



Biodiesel Preparation from Oil Fraction of Crude Pond Palm Oil through ZrO_2/SO_3H^+ -Catalyzed Esterification Followed by KOH-Catalyzed Transesterification

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The synthesis of biodiesel from crude pond palm oil (CPO) fraction has been performed using ZrO_2/SO_3H^+ catalyst. The research was carried out *via* two processes. First process, *i.e.* catalyst preparation of ZrO_2/SO_3H^+ was performed through wet impregnation method by mixing 1 g $ZrOCl_2 \cdot 8H_2O$ with 15 mL (0.5 M) of H_2SO_4 . The second process, involved the synthesis of biodiesel was performed in 2 stages, namely esterification of crude palm oil fraction catalyzed by ZrO_2/SO_3H^+ and transesterification using KOH catalyst. Results showed that ZrO_2/SO_3H^+ has been successfully synthesized from $ZrOCl_2 \cdot 8H_2O$ and H_2SO_4 which have been proven by FT-IR and XRD analysis. Biodiesel could be synthesized by esterification catalyzed by ZrO_2/SO_3H^+ and KOH catalyzed transesterification with 68.96 % conversion. Biodiesel formation is evidenced by the appearance of several peaks corresponding to the peak of methyl palmitate (48.51 %), methyl oleate (46.38 %), methyl stearate (3.84 %), methyl myristate (0.97 %) and methyl laurate (0.3 %). Based on ASTM data, biodiesel can be used as diesel fuel refers to SNI 04-7182-2006.

Keywords: Biodiesel, Crude palm oil pond oil fraction pond, Esterification, Sulfated zirconia.

INTRODUCTION

Biodiesel is one representative of alternative fuel to replace fuel derived from petroleum. Biodiesel can be made using raw material vegetable oils or animal fats. Various vegetable oils have been studied to be developed as a source of biodiesel feedstock, such as palm oil, coconut oil, sunflower seed oil, corn oil and soybean oil. However, use of these oils can cause problems directly related to food competition. During the last few years a lot of raw material of biodiesel coming from used vegetable oil, but in its application, the usage of its material has many constrains related to collection process of raw material.

In this study, the raw material used was oil fraction pond crude palm oil (CPO) that has not been widely studied and developed. Pond crude palm oil fraction is attached to the palm oil mill wastewater (crude palm oil ditch). Crude palm oil pond has free fatty acid content between 40–70 %. The main components consist of crude palm oil pond 95–96 % water, 0.6–0.7 % oil and 4–5 % assorted solids [1]. The use of crude palm oil fractions as raw material for biodiesel will provide the dual advantages eliminating waste pollution to groundwater and rivers, suppress the production cost of crude palm oil (transfer pricing) and obtain the clean development mechanism (CDM).

Its superiority as a raw material for biodiesel, oil fractions of crude palm oil pond has major drawbacks, namely high levels of free fatty acid (FFA) contained therein. With high free fatty acid content, the process of making biodiesel will interfere with the formation of soap in bulk [2]. Soap formation causes a decrease in the methyl ester product and a complicated process for the separation of methyl esters with glycerol. To overcome these problems, in this study, biodiesel production will be done in two stages, namely the stage of esterification using an acid catalyst zirconia sulfated (ZrO_2/SO_3H^+) to reduce levels of free fatty acid fraction crude palm oil pond through the conversion of free fatty acids into methyl esters followed by a stage transesterification with KOH base catalyst to alter triglyceride oil fraction into methyl esters of crude palm oil pond.

Acid catalysts are commonly used in the esterification reaction which is homogeneous acid catalysts, such as strong acids, *i.e.* H_2SO_4 , HF and acid *p*-toluenesulfonate, but is considered less economical catalyst [3]. Sakai *et al.* [4] observed that the lowest production cost is obtained when biodiesel is produced using heterogeneous catalysts capable of reducing downstream processing and purification. Additionally, heterogeneous catalysts also reduce the occurrence of corrosion

[2]. Heterogeneous acid catalyst that is currently been developed, among others, is a group of zeolites and metal oxides (ZrO_2 and SnO_2). However, compared with metal oxides, zeolites have drawbacks as shown by Rothenberg *et al.* [5] related to mass transfer between zeolite micro nature and size of large triglyceride molecules (macromolecules). This limitation has slow process at the stage of diffusion catalysis. With its superiority, we use the heterogeneous catalysts of metal oxide clusters sulfated zirconia ($ZrO_2/SO_3^-H^+$).

Triglyceride transesterification process in order to convert fractions into crude palm oil methyl esters was performed with a strong base catalyst. Strong base catalysts commonly used are NaOH and KOH. Encinar *et al.* [6] reported that compared with NaOH, KOH as catalyst performance is superior to that which produced methyl ester products more and separation of methyl esters of glycerol products more easily. Through a two-stage process that is catalyzed esterification $ZrO_2/SO_3^-H^+$ and transesterification with KOH catalyst is expected to obtain biodiesel with maximum results.

