Synthesis of solid catalyst from egg shell waste and clay for biodiesel production

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Abstract. Until now, energy consumption in Indonesia is almost entirely fulfilled by fossil fuels, thus, its availability will be limited and continue to decrease. To overcome these problems, development and utilization of renewable energy are required, one of which is biodiesel. Biodiesel can be prepared through transesterification reaction of vegetable oil using catalyst. In this research, a solid catalyst for biodiesel synthesis was prepared from chicken egg shell waste and clay. Optimization of the transesterification reaction of coconut (Cocos nucifera) oil to obtain biodiesel was also carried out. The formation of CaO/kaolin catalyst was confirmed based on the results of XRD and SEM-EDS. This catalyst is suitable for biodiesel synthesis from vegetable oils with lower FFA (free fatty acid) levels, i.e. coconut oil with FFA level of 0.18%. Based on FTIR result, FFA level and flame tests, it was found that biodiesel was successfully formed. Synthesis of biodiesel has the optimum conditions on reaction time of 16 hours and temperature of 64 °C, with oil: methanol ratio of 1: 15 and CaO/kaolin catalyst concentration of 0.9% in a reflux system.

1. Introduction
Biodiesel is one of alternative fuel used in diesel engine. Biodiesel can be produced via transesterification reaction between plant oil and short-chain alcohol, such as methanol, with an aid of acid catalyst or base to increase the reaction rate [1]. Indonesia, especially West Java, has a wide variety of plants, thus the plants based oil can be processed as the precursor for biodiesel production. One example of vegetable oil that can be used for biodiesel comes from coconut fruits (Cocos nucifera). Coconut oil contains triglyceride which comprise of various fatty acids and glycerol. Coconut oil contain of 91% saturated fatty acid which consists of caproic acid, caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, and arachidic acid, while the rest of 9% consist of unsaturated fatty acid such as oleic and linoleic acid. The biggest component contained in coconut oil is lauric acid with 55% content [2]. In the early times, biodiesel production via esterification reaction was utilizing homogeneous base catalyst such as NaOH and KOH aqueous solution, because the reaction proceeded in high reaction rate. However, the utilization of this catalyst possesses several drawbacks, i.e. difficult to separate catalyst with reaction products and saponification reaction was
easy to occurred [3]. To overcome this drawbacks, in this research, biodiesel will be produced using heterogeneous base catalyst.

Several research regarding biodiesel production from coconut oil have been done with various FFA (free fatty acid) content from low to high, via esterification/transesterification reaction using homogeneous and/or heterogeneous catalyst [4-7]. In this research, CaO/kaolin catalyst has been synthesized from chicken egg shell waste and kaolin clay. CaO was prepared from the egg shell by high temperature calcination [8]. Activated kaolin was prepared using procedure have been reported [9].

Biodiesel production can be carried out via esterification/transesterification reaction with considering the free fatty acid content in the vegetable oil [10]. Several parameters influencing biodiesel production are water content, free fatty acid content, alcohol concentration, catalyst concentration, reaction temperature, and reaction time [3,11]. Researchers can determine optimum condition for the reaction by manipulating those parameters to obtain good quality and economical biodiesel product. In this research, the free fatty acid (FFA) content change caused by the influence of synthesis time in transesterification of coconut oil catalyzed by CaO/kaolin and KOH (as comparison) is reported. The aim of this research is to observe the amount of fatty acid converted to biodiesel.

