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Synthesis of Heterogeneous Catalysts NaOH/CaO/C from Eggshells for Biodiesel Production Using Off-Grade Palm Oil

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Abstract

A heterogeneous catalyst, such as Calcium Oxide (CaO), is widely used in biodiesel production due to its various advantages over homogeneous ones. The optimum condition for synthesizing this catalyst is determined by calcination temperature and mass ratio. As a result, a modification is required to increase its performance in improving the biodiesel yield. In this study, eggshell waste was modified by calcination, hydration, and dehydration methods integrated with activated carbon and NaOH. It is used as a heterogeneous base catalyst for off-grade palm oil transesterification reactions. The results shows the catalyst with the highest activity is obtained at calcination temperature of 800°C and mass ratio of 7 to 3. This is achieved with transesterification reaction conditions, which include a mole ratio of methanol/oil 6 to 1, catalyst concentration of 6%-wt oil, and temperature 70°C for 3 hours, yielding 79.08% of the biodiesel. Additionally, CaO, Na_2CO_3, and $Ca(OH)_2$ materials were found in the catalyst with a catalyst alkalinity value of H > 9.3 through X-ray diffraction (XRD) analysis. Several methyl esters, such as palmitate and oleate were also found in biodiesel through Gas Chromatography-Mass Spectrometry (GC-MS) analysis.

Keywords: activated carbon, biodiesel, calcium oxide, catalysts, transesterification

1. Introduction

The increase in petroleum consumption leads to oil depletion and necessitate the need for alternative fuel, such as fatty acid methyl ester (FAME), commonly referred to as biodiesel. Palm oil among the raw materials with the potential to be used in the production of the biodiesel.

Off-grade palm oil is a waste product from the palm oil mill (POM). It is mainly obtained from the rest of the sorting process not optimally utilized. The processing of palm fruit into alternative raw materials for biodiesel has a high-profit value. This is due to its sufficient availability, which is 7-10% for a POM with a capacity of 30 tons/hour. Additionally, it is sold for a price of 30-40% cheaper than a decent fruit (on-grade). For this reason, it has the potential to reduce the production cost of biodiesel (Arifin, 2009).

For sufficient production of the biodiesel, a homogeneous or heterogeneous catalyst is required. In general, heterogeneous catalysts are more widely used than homogeneous due to their easy processing. Various heterogeneous catalysts have been studied before, and this study uses a CaO-based catalyst from chicken eggshells.

Eggshells contain a lot of calcium carbonate ($CaCO_3$), probably 94%, as well as other substances such $MgCO_3$ 1%, $Ca_3(PO_4)_2$ 1% and organic ingredients 4% (Wei et al., 2009).

According to Hadiyanto et al. (2017), the use of a carrier helps catalysts to work more effectively. The CaO is mixed with activated carbon and balanced with NaOH solution. Activated carbon has proven to be useful as a carrier for catalysts in gas or liquid phase reactions. It has a large surface area used for emulsification in the transesterification reaction. Besides, it also a porous material with a carbon content of 87%-97% and contains other substances such as hydrogen, oxygen, and sulfur (Ginting et al., 2017).

In this study, a modification of eggshells using a calcination method combined with activated carbon and NaOH is analyzed as a heterogeneous base catalyst in the transesterification reaction of the off-grade palm oil. It is expected to increase the performance of the generated catalyst in boosting the biodiesel yield.

2. Methodology

2.1 Materials

The materials used in this study include off-grade palm oil, methanol (p.a.), activated carbon, distilled water, eggshells, concentrated H_2SO_4, NaOH, KOH, technical ethanol, and phenolphthalein. All chemical are purchase from PT. Praglas Raya, Bandung.

The materials utilized include the 100/200 mesh sieve, furnace, chemical glass 500 mL, measuring cup 100 mL, hot plate, condenser, three-neck flask 500 mL, magnetic stirrer, mechanical stirrer, oven, pipette drops, spindle hydraulic press, stative, thermometer, and analytic scales.