EXPERIMENTAL

The tools used in this study consists of a stirrer hot plate, oven, furnace (furnace), 250 mesh sieve, reflux condenser, three-neck flask, a thermometer, an analytical balance (Mettler AT-200), burette, IR spectrophotometer (Shimadzu FTIR 8201 PC), X-Ray Diffraction (XRD Shimadzu 6000), GC-MS (Shimadzu GCMS-QP2010S), 1H NMR Laboratory of Integrated Science, University of March, the means test ASTM standard (ASTM D 1298, KPI/5.4/TK-02, KPI/5.4/TK-03, KPI/5.4/TK-04) in Laboratory Technology Oil, Gas and Coal, Chemical Engineering Department, Gadjah Mada University, as well as glassware commonly used in chemical laboratories.

The materials used in this study consisted of $ZrOCl_2 \cdot 8H_2O$ obtained from PTAPB-Batan, crude palm oil pond fraction taken from one of the palm oil mills in Rangai Tri Tunggal district, South Lampung, Lampung Province and distilled water. Other chemicals used have a quality proanalysis from Merck, including H_2SO_4 , methanol, KOH, NaOH and phenolphthalein as an indicator.

$ZrO_2/SO_3^-H^+$ catalyst preparation: $ZrO_2/SO_3^-H^+$ catalyst made by the wet impregnation method [7], with slight modifications. A total of 10 g of $ZrOCl_2 \cdot 8H_2O$ put in 150 mL of 0.5 M H_2SO_4 solution is then stirred with a magnetic stirrer for 24 h. Solids produced in the oven at 100 °C for 24 h and then crushed and sieved using a 250 mesh sieve. Solids produced in the calcination temperature variations of 400, 500 and 600 °C for 4 h, then crushed and sieved using 250 mesh sieve. The resulting catalysts were characterized by FT-IR and XRD.

Crude palm oil fraction esterification: As much as 3 L of crude palm pond oil fraction was heated at 130 °C to evaporate water in the crude palm oil fraction and the oil fraction was filtered with a filter paper to separate the large solid impurities. Then, 150 g of oil fraction esterified with methanol, mole ratio of used cooking oil and methanol is 1:12, assuming a molecular weight fractions crude palm oil pond is 860, then the weight of methanol used is 67 g. $ZrO_2/SO_3^-H^+$ catalyst is used as much as 5 % of the total weight of crude palm pond oil fraction and methanol. $ZrO_2/SO_3^-H^+$ catalyst and methanol

were refluxed prior to using a three-neck flask equipped with a magnetic stirrer for 30 min, then crude palm oil fraction which had previously been heated to 45 °C were incorporated gradually into the mixture. The temperature was raised to 60 °C with a magnetic stirrer rotational speed of 600 rpm and maintained for 2 h. Oil was separated from the other components were refluxed with a centrifuge with a rotational speed of 1500 rpm for 20 min.

Determination of free fatty acid oil after esterification:

Free fatty acid content determination used acid-base titration method. A total of 2 g of esterified oil was mixed with 20 mL of 96 % methanol and heated to 45 °C. Then, the mixture was added to 3 drops of phenolphthalein. The mixture was titrated with 0.1 N NaOH until the colour changes to pink that persists for 15 s. Titration was performed 2 times for each sample. Free fatty acid content was determined by the following equation.

Transeserification of esterification oil product: Esterified oil was reacted with methanol with 35 g of oil and methanol in the ratio of 1 : 6. The catalyst used is KOH with 1 % of the total weight of the oil and methanol. Catalyst and refluxing methanol was used prior to using three-neck flask equipped with a magnetic stirrer for 30 min. Then, the oil that had previously been heated to 45 °C was incorporated gradually into the mixture. The mixture was refluxed at 60 °C with a magnetic stirrer having rotational speed of 600 rpm for 2 h. The mixture was refluxed and incorporated into a separating funnel and separated between biodiesel with glycerol. Biodiesel produced evaporated to remove residual methanol and washed with hot distilled water in a separating funnel to dissolve the rest of glycerol. Furthermore, in order to bind, the remnant of water was added to anhydrous Na_2SO_4 . As a control, the manufacture of biodiesel was also performed using $ZrOCl_2 \cdot 8H_2O$ catalyst which has not been activated with sulfuric acid.

Biodiesel product characterization: Analysis of GCMS was used to determine the type of the resulting methyl esters product. 1H NMR was used to analyse the conversion of triglycerides into biodiesel. Quantitatively, the magnitude of the conversion of triglycerides into methyl esters can be determined using the following equation [8]:

$$C_{ME} (\%) = 100 \times (5I_{ME}) / (5I_{ME} + 9I_{TAG})$$

where I_{ME} is integration value of methylester peak, I_{TAG} is integration value of triacylglycerol.

Feasibility test for biodiesel was analyzed by American Standard for Testing Materials (ASTM) method which has been standardized by the National Standardization Agency's quality requirements in accordance with NFPA-04-7182-2006 [9]. As for biodiesel, quality parameters tested include specific gravity, kinematic viscosity, flash point, pour point, cloud point and water content.

