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**ABSTRACT**

Production of biodiesel by catalyst from clam shell with methanol and waste cooking oil as oil resources was carried out. Biodiesel was prepared in two stages that are esterification and transesterification. At stage esterification used  $H_2SO_4$  as a catalyst with mole ratio waste cooking oil and methanol were 1:9. While at phase transesterification used CaO from clam shell *Psammotaea elongata* as a catalyst with mole ratio waste cooking oil and methanol were 1:12. CaO from clam shell catalyst was produced by calcination process on  $1100^\circ C$ . Result of biodiesel is 53.15 % by  $^1H$ -NMR calculation and experimental method is 38.84 %.

**KEYWORDS:** Biodiesel, CaO, esterification, transesterification, waste cooking oil

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**INTRODUCTION**

Increasing concerns about the environmental impact as well as rising oil prices prompted many researchers to identify alternative fuel sources such as biodiesel [1,2,3]. Biodiesel is an alternative diesel fuel, which is generally defined as the mono alkyl esters of vegetable oils and animal fats. Biodiesel has better properties than petroleum diesel as a renewable, biodegradable, the price is relatively stable, does not produce waste which is harmful to the environment [7,8,20]. Application of used cooking oil as a raw material of biodiesel is a good alternative way of handling the waste. However, the used cooking oil has fatty acid content that is higher than the new vegetable oil. Used cooking oil is the oil that comes from the rest of the frying foodstuffs [22]. Transesterification of fat into biodiesel is usually done using a homogeneous catalyst such as sodium hydroxide and potassium hydroxide. However, homogeneous catalysts have the disadvantage that is very hygroscopic, corrosive [10,11,12]. Therefore, the development of heterogeneous catalysts has the advantages given due attention. Some of the advantages of which are not corrosive, it can be used again, the separation easier and friendlier to the environment [4,5,6,9,16,19]. Heterogeneous catalysts typically used in the production of biodiesel, among others, CaO and MgO. Biodiesel production from transesterification of soybean oil with methanol with catalyst CaO,  $Ca(OH)_2$ ,  $CaCO_3$ , at 1 hour reaction produce of FAME (Fatty Acid Methyl Esters) is 93% of CaO, 12% for  $Ca(OH)_2$ , and 0% for  $CaCO_3$ . To produce CaO was made by synthesis of the material  $Ca(NO_3)_2$  and  $Ca(OH)_2$ . But apart from pure material, CaO turns can be made from other sources that contain large  $CaCO_3$ . Some material can be used as a source of CaO, among others from waste egg shells and shells [21]. Based on the above background, this research conducted conversion of used cooking oil into biodiesel using a catalyst shell.

**MATERIALS AND METHODS****1. Materials**

The materials used in this research are: waste cooking oil, clamshell (*Psammotaea elongata*), distilled water, ethanol. p.a. (Merck), Methanol. p.a. (Merck), KOH,  $H_2SO_4$ . p.a (Merck), anhydrous  $Na_2S_2O_4$ , phenolphthalein indicator, Whatman filter paper 40.

**2. Analysis of free fatty acids**

10 gram sample is included in a 250-ml Erlenmeyer flask; add 50 ml of 96% ethanol. The mixture was heated for 10 minutes over a water bath, then added 3 drops of phenolphthalein indicator. Then follow by titration by 0.1 M KOH until the mixture color was changed into pink, then calculated levels of free fatty acids.

### 3. CaO catalyst synthesis of Calm Shells

Calm shells washed with distilled water until clean. Then it was dried in oven at temperature of 150 °C for 1 hour. Shells then crushed until smooth and sieved to 100 mesh sizes. Solids shells that had been sifted and weighed 500 g. CaO synthesis process of shells is done by entering the solids which have been weighed into the calcination apparatus. Calcination process is done by heating the solid at a temperature of 1100 °C for 2 hours.