2.2. Raw materials preparation

The off-grade palm fruit raw material is extracted using the artisanal method. The fruit is first washed away from dirt and crowns. Afterward, it is steamed in the boiler for 120 minutes to make it tender. The fruit is then pressed using a hydraulic spindle tool. The extraction results are inserted into the separating funnel to form two layers of oil and water. The oil obtained is analyzed to find out the levels of FFA and water.

2.3. Catalyst Preparation

The catalyst is prepared through the process of calcination-hydration dehydration of the eggshells, which were calcinated in the furnace at a temperature variation of 800°C, 850°C, and 900°C and mass ratio variations of 7:3, 6:4, and 5:5. Solid-base catalyst NaOH/CaO/C is synthesized using the impregnation method into activated carbon dissolved in 100 mL NaOH 30% in chemical glass and stirred until it is homogeneous. The formed CaO and the activated carbon is weighed following the mass ratio. Solid products are further dehydrated by calcination in a furnace at a temperature of 500°C for 5 hours.

2.4. Esterification Reaction

The esterification reaction is carried out since the off-grade palm oil has an FFA rate of more than 2%. The 50 grams of oil from the extraction are inserted into the esterification reactor equipped with the stirrer and condenser. The process is conducted in batches and placed over the heater to maintain the reaction temperature. At 60°C, the methanol reagent at a molar ratio: oil 12:1 and H2SO4 1%-wt catalyst are added. The reaction lasts for 1 hour with a stirring speed of 400 rpm. Afterward, the mixture is separated using the separating funnel. The upper layer is the H_2SO_4 catalyst while the remaining methanol and the bottom layer are the off-grade palm oil which proceeds to the transesterification reaction stage after the FFA content in the bottom layer is examined.

2.5. Transesterification Reaction

In this phase, 50 grams of the content in the bottom layer of the esterification result is inserted into the transesterification reactor equipped with a condenser and heated over the hot plate to a temperature of 70°C with a methanol mole ratio oil 6 to 1. This was followed by the addition of 6%-wt oil NaOH/CaO/C catalyst. The reaction lasts for 3 hours with a stirring speed of 400 rpm using magnetic stirrer. The initial reaction starting time is calculated after the catalyst, and the reactants are placed into the reactor. Once the reaction is completed, the mixture is cooled, and the catalyst is separated from the solution. The steps above are repeated for the catalyst prepared beforehand. The obtained solution goes to the separation and purification processes to form the biodiesel under the predefined standards.

2.6. Characterization of Catalyst Using X-Ray Diffraction (XRD)

Characterization of catalyst NaOH/CaO/C using X-ray diffraction (XRD) is meant to determine the structure and crystallinity as well as to analyze the presence of CaO material in the synthesized catalysts. The XRD pattern is monitored at an angle of 2θ between 10-100°. Five variations of catalysts are used, including the comparison of NaOH/CaO/C using the variations in mass ratio of 7 to 3, 6 to 4 and 5 to 5 grams at calcination temperature of 800°C for 3 hours and the mass ratio of (7:3) with calcination temperature at 850°C and 900°C.

3. Result and Discussion

3.1. Off-Grade Palm Extraction

Off-grade palm is steamed to soften mesocarp fruit as well as to deactivate the lipase enzyme in preventing elevated oil FFA levels (Budiawan et al., 2013). The fruit is extracted using a pressing machine known as a hydraulic press spindle. It produces 15% or about 150 grams of off-grade palm

oil for 1 kg of fruit. Furthermore, the characterization is conducted, including density, viscosity, water content, and free fatty acid levels. The characteristics of off-grade palm oil are shown in Table 1.