RESULTS AND DISCUSSION

The FTIR spectra of $ZrOCl_2 \cdot 8H_2O$ and ZrO_2/SO_3^- was shown in Fig. 1 that shows the same tape from $ZrOCl_2 \cdot 8H_2O$ and $ZrO_2/SO_3^-H^+$ on which was the wave number of 3417.86 cm^{-1} of OH stretch vibration and 1635,64 cm^{-1} which indicates vibrations of water (H-O-H) [10]. In the spectra of $ZrO_2/SO_3^-H^+$ appears a new band at wavenumber 941.26 and 1126.43

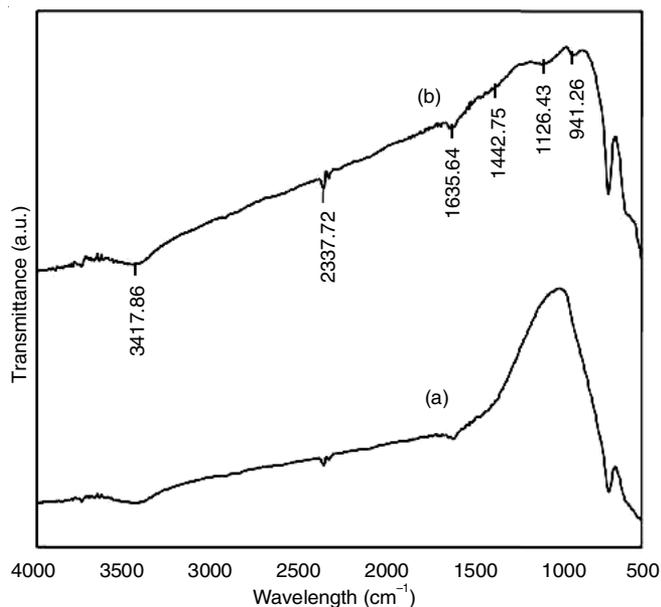


Fig. 1. FTIR Spectra of a) $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and b) $\text{ZrO}_2/\text{SO}_3\text{-H}^+$

cm⁻¹ which is a distinctive ribbon of sulfate ion coordinated to the zirconium cation [11] as well as weak bands at 1442.75 cm⁻¹ is the stretch vibration of S=O [12]. This confirms that the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ sulfate impregnation has been successfully carried out.

X-ray diffraction results of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{ZrO}_2/\text{SO}_3\text{-H}^+$ with calcination temperature variations, namely 400, 500 and 600 °C are shown in Fig. 2. Through figure, it is known that in general, the impregnation process using sulfuric acid does not alter the structure of zirconium oxide. By comparing the diffractogram $\text{ZrO}_2/\text{SO}_3\text{-H}^+$ with the standard ZrO_2 diffractogram $\text{ZrO}_2\text{-1-750}$, the database is known that $\text{ZrO}_2/\text{SO}_3\text{-H}^+$ has a monoclinic phase that can be observed in peak 2 = 28.23; 2 = 31.52; 2 = 25.44; *etc.* Fig. 3 shows a comparison between

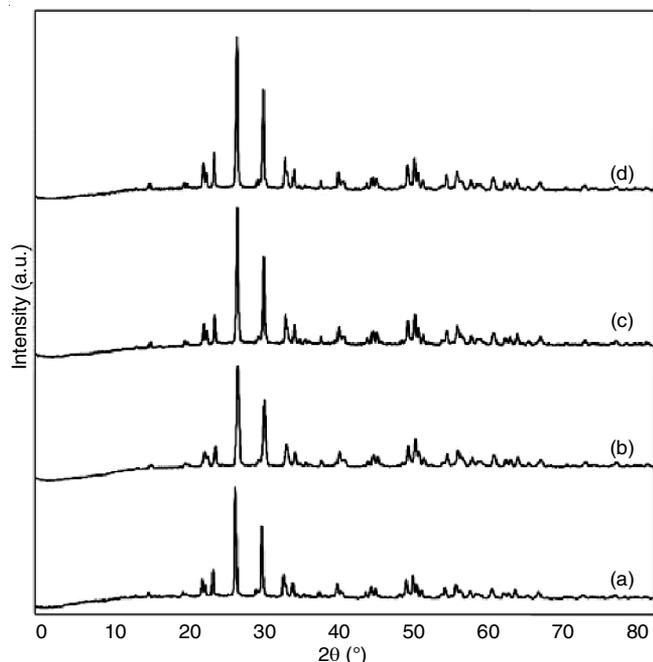


Fig. 2. Diffractograms of (a) $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, (b) $\text{ZrO}_2/\text{SO}_3\text{-H}^+$ at 400 °C, (c) 500 °C and (d) 600 °C

the diffractogram $\text{ZrO}_2/\text{SO}_3\text{-H}^+$ with the standard diffractogram $\text{ZrO}_2\text{-1-750}$ ZrO_2 . Indrati *et al.* [13] stated that ZrO_2 has some kind of crystal structure including monoclinic, tetragonal or a mixture of both, pseudo-hexagonal, rhombohedral or trigonal and cubic where monoclinic structure gives stability to ZrO_2 [7].

