

Conference Paper

Preparation and Characterization of Calcium Oxide Heterogeneous Catalyst Derived from Anadara Granosa Shell for Biodiesel Synthesis

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Abstract The aims of this study were to prepare and characterize environment-friendly calcium oxide (CaO) heterogeneous catalysts from blood cockle (*Anadara granosa*) shells and utilize for the synthesis of biodiesel. In this study, biodiesel was produced by transesterification reaction of waste frying oil with methanol using the CaO catalyst. The catalysts were prepared by crushing and calcining of *Anadara granosa* shells at 800°C and 900°C for 10 hours. The resulting CaO catalyst were characterized using X-ray diffraction (XRD), thermogravimetric analysis (TGA), X-ray fluorescence spectrometry (XRF), and Fourier transform infrared spectroscopy (FTIR). XRD patterns of calcined catalyst showed intense peaks of calcium oxide ($2\theta = 32.24^\circ, 37.38^\circ$ and 64.16°), and it was consistent with XRF results (>99% of CaO found) that revealed calcium was the major element present in the *Anadara granosa* shells. The maximum yield of biodiesel produced was 82.25% under reaction conditions of catalyst loading of 3 wt.%, methanol to oil ratio of 15:1, reaction time of 3 h, temperature of 60°C and using a catalyst calcined at 900°C.

Keywords: Biodiesel, CaO, Heterogeneous catalyst, *Anadara granosa* shell, Waste frying oil

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Received: 1 August 2016
Accepted: 18 August 2016
Published: 6 September 2016

Publishing services provided
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Selection and Peer-review under the responsibility of the ICoSE Conference Committee.

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1. Introduction

Population growth and industrial development has resulted in increased demand for energy. Fossil fuels tend to be environmentally not friendly, and therefore required the development of alternative renewable energy sources that are environmentally friendly and provide a solution to the increasing demand for these fuels. One of the alternatives that can be developed at this time to address these problems is the production of biodiesel from natural sources. Biodiesel, also known as fatty acid methyl ester, is regarded as the best substitute for conventional petro-based diesel fuel since it is nontoxic, biodegradable and renewable [1].

Biodiesel is usually obtained from the transesterification reaction between the oil with methanol in an alkaline or acid catalyst [2]. But the production value is higher than the value derived from the production of petroleum-based fuels. To lower the price and make biodiesel competitive with petroleum, then the selection of basic materials and catalysts which are cheaper to manufacture biodiesel needs into account. The

commonly catalyst used for the transesterification reaction is alkaline catalysts such as KOH and NaOH. Heterogeneous catalyst which has the form of a solid has some advantages: easily separated from the mixture by filtration, do not require a lot of water in the filtration process and can be recycled and reusable [3,4].

Among the heterogeneous catalysts that have been used for the manufacture of biodiesel, calcium oxide (CaO) is an oxide of a strong base which has high catalytic activity. CaO as a base catalyst has many advantages, for example, the low temperature and short time of reaction conditions, as well as the low cost of the catalyst [5]. In addition, the use of CaO catalyst for biodiesel synthesis besides not toxic, the potential for the formation of soap is also very small compared to using base catalyst, i.e. NaOH or KOH [6]. CaO is commercially available with high price, and that the research to obtain CaO with low cost from renewable feedstock is interesting topic until this time. The potential raw material for this purpose is shells from several mollusk and eggshell [7]. Blood cockle (*anadaragranosa*) shells have a good potential to be used as CaO heterogeneous catalysts in the manufacture of biodiesel because it contains calcium carbonate (CaCO₃) that will decompose to CaO at high temperature and its abundance of waste that has not been widely utilized. Moreover, utilization of *anadaragranosa* shells for biodiesel synthesis is expected to reduce the production price and that it will raise the economic value.