### 4. Synthesis of Biodiesel through esterification and transesterification reactions

50 gram sample of clean cooking oil that has been inserted into the tool reflux, then esterified free fatty acids with methanol (the ratio of oil and methanol 1: 9) and added catalyst H<sub>2</sub>SO<sub>4</sub> 1 M as much as 1.25%. Refluxing the mixture at a temperature of 60-65°C for 2 hours. After esterified, the result is transesterified with methanol (comparison oil and methanol 1:12) and added alkaline catalyst CaO shell. Mixture was refluxed back at 60-65°C temperature for 2 hours. The reaction mixture is cooled and formed two layers, namely methyl ester (biodiesel) layer on top, glycerol (the layer below). Layer methyl ester and glycerol is separated from the catalyst using a funnel. Methyl ester was then washed with distilled water in a separating funnel to dissolve the rest of the glycerol. Then, the addition of 1.5 g anhydrous Na<sub>2</sub>SO<sub>4</sub> to tie the remnants of water, then filtered with Whatman filter paper methyl ester 40. The final step is evaporated to remove the remaining methanol.

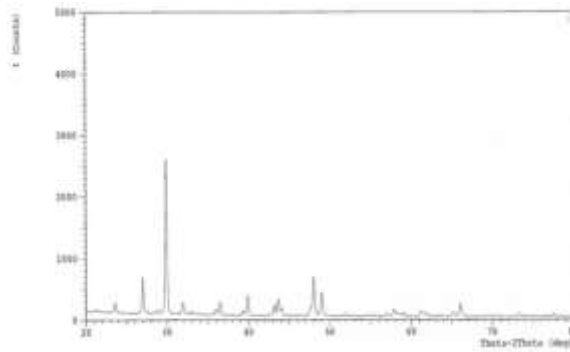
Methyl ester was analyzed by FT-IR, <sup>1</sup>H-NMR.

## RESULTS AND DISCUSSION

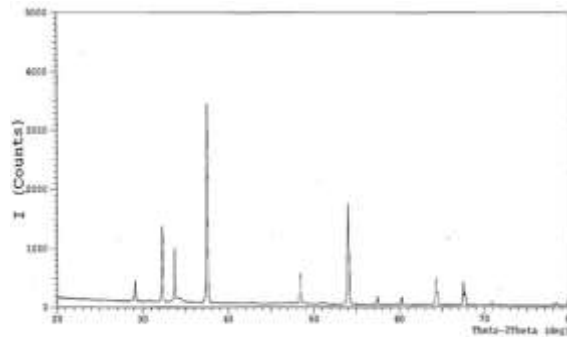
The CaO synthesis process of calm shells (*Psammotaea elongata*) begins with cleaning the shells of dirt are then dried in an oven at 100 °C for 1 hour. Shells (*Psammotaea elongata*) dried later heated in a furnace to a temperature of 600 °C to remove organic impurities attached. The result is then crushed into powder and then calcined at a temperature of 1100 °C for 2 hours to synthesis CaO. With a high temperature heating process can remove CO<sub>2</sub> from the CaCO<sub>3</sub> that can be obtained CaO. Conversion CaO obtained from the calcination 50 g clam shell is 57.88%.

### Characterization of CaO by X-rays (XRD)

CaO produced from the shells (*Psammotaea elongata*) and then tested by X-ray diffraction (XRD) to determine whether the shells that have been formed CaO. XRD results of shells before calcined can be seen in Fig. 1, which shows the characteristic peak 2θ with CaCO<sub>3</sub>. In the picture can be seen the emergence of the peaks of the most powerful with the highest intensity at 2θ = 29.8736 with intensity 1804, 2θ = 47.9622 to 481 intensities, and 2θ = 26.9654 intensity 491. Clam shell generally known to contain CaCO<sub>3</sub> as the main component Ca and the required temperatures above 700 °C to convert CaCO<sub>3</sub> into CaO [3]. The XRD diffractogram results on shells that have been calcined at a temperature of 1100 °C (Fig. 2) showed changes in the diffraction pattern that shown by the peaks of the most powerful is at 2θ = 37.5724 with intensity in 2216, with the intensity of 2θ = 54.0817 1241 and 2θ = 32.4200 intensity 804. XRD results of the shells that have been calcined shows the diffraction pattern similar to the diffraction pattern on a pure CaO. Almost the same diffraction pattern can be seen with the tops of the strongest emerging at 2θ = 37.4728, 53.9871 and 32.3139. Shifting of the pattern that occurred on calm shell after calcined due to heat treatment during calcination at 1100 °C, so that the loss of CO<sub>2</sub> that existed at beginning of the CaCO<sub>3</sub> compounds that produce shells CaO. Diffractogram on solid shells that have been calcined diffraction peaks are narrower and sharper showing that the catalyst obtained have a high degree of crystallinity.