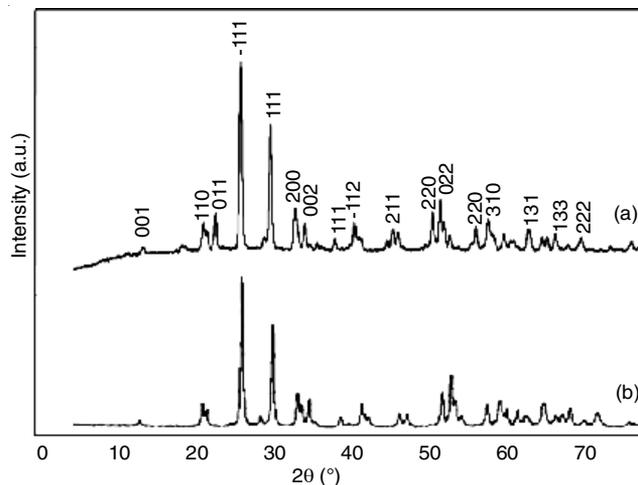


Fig. 3. Diffractograms of (a) $\text{ZrO}_2/\text{SO}_3\text{-H}^+$ at 600 °C and (b) ZrO_2 standard ($\text{ZrO}_2\text{-1-750}$ from database)

Calcination process does not give the effect of a modification phase, in which with increasing calcination temperature, the peak intensity of monoclinic phase increases. From Fig. 2, it appears that the intensity of the peak phase of monoclinic $\text{ZrO}_2/\text{SO}_3\text{-H}^+$ at 400 °C, calcination temperature was lower than $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. It indicates that the impregnation process causes $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and crystallinity decreases due to the presence of sulfate ions on the surface of ZrO_2 , but by calcination at 500 and 600 °C, monoclinic phase increased peak intensity was much higher than $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ because at these temperatures, the regular lattice spacing was caused due to the loss of water.

It can be concluded that impregnation and calcination processes increase the peak intensity which cause the monoclinic phase $\text{ZrO}_2/\text{SO}_3\text{-H}^+$ having the physical stability [7]. The results of FT-IR and XRD have confirmed that $\text{ZrO}_2/\text{SO}_3\text{-H}^+$ is a catalyst that will give good performance with strong acidity and physical stability.

Fig. 4 shows a graph of concentration of the catalyst *versus* free fatty acid content of crude palm oil fractions. Based on these images, it is known that the best type of catalyst in lowering levels of free fatty acid is $\text{ZrO}_2/\text{SO}_3\text{-H}^+$ at 600 °C calcination temperature. These data correspond with the results of characterization using XRD, where $\text{ZrO}_2/\text{SO}_3\text{-H}^+$ peak intensity at 600 °C has the highest monoclinic phase (Fig. 2).

Fig. 4 shows a graph of concentration of the catalyst *versus* free fatty acid content of crude palm oil fractions. Fig. 4 showed that the best catalyst performance in reducing the free fatty acid content was $\text{ZrO}_2/\text{SO}_3\text{-H}^+$ with 5 % concentration at 600 °C. It could reduce levels of free fatty acid fraction crude palm oil of 7.56 % to 0.99 % ($\Delta = 6.57$ % free fatty acid content). The graph shows that increasing the catalyst concentration of 1–5 % will increase the ΔFFA levels. It happened because the

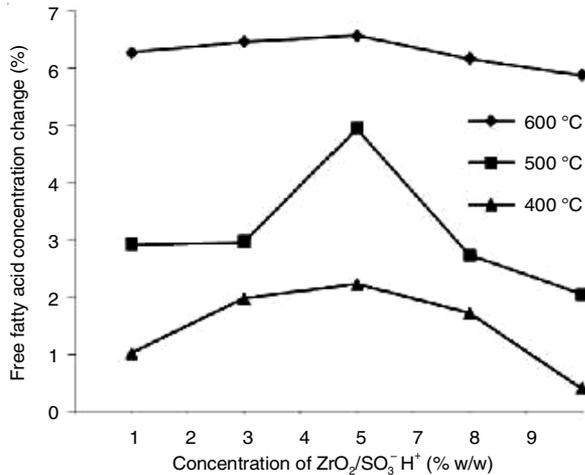


Fig. 4. Concentration of catalyst versus free fatty acid content of crude palm oil fractions

increasing of the amount catalyst sites can be occupied by more reactants, as a result the free fatty acids will react more. In fact, it only applies to a concentration of 5 %, then Δ FFA levels declined. This is presumed to occur because of two factors, the first catalyst $ZrO_2/SO_3^-H^+$ is acidic and is released (leaching) to the acid environment. At a concentration of 5 %, $ZrO_2/SO_3^-H^+$ gives a good performance as a catalyst in lowering levels of free fatty acid, but when the concentration is more than 5 %, $ZrO_2/SO_3^-H^+$ actually increases the acidity of the oil fraction crude palm oil. Nourredine [14] reported that $ZrO_2/SO_3^-H^+$ desorbs sulfuric acid during the reaction so as to provide the reactants. The second factor, the catalytic properties of $ZrO_2/SO_3^-H^+$ decrease due to obstruction (blocking) of the active site as a result of too much amount of catalyst [7]. Reaction mechanisms that occur in the process of esterification between crude palm oil fraction and methanol using solid acid catalysts $ZrO_2/SO_3^-H^+$ are shown in Fig. 5.

