Development of heterogeneous catalyst from chicken bone and catalytic testing for biodiesel with simultaneous processing

Hantoro Satriadi1, Widayat1,*, Hadiyanto1, Aji Prasetyaningrum1, Jufriyah1, Anita Selvia Ningrum1, Risma Oktavia Nirmala Dewi1

1 Department of Chemical Engineering Faculty of Engineering Diponegoro University Jl. Prof. Sudarto SH Tembalang 50275 Semarang
* Corresponding Authors: widayat@live.undip.ac.id

Abstract. The objective of this research is to preparation of heterogeneous catalyst from chicken bone. The catalyst was testing for biodiesel production from used cooking oil. Preparation of heterogeneous catalyst by using chemical and thermal treatment. The catalyst was characterized by morphology analysis and specific surface area. The catalytic testing was used simultaneous reaction of esterification-trans esterification. The solids product of chicken bone was contained CaO composition of 42.25%. The catalyst was impregnated with FeCl3. The results of catalyst characterization were about composition of CaO of 25.60%, FeO of 1.16% and obtained surface area 32.546 m² / g, total pore volume of 0.051 cc / g, average pore radius of 16.150 Å. The performance testing of heterogeneous catalyst was can used in biodiesel production with simultaneous reaction. In esterification and trans esterification, methyl ester can be obtained in biodiesel product.  The biodiesel production conducted at mole ratio of methanol to used cooking oil 6: 1, 3% (w/w) of catalyst to cooking oil, and reaction time of 3 hours, with 22% biodiesel yield.

1. Introduction
At present, public consumption of diesel oil is increasing again. This is in accordance with the survey of the Downstream Oil and Gas Regulatory Agency (BPH MIGAS) that in 2013 the consumption of diesel oil by the public was 78,200 kilolitres. Then in 2014 the consumption of diesel oil by the public decreased by 11.5% to 62,100 kilolitres. In the following year, 2015 again experienced a decline in usage of 22,600 kilolitres, equivalent to 20.3%. Whereas in 2016 diesel oil consumption experienced an increase which was felt to be quite burdensome to the government and made the government have to turn back the brain to reduce diesel oil consumption. The increase in 2016 was 4.6% equivalent to 3,800 kilolitres of diesel oil.

Alternative fuel which is supposed to be able to replace the position of diesel oil or fuel oil which is considered to be high enough, namely biodiesel. Biodiesel is an alternative fuel to replace petroleum fuel derived from vegetable oil. Vegetable oil that has been investigated as a source of biodiesel raw material is quite a lot, but the use of vegetable oils can directly cause problems related to food competition. Then used cooking oil can be used as an alternative biodiesel feedstock [1].

The production of biodiesel with vegetable oil as raw material is aided by a catalyst. One solid catalyst that can be used for biodiesel is a mixture of calcium compounds (CaO, Ca(OH)2, CaCO3). CaO is the most active catalyst compared to Ca(OH)2 and CaCO3 [2]. [3] conducted a study of making biodiesel using CaO catalyst / iron powder which has a basic level of 3 9.3 in the transesterification stage which yields a yield of 69% at optimum conditions at 60⁰C, mole ratio of oil: mol methanol = 1: 6, and catalyst concentration by 3%, according to Helwani et al. [3] the operating conditions that affect the yield produced are the catalyst concentration. CaO catalysts can be synthesized from the shell waste
of molluscs or bone containing Ca which is quite high. One of the natural ingredients derived from waste which is abundant in nature is chicken bones. Chicken bone waste in Indonesia is very abundant because chicken is one of the favourite foods of the Indonesian people because in addition to delicious chicken meat also contains high nutrition. The rest of the chicken bone waste is only garbage that needs special handling. Therefore, it is necessary to find a solution on how to utilize chicken bones that have not been used effectively to be efficient and economically valuable. Bone consists of phosphorus / calcium elements. The calcium element has the potential as a catalyst in the biodiesel production process. Chicken bones can be reproduced into raw materials in the renewal of making homogeneous catalysts for biodiesel.

[4] revealed that the development of CaO as a catalyst in the transesterification process was focused on seeing the ability of CaO as a reusable catalyst. The advantages of using CaO include high alkalinity, low solubility, easier use. However, oxygen (O\textsubscript{2}) ions on the CaO surface easily form hydrogen bonds with methanol or glycerol so that it will complicate the separation process. To overcome this problem, CaO must be impregnated with its backers. [5] CaO catalyst was prepared from limestone with calcination process, the addition methanol would cause excess methanol reacts with glycerol to inhibit the reaction of methanol and reacts, as well as reversing the direction of the reaction, it was produced biodiesel/FAME with 98.89 % of yield. Calcium Oxide has potential catalyst in biodiesel production with transesterification methods. The catalyst has been added with Fe so the catalyst can be reacted in the esterification process. The catalytic catalyst for biodiesel and simultaneous.