Synthesis and characterization of biodiesel using heterogeneous catalysts from blood cockle shells have been studied elsewhere [8]. The different temperature and time of calcination catalyst will result in different catalyst properties and activities to biodiesel conversion. The aim of this study was to synthesize and characterize catalyst derived from blood cockle shells (*anadaragranosa*). The catalyst was tested on the transesterification of waste cooking oil (WCO) to produce biodiesel with the variation parameters of time and temperature reaction in order to obtain the maximum biodiesel production.

2. Materials and Methods

2.1. Materials

Blood cockle shells and WCO samples were collected from households and cafetaria. The chemicals used in this study were methanol (99.8% purity, Sigma Aldrich), potassium hydroxide (KOH) solution prepared to 0.1 N using KOH pellets (99.99% purity, Sigma Aldrich), iso-propanol (99% purity, Merck), phenolphthalein indicator, potassium hydrogen phthalat and distilled water. All the chemicals and reagents were of analytical grade.

2.2. Preparation of CaO catalysts

CaO used in this study comes from the shells waste of blood cockle (*anadaragranosa*). Blood cockle shells were cleaned using water to remove dirt and sand that remains. Then, the shells was washed using distilled water until clean. Shells was coarsely

grounded using a mortar pestle, dried in an oven at a temperature of 110 °C overnight and calcined 10 hours at temperature of 800°C and 900 °C. After calcination, the shells were finely crushed and sifted using a sieve that passes the 200 mesh and stored in a desiccator.

2.3. Catalyst characterization

The properties catalyst derived from *anadaragranosa* shell were characterized including: analysis thermal using Thermal gravimetric and Differential thermal analysis (TG/DTA), crystalline structure using X-ray diffraction (XRD), composition using X-ray fluorescence (XRF) and functional group using Fourier transform infrared spectroscopy (FTIR).

2.4. Synthesis biodiesel

The transesterification reactions of WCO using catalyst derived from *Anadaragranosa* shell was performed in a three-necked batch reactor 500 ml equipped with a thermometer and a reflux condenser. A total of 100 g of the WCO sample was heated above the boiling point of water (temperature 105°C) for 30 minutes, then the oil cooled to a temperature of 50°C. On a separate place a mixture catalyst and methanol was refluxed for 1 hour. Samples of WCO (50°C) was then added to the mixture of catalyst and methanol and stirred for 3 h at a temperature of 60°C. After the reaction completed, the flask was dipped into cold water, and then the mixture was put into a separating funnel and allow to stand at room temperature overnight so that it will form two layers. The next day, the glycerol was removed from the separating funnel. Crude biodiesel was formed, collected and washed with warm water. Yield of biodiesel was calculated according to equation below:

$$Yield (\%) = \frac{Weight\ of\ Biodiesel\ produced}{Weight\ of\ WCO\ used} \times 100 \quad (1)$$

3. Results and Discussion

3.1. Catalyst characterization

Thermogravimetry is a technique to measure the change in weight of a compound as a function of temperature or time. Fig. 1 shows TGA of the decomposition of CaCO₃ derived from *anadaragranosa* shell at atmospheric pressure 1 atm. The decomposition is started at a temperature of ~600°C and completed before 800°C. When CaCO₃ decomposed into CaO and CO₂, the weight of shell reduced to ~58%. Furthermore, the decomposition reaction is endothermic that on reaction it required heat or calorie which is shown in reducing curve of DTA in line with CaCO₃ decomposition. Empikul, et al. [6] characterized solid oxide catalysts derived from the industrial waste shells of egg, golden apple snail, and meretrixvenus using TGA and SDTA. They also found high