Fig. 5 shows H^+ transfer from the Brønsted acid sites on the catalysts towards oxygen of the carbonyl group in acid

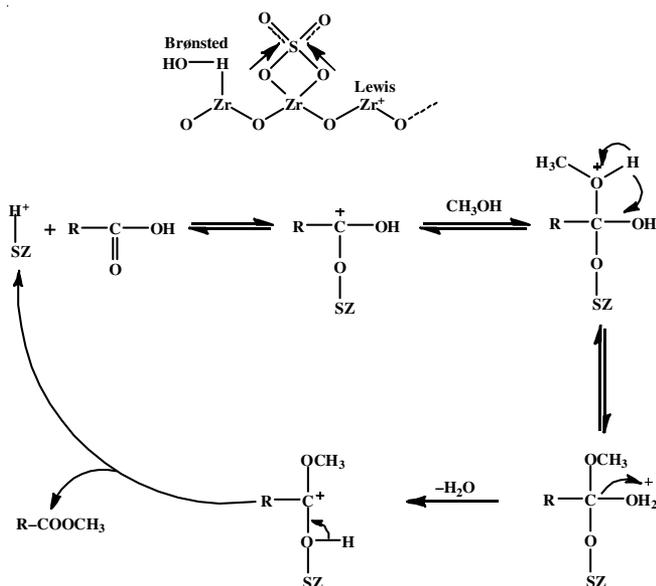


Fig. 5. Illustration of sulfated zirconia (SZ) structure and esterification reaction mechanism of Brønsted acid sulfated zirconia [Ref. 15]

followed by nucleophilic attack of oxygen on methanol. Next, the process of deprotonation and water loss formed ester products [15].

Fig. 6 shows the graph between mole ratio (oil: methanol) versus yield of biodiesel products. From figure, it can be noted that the mole ratio (oil: methanol) which gives the best results of biodiesel product of 1:9 ratio was 90.28 %. Increasing concentration of methanol of 1:3 to 1:9 will also increase biodiesel result due to the reaction equilibrium towards to the right (product of biodiesel), meanwhile the concentration above 1:9 decline in results. It was because competition adsorption of the reactants on the catalyst surface with increasing concentration of methanol in the reaction mixture led to most of the active sites on the catalyst surface is occupied by methanol molecules. As a control, biodiesel production of palm oil fractions was also performed using $ZrOCl_2 \cdot 8H_2O$ that has not been activated by sulphate catalyst. The treatments were administered during the same reaction to both types of the catalyst. The results showed that the catalyst has been activated ($ZrOCl_2 \cdot 8H_2O$ at 600 °C) and provide greater product yield was 90.28 % compared to a catalyst that has not been activated ($ZrOCl_2 \cdot 8H_2O$), i.e. 65.08 %.

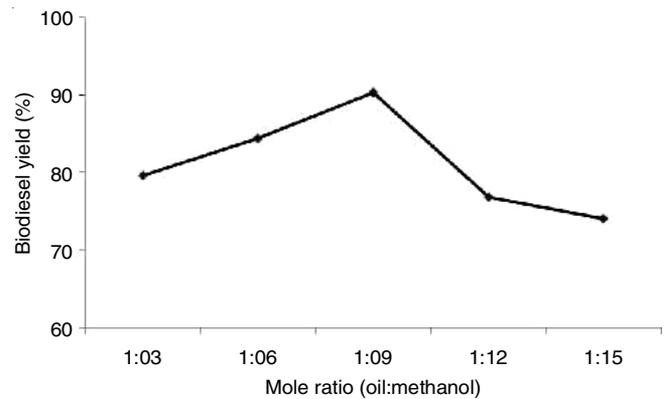


Fig. 6. Mol ratio (oil:methanol) versus biodiesel yield (%)

Fig. 7 shows the chromatogram of biodiesel of oil palm fractions using GC analysis. The figure shows that 5 peaks were detected as methyl esters. Retention time and total area from 5 peaks can be observed in Table-1. Each peak results of GCMS were analyzed and compared with the existing database. The results showed that the compounds synthesized in this study were biodiesel, namely methyl ester. Methyl esters contained in biodiesel are thought to consist of methyl palmitate, methyl oleate and methyl stearate and other methyl ester fraction.

Peak number 3 was the highest area (48.51 %) and its retention time was 22.40 min. It is assumed to be the peak of

TABLE-1
RETENTION TIME AND TOTAL AREA OF
5 PEAKS OF GC CHROMATOGRAM

Peak	Retention time	Total area (%)
1	17.560	0.30
2	20.082	0.97
3	22.404	48.51
4	24.236	46.38
5	24.400	3.84

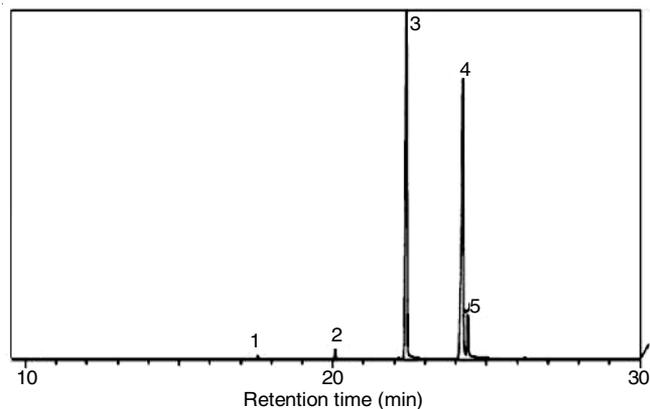


Fig. 7. Chromatogram of biodiesel

methyl palmitate. Comparing the peak number 3 using standard methyl palmitate (Wiley Library), similarity index of 96 % was obtained. Methyl palmitate has a molecular weight of 270 g/mol with the formula $\text{CH}_3(\text{CH}_2)_{14}\text{COOCH}_3$ providing peak $m/z = 270$.

