3.2. Optimization with Calcium Methoxide as Heterogeneous Catalyst for Transesterification Reaction.

3.2.1. Effect of Temperature on TMPTE Yield.
To study the effect of temperature, the reactions were conducted at different temperatures, i.e., 140, 150, 160, 170, 180, and 190 °C. The vacuum pressure was kept fixed at 20 mbar, the molar ratio TMP:POME = 1:3.9, and 0.5% w/w calcium methoxide was employed for these experiments. The samples were collected after 1, 2, 3, and 5 h, and were analyzed to determine the composition of TMPTE by gas chromatography.[20]

The effect of temperature on transesterification of TMP and POME is reported in Figure 2. It is evident that the yield of
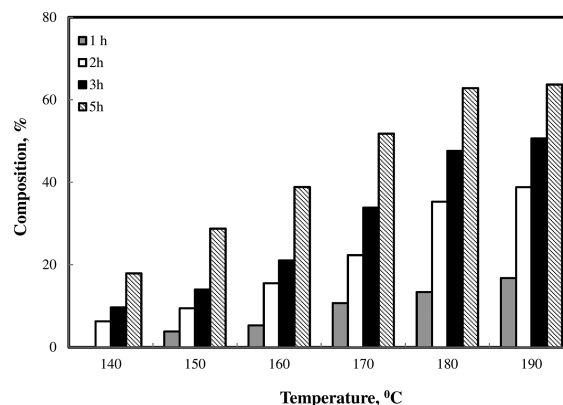
Figure 2. Effect of temperature on TMPTE yield.

TMPTE was low at 140 °C and kept on increasing with the increase in temperature. Initially, there was a constant increase in the TMPTE yield with the increase in temperature, but the less prominent increase in yield was observed at higher temperatures, from 170 to 190 °C after 5 h reaction time. The same trend was noticed in an earlier study,[22] where the yield of triesters increased with the increase in temperature, but after a sharp increase it started to decrease due to saponification caused by the homogeneous sodium methoxide. However, in the current study the saponification factor was expected to be lower and the reaction required comparatively higher temperature to achieve better conversion with solid catalyst. Higher temperatures usually tend to reduce the reaction time for the transesterification reactions, but if the temperature is too high POME might evaporate, resulting in the occurrence of a reverse reaction which eventually reduces the yield of TMPTE. Furthermore, higher temperature favors saponification to take place which lessens the activity of catalyst as well as the yield of TMPTE. The insignificant difference between the yields of TMPTE at 180 and 190 °C in Figure 2 points out that the optimum temperature could range from 170 to 180 °C. Also, the reaction products collected after 5 h of reaction at 180 and 190 °C were sludgy and turbid; hence heavy soap could have formed at such temperatures. Therefore, the optimum reaction temperature is suggested to be 170 °C, providing a good yield without favoring the saponification reaction.

3.2.2. Effect of Molar Ratio of TMP to POME on TMPTE Yield.
The stoichiometric molar ratio between TMP and POME is 1:3, as evident from eq 4; however, the excess amount of POME promotes the forward reaction. The molar ratio of TMP:POME was varied between 1:3, 1:4.5, 1:6, 1:7.5, and 1:9. Other parameters were kept constant at 170 °C, 20 mbar vacuum, and 0.5% w/w calcium methoxide. Reaction was executed for 8 h.

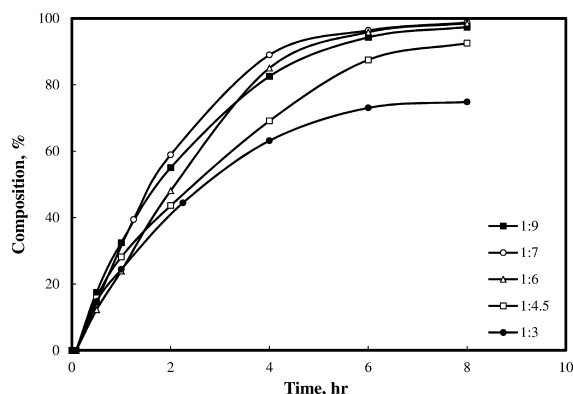The effect of the molar ratio of TMP:POME on the composition of TMPTE is visible from Figure 3. At the