Table 1. Characteristics of off-grade palm oil

Characteristic	Unit	Extraction Result	SNI 01-2901-2006
Color		Reddish Orange	Reddish Orange
Density (40°C)	kg/m^3	892,11	-
Viscocity (40°C)	mm^2/s	29,47	-
Water content	%	1,69	Max 0,5
Free fatty acid levels	%	9,05	Max 0,5

Based on Table 1, the resulting off-grade palm oil has high water content and free fatty acids (FFA) level. The high water content leads to hydrolysis, which forms the FFA (Pahan, 2012). Water reacts with the catalyst and reduces its number (Ulfayana et al., 2015). This high number can be reduced by heating the oil at temperatures exceeding the water boiling point. Furthermore, high FFA levels also require preliminary treatment before the transesterification reaction, which is the esterification process. After this process, the rate of off-grade palm oil FFA decreased from initially 9.05% to 1.48% and met the requirements for the transesterility process, i.e., < 2% (Farag et al., 2013).

3.2. Synthesis of Catalyst NaOH/CaO/C

The use of catalysts NaOH/CaO/C on the transesterification process affect the quality, the number of products, and process conditions. Catalysts are synthesized by calcination - hydration (impregnation) - dehydration. The CaO readily react with CO_2 and H_2O, resulting in a decrease in catalyst selectivity, which affects the resulting product. Glycerol and methanol form an emulsion and complicate the separation process (Liu et al., 2008). At the hydration stage, the impregnation of activated carbon is carried out by the adsorption of CaO alkali metal with a solvent of NaOH 30% to the active carbon solid carrier.

Catalysts are tested on the same transesterification reaction conditions, i.e., with the ratio of methanol to oil (molar) 6:1, catalyst concentration 6%-wt, and reaction temperature of 70°C for 3 hours against all variations of the NaOH/CaO/C.

3.3. Characteristic of Catalyst Base on XRD Pattern.

The pattern XRD analysis of the Catalyst NaOH/CaO/C is shown in Figure 1. Based on the XRD pattern on Figure 1, the highest CaO with an intensity of 100% is found in the 5 to 5 mass catalyst ratio (c) at the peak of 2θ: 30.011° and 2 θ: 41.415°. Also, a peak of Na_2CO_3 indicates the high carbon compound contained in activated carbon impregnated by NaOH. Another compound appearing is $Ca(OH)_2$, indicating that not all of it is converted to CaO during the calcination process.

The comparisons of the XRD pattern of catalysts NaOH/CaO/C prepared using calcination temperature variations of 800°C, 850°C and 900°C with the mass ratio of 7 to 3 are shown in Figure 2.

Based on Figure 2, the highest CaO with a 53.48% intensity appears at a calcination temperature of 900oC (c) with the peak of 2θ: 30.090° and 2θ :28.665°. Furthermore, a peak is also found in other compounds such as sodium carbonate (Na2CO3) and calcium hydroxide Ca(OH)2. The presence of Na2CO3 indicates that CaO has interacted with the surface of activated carbon and NaOH.

Furthermore, the existence of impurities compound such as $Ca(OH)_2$ was attributed to the fact that the sample was opened and led to the absorption of water during the characterization process (Khatsiroh, 2017). The impurities also indicate that not all of them are converted to CaO during the calcination process. Furthermore, the existence of these C-peaks can be caused by the imperfection of $CaCO_3$ decomposition to be CaO. The three samples have similar peaks and phase but with a slightly different intensity due to the increase in mass ratio (Zhang et al., 2014).

3.4. Yield of Biodiesel

The effect of calcination temperature and the NaOH/CaO/C mass ratio on the catalyst activity could be determined through the resulting biodiesel yield indicator. Based on Figure 3, the highest biodiesel yield of 79.08% was obtained at a calcination temperature of 800oC, and the mass ratio of 7:3. The increase in calcination temperature and the mass ratio hugely affect catalyst activity, which in turn impacts biodiesel yield.