Peak number 3 which is supposedly methyl palmitate (methyl hexadecanoic) is also reinforced by the emergence of a mass unit at $m/z = 239$ and $m/z = 74$. Unit mass $m/z = 239$ is an ion that has lost OCH_3 radical (Fig. 8). Unit mass of $m/z = 74$ is an ion fragment from McLafferty containing carbonyl groups and generated from the breakdown through the rearrangement (McLafferty, Fig. 9). Breaking CC bonds in aliphatic esters provides ion series containing oxygen with the formula $[(\text{CH}_2)_n\text{COOCH}_3]^+$ with $n = 2, 3, 4, 5, 6, 7, 8, 9, 10, 11$ and 12 and appeared at $m/z = 87, 101, 115, 129, 143, 157, 171, 185, 199, 213$ and 227 . Peak number 4 is its 46.38 % of total area and 24,236 retention time was estimated as peak of methyl oleate (methyl-10-octadecanoic). Comparing the peak number 4 with standard methyl oleate (Wiley Library), similarity index of 97 % was obtained.

Methyl oleate has a molecular weight of 296 g/mol and the formula is $\text{CH}_3(\text{CH}_2)\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOCH}_3$. The peak with $m/z = 41$ is the uptake of allylic cationic $(\text{CH}_2-\text{CH}=\text{CH}_2)^+$, $(\text{CH}_2=\text{CHCH}_2\text{CH}_2)^+$ which is the result of solving the $m/z = 55$ mass units $m/z = 264$ which indicates that the loss of methyl ester is as many as 32 mass unit (methanol) (Fig. 10).

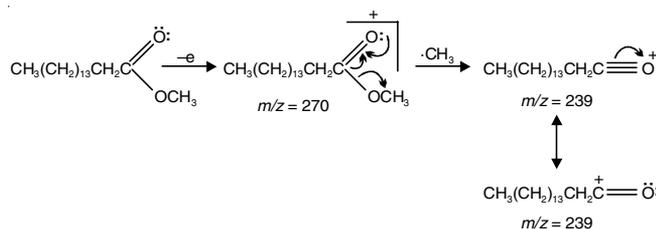


Fig. 8. Fragmentation of methyl palmitate

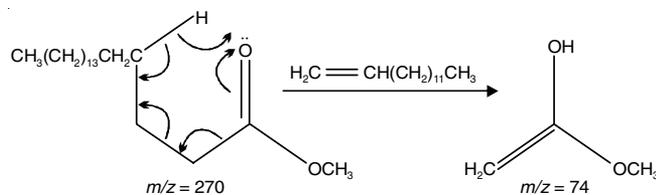


Fig. 9. Methyl palmitate fraction resulted from McLafferty ion

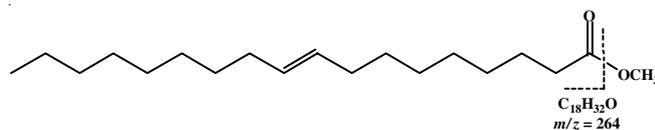


Fig. 10. Methyl oleate fragmentation

Peak number 5 is total area of 3.84 % and a retention time of 24.40. It estimated as peak of methyl stearate (methyl octadecanoic). Comparing the peak number 5 with standard methyl stearate (Wiley Library), similarity index of 96 % was obtained. Methyl stearate has a molecular weight of 298 g/mol with molecular formula $\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3$. Uptake of the molecular ion M^+ appears at $m/z = 298$. Base peak with $m/z = 74$ is the result of breaking through Mc Lafferty rearrangement. Absorption at $m/z = 267$ is the result of solving á (Fig. 11). C-C bond breaking is to give series of aliphatic esters containing oxygen ions with the general formula $[(\text{CH}_2)_n\text{COOCH}_3]^+$ with $n = 2, 3, 4, 5, 6, 7, 9, 10, 11$ and 14 which appeared at $m/z = 87, 101, 115, 129, 143, 157, 185, 199, 213$ and 255 .

