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Synthesis of palm-based ethylhexyl ester as a synthetic base oil for drilling fluids using chemical transesterification

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SUMMARY: In the present study the synthesis of a palm based ethylhexyl ester was examined through a transesterification reaction of palm oil methyl ester (POME) with 2-ethylhexanol (EH). A sodium methoxide in methanol solution was used as a catalyst. The reaction was carried out at a fixed pressure of 1.5 mbar by varying the temperature (80–140 °C), POME/2EH molar ratio (1:1.5–1:2.2), reaction time (0.5–4 h) and catalyst concentration (1–2% w/w). The reaction with 2-ethylhexanol involved a single step reversible reaction, thus, the reaction was completed in a very short time. The optimum conditions were obtained in less than 30 minutes with 1.5 mbar pressure, 70 °C, and 1:2 molar ratio of POME to 2EH. The analysis of the final product (ethylhexyl ester) was performed using gas chromatography which exhibited 98% of ethyl hexyl ester yield. The gas chromatography analysis of ethyl hexyl ester revealed two major esters peaks *i.e.* ethyl hexyl palmitate and ethylhexyl oleate.

KEYWORDS: *Ethylhexyl ester; Gas chromatography; Optimization; Reaction parameters*

RESUMEN: ***Síntesis de ésteres de acetato hexilo, mediante transesterificación química a partir de palma como base sintética de fluidos para sondeos***. En el presente estudio se analizó la síntesis de ésteres de acetato de hexilo de palma mediante reacción de transesterificación de los ésteres metílicos de aceite de palma (PME) con 2-etilhexanol (EH). Como catalizador se utiliza una solución de metóxido de sodio en metanol. La reacción se lleva a cabo a presión fija de 1,5 mbar mediante la variación de temperatura (80–140 °C), relación molar POME/2EH (1:1.5–1:2.2), tiempo de reacción (0,5–4 h) y concentración de catalizador (1–2% w / w). La reacción con 2-etilhexanol implica un solo paso de una reacción reversible, por lo tanto, ésta se completa en un tiempo muy corto. Las condiciones óptimas se obtuvieron en menos de 30 min a 1,5 mbar, 70 °C y una relación molar de 1:2 de POME al 2EH. El análisis del producto final se realizó usando cromatografía de gases que mostró un rendimiento del 98% del etilhexil éster. El análisis de la cromatografía de gases del etilhexil éster muestra dos grandes picos correspondientes a los ésteres palmitato y oleato de etilhexilo.

PALABRAS CLAVE: *Cromatografía de gases; Etilhexil éster; Optimización; Parámetros de reacción*

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1. INTRODUCTION

Nowadays, the use of synthetic ester as a lubricant base oil has become a trend in many industries due to its numerous advantages compared to the lubricants from mineral oil (Sánchez *et al.*, 2011). The need to utilize bio-based resources is of considerable importance due to the high cost and biodegradability issue of petroleum feedstock (Su *et al.*, 2009; García-Zapateiro *et al.*, 2010; Salih *et al.*, 2011).The main factor that has led to synthetic ester being extensively investigated in the past years is a growing interest in reducing impact on the environment (Filippis *et al.*, 1995; Wang and Cao, 2011). The production of synthetic ester from vegetable oils is found to be the most successful invention in terms of environmental friendly products because vegetable oil is biodegradable and shows comparable performance as a replacement for mineral oil lubricants (Salimon *et al.*, 2010). Among these synthetic esters, ethyl hexyl ester shows a promising application and comparable performance for many industries. The synthesis of ethyl hexyl ester can be achieved by an enzymatic or chemical catalyzed process. Linko *et al.*, (1994) used lipase-catalyzed transesterification to produce ethyl hexyl ester from rapeseed oil methyl ester and produced a 90% conversion of ethyl hexyl ester. Tan *et al.*, (2005) also synthesized ethylhexyl oleate using a similar biochemical method and achieved 95% of the desired ester. It has been reported that there are a few drawbacks related to chemical synthesis such as the production of side products and high energy consumption (Chen *et al.*, 1999).However, chemical syntheses are still used widely in the industry because of a faster reaction and production (Uosukainen *et al.*, 1998).