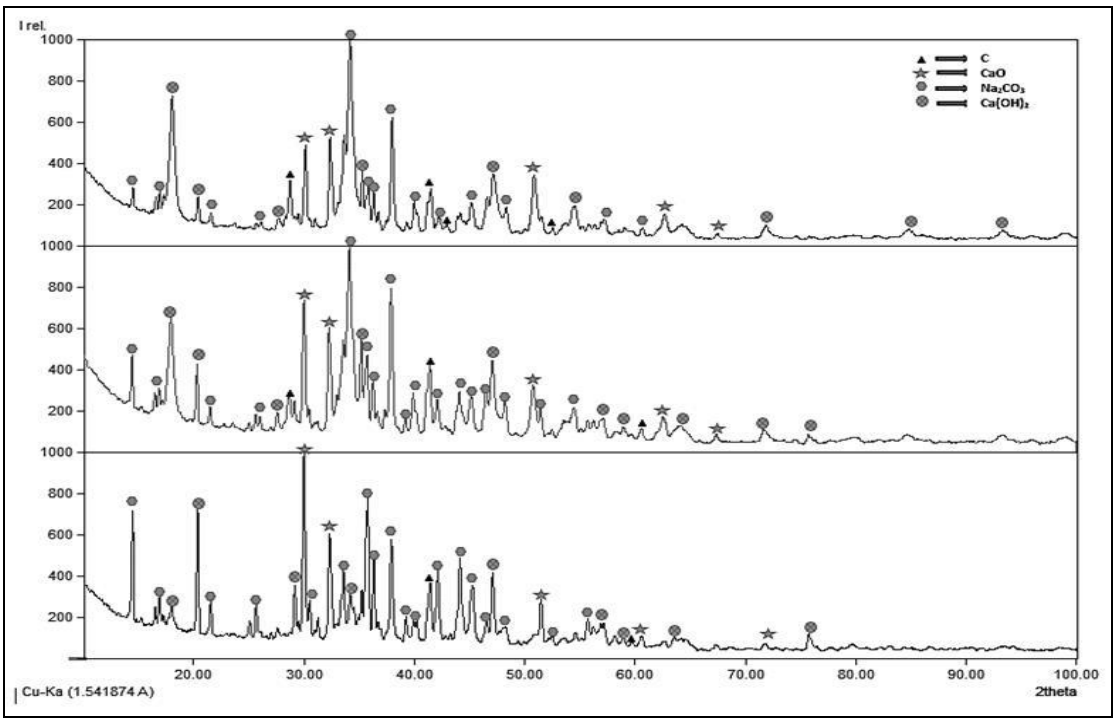

Figure 1. XRD of Catalyst NaOH/CaO/C at 800°C: (a) mass ratio 7:3, (b) mass ratio 6:4, and (C) mass ratio 5:5

