Preparation of CaO/Fly ash as a catalyst inhibitor for transesterification process off palm oil in biodiesel production

Z Helwani¹³, W Fatra², E Saputra¹ and R Maulana¹

¹ Departement of Chemical Engineering, Riau University, Pekanbaru, 28293, Indonesia
² Departement of Mechanical Engineering, Riau University, Pekanbaru, 28293, Indonesia

E-mail: zuhria.helwani@lecturer.unri.ac.id

Abstract. A palm fly ash supported calcium oxide (CaO) catalyst was prepared and used in transesterification from off-grade palm oil for biodiesel production. The catalyst synthesized by loading CaO of calcium nitrate tetrahydrate (Ca(NO₃)₂.4H₂O) into fly ash through impregnation method. The optimum catalyst preparation conditions were determined by influence of calcination temperature and weight ratio of Ca(NO₃)₂.4H₂O and fly ash. Catalyst with highest catalytic activity was achieved when calcined at 800 °C and proportion of Ca(NO₃)₂.4H₂O to fly ash is 80:20. Under the conditions of oil : methanol ratio of 1:6, catalyst dosage of 6 wt% and temperature of 70 °C for 2 h, the biodiesel yield reaches to 71.77%. CaO, SiO₂, Ca(OH)₂ and Ca₂SiO₄ were found in the catalyst through X-ray diffraction (XRD) while the basic strength of the catalyst H₄ in the range 9.3 – 11. Surface area of the developed catalyst is 24.342 m²/g through Brunauer-Emmett-Teller (BET). Characteristics of biodiesel such as density, kinematic viscosity, acid value, flash point has been matched with standard for biodiesel specification of Indonesia.

1. Introduction

Oil-palm off grade is a source of vegetable oil available in large quantities, which is about 7-10 tons produced from palm oil mill with a capacity of 30 tons/hour and sold at prices 30-40% cheaper than good quality CPO [1]. Besides having a great availability and low price, oil-palm off grade has not been utilized to the maximum and potentially be used as raw material for biodiesel. The weakness of oil-palm off grade is to have high levels of FFA. The weakness can be overcome with the use of two-stage reaction due to high FFA levels. FFA can be reduced through esterification reaction before continuing to the transesterification reaction. FFA levels allowed in the transesterification reaction is <2% [2].

The biodiesel production is commonly performed by transesterification of refined vegetable oils with methanol in the presence of homogeneous base catalysts, such as sodium or potassium hydroxides, carbonates or alkoxides. But these catalysts have some problems such as difficulty in removing the catalysts after the reaction, production of large amount of wastewater and emulsification [2]. In order to overcome the drawbacks of homogeneous catalytic process, recently profound
attention has been devoted to the development and application of heterogeneous catalysts for synthesis of biodiesel. The advantage of using heterogeneous catalysts in the transesterification reaction is not corrosive, environmentally friendly, easily separation, high selectivity, reusable, and not a lot of waste [3]. Calcium Oxide (CaO) is one of basic heterogeneous catalyst that most developed, they are CaO, CaCO3 and Ca (OH)2 [4], CaO / Fe3O4 [5], and the CaO/fly ash [6]. However, the use of CaO as a catalyst has disadvantages, the oxygen ions (O²⁻) on the surface easily form hydrogen bonds with methanol or glycerol, increasing the viscosity of glycerol and forms suspensoid with CaO, that it is difficult to be separated [5]. To overcome these problems, CaO may be supported by an active metal [3]. 

CaO catalyst has prepared by supported with palm oil fly ash from the combustion of light fractions of husk and shell at boiler [6]. However, fly ash can be used as a source of silica in the catalyst preparation, whereas it can acts as adsorbent, either as an active sites in the reaction. High silica content in CaO will improve the mechanical, hardness properties and morphology [7]. On the other hand, high mechanical properties of the catalyst will prevent leaching [8].