*Fig.1. Diffractogram CaO before calcination*



*Fig. 2. Diffractogram CaO after calcination*

## Synthesis of Biodiesel

### Esterification process

Used cooking oil as raw material for research is a waste frying prepared covering the heating process to remove water and filtered to remove other impurities. The esterification process is carried out by reacting used cooking oil and methanol (1: 9), as the catalyst used sulfuric acid 1 M. The reaction is done at a temperature of 60-65 °C for 2 hours will form two layers, namely a mixture of methanol and methyl esters in the top coat off and triglycerides in the bottom layer. The bottom layer is separated from the top layer later in the transesterification. Esterification reaction aimed to change the free fatty acids with the aid of an acid catalyst to form an ester, a byproduct of this reaction is the formation of water, which can be reduced with excess methanol, because the water that is formed will dissolve in methanol and will not inhibit the subsequent reaction process. Sulfuric acid catalyst used in this reaction serves to improve the process of converting free fatty acids into methyl esters, because acid catalyst esterification reaction process can take place quickly.

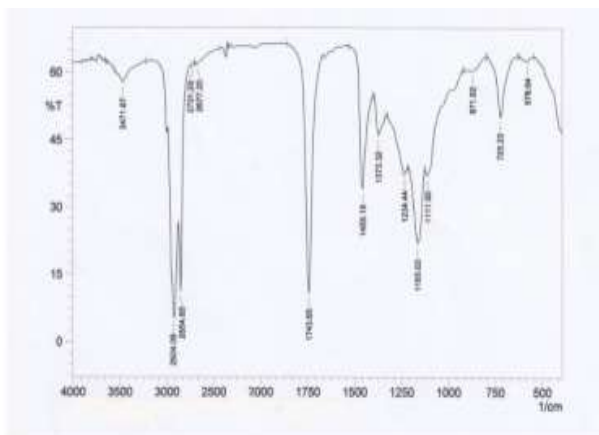
### Transesterification process

Transesterification process is performed by reacting the lower layer containing the results of esterification of triglycerides with methanol, is used as the base catalyst heterogeneous catalysts CaO 10%. Comparison of oil and methanol is 1:12. The reaction was performed at a temperature of 60-65 °C for 5 hours was obtained two layers. CaO heterogeneous basic catalysts are solids so easily separated from the reaction and can be reused. Then washed with water to remove the glycerol and then water was removed with anhydrous Na<sub>2</sub>SO<sub>4</sub>. Furthermore, evaporated to remove methanol and then filtered with Whatman filter paper 40 and obtained methyl ester (biodiesel) (Fig. 12)

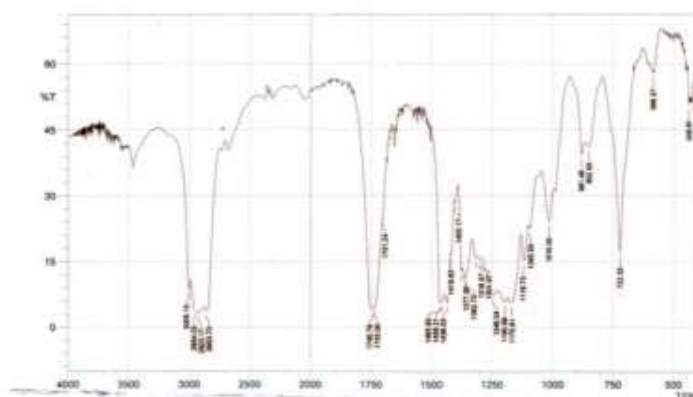
which will then be tested physical and chemical properties. Conversion of methyl ester (biodiesel) from using cooking oil through esterification process and transesterification experimentally by 38.84%.

### Characterization of Biodiesel

Analysis of biodiesel with FT-IR spectroscopy. FT-IR testing done to prove the existence of the product ester transesterification. Presence of ester, can be seen from uptake in group C = O and CO. Fig. 3 and 4 show the comparison between the spectra of spectra used cooking oil and biodiesel.