Figure 3. Effect of molar ratio on TMPTE yield.

stoichiometric ratio of 1:3, a yield of 75% triesters was obtained after 8 h reaction time. However, when the ratio was increased to 1:4.5, the yield increased drastically to above 90%. At TMP to POME ratio above 1:6, more than 98% yield of triesters was achieved. Generally, a better product yield is obtained by keeping the molar ratio of reactants higher than the stoichiometric values since the reaction is driven more toward completion.[23] The heterogeneous form of the catalyst and the immiscibility of reactants at the start of the reaction are the governing aspects which ensure a better diffusion among all involved components with excess of any reactant in the reaction. However, the effect of excess reactant was hindered at molar ratios of 1:7.5 and 1:9, as illustrated in Figure 3. This probably happened because the mass transfer had been constrained by the limited catalyst surface area for the reaction and therefore the yield was more or less the same compared to that for 1:6. Therefore, 1:6 can be considered as the optimized molar ratio of TMP:POME within the studied parameters.

3.2.3. Effect of Vacuum on TMPTE Yield. The effect of vacuum on the rate of transesterification of TMP and POME was studied at 10, 20, 50, 70, and 100 mbar, as demonstrated in Figure 4. Experiments were performed at fixed conditions of
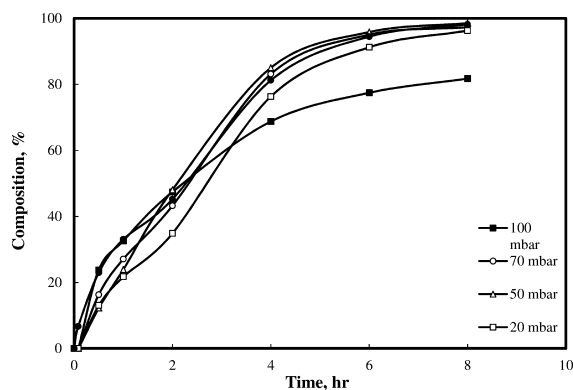

Figure 4. Effect of vacuum on TMPTE yield.

temperature 170 °C, TMP:POME molar ratio 1:6, and 0.5% w/w catalyst loading.

High vacuum facilitates the efficient removal of methanol from the system which in turn favors the forward reaction in eqs 1−3. However, high vacuum requires high energy and high equipment cost for an industrial scale processing plant, especially when the vacuum level has to go below 20 mbar. At a vacuum level below 20 mbar, vacuum booster (special high

energy consumption equipment) is normally required. Also, a higher vacuum level reduces the boiling point of the POME. At 4.9 mbar, the boiling point of methyl oleate (C18:1) is approximately 175 °C as predicted using the Antoine equation. Therefore, the vacuum needs to be optimized rather than just increasing, to enhance the removal of methanol, considering both the process feasibility and the practicability for industrial applications at the same time.

It is evident from Figure 4 that the yield of TMPTE increased when the vacuum was amplified from 100 to 70 mbar, and then to 50 mbar. With the further increase in vacuum to 20 and 10 mbar, the change in yield was less prominent. The removal rate of methanol was comparatively low at 100 mbar, resulting in a relatively lower specific reaction rate to the right (eqs 1−3). It appeared to be the same at 70 mbar, even though a slightly higher yield was observed due to more efficient removal of methanol. From 50 to 10 mbar, the insignificant change in product yield was probably due to the limitation of the process and phase equilibrium between methanol and esters at that specific range of reaction conditions. Therefore, 50 mbar can be regarded as the optimized vacuum for the system, under these specific conditions, which generates a suitable yield of high oleic TMPTE and ensures the feasibility for industrial practice.