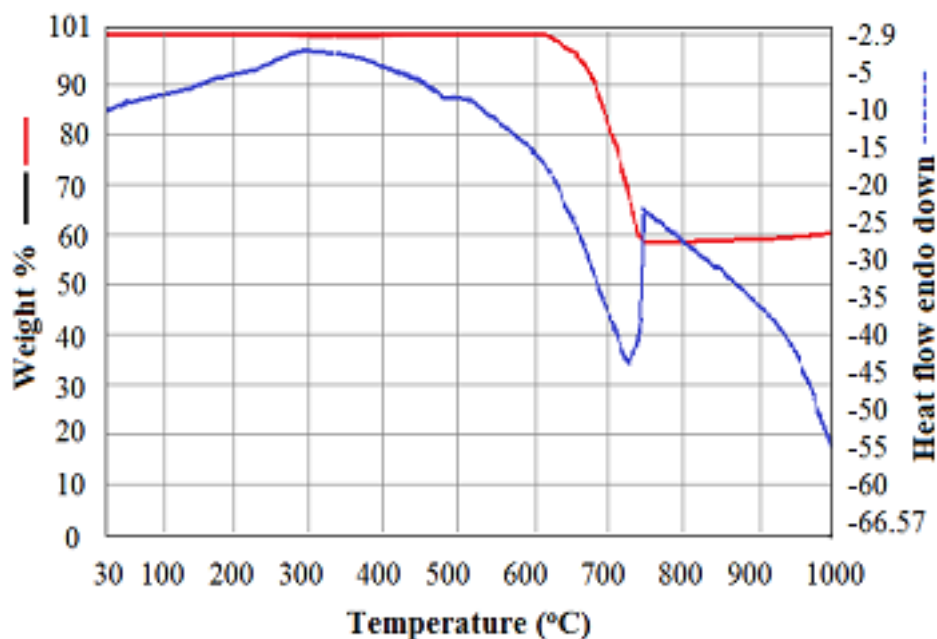


Figure 1: TG/DTA curves of *AnadaraGranosa*.

temperature range is required to transform CaCO_3 to CaO (above 700°C). Nakatani et al. [9] reported that the transformation of oyster shell composed of CaCO_3 to CaO required the combustion temperature at 700°C or above. From TGA curve (Fig. 1) it can be noted that the decomposition raw material (*anadaragranosa* shell) should be completed on calcination at 800°C for 10 h, however, from XRD there was still CaCO_3 peaks appeared (Fig. 2).

The result of XRD analysis of CaO catalyst derived from *Anadaragranosa* shell calcinated at 800°C and 900°C for 10 h was presented in Fig.2. It is seen from the figure that CaO was formed on calcination at 800°C and 900°C for 10 h. This is indicated by presence of diffraction peaks 2θ at 32.24° , 37.39° , 53.88° , 64.18° , 67.40° , 79.66° and 88.50° . The CaO diffraction pattern is in accordance with the standards of JCPDS. Catalyst calcining at 800°C for 10 h contained mineral of *Calcite* (CaCO_3) at 2θ of 29.35° and 47.12° (Fig. 2a). This shows that the decomposition of CaCO_3 to CaO on calcination of *anadaragranosa* shell at 800°C for 10 h still not completed. This is because cockle shell type of *Anadaragranosa* has a very hard shell layer so it is difficult to decompose at a temperature of 800°C . On the other hand, some peaks of Ca(OH)_2 were also appeared at 2θ of 17.87° , 28.55° , 34.18° , 47.51° and 50.71° . The formation of Ca(OH)_2 is due to the reaction between CaO with H_2O in the air. The XRD analysis of *anadaragranosa* shell calcined at 800°C and 900°C for 3 h has been reported [8]. The XRD pattern of catalyst derived from the shell calcined 800°C for 3 h still showed more CaCO_3 peaks compared to the XRD result of this study. Moreover, the intensity Ca(OH)_2 peak from the shell calcined 900°C for 3 h is much higher than that in this study.

The FTIR spectra of CaO catalyst derived from *Anadaragranosa* shell calcined 10 h at 800°C and 900°C were shown in Fig. 3. The FTIR spectra of raw and decomposed sample were obtained using KBr method at room temperature and the spectra were