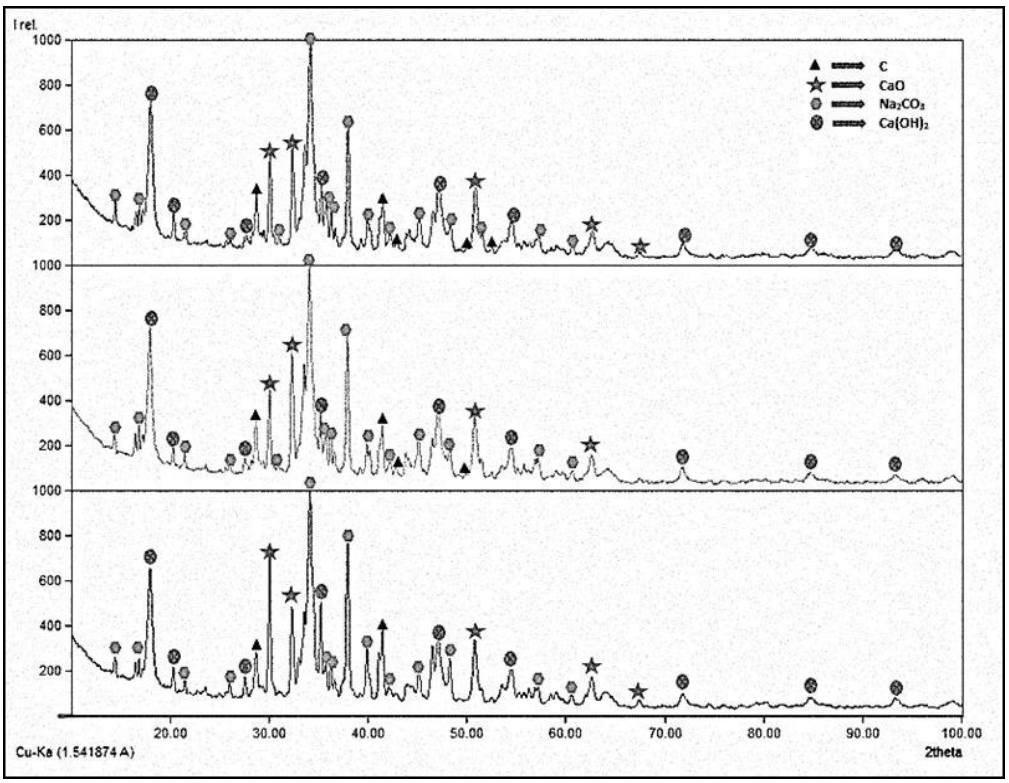

Figure 2. XRD Pattern of Catalyst NaOH/CaO/C (7:3) with calcination temperature (a) 800°C, (b) 850°C and (C) 900°C

The catalytic activity is increased due to the optimal CaO composition distributed evenly into the micro-pore active carbon and formed a larger surface area, increasing the alkaline side of the catalyst (Liu et al. 2010). Besides, with the increase of calcination temperature, the catalyst gradually transforms into a stable crystal with the surface area also increased (Tang et al., 2012).

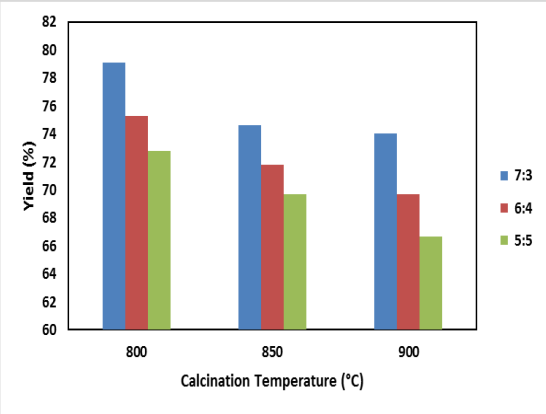

Figure 3. Relationship between calcination temperature and biodiesel yield on a wide variety of catalyst mass ratios

However, biodiesel yield in this study decreases with the increase in calcination temperature and mass ratio, which is beyond the optimum standard. This causes the CaO to accumulate and forming agglomeration on the catalyst surface, preventing contact between the active sites with the reactants (Liu et al., 2010). Additionally, the agglomeration covers the micropore catalyst, making the surface area small and reduced the active alkaline (Liu et al., 2010; Hu et al., 2011; Tang et al., 2012).

3.5. Biodiesel Characteristics

Biodiesel characterization is required to compare the features of the biodiesel produced by Indonesians to the quality standard of SNI 7182:2015 through the Decree of Directorate General of New Renewable Energy and Energy Conversion (EBTKE) Number 723/K/10/D.E/2013. This quality standard was compiled by the Technical Committee of 27-04 Bioenergy in the Consensus Forum on 22 December 2014 in Jakarta (BSN, 2015). The characteristics tested include density, kinematic viscosity, acid number, and flashpoint as the most critical parameter (Romero et al., 2010).

The biodiesel is tested using all variations of catalysts, and the result is shown in Table 2. As shown in Table 2, biodiesel density obtained is 858 kg/m, a value which meets the SNI standard. Density is a comparison of mass per unit volume. Biodiesel density beyond the standard causes imperfect combustion reactions which increase emissions and engine wear (Budiawan et al., 2013). This is influenced by the molecular weight of its components. The heavier the components, the higher the density value (Febrian, 2016).