*Fig. 3 FT-IR spectra on used cooking oil*

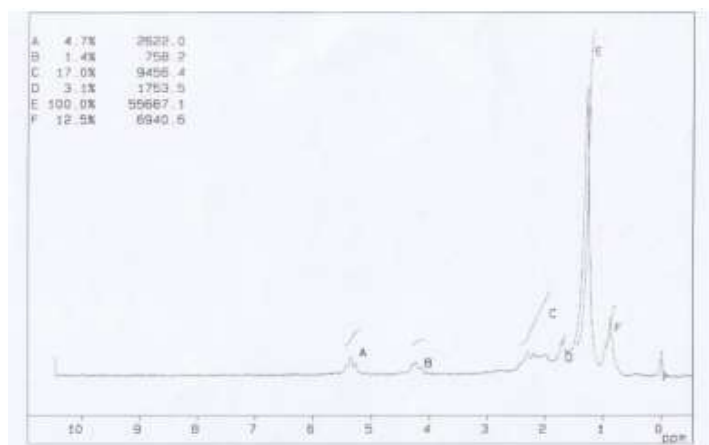


*Fig. 4 FT-IR spectra on biodiesel*

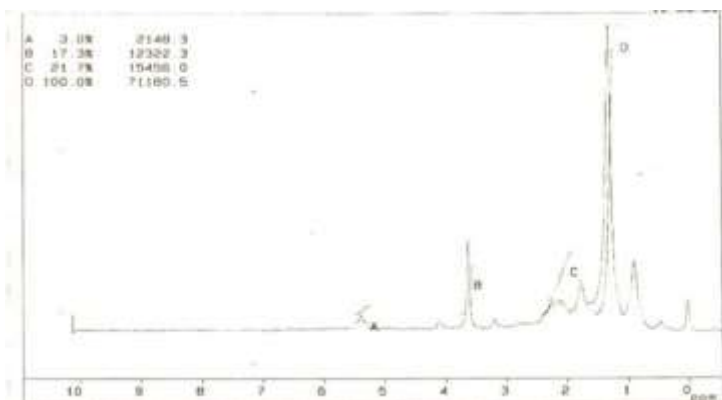
There are changes in absorption in both spectra. On biodiesel, absorption in the region from 1735 to 1740.79  $\text{cm}^{-1}$  wave number is the range for the group C=O (carbonyl group), absorption in the wave number region from 1170.81 to 1195.85  $\text{cm}^{-1}$  is a CO group which is a methyl ester and aliphatic CH in the region of wave number 2857.73 to 2954.03  $\text{cm}^{-1}$ . While on used cooking oil, absorption at the wave number 1743.65 area is the range of C = O (carbonyl group), absorption in the region number wave 1165.00  $\text{cm}^{-1}$  is the range of the CO group.

### Analysis of biodiesel by $^1\text{H-NMR}$ spectroscopy

Biodiesel has been obtained through esterification and transesterification then analyzed by  $^1\text{H-NMR}$  spectroscopy to determine the conversion presentation of biodiesel from the used cooking oil. On used cooking oil  $^1\text{H-NMR}$  spectra (Fig. 5) can be seen a proton from the group glycerides shown in area 4 to 4.3 ppm and 5-6 ppm.



*Fig. 5 Waste cooking oil <sup>1</sup>H-NMR spectra*



*Fig. 5 Biodiesel <sup>1</sup>H-NMR spectra*

On the results of <sup>1</sup>H-NMR spectra of biodiesel (Fig. 6) visible presence from methyl ester protons at 3.7 ppm and regional groups in the region of 5-6 ppm glycerides. On emerging area of 1-2 ppm peak width and height, this peak occurs because the protons in the CH fatty acids are so close that the chemical shift is also a result too close to the tops will merge into a singlet in which the tops of the middle of a multiplet also symptoms of tilting or leaning [14,15]. Conversion of methyl ester (biodiesel) which is formed can be determined by using the equation 1 and equation 2 theoretically. Biodiesel obtained spectra (Fig. 6) shows the spectra of glycerol at 5-6 ppm. Conversion was obtained methyl esters (biodiesel) from <sup>1</sup>H-NMR calculated is 53.15%.

#### **Spectroscopic analysis of biodiesel by GC-MS**

The results of spectroscopic analysis by GC-MS showed the content of methyl palmitate (C<sub>17</sub>H<sub>34</sub>O<sub>2</sub>) of 3.47%, methyl linoleic (C<sub>19</sub>H<sub>34</sub>O<sub>2</sub>) of 4.57%, methyl oleate (C<sub>19</sub>H<sub>36</sub>O<sub>2</sub>) amounted to 9.93%, and methyl stearate (C<sub>19</sub>H<sub>38</sub>O<sub>2</sub>) of 2.65%.