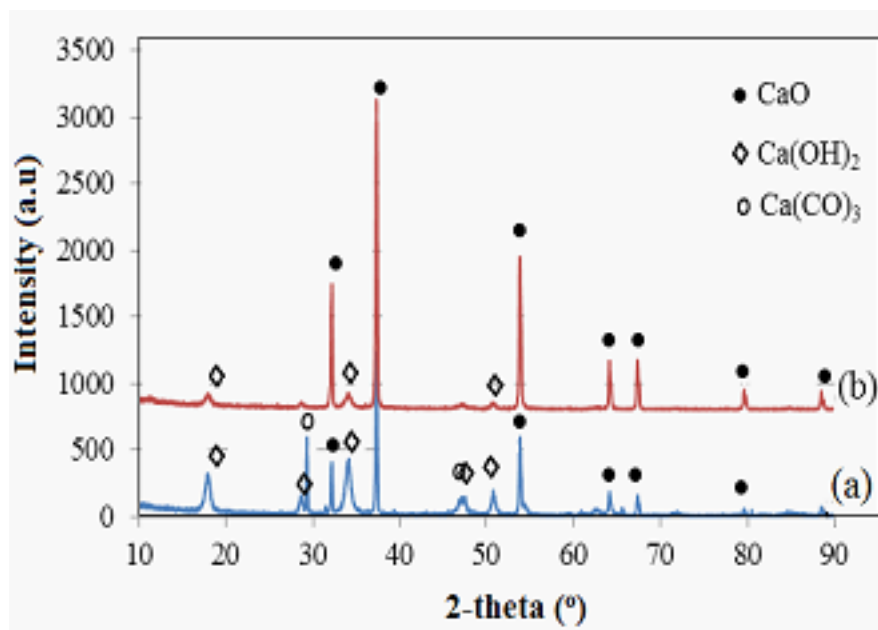


Figure 2: XRD pattern of *Anadara granosa* shell calcined 10 h (a).800°C and (b). 900°C.

Calcination temperature	Composition, weight fraction (wt.%)							
	CaO	K ₂ O	SrO	Cl ₂ O	Fe ₂ O ₃	MnO	SO ₃	SnO ₂
800°C	99.14	0.29	0.25	0.13	0.02	0.02	0.12	-
900°C	99.09	0.37	0.28	0.12	0.03	0.03	-	0.02

TABLE 1: XRF analysis of *Anadara Granosa* shell calcined 10 h at 800°C and 900°C.

recorded at 400-4000 cm⁻¹. The raw material (uncalcined) shell showed spectral FTIR bands corresponded to CaCO₃. The broad transmission band at approximately 3379 cm⁻¹ can be attributed to OH stretching vibration from water. Sharp peaks at 2517, 1735, 1461 and 861 cm⁻¹ were characteristic peaks of C-O stretching and bending modes of CaCO₃. Similar peaks also observed by Margaretha et al. [3] using *Pomacea* sp. shell as catalyst. Besides, the characteristic absorption of C=O between 2000 and 1500 cm⁻¹ indicates the presence of calcium carbonate over the catalysts. On calcining the raw material to 800°C and 900°C for 10h all those bands disappeared. The broad band at ~1621 cm⁻¹ and sharp band at 3641 cm⁻¹ are associated with OH stretching vibration mode of water physisorbed on the surface of the CaO. This is related to OH in Ca(OH)₂ as shown in the XRD pattern. Furthermore, broad bands of CaO appeared at around 530 cm⁻¹ (for catalyst calcined 800°C) and 500 cm⁻¹ (for catalyst calcined 900°C).

The determination of chemical composition of catalyst was performed using X-ray fluorescence (XRF) and the results are shown in Table 1. It can be seen from the table that the majority composition of the catalyst was calcium oxide (CaO). The table shows the results of quantitatively characterization by XRF in which the chemical composition of calcium oxide (CaO) has the largest percentage by weight with the percentages of CaO obtained were 99.14 % and 99.09 % respectively. Besides CaO,