Table 2. Biodiesel Characteristic

Characteristic	Unit	Analysis Result	SNI 7182:2015
Density (40°C)	kg/m^3	858	850-890
kinematic viscosity (40°C)	mm^2/s	4.73	2.3-6.0
Flashpoint	°C	138	Min. 100
Acid number	mg-KOH/g	0.43	Max. 0.5

The kinematic viscosity of biodiesel in this study amounted to 4.73 mm^2/s, which is also within the SNI range. The high viscosity affects the injection equipment and raises the strong pull in the injection pump, affecting the high pressure and volume, especially at low engine temperatures (Romero et al., 2010).

The acid number indicates the content of free fatty acids in the biodiesel. The higher the acid number, the more the free fatty acids content, and this determines the quality of biodiesel. The large acid number increase the corrosion rate of the vehicle engine. The higher the acid figure, the higher the corrosive (Haryanto et al., 2015). The biodiesel acid number is obtained at 0.43 MG-KOH/G or below the maximum limit of SNI, which is 0.5 mg-KOH/g. It shows it is not corrosive and cannot damage the injector machine (Budiawan et al., 2013).

The flashpoint often indicates the high-low volatility and flammability of a fuel. The result of biodiesel flashpoint of this study was 138°C, a value that meets the quality standards based on SNI, which is 100°C. This shows that biodiesel is safe in both carriage and oil storage.

From Figure 4, the highest peaks of the methyl palmitic with a biodiesel composition

of 46.50%, displayed with the number 1. The methyl oleate with a composition of 43.64% displayed the number 3. The result of conversion from the carboxylic acid group to methyl ester in the biodiesel production process was 100%. Its rate meets the quality standard of biodiesel established (SNI 7182:2015), and this means the resulting biodiesel product is pure. Based on the results of the GC-MS analysis, NaOH/CaO/C catalysts might be used as a catalyst in biodiesel production. The biodiesel composition of the GC-MS test analysis results is shown in Table 3.

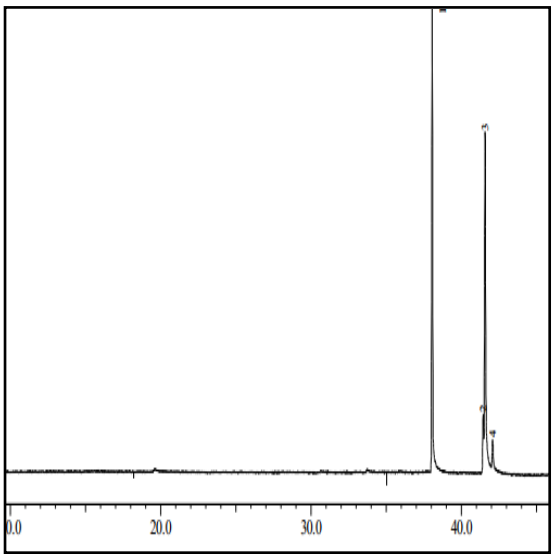

Figure 4. Analysis Result of GC-MS Biodiesel

Table 3. The composition of methyl ester in biodiesel

No	Component of ME	Concentration (%)
1	Methyl Palmitate	46.50
2	Methyl Linoleate	6.27
3	Methyl Oleate	43.64
4	Methyl Tetrakosanoate	3.60
	Total	100.00

4. Conclusion

Heterogeneous catalysts NaOH/CaO/C might be synthesized and used in the transesterification process of biodiesel production from off-grade palm oil. The results of XRD analysis shows the catalysts with peaks are C, CaO, Na_2CO_3, and $Ca(OH)_2$. The highest biodiesel yield is 79.08% using calcination catalysts with a temperature of 800°C and a mass ratio of 7 to 3.