Fly ash, the chief inorganic waste arises through palm oil mill waste boiler ashes, has a typical chemical composition (on dry basis): 55.19% SiO2, 30.01% Al2O3, 4.58% Fe2O3, 2.12% Na2O, 0.77% CaO, 1.91% MgO, 2.74% TiO2, 1.28% BaO and 1.40% K2O. The presence of high amount of SiO2 and Al2O3 prompts its potential applicability as a low-cost catalyst support. In a very recent publication, fly ash supported calcium oxide has been employed as a recyclable solid base catalyst for Knoevenagel condensation reaction [7]; however, the CaO was derived from reagent grade CaCO3 which might increase the cost of catalyst preparation.

Calcination and temperature time can affect the formation of CaO [10]. The study by Ho et al. (2014) found that the higher calcination temperature and the longer time of calcination, the yield of biodiesel tends to decrease. Calcination temperature depends on the primary material (precursor) for the formation of CaO. The basic strength explains the active site of catalyst for the transesterification. The basic strength determined using Hammett indicators such as phenolphthalein (H_ = 9.8), Nile blue (H_ = 10.1) and 2,4-Dinitroaniline (H_ = 18.4). Kesic et al. (2012) using CaO:ZnO, with optimum conditions of yield biodiesel reached 99%. The higher basic strength, the higher catalytic activity of catalyst. Tang et al. (2012) using a catalyst CaO/Fe3O4 to see the effect of the molar ratio of n(Ca): n(Fe) at the calcination temperature of 600 °C for 6 h. The optimum conditions are obtained with a molar ratio of Ca:Fe by 5:1, the yield increases with increasing biodiesel content of Ca.

Ho et al. (2012) studied the effect of CaO catalyst using bottom ash, ash boiler, and fly ash palm as its support material. CaO was obtained from calcium carbonate (CaCO3) calcination with temperature of 800, 900 and 1000 °C. The optimum temperature condition of catalyst preparation were obtained at a temperature of 800 °C for 30 minutes, by addition of 15%-w calcined CaCO3 into fly ash palm. The catalyst was to use for transesterification process of CPO and obtained the conversion result of 94.48%. The use of fly ash as a CaO support material can provide a larger catalyst surface area. The larger surface area of the catalyst would achieve better productivity of catalyst. The extended research was conducted by Ho et al. (2014) reviewing the development and evaluation of the CaO/palm fly ash catalyst. The catalyst was prepared by a wet impregnation method of CaCO3 and fly ash with composition 45% wt% and 55 wt %, respectively. CaCO3 was calcined at 800 °C for 1.5 h. Catalyst was used in transesterification process of CPO with methanol in the biodiesel production. The optimum condition of the transesterification reaction was reached at 60 °C, with a stirring rate of 700 rpm, and catalyst composition of 6 wt% of oil with molar ratio of methanol: oil = 12 : 1. Hence, these condition was obtained the biodiesel yields approximately 75.73%.

CaO can be synthesized using a thermal decomposition process of CaCO3 with calcination [9]. However, high calcination temperatures require more energy to decompose CaCO3 into CaO. Ho et al. (2014) obtained CaO from the precursor CaCO3 with the highest concentration of 39%-w after calcination at 1000 °C [6]. Nugraha et al. (2016) have been used CaO catalysts from precursors of calcium nitrate tetrahydrate (Ca(NO3)2·4H2O) and fly ash as support [10]. The advantage of Ca(NO3)2·4H2O can be directly use without calcination with high temperature to obtain CaO.
Preparation of catalyst using wet impregnation method with composition 50% wt% \( \text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O} \) and 50 wt% fly ash. The amount of CaO in the catalyst was 17.07%. Catalysts are used in the transesterification of biodiesel production from off-grade palm oil. The optimum condition was obtained at 60 °C, CaO/fly ash concentration of 7% -w of oil with mole ratio of methanol: oil 8: 1. The highest biodiesel yield was 61.72%.