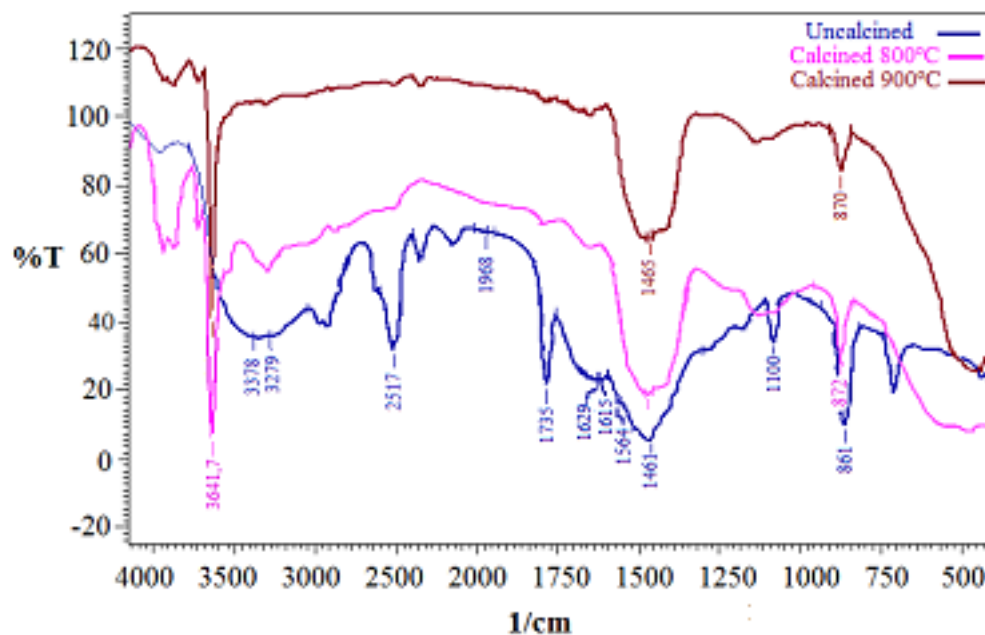


Figure 3: FTIR of *Anadaraganosashells:raw*, calcined 10 h at 800°C and 900°C.

catalyst from this *Anadaraganosa* shells also contained small amounts of oxides such as K_2O , SrO , Cl_2O , Fe_2O_3 and MnO .

3.2. Transesterification of WCO

The catalyst used for producing biodiesel in this study was derived from blood coke shells (*Anadaraganosa*) calcined at 800°C and 900°C for 10 hours. Transesterification was done using basic materials of waste cooking oil (WCO) and methanol. The yield of biodiesel produced here can be seen in Figure 4. Figure 4a shows the effect of reaction time on the biodiesel yield. It can be seen from the figure that the yield of biodiesel increased with increasing reaction time. The longer the reaction time of transesterification then the more the opportunity of reactant molecules to collide, so the yield of biodiesel results increased. The optimum biodiesel result was obtained at a reaction time of 3 h, and a longer time the yield will decline. This is because in the early stages of the transesterification reaction, the biodiesel production took place rapidly and then the rate declined until it reaches equilibrium at the reaction time of 3 hours. If reaction time is too long it will result in the formation of glycerol and emulsion in the product, increasing the viscosity and affect the purity of biodiesel. Maximum yield biodiesel synthesized using the catalyst calcination at 800°C is 79.28 %. This result is lower than the biodiesel results obtained with the use of catalyst calcination at 900°C for 10 h (82.25%). The low biodiesel obtained using catalyst calcined at 800°C is due to incomplete decomposition of $CaCO_3$ to CO_2 and CaO .

In addition to reaction time, the temperature of transesterification reaction affects the biodiesel yield. In order to get the optimum biodiesel reaction conditions it must be maintained at a temperature around the boiling point of methanol (around 64°C) [1]. In this study, transesterification process was carried out at temperature from 50°C