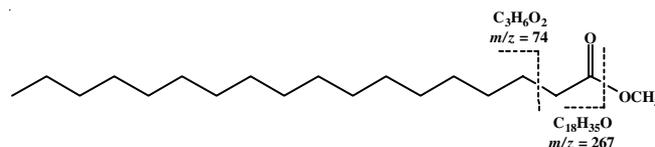
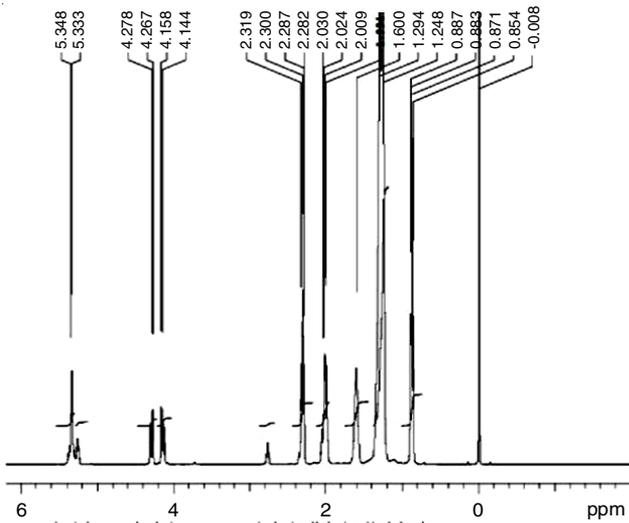
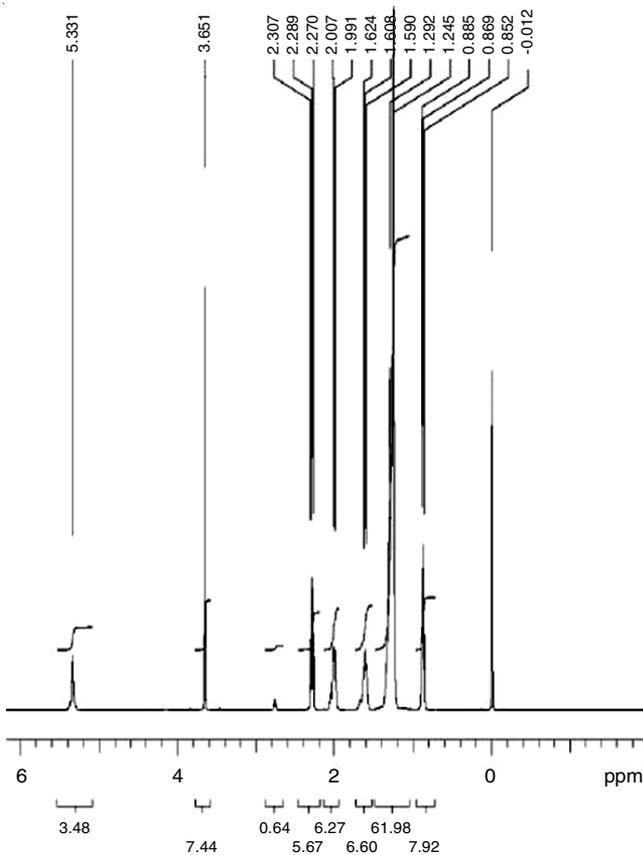


Fig. 11. Methyl stearate fragmentation

In ^1H NMR spectra interpretation, calculated peak is a peak at a chemical shift of 4.1 to 4.4 ppm which is the spectra of glyceride group proton and 3.7 ppm which is the spectra of methoxy group proton [16]. Fig. 12 shows ^1H NMR spectra of oil fractions crude palm oil pond where the typical peak of triglycerides appears with chemical shift of about 4.1 to 4.4 ppm with the integration value of 1.86. Fig. 13 shows that the ^1H NMR spectra of palm oil biodiesel oil fraction and triglyceride peaks no longer appear. At 3.7 ppm, chemical shift peak showed typical biodiesel with the integration value of 7.44. Comparing the ^1H NMR spectrum of the oil fraction of palm oil biodiesel oil fraction with crude palm oil proved that the triglycerides contained in the oil fraction have been converted into palm oil methyl ester. Integration value of triglycerides peak and methyl esters can be used to determine the amount of conversion of triglycerides into biodiesel. Substituting the value of integration into the Knothe equation [8], it was noted that the conversion occurred at 68.96 %. It is concluded that although the percent of product yield is quite high, but the conversion of triglycerides into biodiesel is not maximized. It can be caused by several factors, among others, the mixing process is not perfect and is not yet known in the reaction time required to produce the best conversion of methyl ester. As a result, further research is always needed.

Feasibility test for biodiesel was made by comparing biodiesel product with biodiesel feasibility standards based on SNI 04-7182-2006 using several parameters, namely the specific density (60/60°F, g/cm^3), kinematic viscosity (40 °C, mm^2/s), flash point, pour point, cloud point and water content. Table-2 shows the comparison of the four values of these parameters between standard diesel oil SNI 04-7182-2006,

Fig. 12. 1H NMR oil spectra from crude palm oil fractionFig. 13. 1H NMR biodiesel spectra of crude palm oil fraction

test results on the biodiesel fraction of crude palm oil and crude palm oil pond itself.

Table-2 shows that the esterification followed by transesterification process has changed the physical properties of crude palm oil fractions towards the desired properties in the utilization of the product as diesel fuel. The results testing using ASTM D 1298 method showed specific density value (60/60 °F) of biodiesel crude palm oil fraction pond was 0.8726. This value was fulfilled as standard diesel oil based on SNI 04-7182-2006.