2. Methods

Activated kaolin was obtained by chemical activation under alkaline condition. Kaolin clay was calcined in 800 °C for 10 hours, soaked in NaOH 0.4 M in 50 °C for 6 hours, washed, and then calcined in 500 °C for 6 hours. Calcium oxide (CaO) was obtained from chicken egg shell waste by washing, drying, milling, and calcination in 900 °C for 4 hours. CaO/kaolin solid catalyst was synthesized using wet impregnation method by mixing CaO from chicken egg shells and activated kaolin clay. Coconut oil transesterification was performed using the synthesized catalyst to investigate the activity of the catalyst. The transesterification was also carried out using KOH catalyst to obtain comparison data. The materials used to synthesize CaO/kaolin catalyst was chicken egg shell, kaolin, NaOH, and aquadest. The catalyst is made by composition of 15 mmol CaO for each 1 gram of activated kaolin. The mixture was soaked in NaOH 0.02 M in 70 °C for 4 hours, left along for 24 hours, centrifuged, dried in 100 °C for 20 hours, and calcined in 900 °C for 2 hours to obtain the CaO/kaolin catalyst. Materials used for biodiesel synthesis was methanol, commercial coconut oil, and KOH. The transesterification reaction was observed with variation of synthesis time i.e. 4, 6, 8 and 16 hours at 64°C, with oil: methanol ratio of 1:15 and CaO/kaolin catalyst concentration of 0.9% in a reflux system. FFA content measurement in the mixture was performed to observe the completion of transesterification reaction. Biodiesel obtained from optimum reaction condition was separated from the mixture using separation funnel for further analysis. The structure of activated kaolin and the synthesized CaO/kaolin catalyst was characterized using X-Ray Diffraction (XRD). Catalyst surface morphology is observed by using scanning electron microscopy (SEM). Catalyst chemical composition was characterized using energy-dispersive X-ray spectroscopy (EDS). The biodiesel was characterized using Fourier Transform Infrared (FTIR). Free fatty acid (FFA) content analysis and flame test were also performed.

3. Results and Discussion

In this research, activated kaolin was obtained from metakaolin wet impregnation using NaOH 0.4 M [9]. NaOH addition can change Si/Al ratio, thus metakaolin was transformed to the mixture of LTA, sodalit, and cancrinite [12]. NaOH is also used to dissolve the impurities in the kaolin surface to increase the number of pores in the kaolin. The XRD spectrum of the activated kaolin (Figure 1a)) showed peaks at 2θ = 8.8°; 18.1°; 20.06°; 23.3°; 26.65°; and 31.4°. The peaks pattern in the XRD spectrum of activated kaolin is in agreement with XRD spectrum of activated kaolin obtained by chemical activation under alkaline condition from previous research by Belver, et al. [12]. XRD spectrum comparison of the produced activated kaolin with literature data base [13], showed that kaolin activation by NaOH 0.4 M was lead to the LTA and sodalit mixed structure.
CaO/kaolin catalyst was synthesized by mixing CaO precursor and activated kaolin in NaOH solution. The addition of activated kaolin to CaO can lower the high basicity of CaO. XRD spectrum of the synthesized catalyst can be seen in figure 1(b). The peaks appeared at $2\theta = 8.88^\circ; 17.7^\circ; 19.86^\circ; 20.96^\circ; $ and $26.66^\circ$ showed that the catalyst consists of three main components/phases i.e. silica, calcite, and CaO [14]. The components was part of the activated kaolin and chicken egg shell.

![Figure 1. XRD spectrum of (a) activated kaolin and (b) CaO/kaolin catalyst](image)

Surface morphology and percent elemental composition of the catalyst can be seen in Figure 2. The surface morphology of CaO/kaolin catalyst showed that the catalyst surface has pores/cavities with diameter between 2-10 μm approximately. The catalyst formed small aggregates with irregular shape similar to stacked plates with diameter around 5 μm. Based on EDS data, the CaO/kaolin catalyst was consist of three elements, i.e. calcium (44.56%), silicone (17.60%) and oxygen 37.84%.