Ethylhexyl esters are used widely as coolants and lubricants for the machining of metals (Herrmann *et al.*, 2007). The presence of 2-ethylhexyl ester in the oxidative polymerization for drying printing ink and printing with ink containing the drier gives environmental friendly properties to the ink (Nomura *et al.*, 2005). Above all, ethylhexyl ester shows a great performance as a lubricant and proves to be a high demand biolubricant for many industries (May *et al.*, 2005). Asadaukus and Erhan (1999) use ethyl hexyl ester to improve the pour point properties of the biolubricant. Apart from being used as additives, the lubrication properties of the ethyl hexyl ester found to be promising in a base oil for synthetic drilling fluid (Berthezene *et al.*, 1999). These synthetic esters are also widely used as cold cleaning agents for predominantly oil contaminated metal surfaces (Nieendick *et al.*, 1995). The method for the production of ester by means of a transesterification reaction was described by Yunus *et al.*, (2005). Waskitoaji *et al.*, (2012) successfully synthesized 95% ethyl hexyl oleate from palm oil in a 4 h reaction time. Sern *et al.* (2008) also successfully synthesized 95% of 2-ethylhexyl palmitate for a lubricant pour point study. The main objective of the current research was to synthesize the palm oil-based ester for a drilling fluid from palm oil methyl ester and 2-ethylhexanol. Since most of the earlier synthesis work required at least 4 hours to complete and took place at higher temperatures, the focus of our study was also to optimize the process conditions so that both reaction time and temperature can be reduced. In addition, other contributing parameters such as catalyst amount and reactant molar ratio were also investigated.

2. MATERIALS AND METHODS

2.1. Materials

Palm oil methyl ester (POME) was obtained from Carotech Sdn. Bhd. (Ipoh, Perak, Malaysia). 2-ethylhexanol, sodium methoxide and other chemicals were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO).*N*,*O*-Bis (trimethylsilyl) trifluoroacetamide (BSTFA) was purchased from Fluka Chemie AG (Buchs, Switzerland). The fatty acid (FA) compositions of these samples were determined according to the standard methods for the analysis of oils and fats (15): POME (wt%): C12:0, 0.9; C14:0, 1.5; C16:0, 41.5; C16:1,0.3; C17:0, 0.1; C18:0, 2.7; C18:1, 40.6; C18:2, 11.9; C18:3,0.5; The calculated mean M.W. of the esters were determined from the FA compositions i.e. POME, 287.

2.2. Experimental conditions

The experiments were devised to determine the effect of temperature, POME/2-ethylhexanol (2EH) molar ratio, reaction time and catalyst concentration on the synthesis of 2-ethyl hexyl ester. Throughout the laboratory scale studies, the pressure (1.5 mbar) was kept constant. The reaction temperatures varied from 80, 100, 120 and 140 °C. The molar ratio of POME/2EH varied from 1:1.5, 1:2 and 1:2.2. The reaction time varied from 0.5, 1, 2, 3 and 4 h. The amount of catalyst varied from 1, 1.5 and 2% w/w.

2.3. Synthesis of palm-based ethyl hexyl esters

The transesterification reaction was carried out according to the procedures described by Yunus *et al.* (2004). Briefly, 100 g of palm oil methyl ester (POME) were placed in a 500 mL three-neck flask equipped with a magnetic stirrer, thermometer, sampling port and reflux condenser. The three neck flask acted as a reactor and the flask was immersed in the silicon oil bath. The set up was connected to the vacuum pump with a relief valve and a vacuum trap from the condenser. POME was heated to slightly above 100 °C to remove all the water content in the solution as well as in the flask under vacuum pressure. After one hour, a certain amount of

2-ethylhexanol was added to the POME after which the temperature was dropped to below 100 °C. 2 % w/w of sodium methoxide based on the total mass of the reactant was then added to the mixture. The reaction temperature had to be kept below 100 °C when the catalyst was added to the mixture. This was to avoid any spill over because sodium methoxide is highly reactive at high temperatures. The reaction product was purified by vacuum filtration and the methyl ester removal step. The vacuum filtration was used to separate the catalyst and the liquid product mixture. The liquid product mixture collected in the conical flask was purified further to remove the excess methyl ester. The liquid product was distilled at a temperature between 200–230 °C under vacuum to obtain the final purified product.