Thus, the present work attempts to develop and characterize a novel low cost, highly efficient supported base catalyst through utilization of the two waste materials viz. fly ash and \( \text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O} \) as a precursor to derived CaO for transesterification of oil-palm off grade to yield biodiesel.

2. Experimental

2.1. Preparation of off grade fruit bunch oil
The first step is the washing of the fruit from the dirt. Furthermore the fruit steamed as much as 3 kg in the stall for 120 minutes. After that, the fruit is pressed using a spindle hydraulic press. The extraction results are inserted into the separating funnel. The oil obtained is then analyzed to determine the level of FFA and moisture content.

2.2. Preparation of CaO/fly ash catalyst

2.3. Biodiesel Production
The extraction oil is weighed as much as 60 grams and fed into the esterification reactor. After the temperature reaches 60 °C, methanol reactants with a mole ratio of methanol: oil = 12: 1 and a 1% -w \( \text{H}_2\text{SO}_4 \) catalyst are added. The reaction lasts for 1 hour and the speed of stirrer 400 rpm. The mixture of \( \text{H}_2\text{SO}_4 \) catalyst and residual methanol is separated by separating funnel. The lower layer is checked for FFA content [11], then proceed to the transesterification reaction stage. The lower layers of esterification product separation were fed into 50 g of transesterification reactor, heated to 70 °C, methanol was added with the mole ratio of methanol: oil = 6: 1, CaO / fly ash catalyst of 6% -w oil and 400 rpm stirring rate. After 3 hours, the mixture is cooled and filtered. The catalyst precipitate is separated from the filtrate. The obtained filtrate proceeds to the process of separation and purification of biodiesel.

2.4. Catalyst Characterization
There are a few characterization method for photocatalyst such as X-Ray diffraction (XRD) and scanning electron microscopy (SEM) observation to study composition and morphology which contain important information. XRD measurement was conducted by using Shimadzu XRD 600 X-ray diffractometer (30 kV, 30 mA). The morphology of the prepared sample was recorded by Scanning electron microscope (SEM) using a Philips XL-30 (15 kV, 70 Pa). A prepared sample was filled through gold sputtering in the surface of CaO/Fly ash. The picture was gained through scanning electron microscope gained at 15 kV with 10000 times enlargement.

3. Result and Discussion

3.1. Extraction of CPO Off-grade
The CPO off-grade fruit was extracted using a spindle press tool and produced an off-grade palm oil of 18.53% or about 556 g. High FFA therefore through esterification process before transesterification. FFA levels of CPO off-grade which initially was 6.19% decreased to 0.96%. Characteristics of CPO off-grade are shown in Table 1.
Table 1. Characteristics of Crude Palm Oil Off-grade.

| No | Characteristic          | Unit | Characterization | Standard CPO SNI 01-2901-2006 |
|----|-------------------------|------|------------------|--------------------------------|
| 1  | Density (40 °C)         | kg/m³| 892.11           | -                              |
| 2  | Viscosity (40 °C)       | mm²/s| 29.47            | -                              |
| 3  | Moisture                | %    | 3.5              | Max 0.5                        |
| 4  | FFA                     | %    | 6.19             | Max 0.5                        |
| 5  | Color                   |      | Orange           | Orange                         |

3.2. Basic Strength
Fly ash (FA) and CaO/FA on variation of weight ratio of Ca(NO₃)₂·4H₂O:FA 80:20, calcination temperature 800, 850 and 900 °C tested using Hammett indicator i.e phenolphthalein. Based on the result, FA does not show the color change. This indicates that the FA has a strong base of H_ <8.2. High SiO₂ content causes FA to have no alkaline properties, does not contain oxide ions and does not react with acids. Instead, it is a weak acid and reacts with a strong base. Therefore, the FA is particularly suitable as a support material [12]. However, the 3 variations of the catalyst CaO/FA show the change to purple. This indicates that the catalyst has a basic strength of H_ > 9.3 [13]. According to Ho et al. (2014) a strongly developed base catalyst of H_ > 9.3 is considered a relatively strong base catalyst for the transesterification process although its basic strength is lower than pure CaO (15 <H_ <18.4) [6].