![Figure 2. SEM image (a) and EDS data for CaO/kaolin catalyst](image)

The FFA content in oil and reaction mixture can be calculated based on the highest component in oil i.e. lauric acid with molar mass of 200 g/mol. FFA content in the starting coconut oil was measured to be 0.18%. The coconut oil was directly used for transesterification reaction without lowering the FFA content. The transesterification was performed in two separated coconut oil samples, each using CaO/kaolin catalyst and KOH as comparison. Transesterification reaction with variation of reaction time gave influence to the increasing FFA content in the oil. The longer duration of reaction time results in higher FFA content. This finding confirms that coconut oil hydrolysis by catalyst and KOH...
was taking place which will be followed by esterification with methanol to produce biodiesel. The increase of FFA content occurred significantly in 16 hours reaction time. The FFA content was increased from 0.18% to 0.40%. This showed that the optimum reaction time for esterification reaction was 16 hours.

Coconut oil transesterification using KOH results in two phase of immiscible solution which then separated using separation funnel. The first phase was clear solution containing methyl ester, and the second phase was white turbid solution containing glycerol. Transesterification using CaO/kaolin catalyst results in three phase of solution i.e. the clear solution containing methyl ester, the white turbid solution containing glycerol, and solid catalyst deposit. The solid catalyst was separated using filtration, and the two phase of solution was separated using separation funnel. Solution containing methyl ester was characterized using FTIR. FTIR spectrum of solution containing methyl ester produced using CaO/kaolin catalyst and KOH catalyst can be seen in Figure 3.

![FTIR spectra of biodiesel product catalyzed by CaO/kaolin (red line) and KOH (black line)](image_url)

**Figure 3.** FTIR spectra of biodiesel product catalyzed by CaO/kaolin (red line) and KOH (black line)

FTIR spectrum of biodiesel produced in this research showed absorption of C=O functional group vibration at 1749.44 cm\(^{-1}\), C-O vibration at 1111; 1159.22; and 1230.58 cm\(^{-1}\), C-H stretching at 1375.25 cm\(^{-1}\), alkane C(sp\(^3\))-H stretching at 2677.20; 2852.72; and 2924.09 cm\(^{-1}\), and also C(sp\(^2\))-H at 881.47 cm\(^{-1}\). This results suggest that the methyl ester was formed by using CaO/kaolin catalyst and KOH. Absorption spike at 3400 cm\(^{-1}\) showed that the product mixture contains free fatty acid (FFA). Moreover, absorption spike at 1575.84 and 1541.12 cm\(^{-1}\) suggest the existence of carboxylate group in the solution containing methyl ester produced using CaO/kaolin catalyst. Based on above results, further purification of the methyl ester products is still needed.

Analysis of biodiesel physical properties was performed by flame test. The flame intensity produced by combustion of biodiesel produced by using CaO/kaolin catalyst was compared with the flame intensity from solar diesel fuel combustion and coconut oil combustion. It was found that
biodiesel flame intensity is not as bright as solar diesel fuel. This was probably caused by cetane number in biodiesel that was not good enough. The purity of the solution and length of carbon chain in methyl ester also can affect the flame intensity of combustion. However, the combustion of biodiesel is clean (no smoke and ash observed qualitatively). The biodiesel capilarity through the burner is quite good and the biodiesel is also not coagulate in 5°C temperature for 24 hours. The synthesized biodiesel has lower viscosity compared to the starting material. Meanwhile, no flame produced from coconut oil (Cocos nucifera) combustion.

4. Conclusion
CaO/kaolin solid catalyst was synthesized and used to catalyze the transesterification reaction between coconut (Cocos nucifera) oil and methanol to produce biodiesel. Based on XRD, SEM, and EDS characterization results, CaO/kaolin catalyst was successfully formed. This catalyst can be used to catalyze biodiesel synthesis from vegetable oil with low FFA content, for example coconut oil (Cocos nucifera) with 0.18% FFA content. Based on FTIR spectrum, FFA content measurement, and flame test, it was suggested that biodiesel was successfully formed. Biodiesel synthesis has optimum reaction time of 16 hours at 64°C with oil: methanol ratio 1:15 and and CaO/kaolin catalyst concentration of 0.9% in a reflux system. Coconut oil was converted to biodiesel with higher intensity using CaO/kaolin catalyst than using KOH.

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