2.4. Gas chromatography analysis

The analysis of the reaction product was done using Gas chromatography. According to Yunus (2003) one drop of sample of approximately 0.03±0.005 g was weighed into an auto sampler vial. 1 mL of ethyl acetate was added into the vial with 0.5 mL of N,O-Bis (trimethylsilyl) trifluoroacetamide (BSTFA) and swirled for a few minutes. The prepared sample was then heated in a water bath at 40 °C for 10 min to confirm that the sample was silylated. The sample was cooled down to room temperature before injection into the GC system.

Separation on the GC system was performed using a capillary column SGE 12 m x 0.53 mm, i.d. 0.15 µm (SGE, Melbourne, Australia). The oven temperature was set initially at 80 °C, held for 3 min and then increased at 6 °C min^{-1} to 340 °C and held for another 8 min. The injector and detector temperature were set at 320 °C and 340 °C, respectively. Hydrogen gas was used as the carrier gas at a flow rate of 26.7 $\text{mL}\cdot\text{min}^{-1}$ and a pressure of 4.13 psi. The inlet ratio was set at 1:1, and 1.0 mL of sample was injected into the GC system. This procedure provides a complete separation of the sample methyl ester and monoesters.

2.5. Evaluation of ethylhexyl ester properties

The kinematic viscosities at 40 °C and 100 °C were measured based on the ASTM D445 method. The flash point of the sample was measured using Semi-Automatic Pensky-Martens Flash Point Tester, while the pour point test used Petrotest PM4 according to the ASTM D 93 method.

2.6. Statistical analysis

Three different samples of each of the ethyl hexyl ester were analyzed independently in triplicate. Data are presented as mean values±SD of triplicate determinations.

3. RESULTS AND DISCUSSION

The effects of various reaction variables contributing towards the conversion of palm oil methyl ester (POME) with 2-ethylhexanol (2EH) into ethyl hexyl ester were evaluated. Among the main variables affecting the transesterification were reaction temperature, molar ratio of POME to 2EH, amount of catalyst, and reaction time. The reactions were conducted under constant vacuum pressure at 1.5 mbar.

3.1. Effect of reaction time

The reaction time was varied at 0.5, 1, 2, 3 and 4 hours while other parameters were constant. The molar ratio of POME:2EH was 1:2, the temperature of reaction was 80 °C in the presence of a sodium methoxide catalyst (2% w/w). The pressure of the reaction was fixed throughout the study. Figure 1 depicts the results obtained at 0.5, 1, 2, 3 and 4 hours of reaction time, respectively. The results from the GC chromatograms at 0.5, 1, 2, 3 and 4 hour time reaction time showed exactly the same pattern in which all peaks appeared at the same time ranges and intensities compared to the results at 4 hours' reaction time (Figure 2).

The final monoester conversion improves slightly with time until 2 hours of reaction, after which the improvement is marginal, as shown in Figure 1. Nevertheless, the difference in ester conversion was only 1.8% when the time was increased to 2 hours. The reaction can be considered almost complete after 1 hour of reaction time. Consequently, the reactions in the subsequent experiments were conducted in 1 hour. This is a marked improvement over the current method by Waskitoaji *et al.* (2012) who took 4 hours to successfully synthesize 95% ethyl hexyl oleate from palm oil oleic acid. In another study, Lamsa *et al.* (1994) obtained up to 90% conversion of 2-ethyl-1-hexanol esters from rapeseed oil in 8 hrs.

3.2. Effect of reaction temperature

The temperature of the reaction varied from 80 °C, 100 °C, 120 °C and 140 °C. The temperature interval of 20 °C was selected because the improvement in the conversion is only observable if the interval is large enough. The other reaction parameters were similar to the previous experiments except for the fact that the temperature and the reaction time was fixed at 1 hour.