2. Experimental Methods

2.1. Materials
Chicken bones, FeCl\textsubscript{3}.6H\textsubscript{2}O, distilled water, used cooking oil, methanol, oleic acid, olive oil, indicator PP.

2.2. Catalyst Preparation
The chicken bone waste is washed before it is superheated steamed for ± 30 minutes. Chicken bones are mashed with a machine until they become chicken bone powder. The powder is dried in an oven at 100 °C for an hour and later calcined at 800°C for 3 hours straight, which is then characterized by SEM-EDX and BET. 4 grams of FeCl\textsubscript{3}.6H\textsubscript{2}O added with100 ml of distilled water and mixed at 30 minutes. 80 grams of CaO was added in FeCl\textsubscript{3} solution. The Ca-Fe\textsubscript{2}O\textsubscript{3} mixture was impregnated at 80°C for 8 hours then filtered using filter paper. The filtered catalyst was dried in the oven for ± 1.5 hours at 100°C. The drying catalysts are calcined at 600°C for 3 hours and characterized by SEM-EDX and BET.

2.3. Biodiesel Production
1 mole cooking oil is put into the reactor. 6 moles of methanol are mixed into used cooking oil. 3% of the catalyst is added to the mixture of used cooking oil and methanol. The three mixtures were heated at 65 °C for 3 hours. The separation of products is done by using separator. Biodiesel is produced, and then GC-MS analysis is carried out. Do the same steps as above for other variables in table 1.

3. Result and Discussion

3.1. SEM-EDX analysis of Catalyst CaO and Ca-Fe\textsubscript{2}O\textsubscript{3}
Fig. 1 shows the morphology of the CaO catalyst which looks spherical in size that is not uniform [6] Akin to the appearance of the Ca-Fe\textsubscript{2}O\textsubscript{3} catalyst, which is spherical and elongated and irregular morphological morphologies. Elongated and irregular morphology is the morphology of the phosphate element [7] which is the second most important element of the analysis of catalyst composition. The morphology of the Fe on the Ca-Fe\textsubscript{2}O\textsubscript{3} catalyst is not clearly visible nor is its shape. This is due to the very small amount of FeCl\textsubscript{3}.6H\textsubscript{2}O which is impregnated into CaO, so that the morphology of the Fe element tends to be unclear.
Based on the results of EDX analysis (Table 1), the solids product of chicken bone was contained CaO composition of 42.25%. The catalyst was impregnated with FeCl₃. The results of catalyst characterization were about composition of CaO of 25.60%, FeO of 1.16%. The presence of these elements is indicated to come from the raw material (chicken bone) content. The presence of O (oxygen) is probably due to oxidation process.

**Table 1. EDX Analysis Results of CaO and Ca-Fe₂O₃.**

| Catalyst       | Element (%mass) | CaO   | FeO  |
|----------------|-----------------|-------|------|
| CaO            | 42.25           | -     | -    |
| Ca-Fe₂O₃       | 25.60           | 1.16  | -    |

3.2. **Surface Area on Catalyst CaO and Ca-Fe₂O₃**

**Table 2. BET analysis results.**

| Catalyst       | Surface area (m²/g) | Pore Volume (cc/g) | Pore Radius (Å) |
|----------------|---------------------|--------------------|-----------------|
| CaO            | 29.440              | 0.047              | 16.993          |
| Ca-Fe₂O₃       | 32.546              | 0.051              | 16.150          |

Table 3 shows the surface area representing the active surface that can occur when in contact with the reactants in the process reaction. The greater the active surface of the catalyst, the better catalyst activity is expected [8]. The calcination process of CaO and Ca-Fe₂O₃ catalysts that occurs at temperatures of 800°C and 600°C also causes changes from non-porous material to porous material. This is indicated by the change in the adsorption-desorption of N₂ gas isotherms. The increase in the surface area of Ca-Fe₂O₃ is caused by the desorption of CO₂ and H₂O gas molecules from the surface of Ca-Fe₂O₃. Based on differences in calcination temperature, it can be seen that when the calcination temperature is more than 700°C, the surface area will decrease. According to [9], particles will change at temperatures higher than 700°C. This is because at high temperatures, kinetic energy will increase and then the constituent atoms will diffuse with particles adjacent to each other and bind to each other (agglomeration).
3.3. Effect of Catalyst concentration and mole ratio of oil with moles of methanol of yield produced in biodiesel production