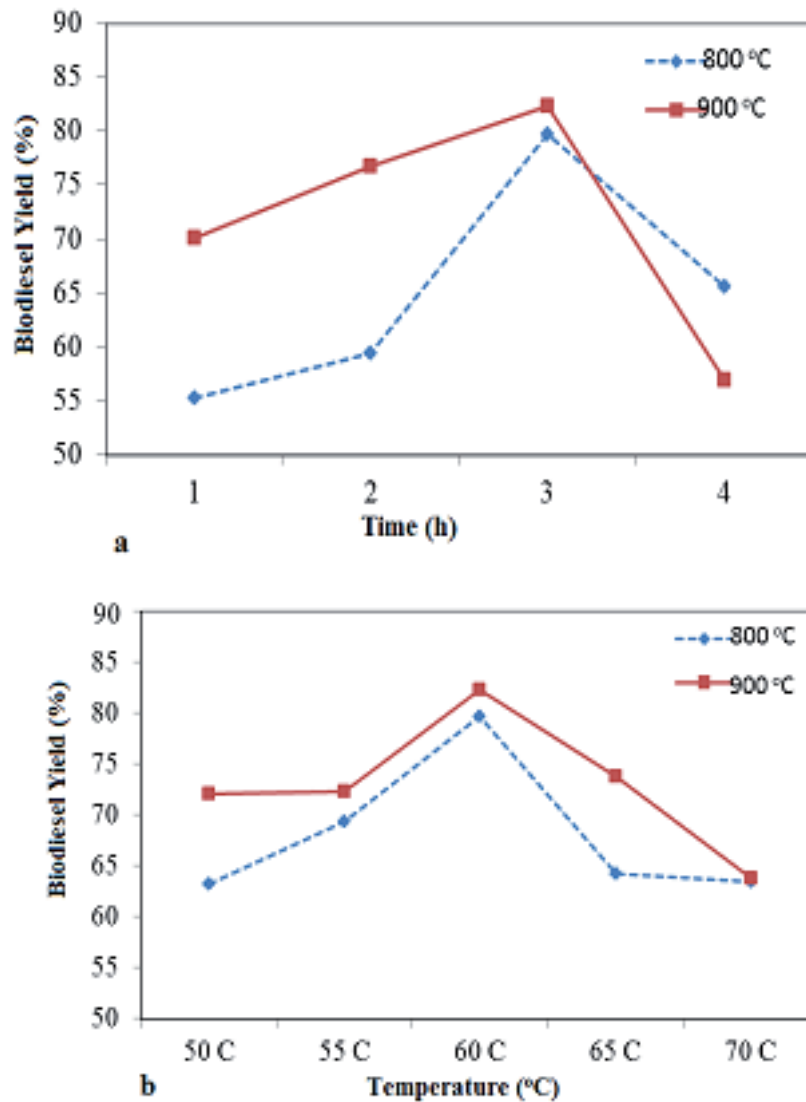


Figure 4: Biodiesel yield at different time (a) and temperature (b) reaction (weight of catalyst 3 g, molar ratio of methanol to oil 15:1).

to 70°C. The yield of biodiesel produced can be seen in Figure 4b. It can be seen that the yield of biodiesel increased as the temperature increased, and the maximum yield was at the reaction temperature of 60°C which is 82.25%. It also shows that the rise in temperature after reaching optimum condition do not lead to increase the results of biodiesel, and even became more decreased. This is because if the reaction temperature is too high it can lead to evaporate or loss of methanol and that the yield biodiesel will reduce.

4. Conclusion

Based on the results of research conducted, it can be concluded that the minimum temperature *Anadaragranosashell* decomposited to obtain Calcium oxide was 800°C. The higher decomposition temperature used will improve the crystallinity of CaOas

shown on the XRD diffractogram. The formation of CaO was also supported by FTIR spectra in the area around 500 cm^{-1} which indicate the presence of Ca-O vibration. It is confirmed by the XRF data showing the percentage of CaO in the samples $> 99\%$. The maximum biodiesel yield was 82.25% which was produced in the transesterification reaction using catalyst CaO from shell of *anadaragranosa* calcination at 900°C for 10 h, under reaction conditions of catalyst loading of 3 wt.%, methanol to oil ratio of 15:1, reaction time of 3 h and temperature of 60°C .

5. Acknowledgements

The authors gratefully acknowledge the financial support of Riau University under PUPT Grant.

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