3.2.4. Effect of Catalyst Loading on TMPTE Yield. The mass ratio of calcium methoxide to the reaction mixture was varied within the range 0.1−0.5% as illustrated in Figure 5, while other
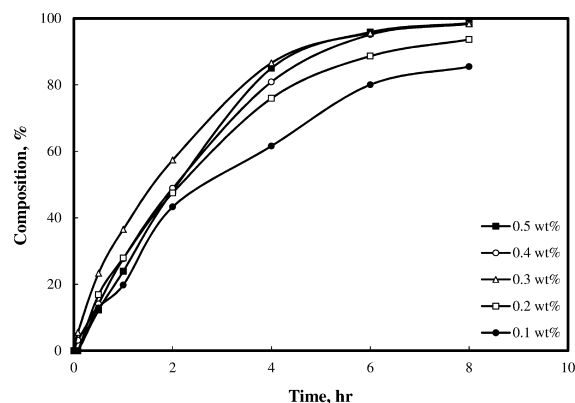

Figure 5. Effect of catalyst loading on TMPTE yield.

parameters such as temperature, molar ratio TMP:POME, and pressure were kept fixed at 170 °C, 1:6, and 50 mbar, respectively. Reaction was conducted for the time period of 8 h. An earlier study reported the increase in the yield of biodiesel with the increase in amount of calcium methoxide.[19] However, no data have been reported yet concerning the effect of the amount of calcium methoxide on the yield of TMPTE.

In this study, the increase in amount of calcium methoxide from 0.1 to 0.2% and then to 0.3% showed a noticeable increase in the yield of TMPTE. On increasing the catalyst above 0.3%, the yield of TMPTE remained more or less the same at around 97%. A much similar result was noticed when calcium methoxide was used for transesterification of soybean oil to biodiesel, where a higher amount of catalyst delivered only a slight increase in the yield of product.[19] When homogeneous sodium methoxide was employed for transesterification of POME to TMPTE, 0.8% w/w catalyst was required to achieve 90% conversion to triesters.[22] However, under the current experimental conditions, the addition of 0.3% catalyst by weight

of reaction mixture has generated an effective yield, and therefore it can be regarded as an optimized parameter for these conditions.

3.3. Saponification by Calcium Methoxide under Optimum Reaction Conditions. The quantity of saponification generated by the heterogeneous calcium methoxide was determined by utilizing the optimum experimental conditions investigated under section 3.2, for the transesterification between TMP and high oleic POME. Almost 52% of calcium methoxide got converted into soap at the end of 8 h reaction time, and at the same point the yield of TMPTE was more than 98%. In contrast to sodium methoxide under its respective optimum conditions for this transesterification reaction, calcium methoxide showed a markedly lower tendency to transform into soap. Judging by the amount of catalyst used at the start of reaction, 0.3% w/w calcium methoxide producing 9.2 mg of soap/g of product at the end of reaction seems to be a more appropriate choice for transesterification compared to 0.9% w/w sodium methoxide producing 46 mg/g soap. Finally, 0.3% w/w calcium methoxide generated almost the same yield of TMPTE at the end of the reaction as obtained by a higher amount of sodium methoxide under optimum conditions.