## CONCLUSION

Based on the results obtained, it can be summed up as follows: CaO can be generated shell at a temperature of 1100 °C as much as 57.884%. Converting used cooking oil into biodiesel amounting to 38.838%. The biodiesel constituent fatty acids obtained from the GC-MS analysis is methyl oleate (C<sub>19</sub>H<sub>36</sub>O<sub>2</sub>) (42.77%), methyl palmitate (C<sub>17</sub>H<sub>34</sub>O<sub>2</sub>) (36.85%), linoleic methyl (C<sub>19</sub>H<sub>34</sub>O<sub>2</sub> retention 22.206 min (11.54%).

## REFERENCES

- [1] Basha, S.A., Gopal, K.R., Jebaraj, S., 2009, A review on biodiesel production, combustion, emissions and performance, *Renewable and Sustainable Energy Reviews* 13: 1628–1634.
- [2] Balat M, Balat H., 2010, Progress in biodiesel processing. *Appl Energy* ;87:1815–35.
- [3] Bhatti, H.N., Hanif, M.A., Qasim, M., Ata-ur-Rehman, 2008, Biodiesel production from waste tallow, *Fuel*, 87:2961–2966.
- [4] Byun, M.W., Kang, I.J, Kwon, J.H., Hayashi, Y, Mori, T., 1995, Physicochemical properties of soybean oil extracted from [gamma]-irradiated soybeans. *Radiat Phys Chem* 46:659–62.
- [5] Carrero, A., G. Vicente, R. Rodríguez, M. Linares, G.L. del Peso, 2011, Hierarchical zeolites as catalysts for biodiesel production from *Nannochloropsis* microalga oil, *Catalysis Today* 167, 148–153
- [6] Chakraborty, R., S. Bepari, A. Banerjee, 2011, Application of calcined waste fish (*Labeo rohita*) scale as low-cost heterogeneous catalyst for biodiesel synthesis, *Bioresource Technology* 102, 3610–3618
- [7] Chisti, Y., 2007, Biodiesel from microalgae, *Biotechnology Advances* 25, 294–306
- [8] Demirbas, A., 2009, Progress and recent trends in biodiesel fuels, *Energy Conversion and Management* 50:14–34.
- [9] Eckey, E.W., 1956, Esterification and interesterification. *JAACS*, 33:575–9.
- [10] Freedman, B., Pryde, E.H., Mounts, T.L., 1984, Variables affecting the yields of fatty esters from transesterified vegetable oils, *Journal of the American Oil Chemists Society* 61: 1638–1643.
- [11] Granados, M.L., Poves, M.D.Z., Alonso, D.M., Mariscal, R., Galisteo, F.C., R. Moreno-Tost, Santamaría, J., Fierro, J.L.G., 2007, Biodiesel from sunflower oil by using activated calcium oxide, *Applied Catalysis B: Environmental* 73:317–326.
- [12] Guru, M., Koca, A., Can, O., Çinar C., Sahin, F., 2010, Biodiesel production from waste chicken fat based sources and evaluation with Mg based additive in a diesel engine, *Renewable Energy*, 35:637–643
- [13] Kawashima, A., Matsubara, K., Honda, K., 2008. Development of heterogeneous base catalysts for biodiesel production. *Bioresour. Technol.* 99, 3439–3443.
- [15] Knothe, G., 2010, Biodiesel and renewable diesel: A comparison, *Progress in Energy and Combustion Science* 36:364–373.
- [16] Liu, X., He, H., Wang, Y., Zhu, S., Piao, X., 2008, Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst, *Fuel* 87:216–221.
- [19] Ma, F., Hanna, M.A., 1999, Biodiesel production: a review. *Bioresource Technology*, 70: 1-15.
- [20] Singh, S.P., Singh, D., 2010, Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review, *Renewable and Sustainable Energy Reviews*, 14:200–216.
- [21] Viriya-empikul, N., Krasae, P., Puttasawat, B., Yoosuk, B., Chollacoop, N., Faungnawakij, K., 2010, Waste shells of mollusk and egg as biodiesel production catalysts, *Bioresource Technology* 101: 3765–3767.
- [22] Zhang, Y., Dube, M.A., McLean, a, D.D., Kates, M., 2003, Biodiesel production from waste cooking oil, *Bioresource Technology*, 89:1–16.

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