Based on the results testing using IKU/5.4/TK-02 method, value of kinematic viscosity obtained at 40 °C was 5.022 mm²/s which indicates that these parameters have met the appropriate standard diesel oil SNI 04-7182-2006. Kinematic viscosity is one of the test parameters that indicates the resistance of a fuel to flow. Lubrication viscosity grades will influence fuel injectors, a high viscosity of biodiesel fuels cause difficult sprayed or atomized. This resulted in no tangible result of the injection of volatile fog, but rather tend to form droplets that are difficult for burning fuel, thus affecting the working speed of fuel injection equipment.

Testing result using IKU/5.4/TK-04 shows that the value of crude palm oil biodiesel pour point was at 9 °C. This value also complies with standard diesel oil-based SNI 04-7182-2006. Pour point indicates the lowest temperature at which the fuel can still be streamed or poured. High pour point leads to difficult ignited engines at low temperatures. Crude palm oil biodiesel pour point value at 9 °C indicates that palm oil biodiesel pond is suitable for both in the tropics and areas that tend to be cold.

Flash point value of crude palm oil biodiesel using IKU/5.4/TK-03 method was obtained at 240.5 °C. This value is in accordance with standard diesel oil in accordance with NFPA-04-7182-2006. The high flash point of crude palm oil biodiesel showed that the residual methanol contained in just a few products. A large amount of methanol in the biodiesel will lower the flash point [17]. Methanol is volatile and flammable, so the higher the methanol content, the lower the flash point. Flash point is the lowest temperature at which a fuel can still be lit. Determination of flash point is based on security process in the storage and handling of fuel. High flash point that will facilitate the process of saving fuel is because the fuel is not flammable at room temperature.

Cloud point is one of the indicators used to measure the performance of biodiesel at low temperatures. Cloud point indicates the temperature at which the fuel starts to look like a murky haze. Value test cloud point of crude palm oil biodiesel

TABLE-2
PHYSICAL PROPERTIES COMPARISON BETWEEN STANDARD DIESEL OIL,
CRUDE PALM OIL BIODIESEL AND CRUDE PALM OIL POND (CPO)

Parameter	Diesel oil*	Biodiesel from pond-CPO	Oil fraction of pond-CPO
Specific density (60/60 °F)	0.85-0.92	0.8726	0.9134
Kinematic viscosity at 40 °C (mm ² /s)	2.3-6.0	5.022	40.21
Pour point (°C)	Max. 18	9	18
Flash point (°C)	Min. 100	240.5	252.5
Cloud kabut (°C)	Max. 18	6	–
Conradson carbon residue (% wt)	Max. 1	0.248	–
Water content (% vol)	Max. 0.05	0.1	0.24

*SNI-04-7182-2006 by National Standardization Agency of Indonesia.

was obtained at 6 °C and found to be according to SNI 04-7182-2006 standards.

The test results of water content for crude palm oil biodiesel was 0.1 %. This value does not meet the standard of SNI 04-7182-2006. This is likely to occur because of the lack of anhydrous Na₂SO₄ which was added to absorb the water contained in palm oil biodiesel. According to Suhartanta and Arifin [18], high water content will cause the absorption of heat energy in the combustion process is large enough so that the heat generated from the combustion process decreases.

Based on the value of the six test parameters, it is known that palm oil biodiesel used is appropriate as diesel oil based SNI 04-7182-2006. Crude palm oil biodiesel pond has a specific density value, kinematic viscosity, pour point, flash point and cloud point of diesel oil that meets the standards [19,20].

Conclusion

Impregnation process of sulfate groups on ZrOCl₂·8H₂O had been done successfully. It was evidenced by the appearance of new bands in the IR spectrum of ZrO₂/SO₃⁻H⁺ at 941.26 and wave number of 1126.43 cm⁻¹ which is typical of sulfate ion coordinated to the zirconium cation as well as weak band at 1442.75 cm⁻¹ which is the vibration of S=O stretch. Esterification process using 5 % of ZrO₂/SO₃⁻H⁺ catalyst at 600 °C can decrease free fatty acid of crude palm oil content from 7.56 to 0.991 %. The best oil and methanol mole ratio of 1:9 produces biodiesel as much as 90.28 %. GCMS results showed that the content of palm oil biodiesel pond consists of methyl palmitate (48.51 %), methyl oleate (46.38 %), methyl stearate (3.84 %), methyl myristate (0.97 %) and methyl laurate (0.3 %). ¹H NMR results showed that the triglyceride conversion to biodiesel has been successful as evidenced by the appearance of a typical triglyceride peak at 4.1–4.4 ppm chemical shift in the spectrum of crude palm oil typical and also methoxy peak at 3.7 ppm chemical shift in the spectrum of palm oil biodiesel pond with greater conversion as much as 68.96 %. Based on SNI 04-7182-2006, physical properties of palm oil biodiesel fullfil the criteria of the crude palm oil pond specific density (60/60 °F) of 0.8726, kinematic viscosity of 5.022 mm²/s, pour point at 9 °C, flash point at 240.5 °C and cloud point at 6 °C, while the value of the water content of crude palm oil biodiesel was 0.1 % that was not fulfilled with the standard criteria.

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