3.3. X-Ray Diffraction (XRD)
The catalysts used in the test using XRD method were five variations, i.e catalyst with percent weight ratio of Ca(NO₃)₂·4H₂O:fly ash of 70:30, 80:20, and 90:10 calcined at 800 °C. The comparison of XRD pattern three different composition of catalyst is shown in Figure 1.
Figure 1. XRD Patterns of 800 °C Calcination Temperature Catalysts on Variations Ca(NO\textsubscript{3})\textsubscript{2}.4H\textsubscript{2}O : FA a) 70:30, b) 80:20 and c) 90:10.

Figure 1 (a) there is a peak of the highest crystals with an intensity of 1157.63 indicating the CaO content of the catalyst at 2θ: 32.29°. Next the CaO peak appears at 2θ: 54.23° and 64.67°. In addition, there is a SiO\textsubscript{2} peak at 2θ: 26.59°, 39.38° and 75.51°, indicating the high content of silica compound from impregnated fly ash. Other compounds are dicalcium silicate (Ca\textsubscript{2}SiO\textsubscript{4}) at 2θ: 29.62°, 39.38° and 75.51°.

Figure 1 (b) it still shows the highest CaO content at 2θ: 37.35° with an intensity of 1647.77 and subsequently at 2θ: 32.19° and 53.85° (JCPDS File No. 37-1497). There is a SiO\textsubscript{2} peak at 2θ: 26.58° and 39.38° (JCPDS File No. 29-0085) where the silica intensity is reduced because the weight percent or fly ash content is also reduced in the catalyst. Dicalcium silicate peak (Ca\textsubscript{2}SiO\textsubscript{4}) appears at 2θ: 32.46°, 41.14° and 46.71°. Other compounds are calcium hydroxide (Ca(OH)\textsubscript{2}) at 2θ: 18.06°, 34.10° and 64.29°.

Figure 1 (c) the XRD pattern shows the SiO\textsubscript{2} peak at 2θ: 26.58° the silica intensity decreases because of the small fly ash content in the catalyst. The Ca(OH)\textsubscript{2} peak appears at 2θ: 17.98°, 34.02° and 62.49°. The highest peak is CaO at 2θ: 32.19° with intensity 958.03 and then at 2θ: 37.35° and 53.85° (JCPDS File No. 37-1497). CaO intensity decreases because CaO has reacted with SiO\textsubscript{2} from fly ash in the impregnation process to form dicalcium silicate (Ca\textsubscript{2}SiO\textsubscript{4}). So the intensity of Ca\textsubscript{2}SiO\textsubscript{4} is greater and the peak is increasing at 2θ: 23.26°, 29.62°, 41.18° and 47.56°. The presence of dicalcium silicate indicates that CaO has interacted with the fly ash surface, resulting in a reaction as in the following equation 1:

\[ 2\text{CaO} + \text{SiO}_2 + \text{H}_2\text{O} \rightarrow (\text{CaO})_2(\text{SiO}_2)(\text{H}_2\text{O}) \] ................................. (3.1)

In the presence of water molecules, CaO and SiO\textsubscript{2} react to form dicalcium silicate hydrate (Ca\textsubscript{2}SiO\textsubscript{4}H\textsubscript{2}O). However calcination at 800-900 °C will released the water molecule and produced
dicalcium silicate (Ca$_2$SiO$_4$) [14]. The more dicalcium silicate (Ca$_2$SiO$_4$) formed by the reaction with fly ash shows the more CaO impregnated on the fly ash surface, the active side of the catalyst becomes more numerous. With the increase of the active side of the catalyst, the likelihood of the reaction is higher, the resulting product more and more. Meanwhile, according to Setiawan et al. (2014) CaO component will be impregnated in the SiO$_2$ pores present in fly ash [15].