References

Arifin, J.K. 2009. Pemanfaatan Buah Sawit Sisa Sortiran sebagai Sumber Bahan Baku Asam Lemak. *Tesis*. Program S2 Teknik Kimia Universitas Sumatra Utara. Medan.

Budiawan, R. Zulfansyah, Fatra, W. dan Helwani, Z. (2013) *Off grade* Palm Oil as A Reneweble Raw Material for Biodiesel Production by Two-Step Processes. *ChESA Conference.* Januari. Banda Aceh. 7:40-50.

Farag, H.A., El-Maghraby. dan N.A. Taha. (2013) Kinetic Study of Used Vegetable Oil for Esterification and Transesterification Process of Biodiesel Production. *International Journal of Chemical and Biochemichals Sciences,* 3, 1-8.

Ginting, S.O., D. Tarigan dan N. Hindryawati. (2017) Impregnasi Natrium Oksida pada Karbon Aktif Cangkang Jengkol sebaga Katalis dalam Pembuatan Biodiesel. Prosiding Seminar Nasional Kimia. ISBN 978-602-50942-0-0.

Hadiyanto, H., A.H. Afianti, U.I. Navi'a, N.P. Adetya, W. Widayat dan H. Sutanto. (2017) The Development of Heterogeneous Catalyst C/CaO/NaOH from Waste of Green Mussel Shell (Permavaridis) for Biodiesel Synthesis. Journal of Environmental Chemical Engineering. 2017 Vol.5 No.5 pp.4559-4563

Helwani, Z., N. Aziz, J. Kim dan M.R. Othman. (2016) Improving The Yield of Jatropha Curcas's FAME through Sol-Gel Derived Meso-porous Hydrotalcites. *Renewable Energy*. 86:68-74.

Ho, W.W.S., H.K. Ng, S. Gan dan S.H. Tan. (2014) Evaluation of Palm Oil Mill Fly Ash Supported Calcium Oxide as a Heterogeneous Base Catalyst in Biodiesel Syinthesis from Crude Palm Oil. *Energy Conversion and Management*. 88: 1167-1178

Hu, S., Guan, Y. dan Han, H. (2011) Nano-Magnetic Catalyst KF/CaO-Fe_3O_4 for Biodiesel Production. Applied Energy. 88:2685-2690.

Kesic, Z., Lukic, I., Zdujic, M., Liu, H. dan Skala, D. (2012) Mechanochemically

Synthesized CaO.ZnO Catalyst for Biodiesel Production. *Procedia Engineering*. 42:1169-1178.

Liu, X., He, H., Wang, Y., Zhu, S. dan Piao, X. (2008) Transesterification of Soybean Oil to Biodiesel Using CaO as a Solid Base Catalyst. *Fuel*. 87:216-221.

Liu, C., Pengemei, Lv., Yuan, Z., Yan, F. dan Luo, W. (2010) The Nanometer Magnetic Solid Base Catalyst for Production of Biodiesel. *Renewable Energy*. 35:1531-1536.

Pahan, I. (2012) Panduan Lengkap: Kelapa Sawit. Penebar Swadaya. Jakarta.

Tang, S., Wang, L., Zhang, Y., Li, S., Tian, S. dan Wang, B. (2012) Study on Preparation of Ca/Al/Fe_3O_4 Magnetic Composite Solid Catalyst and Its Application in Biodiesel Transesterification. *Fuel Processing Technology*. 95:84-89.

Ulfayana, S. dan Helwani. Z. (2015) Natural Zeolite for Transesterification Step Catalysts in Biodiesel Production from Palm *Off grade*. *Abstract Book: Regional Conference on Chemical Engineering*. Desember. Yogyakarta. 7:22.

Wei, Z., Xu, C. dan Li, B. (2009) Application of waste eggshell as low-cost solid catalyst for biodiesel production, *Bioresource Technology*. 100(11), 2883–2885.