From the GC chromatogram, the results for 80 °C and 140 °C reaction temperature showed no difference in the peak positions and intensities. The ester conversions at 100 °C, 120 °C and 140 °C were 98.7, 98.9 and 98.8%, respectively. The results for temperature manipulated reactions are illustrated in Figure 3. Similar to the previous results, no marked

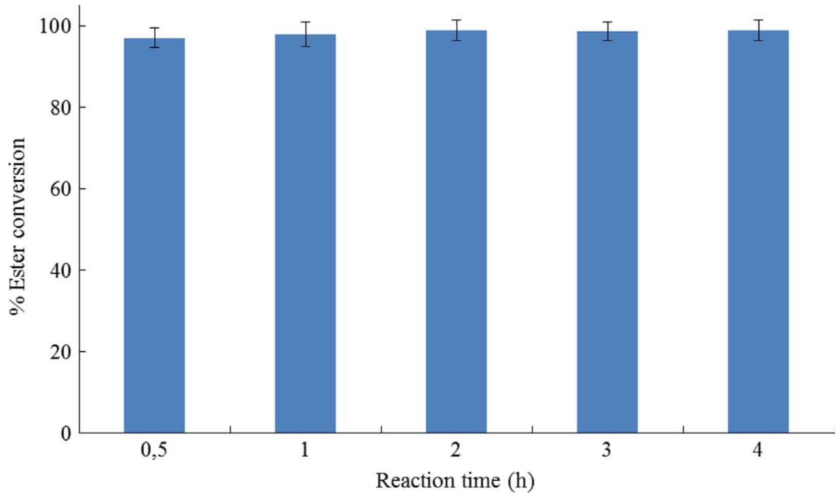

Figure 1. Percentage of ester conversion versus reaction time.

difference was observed for the ester conversions at these temperatures. Therefore, it can be concluded that the reaction was already complete after one hour and the lowest temperature to attain this completion was 80 °C and could possibly be lower. However, according to a recent study on the esterification of oleic acid from palm oil with 2-ethylhexanol, the best operating temperature was 160 °C using 1.0% catalyst (Waskitoaji *et al.*, 2012). Not only was the conversion obtained in this study higher than 98.9% but our operating temperature was also much lower at 80 °C.

3.3. Effect of POME:2EH molar ratio

Since POME is the limiting reactant, the amount of POME was fixed and the ratio of 2-ethylhexanol (2EH) to POME was manipulated between 1.5 and 2.2.

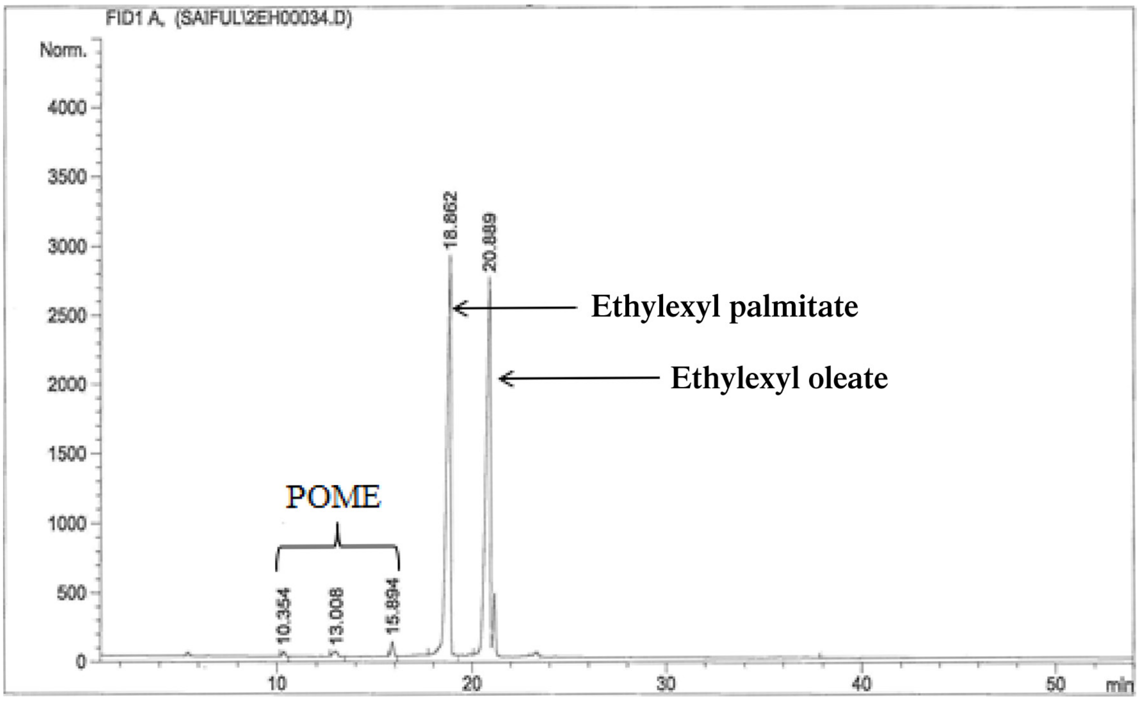

Figure 2. GC chromatogram for ethyl hexyl esters.