Then another catalyst variation is a catalyst with a weight percent ratio of Ca(NO$_3$)$_2$.4H$_2$O : fly ash precursor of 80:20 calcined at 850 and 900 °C. The XRD pattern of the catalyst is shown in Figure 2.

Figure 2 (b) shows the highest CaO content at 2θ: 32.22° with an intensity of 1186.53 and then at 2θ: 37.37° and 53.89°. The higher calcination temperature at 850 °C makes SiO$_2$ more reactive with CaO to form Ca$_2$SiO$_4$ at 2θ: 28.32°, 33.10°, 41.14° and 46.71° so that no SiO$_2$ peaks appear. According to Soleimani et al. (2012) the SiO$_2$ intensity decreases after calcination because Si-O-Si or Si-O-Al bonds become loose so that there will decrease the amount of crystals and new crystalline formation during the calcination process [16]. Meanwhile, other compounds are Ca(OH)$_2$ at 2θ: 17.95° and 63.93°.

Figure 2 (c), the highest peak is CaO at 2θ: 32.29° with an intensity of 1491.24 and then at 2θ: 37.46°. The higher calcination temperature at 900 °C makes SiO$_2$ more reactive with CaO to form Ca$_2$SiO$_4$ at 2θ: 28.32°, 33.10°, 41.14°, 46.71° and 51.89°. Another compound is Ca (OH)$_2$ at 2θ: 18.08°.

The presence of Ca(OH)$_2$ compounds is thought to have formed due to contact between the surface of CaO and water vapor (H$_2$O) solids from free air. Kouzu et al. (2008) also reported that the highest order of base strength was in CaO, then Ca(OH)$_2$ and the lowest was CaCO$_3$. Thus, the presence of Ca(OH)$_2$ compound on the surface of CaO solids results in a decrease of base strength on the catalyst [4].

From the result of XRD pattern in Figure 2 (a) - (c) shows the intensity and the peak of Ca(OH)$_2$ decreases. This is due to the high temperature of calcination which causes Ca(OH)$_2$ to decompose into CaO. This corresponds to the purpose of calcination to modify the chemical composition of the
catalyst by heating at high temperatures. Thus, the intensity of CaO increases with increasing calcination temperature (Wong et al., 2014). On the other hand, the temperature of calcination is required to increase the mechanical forces preventing leaching [12].

3.4. Brunauer-Emmet-Teller (BET)
The catalysts were characterized by 2 variations, CaO/FA catalysts with a calcination temperature at 800 and 850 °C and a weight ratio of Ca(NO$_3$)$_2$.4H$_2$O: FA of 80:20 are shown in table 2.

Table 2. Catalyst Surface Area of the catalys FA/CaO at Ratio Ca(NO$_3$)$_2$.4H$_2$O: FA 80:20.

| Catalyst                  | Calcination Temperature (°C) | Surface Area (m$^2$/g) |
|---------------------------|------------------------------|------------------------|
| CaO/fly ash 80:20         | 800                          | 24.342                 |
|                           | 850                          | 909.781                |

Based on the result of BET in table 2, the large catalyst surface area in the temperature 850 °C is 909.781 m$^2$/g. This is due to an increase in the temperature of calcination, then the catalyst gradually turns into a stable crystal and increased surface area [17]. Closing of pores from fly ash by CaO crystals causes a decrease in the surface area of the catalyst [13]. Therefore, the magnitude of catalyst surface area obtained due to the possibility of CaO is not evenly distributed across the pores and fly ash surfaces in the impregnation process.