Figures 2 and 3 show the relationship between catalyst concentration and mole ratio of oil and methanol to biodiesel yield. The maximum yield is obtained at the mole ratio of oil and methanol by 1:8 with a catalyst ratio of 3% (w/w) with a yield of 22%. Mole ratio of methanol and oil affects the yield of biodiesel. In the reaction stoichiometry, one mole of oil requires three moles of alcohol to produce three moles of methyl ester and 1 mole of glycerol [10]. The addition of the number of moles is intended so that the reaction moves towards the product because the reaction that occurs is an equilibrium reaction. The result shows that the more methanol is added, the yield decreases after the ratio of oil and methanol at 1:8. This is because methanol can act as an emulsifier in the reaction mixture and too much methanol will cause glycerol to be coated in methanol so that emulsions between the catalyst and methanol and glycerol are formed which will inhibit this simultaneous reaction.

The addition of catalyst concentration can also increase the yield of the biodiesel produced. However, after maximum conditions are reached, the yield of the produced biodiesel will start to decrease. [11] said the yield of biodiesel increased when the catalyst was added up to 3%-b, whereas when the catalyst was used in small amounts (<1%-b) the yield of biodiesel produced was not large. The addition of a catalyst of more than 3%-b does not give an increase in the yield of the biodiesel.

4. Conclusion
From the results of the catalyst characteristics analysis showed that CaO catalyst which has spherical morphology and Fe morphology that is not very visible due to its very low levels, and catalyst surface area Fe₂O₃ has increased to prove that CaO after the impregnation and calcination process has a more
reactive catalyst property. The performance testing of heterogeneous catalyst was can used in biodiesel production with simultaneous reaction. In esterification and trans esterification, methyl ester can be obtained in biodiesel product. The biodiesel production conducted at mole ratio of methanol to used cooking oil 6: 1, 3% (w/w) of catalyst to cooking oil, and reaction time of 3 hours, with 22% biodiesel yield.

Acknowledgement
I did like to express my gratitude to Faculty og Engineering Diponegoro University for funding that had given.

References
[1] Liu S, McDonald T and Wang Y 2010 Producing biodiesel from high free fatty acids waste cooking oil assisted by radio frequency heating Fuel 89 10 2735-40
[2] Arzamendi G, Arguinarena E, Campo I, Zabala S and Gandia L M 2008 Alkaline and alkaline-earth metals compounds as catalysts for the methanolysis of sunflower oil Catal. Today 133 305-13
[3] Helwani Z, Othman M, Aziz N, Kim J and Fernando W 2009 Solid heterogeneous catalysts for transesterification of triglycerides with methanol: a review Appl. Catal. A Gen. 363 1-2 1-10
[4] Hu S, Guan Y, Wang Y and Han H 2011 Nano-magnetic catalyst KF/CaO–Fe3O4 for biodiesel production Appl. Energy 88 8 2685-90
[5] Widayat W, Darmawan T, Rosyid R A and Hadiyanto H 2017 Biodiesel Production by Using CaO Catalyst and Ultrasonic Assisted J. Phys. Conf. Ser. 877 1 012037
[6] Mirghiasi Z, Bakhtiari F, Darezereshki E and Esmailzadeh E 2014 Preparation and characterization of CaO nanoparticles from Ca (OH) 2 by direct thermal decomposition method J. Ind. Eng. Chem. 20 1 113-7
[7] Huang X, Andina D, Ge J, Labarre A, Leroux J-C and Castagner B 2017 Characterization of calcium phosphate nanoparticles based on a PEGylated chelator for gene delivery ACS Appl. Mater. Interfaces 9 12 10435-45
[8] Özkar S 2009 Enhancement of catalytic activity by increasing surface area in heterogeneous catalysis Appl. Surf. Sci. 256 5 1272-7
[9] Dong W, Wu S, Chen D, Jiang X and Zhu C 2000 Preparation of α-Fe2O3 nanoparticles by sol-gel process with inorganic iron salt Chem. Lett. 29 5 496-7
[10] Liu J-K, Zhao S-M, Xiong S-B and Zhang S-H 2009 Influence of recooking on volatile and non-volatile compounds found in silver carp Hypophthalmichthys molitrix Fish. Sci. 75 4 1067-75
[11] Wei Z, Xu C and Li B 2009 Application of waste eggshell as low-cost solid catalyst for biodiesel production Bioresour. Technol. 100 11 2883-5