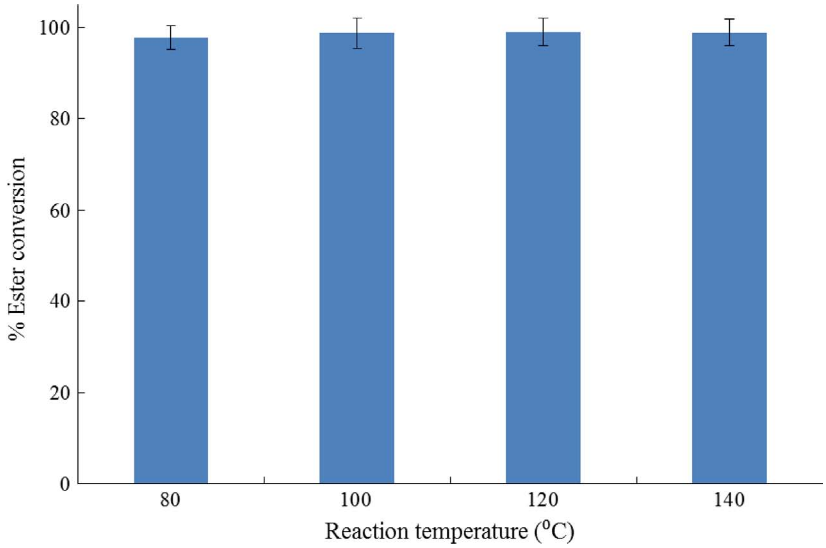

Figure 3. Percentage of ester conversion versus reaction temperature.

The reaction temperature was fixed at 80 °C, 2 % catalyst and 1 hour reaction time. The effect of molar ratio between POME and 2EH was studied because the equilibrium in the transesterification might be influenced by employing an excess of one reactant (Liu *et al*., 2006). Figure 4 shows the percentages of ester conversion according to reactant molar ratio.

The transesterification reaction is highly reversible, thus the alcohol should be in excess and that is why ratios 1:2, 1.5 and 2.2 were selected to study the effect of the reactant molar ratio. The results on the reaction conversion (2EH ester) showed only a slight improvement at molar ratio, 1:2.2, in which the 2EH ester percentage was 99.9%. For molar ratio 1: 1.5, 97.6% of 2EH ester was obtained, while at 1:2, the conversion was 98.8%, which is also very high. Comparatively, the ratio 1:2 is preferable because of the highly reversible nature of the reaction. A similar trend was observed by Waskitoaji *et al.* (2012) who found that the effect of molar ratio between oleic acid and alcohol has a marginal effect on ester conversion. Tan *et al*., (2006) reported a higher synthesis of 2-ethyl hexyl pamitate (>95%) at a molar

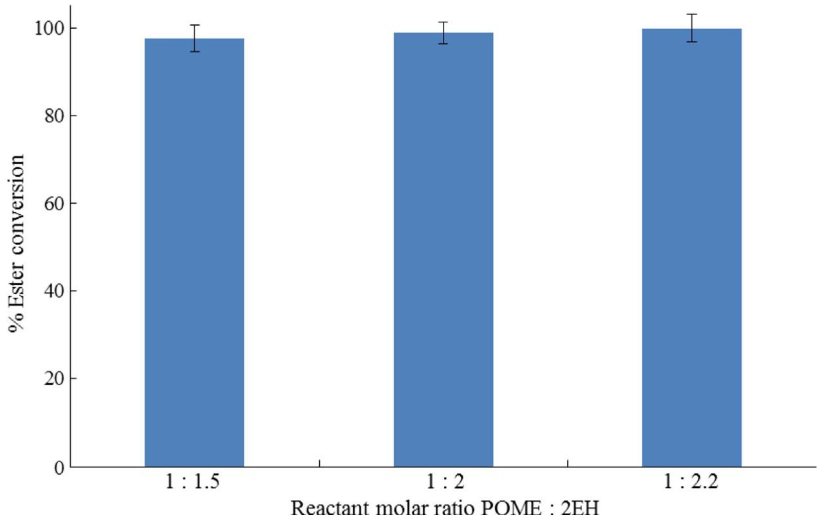

Figure 4. Percentage of ester conversion versus reactant molar ratio.