3.5. Transesterification Reaction
The lowest biodiesel yield obtained was 45.19% using a catalyst of calcination temperature of 900 °C and the ratio of Ca(NO$_3$)$_2$.4H$_2$O: FA by 90:10, where the CaO content in the catalyst was 68.11%. The highest biodiesel yield was obtained by 71.77% using a catalyst calcined at 800 °C and the ratio of Ca(NO$_3$)$_2$.4H$_2$O: FA by 80:20, where CaO content in the catalyst was 48.69%. Catalyst Ca(NO$_3$)$_2$.4H$_2$O: FA 80:20 has a high CaO content among other catalysts, thus providing a higher basic strength. The larger the basic strength, the higher the catalytic activity of the catalyst so that the yield of biodiesel produced is also higher [18].

The calcination temperature of 800 °C did not cause the chemical structure of the catalyst to change which caused the deactivation of the catalyst. The surface area of the catalyst at a temperature of 850 °C which is too large causes the distribution of active sites uneven across the pore and the catalyst surface so that it does not react entirely [19]. Meanwhile, according to Liu et al. (2010) the amount of CaO is too small then the active side of the catalyst is less so the resulting yield is small [3]. Thus, the surface area (BET) does not significantly affect the activity of the CaO/FA catalyst.

On the other hand, the high temperature calcination of 900 °C of catalyst with a weight ratio of Ca(NO$_3$)$_2$.4H$_2$O: FA 90:10 lowers the catalyst base side. Further increase of the calcination temperature causes the active component parts of the catalyst to be lost and cause catalyst agglomeration. Too high CaO contained in the catalyst of 68.11% cause CaO intensity decreases due to CaO has been much reacted with SiO$_2$ from fly ash to form Ca$_2$SiO$_4$ thereby decreasing its strong base. The excess of CaO in the catalyst may lead to the possibility that the surface of the CaO solid can no longer decompose methanol into a methoxide ion so that the transesterification reaction cannot proceed well [20].

3.6. Characteristics of Biodiesel
Biodiesel results are tested and characterized prior to use to the machine to work optimally and more durable. The specifications or quality standards of biodiesel obtained compared to the characteristics of biodiesel based on SNI 7182: 2015 are shown in Table 3.
Table 3. Characteristics of Biodiesel.

| No | Characteristics            | Unit       | Result       | SNI 7182:2015 |
|----|----------------------------|------------|--------------|---------------|
| 1  | Density                    | kg/m³      | 860.49       | 850 – 890     |
| 2  | Kinematic Viscosity        | mm²/s      | 3.75         | 2.3 – 6.0     |
| 3  | Flash point                | °C         | 125          | Min. 100      |
| 4  | Acid Number                | mg-KOH/g-biodiesel | 0.24 | Max. 0.5 |

Biodiesel with highest yield using catalyst FA/CaO calcined at 800 °C and ratio of Ca(NO₃)₂·4H₂O: FA of 80:20 identified its methyl ester using Gas Chromatography - Mass Spectrometry (GC-MS) at UPT Diponegoro University Integrated Laboratory. The results of the sample analysis with GC-MS can be seen in the methyl ester chromatography of the CPO off-grade shown in Figure 3.

This identification aims to determine the composition of the suspected compounds as methyl esters of the synthesis. The result of GC-MS fragmentation pattern analysis as shown in Figure 3 shows that large methyl esters have retention time (tr) (39.407; 43.167; 43.402 and 44.095) minutes. The graph of biodiesel characterization results using GC-MS shows the chemical composition and methyl ester conversion as shown in Table 4.