4. CONCLUSION

This study effectively demonstrated that calcium methoxide serve as an effective catalyst for chemical transesterification of TMP with high oleic POME to attain more than 98% yield of TMP triesters. The optimized conditions determined for the reaction were 170 °C, molar ratio TMP:POME of 1:6, reduced pressure of 50 mbar, and amount of catalyst 0.3% by weight of reaction mixture. The effective results were obtained after 8 h reaction time. Around 52% of calcium methoxide got converted into soap at the end of reaction under these conditions. The results showed that calcium methoxide has excellent catalytic activity and stability for the reaction and produces less soap compared to homogeneous catalyst.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: robiah@eng.upm.edu.my. Fax: +60386567120.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Schneider, M. P. Plant-oil-based lubricants and hydraulic fluids. *J. Sci. Food Agric.* **2006**, *86*, 1769.
(2) Wilson, B. Lubricants and functional fluids from renewable sources. *Ind. Lubr. Tribol.* **1998**, *50*, 6.
(3) Sharma, B. K.; Adhvaryu, A.; Liu, Z.; Erhan, S. Z. Chemical modification of vegetable oils for lubricant applications. *J. Am. Oil Chem. Soc.* **2006**, *83*, 129.
(4) Wagner, H.; Luther, R.; Mang, T. Lubricant base fluids based on renewable raw materials: Their catalytic manufacture and modification. *Appl. Catal., A* **2001**, *221*, 429.
(5) Hwang, H. S.; Erhan, S. Z. Modification of epoxidized soybean oil for lubricant formulations with improved oxidative stability and low pour point. *J. Am. Oil Chem. Soc.* **2001**, *78*, 1179.
(6) Hwang, H. S.; Adhvaryu, A.; Erhan, S. Z. Preparation and properties of lubricant basestocks from epoxidized soybean oil and 2-ethylhexanol. *J. Am. Oil Chem. Soc.* **2003**, *80*, 811.
(7) Lathiand, P. S.; Mattiasson, B. Green approach for the preparation of biodegradable lubricant base stock from epoxidized vegetable oil. *Appl. Catal., B* **2007**, *69*, 207.
(8) Sharma, B. K.; Doll, K. M.; Erhan, S. Z. Ester hydroxy derivatives of methyl oleate: Tribological, oxidation and low temperature properties. *Bioresour. Technol.* **2008**, *99*, 7333.
(9) Campanella, A.; Rustoy, E.; Baldessari, A.; Baltanás, M. A. Lubricants from chemically modified vegetable oils. *Bioresour. Technol.* **2010**, *101*, 245.
(10) Linko, Y. Y.; Tervakangas, T.; Lämsäand, M.; Linko, P. Production of trimethylolpropane esters of rapeseed oil fatty acids by immobilized lipase. *Biotechnol. Tech.* **1997**, *11*, 889.
(11) Hillion, G.; Prioriol, D. Synthesis of a high-grade lubricant from sunflower oil methyl esters. *OCL: Ol., Corps Gras, Lipides* **2003**, *10*, 370.
(12) Sulaiman, S. Z.; Chuah, A. L.; Fakhru'l-Razi, A. Batch production of trimetylolpropane ester from palm oil as lubricant base stock. *J. Appl. Sci.* **2007**, *7*, 2002.
(13) Kamil, R. N. M.; Yusup, S.; Rashid, U. Optimization of polyol ester production by transesterification of Jatropha-based methyl ester with trimethylolpropane using Taguchi design of experiment. *Fuel* **2011**, *90*, 2343.
(14) Uosukainen, E.; Linko, Y. Y.; Lämsä, M.; Tervakangas, T.; Linko, P. Transesterification of trimethylolpropane and rapeseed oil methyl ester to environmentally acceptable lubricants. *J. Am. Oil Chem. Soc.* **1998**, *75*, 1557–63.
(15) Gryglewicz, S.; Piechocki, W.; Gryglewicz, G. Preparation of polyol esters based on vegetable and animal fats. *Bioresour. Technol.* **2003**, *87*, 35.
(16) Yunus, R.; Fakhrul-Razi, A.; Ooi, T. L.; Iyuke, S. E.; Idris, A. Preparation and characterization of trimethylolpropane esters from palm kernel oil methyl esters. *J. Oil Palm Res.* **2003**, *15*, 42.
(17) Kouzu, M.; Kasuno, T.; Tajika, M.; Yamanaka, S.; Hidaka, J. Active phase of calcium oxide used as solid base catalyst for transesterification of soybean oil with refluxing methanol. *Appl. Catal., A* **2008**, *334*, 357.
(18) Martyanov, I. N.; Sayari, A. Comparative study of triglyceride transesterification in the presence of catalytic amounts of sodium, magnesium, and calcium methoxides. *Appl. Catal., A* **2008**, *339*, 45.
(19) Liu, X.; Piao, X.; Wang, Y.; Zhu, S.; He, H. Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol. *Fuel* **2008**, *87*, 1076.
(20) Yunus, R.; Lye, O. T.; Fakhru'l-Razi, A.; Basri, S. A simple capillary column GC method for analysis of palm oil-based polyol esters. *J. Am. Oil Chem. Soc.* **2002**, *79*, 1075.
(21) Soriano, N. U., Jr.; Venditti, R.; Argyropoulos, D. S. Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification. *Fuel* **2009**, *88*, 560.
(22) Yunus, R.; Fakhrul-Razi, A.; Ooi, T. L.; Iyuk, S. E.; Idris, A. Development of optimum synthesis method for transesterification of palm oil methyl esters and trimethylolpropane to environmentally acceptable palm oil-based lubricant. *J. Oil Palm Res.* **2003**, *15*, 35.
(23) Ramadhas, A. S.; Jayaraj, S.; Muraleedharan, C. Biodiesel production from high FFA rubber seed oil. *Fuel* **2005**, *84*, 335.