ratio of alcohol/acid, 1:1.3 and when the reaction was carried out for 6–10 hrs.

3.4. Effect of amount of catalyst

A homogenous sodium methoxide catalyst (CH_3ONa) in methanol solution was used in the transesterification to produce 2EH ester. The amount of catalyst depends on the total mass of the reactant and is measured by weight percentage. In this study, 1%, 1.5% and 2% *w/w* of catalyst were used in the synthesis with 80 °C reaction temperature, the ratio POME:2EH was 1:2 and reaction time was 1 hour. The GC result showed that the 2EH conversion for 1% catalyst was 88% and 94% for 1.5% catalyst. These conversions are slightly lower than the conversion of monoester at 2% catalyst. However, the use of a large amount of catalyst may induce soap formation during the reaction. Fortunately, in this study, the amount of soaps formed by using 2%, 1.5% and 1% catalyst are almost similar, hence 2% catalyst was selected because a higher conversion of 2EH ester was achieved. The results are shown in Figure 5. The previous study using sulphuric acid as catalyst found the optimum catalyst to be 1% (Waskitoaji *et al.*, 2012).

Consequently, further experiments were conducted at lower temperatures of 70 °C and 60 °C. The result for 70 °C reaction showed that the conversion of 2EH ester was 97%, which is very good, but at 60 °C reaction, only a small conversion was detected. To find the exact time required for the reaction to complete, the sample was taken at times 3, 5, 7, 10, 15, 20, 25, 30, 40, 50, 60, 120, 180 and 240 min. The condition of the experiment was fixed except for the temperature of the reaction varying from 70 °C to 100 °C as is given in Table 1.

The result of the time sampling in Figure 6 shows that there is no distinct difference in the percentage of ester conversion and also, the time taken to complete the reaction was only 3 minutes. Thus, the optimum conditions for the synthesis were: reaction temperature of 70 °C; reaction time below 10 minutes; 1:2, POME:2EH molar ratio; 2 % w/w sodium methoxide catalyst and 1.5 mbar vacuum pressure. However, Waskitoaji *et al.*, (2012) reported that the esterification of 2-ethyl hexyl oleate was best carried out at 160 °C in 4 h, with 1.0% catalyst. Most of the researchers reported the conversion of fatty acid esters of 2-ethyl-1-hexanol by using an enzymatic catalyst (Linko *et al.*, 1994; Lamsa *et al.*, 1994; He *et al.*, 2002; Tan *et al.*, 2006). The time taken to achieve 90% conversion was 8 hours and required at least 3.4% catalyst (Lamsa *et al.*, 1994).

3.5. GC analysis and properties of ethyl hexyl esters

The purity of the 2-ethyl hexyl esters was determined by GC. The GC chromatogram revealed five distinct peaks with two different intensities, peaks at retention times 10.35, 13.0 and 15.89 (Figure 2) have less intensities (50 to 100 pA) compared to peaks at 18.8 and 20.9 minutes with intensities 2500 to 3000 pA. The GC chromatogram of fatty acid methyl ester standards depicted peaks at retention times between 12 to 15 minutes, while peaks