Table 4. Chemical Composition of Palm Oil and Biodiesel.

| Komposisi          | Methyl Palmitate (C16:0) | Methyl Stearate (C18:0) | Methyl Oleate (C18:1) | Methyl Linoleate (C18:2) | Reference        |
|--------------------|--------------------------|------------------------|-----------------------|--------------------------|------------------|
| Sludge Palm Oil    | 42.84%                   | 4.21%                  | 39.58%                | 9.92%                    | [21]             |
| CPO Off-Grade      | 33.74%                   | 3.10%                  | 36.04%                | 7.91%                    | The Result of Research |

It can be seen in table 4 that the largest composition of biodiesel is methyl palmitate of 42.84%. While the least composition on biodiesel is methyl stearate of 3.10%. The conversion of the carboxylic acid group to methyl ester in the biodiesel production process reaches 80.79%. This indicates that the biodiesel product produced is not very pure or still other impurities such as catalyst residue, water, methanol and glycerol. This is evidenced by the presence of glycerol that is converted from GC-MS yield of 7.27%. The residual methanol on the use of the catalyst shows that between oil and methanol does not react completely. Substantial amounts of methanol and glycerol form emulsions with the catalyst thus affecting the yield of biodiesel and the conversion of methyl esters.
4. Conclusion
Biodiesel can be produced from CPO off-grade using a CaO/Fly ash catalyst at the transesterification. Heterogeneous CaO/fly ash can be synthesized and have a basic strength value of H<sub>t</sub> > 9.3 using the Hammett phenolphthalein. The highest yield of biodiesel was obtained 71.77% using catalyst at 800 °C calcination temperature and weight ratio of Ca(NO<sub>3</sub>)<sub>2</sub>:4H<sub>2</sub>O: FA 80:20, CaO level in catalyst was 48.69%. The higher the calcination temperature, the lower the yield of biodiesel. The biodiesel yield tends to increase with increasing CaO levels in the catalyst. The activity of the CaO/fly ash is not affected by its surface area (BET) but is affected by its basic strength.

References
[1] Arifin, J.K., 2009. Pemanfaatan Buah Sawit Sisa Sortiran sebagai Sumber Bahan Baku Asam Lemak. *Tesis.* Program S2 Teknik Kimia Universitas Sumatra Utara. Medan.
[2] Helwani, Z., M. R. Othman, N. Aziz, J. Kim and W. J. N. Fernando. 2009. Solid Heterogeneous Catalyst for Transesterification of Triglycerides with Methanol : A Review. *Applied Catalysis A : General.* 369: 1 -10.
[3] Liu, X.J., He, H.Y., Y. Wang and S. Zhu. 2008. Transesterification of Soybean Oil to Biodiesel Using CaO as A Solid Base Catalyst. *Fuel.* 87 :216-221.
[4] Kouzu, M., T. Kasuno, M. Tajika, Y. Sugimoto, S. Yamanaka and J. Hidaka. 2008. Calcium Oxide as Solid Base Catalyst for Transesterification of Soybean Oil and its Application to Biodiesel Production. *Fuel.* 87:2798 -2806.
[5] Liu, C., L.V., Pengmei. Yuan, Z., F. Yan and W. Luo. 2010. The Nanometer Magnetic Solid Base Catalyst for Production of Biodiesel. *Renewable Energy.* 15 : 1531-1536.
[6] Ho, W.W.S., H.K. Ng, S.Gan and S.H. Tan. 2014. Evaluation of Palm Oil Mill Fly Ash Supported Calcium Oxide as A Heterogenous Base Catalyst in Biodiesel Synthesis from Crude Palm Oil. *Energy Conversion and Management.* 88 : 1167-1178.
[7] Zahrina, I., Yelmida and F. Akbar. 2012. Sintesis ZSM-5 dari Fly Ash Sawit Sebagai Sumber Silika dengan Variasi Nisbah Molar Si/Al dan Temperatur Sintesis. *Jurnal Rekayasa Kimia dan Lingkungan.* 9 : 94-99.
[8] Nugraha, P. Z., Z. Helwani and E. Saputra. 2016. Penggunaan Katalis Fly Ash yang Diimpregnasi dengan CaO dari Ca(NO<sub>3</sub>)<sub>2</sub> pada Tahap Transesterifikasi Minyak Sawit Off-grade Menjadi Biodiesel. *Jom FTEKNIK.* 3 (1).
[9] Budiawan, R. Zulfansyah, W. Fatra and Z. Helwani. 2013. Off Grade Palm Oil as A Renweable Raw Material for Biodiesel Production by Two-Step Processes. *ChESA Conference.* Januari. Banda Aceh. 7 : 40-50.
[10] Marinkovic, D.M., M.V. Stankovic, A.V. Velickovic, J.M. Avramovic, M.R. Miladinovic, O.O. Stamenkovic, V.B. Veljkovic and D.M. Jovanovic. 2016. Calcium Oxide as a promising heterogenous catalyst for biodiesel production: Current state and perspectives. *Renewable and Sustainable Energy Reviews.* 56 : 1387-1408.
[11] Hindryawati, N., G. P. Maniam, Md. R. Karim and K. F. Chong. 2014. Transesterification of used cooking oil over alkali metal (Li, Na, K) supported rice husk silica as potential solid base catalyst. *Engineering Science and Technology, an International Journal.* 1-9.
[12] Helwani, Z., N. Aziz, J. Kim and M. R. Othman. 2016. Improving The Yield of Jatropha Curcas’s FAME through Sol-Gel Derived Meso-porous Hydrotalcites. *Renewable Energy.* 86: 68-74.
[13] Ho, W.W.S., H.K. Ng and S. Gan. 2012. Development and characterization of novel heterogeneous palm oil mill boiler ash-based catalyst for biodiesel production. *Bioresource Technology.* 125 : 158-164.
[14] Setiawan A., Widiyastuti, S. Winardi and A. Nugroho. 2014. Kinetika Reaksi Sintesis Biomaterial Hydroxyapatite Dengan Prekursor Nitrat dan Asetat. *Reaktor.* 15 (2) : 104-110.
[15] Soleimani, M.A., R. Naghizadeh, A.R. Mirhabibi and F. Golestanifard. 2012. Effect of Calcination Temperature of The Kaolin and Molar Na₂O/SiO₂ Activator Ratio on Physical and Microstructural Properties of Metakaolin Based Geopolymers. *Iranian Journal of Materials Science & Engineering*. Vol. 9, Number 4.