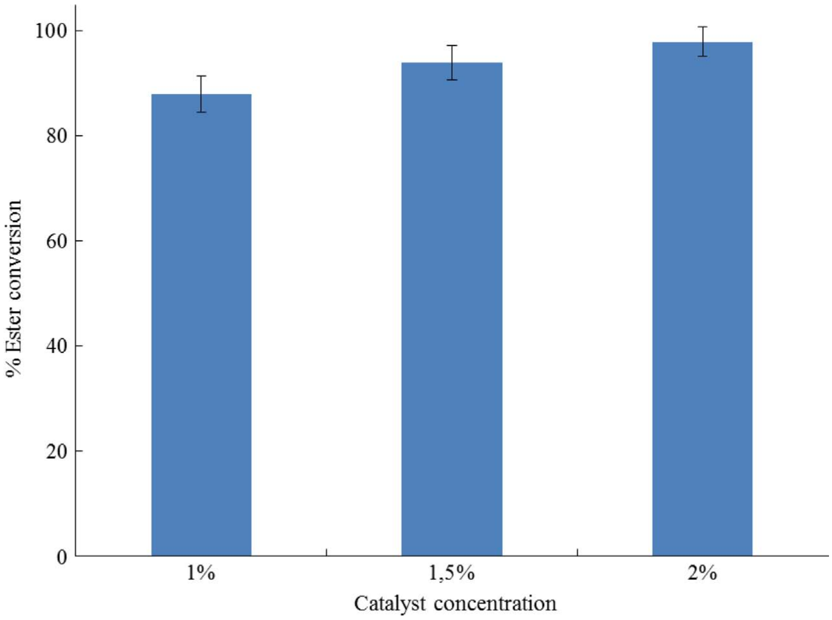

FIGURE 5. Percentage of ester conversion versus w/w% catalyst.

Table 1. The condition of 2EH ester transesterification

Operating Variables	Value
Temperature (°C)	70, 80,90, 100
Molar ratio of POME : 2EH	1:2
Catalyst w/w (%)	2
Vacuum pressure (mbar)	1.5

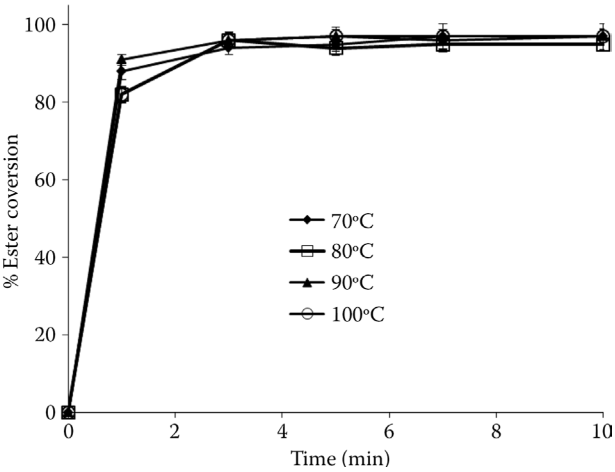

Figure 6. Percentage of ester conversion versus reaction time.

appearing between18 to 21 minutes belong to monoesters. From this data, the transesterification process was considered successful because the majority of the reaction product consists of monoesters which were the desired products. Accordingly, the peak at 18.8 belongs to ethyl hexyl palmitate and the peak at 20.9 represents ethyl hexyl oleate. The total percentages of monoesters in this sample were 98.8% and 1.2% for unreacted palm oil methyl ester.

The basic properties of the ester oil were tested and the results show that the kinematic viscosity of the oil at 40 °C and 100 °C were 8.24 mm^{2}·s^{-1} and 3.03 mm^{2}·s^{-1}, respectively. The flash point was >200 °C and the pour point was –15 °C.

4. CONCLUSIONS

In this study, the synthesis of ester as a biodegradable base oil was conducted by means of a transesterification reaction of palm oil methyl ester (POME) with 2-ethylhexanol (2EH). Based on the results, a complete conversion of 2-ethylhexanol to palm based ethyl hexyl ester was obtained in less than 30 min under these conditions: temperature of reaction, 70 °C-100 °C, reactant molar ratio 2:1 and using 2% (w/w) sodium methoxide as catalyst. The pressure of the reaction was fixed at 1.5 mbar. Temperature has a marginal effect on the reaction conversion; the product yield showed no significance difference at 70 °C to 100 °C. Thus, 70 °C was selected for the optimum condition since it requires the least amount of energy for the reaction to occur. The reaction product was monoester as identified using GC. No intermediate compound was produced; all reactants were converted into monoesters of ethyl hexyl oleate and ethyl hexyl palmitate. The complete conversion for the reaction was achieved in less than 10 minutes, where 98% w/w palm based ethyl hexyl ester was successfully synthesized.

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