[16] Tang, S., L. Wang, Y. Zhang, S. Li, S. Tian, and B. Wang. 2012. Study on Preparation of Ca/Al/Fe₃O₄ Magnetic Composite Solid Catalyst and Its Application in Biodiesel Transesterification. *Fuel Processing Technology*. 95 : 84-89.

[17] Kesimal, Z., I. Lukic, M. Zdujic, H. Liu and D. Skala. 2012. Mechanochemically synthesized CaO-ZnO catalyst for biodiesel production. *Procedia Engineering*. 42 : 1278-1287.

[18] Wong, Y.C., Y.P. Tan, Y.H. Taufiq-Yap and I. Ramli. 2014. Effect of Calcination Temperatures of CaO/Nb₂O₅ Mixed Oxides Catalysts on Biodiesel Production. *Sains Malaysiana*. 43 (5) : 783-790.

[19] Samik, R. Ediati and D. Prasetyoko. 2014. Review: Pengaruh Kebasaan dan Luas Permukaan Katalis Terhadap Aktivitas Katalis Basa Heterogen untuk Produksi Biodiesel. *Jurusan Kimia Fakultas MIPA Institut Teknologi Sepuluh Nopember*, Surabaya.

[20] Fanny W. A., Subagjo and T. Prakoso. 2012. Pengembangan Katalis Kalsium Oksida untuk Sintesis Biodiesel. *Jurnal Teknik Kimia Indonesia*. 11 (2) : 66-73.

[21] Hayyan, A., Md. Z. Alam, M.E.S. Mirghani, N.A. Kabbashi, N.I.N.M. Hakimi, Y.M. Siran and S. Tahiruddin. 2010. Sludge Palm Oil as A Reneweble Raw Material for Biodiesel Production by Two Step Processes. *Bioresource Technology*. 101 : 7804 – 7811.